

# **Quality Assurance Project Plan**

## For Monitoring By The

### San Joaquin County & Delta Water Quality Coalition

(Revision 2.0)

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For The

**Irrigated Lands Regulatory Program**  
Central Valley Regional Water Quality Control Board  
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SWAMP Project ID: SJCDWQC\_08

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# GROUP A: PROJECT MANAGEMENT

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### San Joaquin County & Delta Water Quality Coalition

<u>Title:</u>	<u>Name:</u>	<u>Signature:</u>	<u>Date*:</u>
Steering Committee Co-Chairman	Mike Wackman	_____	_____

### Michael L. Johnson, LLC

<u>Title:</u>	<u>Name:</u>	<u>Signature:</u>	<u>Date*:</u>
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Project QA Officer	Melissa Turner	_____	_____

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### Central Valley Regional Water Quality Control Board (CVRWQCB)

<u>Title:</u>	<u>Name:</u>	<u>Signature:</u>	<u>Date*:</u>
Regional Board Coalition Liaison	Chris Jimmerson	_____	_____
Regional Board ILRP Monitoring Assessment Supervisor	Susan Fregien	_____	_____
QA Officer	Leticia Valadez	_____	_____

\* This is a contractual document. The signature dates indicate the earliest date when the project can start.

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## LIST OF ACRONYMS

AMR	Annual Monitoring Report	MPN	Most Probable Number
APC	Atmospheric Pressure Chemical Ionization	MRP	Monitoring and Reporting Program Order No. R5-2008-0005
APPL	Agriculture and Priority Pollutants Laboratories Inc.	MRPP	Monitoring and Reporting Program Plan
BU	Beneficial Use	MS	Matrix Spike <u>or</u> Mass Spectrometry
CCC	Continuing Calibration Check	MSD	Matrix Spike Duplicate
CD-ROM	Compact Disc Read-Only Memory	MUN	Municipal and Domestic Supply (beneficial use)
COC	Chain of Custody	NA	Not Applicable
CRM	Certified Reference Material	NCL	North Coast Laboratories Ltd.
CVRWQCB	Central Valley Regional Water Quality Control Board	ND	Not Detected
CWA	Clean Water Act	NDIR	Non-dispersive Infrared
DAI	Direct Aqueous Injection	NM	Normal Monitoring
DDD	Dichlorodiphenyldichloroethane	OP	Organophosphate
DDE	Dichlorodiphenyldichloroethylene	PCD	Post Column Detection
DDT	Dichlorodiphenyltrichloroethane	PDF	Portable Document Format
DI	Deionized	PR	Percent Recovery
DO	Dissolved Oxygen	QA	Quality Assurance
DQO	Data Quality Objective	QAPP	Quality Assurance Project Plan
E	Environmental sample	QC	Quality Control
EC	Specific Conductance	QMR	Quarterly Monitoring Report
ECD	Electron Capture Detector	RL	Reporting Limit
EDD	Electronic Data Deliverable	RPD	Relative Percent Difference
EPA	Environmental Protection Agency	RS	Resample
ESI	Electrospray Ionization	RSD	Relative Standard Deviation
FB	Field Blank	SIM	Selective Ion Monitoring
FD	Field Duplicate	SJCDWQC	San Joaquin County & Delta Water Quality Coalition
FDe	Fluorescence Detection	SOP	Standard Operating Procedure
GC	Gas Chromatography	SPE	Solid Phase Extraction
GPS	Global Positioning System	SRM	Standard Reference Material
HDPE	High Density Polyethylene	SWAMP	Surface Water Ambient Monitoring Program
HPLC	High Performance Liquid Chromatography	TDS	Total Dissolved Solids
ID	Identification	TIC	Technical Issues Committee
ICP-MS	Inductively Coupled Plasma Mass Spectrometry	TIE	Toxicity Identification Evaluation
ILRP	Irrigated Land and Regulatory Program	TKN	Total Kjeldahl Nitrogen
LC	Liquid Chromatography	TOC	Total Organic Carbon
LCS	Laboratory Control Spike	TSS	Total Suspended Solids
LCSD	Laboratory Control Spike Duplicate	VOA	Volatile Organic Analyte
MCL	Maximum Contaminant Level	WQTL	Water Quality Trigger Limit
MDL	Method Detection Limit		
MLJ-LLC	Michael L. Johnson, LLC		

## LIST OF UNITS

cfs	cubic feet per second
cm	centimeter
kg	kilogram
L	Liter
lbs	pounds
mg	milligram
mL	milliliter
ng	nanogram
NTU	Nephelometric Turbidity Units
pH	Power of Hydrogen
sec	second
TUa	Toxic Unit (acute)
µg	microgram
µm	micrometer
µS	microsiemen

### 3. Distribution List

Distribution list of the 2008 San Joaquin County & Delta Water Quality Coalition QAPP.

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#### 4. PROJECT/TASK ORGANIZATION

##### 4.1 Involved parties and roles.

The San Joaquin County & Delta Water Quality Coalition (SJCDWQC, or Coalition) is a consortium of farms and farmers obligated to monitor agricultural wastewater discharge from member areas. The broad goal of the SJCDWQC is to conform to the Conditional Waiver of the Irrigated Lands Regulatory Program (ILRP) developed by the Central Valley Regional Water Quality Control Board (CVRWQCB) and thereby improve water quality. Monitoring and active outreach are developed by the SJCDWQC Steering Committee. Constituents monitored and associated water quality trigger limits (WQTLs) are defined by the CVRWQCB; the CVRWQCB also reviews and approves all monitoring and activities of the SJCDWQC. To facilitate compliance with the ILRP, the SJCDWQC hired Michael L. Johnson LLC (MLJ-LLC) to provide technical support and sampling services. MLJ-LLC initiates and maintains working contracts with the necessary laboratories, including Agriculture and Priority Pollutants Laboratories Inc. (APPL) in Clovis, Caltest Laboratories (Caltest) in Napa, AQUA-Science in Davis, and North Coast Laboratories Ltd. (NCL) in Arcata.

##### 4.2. Responsibilities of involved parties.

MLJ-LLC is responsible for providing technical support for the selection of sampling locations, techniques and sample collection, including delivery of samples to laboratories, synthesis of data from laboratories, and report submission to the CVRWQCB. MLJ-LLC will submit data to the CVRWQCB and will maintain copies of chains of custody (COC) forms and field sheets at their office. MLJ-LLC will maintain an ILRP SWAMP Comparable database in which the field results and laboratory results are recorded. MLJ-LLC will also submit to the CVRWQCB the reports listed in Table 20. The laboratories mentioned above will provide analytical services for this project in accordance with all method and quality assurance (QA) requirements found in this QAPP, and will return data to MLJ-LLC in both hardcopy and in approved electronic data deliverable (EDD) format.

**Table 1. (Element 4) Personnel responsibilities.**

<b>Name</b>	<b>Organizational Affiliation</b>	<b>Title</b>	<b>Contact Information (Telephone number, fax number, email address.)</b>
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#### 4.3 Quality Assurance Officer role.

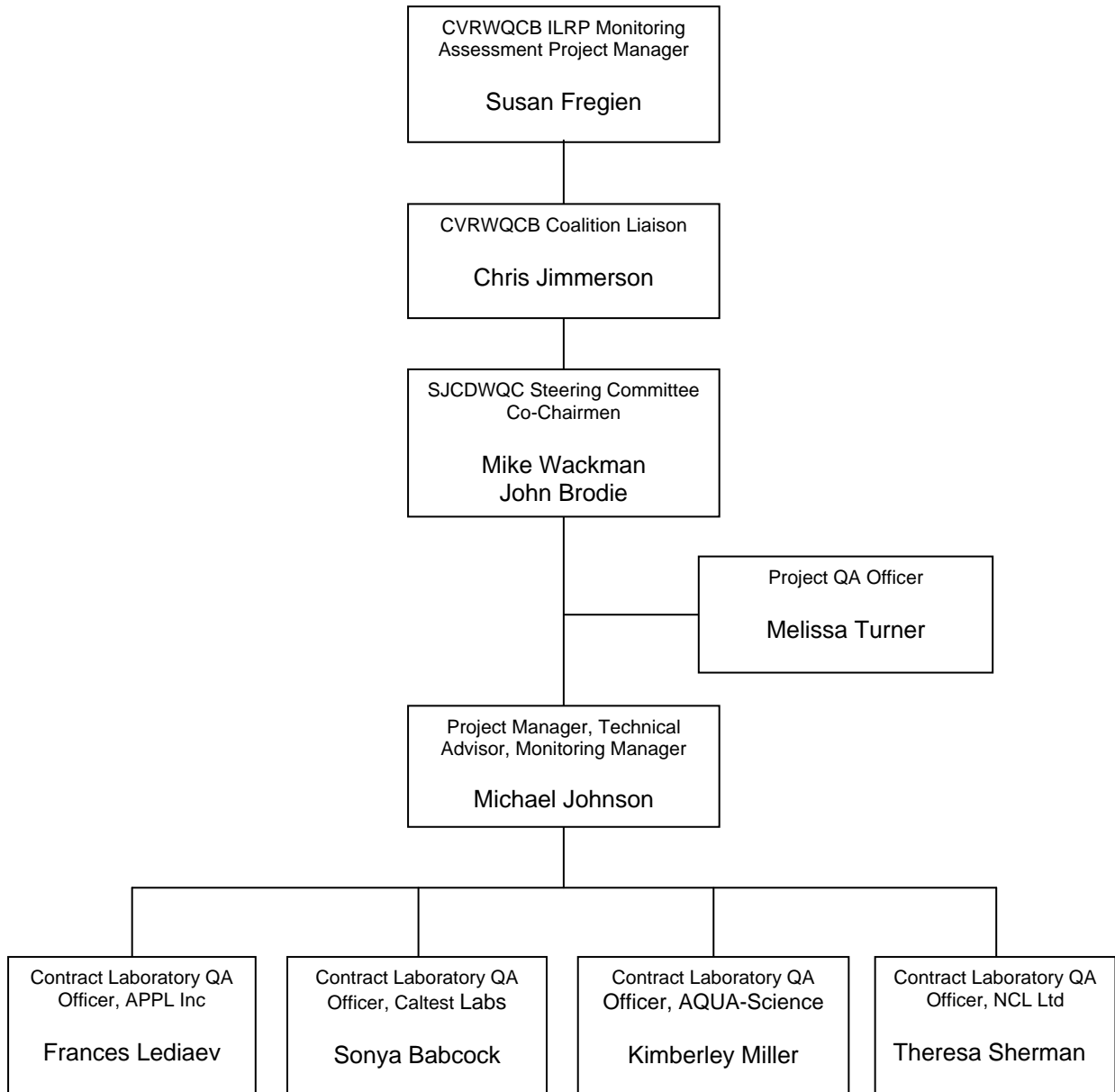
The project QA Officer, Melissa Turner of MLJ-LLC, is responsible for establishing the QA/QC guidelines for field sampling and analysis procedures in this QAPP. In addition to procedural QA/QC, Melissa Turner tracks the percentage of QA/QC samples analyzed during the time frame specified within this QAPP to maintain more than the minimum of 5% field QA/QC samples and 5% or 1 per batch lab QA/QC samples where applicable. Melissa Turner is responsible for reviewing laboratory protocol to confirm laboratory compliance with ILRP analysis guidelines and she is ultimately responsible for reviewing hard-copy and electronic data both for accuracy and SWAMP comparability.

#### 4.4 Persons responsible for QAPP update and maintenance.

Melissa Turner, MLJ-LLC and project QA Officer, is responsible for creating, maintaining, and updating the official approved QAPP. Changes and updates to this QAPP may be made after a review of the evidence for change by CVRWQCB's Project Manager and Quality Assurance Officer, and with the concurrence of the SJCDWQC Steering Committee. The MLJ-LLC QA Officer will be responsible for making the changes, submitting drafts for review, preparing a final copy, and submitting the final version for signature.

4.5 Organizational chart and responsibilities

Figure 1. Organizational chart.



#### 4.6. Project team members and project advisors.

The SJCDWQC monitoring project team is composed of the SJCDWQC Steering Committee (co-chairmen: Mike Wackman & John Brodie) and the QA Officer Melissa Turner of MLJ-LLC. Michael Johnson of MLJ-LLC provides technical support to the SJCDWQC while also managing the monitoring and compiling the data. MLJ-LLC manages the contract laboratories and their individual QA Officers listed in Section 3.1.

## 5. PROBLEM DEFINITION/BACKGROUND

### 5.1 Problem statement.

Agricultural lands are source of water discharged to waters of the State. The discharged water may be initially taken into the irrigation system and subsequently discharged as a result of a variety of practices including flood irrigation or as tail water from furrow irrigation. Discharge may also be the result of rains during the storm season. Once water has passed through an irrigation system its physical properties can change, and on occasion its chemical content may change as well. Examples of the physical changes include increasing water temperature, lowered dissolved oxygen, or increased turbidity. Examples of chemical changes include flushing nutrients, pesticides, or salts from fields into the receiving water body. The effect of return flow on a water body can be reduced water quality sufficiently to limit the potential of the water to be used for this same or other beneficial uses. This project is undertaken to characterize discharge from irrigated agriculture and determine if the discharge is impairing beneficial uses of water bodies. Once impaired water bodies are identified, it is the responsibility of the Coalition to contact members and suggest alternative practices or solutions that may prevent further degradation.

### 5.2 Decisions or outcomes.

The Amended Coalition Group Conditional Waiver of Waste Discharge Requirements for Discharges from Irrigated Lands, Order No. R5-2006-0053 (hereafter referred to as the Conditional Waiver), Monitoring and Reporting Program, Order No. R5-2008-0005 (Order), regulates discharge from agricultural lands. The results of the monitoring outlined in this QAPP will allow the SJCDWQC to determine which water bodies are impaired and institute appropriate outreach measures. Impairment is based on Conditional Waiver WQTLs which were developed based on the CVRWQCB Basin Plan. The WQTL's are set at a level to protect the most sensitive beneficial use for a given constituent.

### 5.3 Water quality or regulatory criteria.

Under the guidelines established by the Conditional Waiver the CVRWQCB set specific WQTLs for a number of parameters and compounds; no waters within Coalition boundaries should exceed these WQTLs. To determine if water discharged within the Coalition area meets the WQTLs, the Coalition conducts monthly monitoring based on the MRPP.

This ongoing project will continue to monitor water quality within the SJCDWQC region (defined in the SJCDWQC Watershed Evaluation Report, submitted April 1, 2004) by regularly analyzing water samples collected from sites within subwatersheds in the region. Field parameters will be measured *in situ*, while physical parameters and chemical content will be analyzed in a laboratory environment. The sampling methods used are adapted from those used in the past by MLJ-LLC; the laboratory analytical methods used are approved EPA methods specific to each compound or test. All methods are explained in detail in the appendices of this QAPP.

Previous monitoring by the SJCDWQC under the Conditional Waiver has characterized water quality issues within the Coalition area as a result of agricultural discharge. Regular monitoring allows Coalition members to take active steps and focus efforts and funding to prevent discharge of waste. Ultimately, the goal of the SJCDWQC is to achieve 100% compliance with all WQTLs through a combination of approaches including but not limited to refining or implementing management practices by the growers responsible for the discharges. The monitoring program will help identify areas in which management practices or different pesticide application practices may be most effective, and also identify areas in which water quality meets the defined objectives. The specific WQTLs that the project has agreed to meet are periodically reviewed and updated; at the time of this QAPP submittal, the WQTLs for each constituent are shown in Table 13 and Table 14 (Element 13), but are subject to change.

## 6. PROJECT DESCRIPTION

### 6.1 Work statement and produced products.

Ambient water and sediment quality monitoring for agricultural discharge will occur using three types of monitoring: Core Monitoring Assessment Monitoring, and Management Plan Monitoring. Combined, these three levels of monitoring are designed to characterize the discharge from irrigated agriculture as a result of irrigation and storm water runoff. Core Monitoring will occur at sites that have undergone intensive monitoring in the past to assess general water quality trends over time. Assessment Monitoring will occur at sites that have not been well characterized by previous monitoring. Samples collected from Assessment Monitoring locations will be analyzed for a large suite of constituents to adequately characterize water quality at those sites. This monitoring strategy allows for comprehensive monitoring in the short term and general trend monitoring over successive years.

The Coalition area has been divided into six zones based on hydrology, crop types, land use, soil types, and rainfall. For a description of each zone's land use, hydrology, precipitation, soil types and crop patterns refer to the Description of Coalition Area section of the Monitoring and Reporting Program Plan (MRPP). The zone names are based on the Core Monitoring location within that area and include: 1) Mokelumne River @ Bruella Zone, 2) French Camp @ Airport Way Zone, 3) Terminous Tract Drain @ Hwy 12 Zone, 4) Roberts Island Drain @ Holt Ave Zone, 5) Lower San Joaquin Zone, and 6) Contra Costa Zone. Each zone will be monitored at one Core Monitoring location and one Assessment Monitoring location. The Assessment Monitoring location will rotate every two years except for Lower San Joaquin Zone and Contra Costa Zone. The Coalition has not previously sampled within the Lower San Joaquin Zone due to the limited amount of agricultural discharge and therefore there will be three Assessment Monitoring locations. Two sites will be monitored within this zone as Assessment Monitoring locations from October 2008 to December 2010 to characterize irrigated agriculture for this entire zone. In 2010 one site will be selected to become the Core Monitoring location and the third site will rotate into the Assessment Monitoring rotation in January 2011. The Contra Costa Zone will not have any Core or Assessment Monitoring locations due to the large amount of urban within the zone. The Coalition will continue to conduct Management Plan monitoring within this zone for previously sampled location (Sand Creek @ Hwy 4 Bypass).

To allow the Coalition to monitor a large number of waterbodies across the six zones, the Assessment Monitoring sites will be rotated every two years. If an Assessment Monitoring site exhibits more than one water quality exceedance within the two years of monitoring, it will become part of the SJCDWQC Management Plan monitoring which requires additional monitoring beyond the initial two years. For site subwatersheds that are currently under a management plan, the Coalition will continue to monitor at that location for the constituents within the management plan for which it is listed. For additional details on the monitoring strategy of the Coalition, refer to the MRPP.

Toxicity tests to assess survival or growth relative to a control sample will occur during assessment monitoring. Highly toxic samples that reduce survival >50% relative to the control or for algae exhibit suppressed growth of >50% relative to the control will undergo a Toxicity Identification Evaluation (TIE), and in cases where there is no survival or growth a dilution series is initiated. The results of toxicity tests will be compared to the results of water column chemical analyses to support a stronger interpretation of each toxicity result.

In addition to the water column analyses the Coalition will conduct sediment quality monitoring twice per year between the dates listed in Table 4. Sediment sampling will consist of a toxicity test to *Hyalella azteca* and additional physical parameters identified in Table 2. Samples which show statistically significantly toxicity to *H. azteca* and exhibit a >20% reduction in survival compared to the control will require pesticide analysis of the pesticides listed in Table 2.

During a calendar year MLJ-LLC will provide the CVRWQCB with exceedance reports within five business days of receiving field and analytical results, as well as three quarterly data deliveries and one annual report. Report requirements are described in the MRPP.

## 6.2 Constituents to be monitored and measurement techniques

All constituents listed in the MRP are included in Table 2 except for fecal coliform (Group A pesticides are listed in Table 3). The Coalition has been monitoring for *E. coli* since 2004 using the water quality trigger limit (WQTL) WQTL of 235 MPN/100mL (a fecal coliform number). *E. coli* is a sub-category of fecal coliform and therefore if the amount of *E. coli* detected in a sample is above the WQTL than it is assumed that the fecal coliform is also above the WQTL and the sample is treated as exceeding a fecal coliform WQTL. It is not necessary therefore to also collect a sample for fecal coliform analysis.

A total of 17 constituents and parameters will be measured at each visit to each Core site, including a three-species water column toxicity test. At each visit to each Assessment site, and every third year for each Core site, a total of 63 constituents and parameters will be measured. Twice per year, once in the storm season and once during irrigation season, sediment will be analyzed for toxicity, total organic carbon, and grain size. Those sediment samples which are demonstrated to be toxic will be analyzed for each of eight pesticides. Measurement techniques for water and sediment constituents vary by analyte and all are listed with the full constituent list in Table 2.

**Table 2. (Element 6) Constituents and parameters.**

Constituents and parameters measured, grouped by category. Laboratory SOPs are available in the appendices.

Constituent	Matrix	Analyzing Lab	Method	Analysis Type	Assessment (A) and/or Core (C) Monitoring
Physical Parameters					
Photo Monitoring	NA	NA	Digital capture	NA	With every event
Flow	Fresh Water	Field Measure	USGS R2Cross streamflow Method	Electromagnetic Induction	A, C
pH	Fresh Water	Field Measure	EPA 150.1	Glass Electrode	A, C
Electrical Conductivity	Fresh Water	Field Measure	EPA 120.1	Electrode Cell	A, C
Dissolved oxygen	Fresh Water	Field Measure	SM 4500-O	Steady State Polarographic	A, C
Temperature	Fresh Water	Field Measure	SM 2550	Thermistor	A, C
Turbidity	Fresh Water	Caltest	EPA 180.1	Nephelometric	A, C
Total Dissolved Solids	Fresh Water	Caltest	SM2540C	Filtration/Evaporation	A, C
Total Suspended Solids	Fresh Water	Caltest	SM2540D	Filtration/Dry Weight	A, C
Hardness	Fresh Water	Caltest	SM2340C	Na <sub>2</sub> EDTA Titration	A, C
Total Organic Carbon	Fresh Water		SM5310B	NDIR Detection	A, C
Pathogens					
Escherichia coli	Fresh Water	Caltest	SM 9223B	Colilert media	A, C
Toxicity					
Water Column Toxicity	Fresh Water	AQUA-Science	EPA 821-R-02-012	Acute 96 Hour Survival	A
	Fresh Water	AQUA-Science	EPA 821-R-02-013	Chronic 96 Hour Growth	A
Sediment Toxicity	Sediment	AQUA-Science	EPA 600/R-99-064	Acute 10 day Survival	A
Carbamates					
Aldicarb	Fresh Water	APPL Inc	EPA 8321	HPLC, ESI/APC, LC/MS	A
Carbaryl	Fresh Water	APPL Inc	EPA 8321	HPLC, ESI/APC, LC/MS	A
Carbofuran	Fresh Water	APPL Inc	EPA 8321	HPLC, ESI/APC, LC/MS	A
Methiocarb	Fresh Water	APPL Inc	EPA 8321	HPLC, ESI/APC, LC/MS	A
Methomyl	Fresh Water	APPL Inc	EPA 8321	HPLC, ESI/APC, LC/MS	A
Oxamyl	Fresh Water	APPL Inc	EPA 8321	HPLC, ESI/APC, LC/MS	A
Organochlorines					
DDD	Fresh Water	APPL Inc	EPA 8081A	GC,ECD	A
DDE	Fresh Water	APPL Inc	EPA 8081A	GC,ECD	A
DDT	Fresh Water	APPL Inc	EPA 8081A	GC,ECD	A
Dicofol	Fresh Water	APPL Inc	EPA 8081A	GC,ECD	A
Dieldrin	Fresh Water	APPL Inc	EPA 8081A	GC,ECD	A
Endrin	Fresh Water	APPL Inc	EPA 8081A	GC,ECD	A
Methoxychlor	Fresh Water	APPL Inc	EPA 8081A	GC,ECD	A
Organophosphates					
Azinphos-methyl	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Chlorpyrifos	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Diazinon	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Dichlorvos	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Dimethoate	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Dimeton-s	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Disulfoton	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Malathion	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Methamidphos	Fresh Water	APPL Inc	EPA 8321	HPLC, ESI/APC, LC/MS	A
Methidathion	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Parathion, methyl	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Phorate	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Phosmet	Fresh Water	APPL Inc	EPA 8141A	Capillary Column, GC/MS	A
Herbicides					
Atrazine	Fresh Water	APPL Inc	EPA 619	GC	A
Cyanazine	Fresh Water	APPL Inc	EPA 619	GC	A
Diuron	Fresh Water	APPL Inc	EPA 8321	HPLC, ESI/APC, LC/MS	A
Glyphosate	Fresh Water	NCL Ltd	EPA 547	DAI HPLC, PCD, FD	A



Constituent	Matrix	Analyzing Lab	Method	Analysis Type	Assessment (A) and/or Core (C) Monitoring
Linuron	Fresh Water	APPL Inc	EPA 8321	HPLC, ESI/APC, LC/MS	A
Paraquat dichloride	Fresh Water	APPL Inc	EPA 549.1	SPE, HPLC, UV detection	A
Simazine	Fresh Water	APPL Inc	EPA 619	GC	A
Trifluralin	Fresh Water	APPL Inc	EPA 8141	Capillary Column, GC/MS	A
Metals					
Arsenic	Fresh Water	Caltest	EPA 200.8	ICP-MS (Collision Cell)	A
Boron	Fresh Water	Caltest	EPA 200.8	ICP-MS (Collision Cell)	A
Cadmium	Fresh Water	Caltest	EPA 200.8	ICP-MS (Collision Cell)	A
Copper	Fresh Water	Caltest	EPA 200.8	ICP-MS (Collision Cell)	A
Lead	Fresh Water	Caltest	EPA 200.8	ICP-MS (Collision Cell)	A
Molybdenum	Fresh Water	Caltest	EPA 200.8	ICP-MS (Collision Cell)	A
Nickel	Fresh Water	Caltest	EPA 200.8	ICP-MS (Collision Cell)	A
Selenium	Fresh Water	Caltest	EPA 200.8	ICP-MS (Reaction Cell)	A
Zinc	Fresh Water	Caltest	EPA 200.8	ICP-MS (Collision Cell)	A
Nutrients					
Total Kjeldahl Nitrogen	Fresh Water	Caltest	SM4500NH3 C	Tecator Auto Titration	A, C
Nitrate (as N)+ Nitrite (as N)	Fresh Water	Caltest	EPA 353.2	Colorimetric, Automated Cadmium Reduction	A, C
Total Ammonia	Fresh Water	Caltest	SM4500NH3 C	Tecator Auto Titration	A, C
Total Phosphorus	Fresh Water	Caltest	SM4500PE	Colorimetric Analysis	A, C
Soluble Orthophosphate	Fresh Water	Caltest	SM4500PE	Colorimetric Analysis	A, C
Sediment					
Bifenthrin	Sediment	Caltest	GCMS-NCI-SIM	GC/MS/SIM	A <sup>1</sup>
Cyfluthrin	Sediment	Caltest	GCMS-NCI-SIM	GC/MS/SIM	A <sup>1</sup>
Cypermethrin	Sediment	Caltest	GCMS-NCI-SIM	GC/MS/SIM	A <sup>1</sup>
Deltamethrin: Tralomethrin	Sediment	Caltest	GCMS-NCI-SIM	GC/MS/SIM	A <sup>1</sup>
Esfenvalerate	Sediment	Caltest	GCMS-NCI-SIM	GC/MS/SIM	A <sup>1</sup>
Lambda-Cyhalothrin	Sediment	Caltest	GCMS-NCI-SIM	GC/MS/SIM	A <sup>1</sup>
Permethrin	Sediment	Caltest	GCMS-NCI-SIM	GC/MS/SIM	A <sup>1</sup>
Fenpropathrin	Sediment	Caltest	GCMS-NCI-SIM	GC/MS/SIM	A <sup>1</sup>
Chlorpyrifos	Sediment	Caltest	GCMS-NCI-SIM	GC/MS/SIM	A <sup>1</sup>
Total Solids	Sediment	Caltest	SM2540B	Gravimetric	A
Total Organic Carbon	Sediment	Caltest <sup>2</sup>	Walkley Black	Oxidation & Titration	A <sup>5</sup>
Grain Size	Sediment	Caltest <sup>2</sup>	ASTM D-422-63 <sup>3</sup> , ASTM D4464M-85 <sup>4</sup>	Dry Sieve <sup>3</sup> & Laser Light Scattering <sup>4</sup>	A <sup>5</sup>

NDIR: Non-dispersive infrared

HPLC: High performance liquid chromatography

ESI: Electrospray ionization

APC: Atmospheric pressure chemical ionization

LC: Liquid chromatography

MS: Mass spectrometry

ICP-MS: Inductively coupled plasma mass spectroscopy

<sup>1</sup> If needed based on criteria described in text above

<sup>2</sup> Subcontracted to PTS Geo Laboratories

<sup>3</sup> For particle sizes 6.351-0.037 mm

<sup>4</sup> For particle sizes 0.4-2000 µm

<sup>5</sup> Simultaneous with sediment toxicity sampling

GC: Gas Chromatography

ECD: Electron capture detector

DAI: Direct aqueous injection

PCD: Post column detection

FDe: Fluorescence detection

SPE: Solid phase extraction

SIM: Selective Ion Monitoring

Special project monitoring will include specific targeted studies for the implementation of a Management Plan that results from more than one exceedance within three years of either Core or Assessment Monitoring. Monitoring for Management Plans may include more extensive monitoring than what is required in the Core Monitoring or Assessment Monitoring schedules. The schedule for Special Project Monitoring will be determined as outlined in the SJCDWQC Management Plan which is updated on a yearly basis. Special project monitoring may also occur in areas where targeted source identification studies must take place or Total Maximum Daily Load (TMDL) studies are required (refer to the Special Project Monitoring section of the MRPP for a list of all 303(d) listed water bodies). Of all 303(d) listed causes of impairment, the Coalition has monitored for all constituents in all portions of the Delta with the exception of the Group A pesticides and diazinon in Zone 4 (which would be representative of the reach of Five Mile Slough from Alexandria Place to Fourteen Mile Slough).

The Coalition will monitor Group A pesticides at four sites: Mokelumne River @ Bruella Road, Duck Creek @ Highway 4, Drain @ Woodbridge Road, and Roberts Island Drain @ Holt Road. Of these four, the Drain @ Woodbridge Road is a new site and will have the full Assessment Monitoring, the other three sites are Core Monitoring sites and will have Group A pesticides added to the suite of constituents. These four sites will be representative of 303(d) listed sites in the four portions of the Delta in the Coalition region. Group A pesticides are considered legacy pesticides and the most recent use of any Group A pesticide was in 2006 (endosulfan). Therefore, if the Coalition does not detect any Group A pesticides during 2008/2009 monitoring, the Coalition will have demonstrated that these pesticides are not negatively affecting water quality and will discontinue monitoring for Group A pesticides in 2010. The status of TMDLs and 303(d) listed water bodies and their associated constituents will be reviewed annually in the Annual Monitoring Report.

**Table 3. (Element 6) Additional constituents monitored for CWA 303(d) compliance.**

Site Name	Constituent	Matrix	Analyzing Lab	Method	Analysis Type	Assessment (A) and/or Core (C) Monitoring
Mokelumne River @ Bruella Rd	Aldrin	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies
	Chlordane	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies
	Heptachlor	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies
Duck Creek @ Highway 4	Heptachlor epoxide	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies
	Hexachlorocyclohexane (alpha-BHC)	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies
Drain @ Woodbridge Rd	Hexachlorocyclohexane (beta-BHC)	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies
	Hexachlorocyclohexane (gamma-BHC; Lindane)	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies
Roberts Island Drain @ Holt Rd	Hexachlorocyclohexane (delta-BHC)	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies
	Endosulfan	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies
	Toxaphene	Fresh Water	APPL Inc	EPA 8081A	GC, ECD	As needed to characterize 303d listed waterbodies

### 6.3 Project schedule

The project will advance with deliverable dates outlined in the table below. The table provides dates for the first year this QAPP is active. Beyond 2009 the year advances but the month and day of each date will remain roughly the same. If in subsequent years the deliverable due date is not a weekday it will change to the first business day after the due date.

**Table 4. (Element 6) Project schedule timeline.**

Activity	Date (MM/DD/YY)		Deliverable	Deliverable Due Date
	Anticipated Date of Initiation	Anticipated Date of Completion		
Prior Year Monitoring	01/01/09	12/31/09	Annual Monitoring Report	03/01/10
Quarter 1 Monitoring, Monthly	01/01/09	03/31/09	Quarterly Monitoring Data Report	06/01/09
Sediment Monitoring #1	03/01/09	04/30/09	Results included in Quarterly Monitoring Report	Either 06/01/09 or 09/01/09
Quarter 2 Monitoring, Monthly	04/01/09	06/30/09	Quarterly Monitoring Data Report	09/01/09
Quarter 3 Monitoring, Monthly	07/01/09	09/30/09	Quarterly Monitoring Data Report	12/01/09
Sediment Monitoring #2	08/15/09	10/15/09	Results included in Quarterly or Annual Monitoring Report	Either 12/01/09 or 03/01/10

#### 6.4 Geographical setting.

The Coalition region includes parts of San Joaquin, Contra Costa, Alameda and Calaveras counties and comprises approximately 1,057,350 acres of which 548,362 (52%) are considered irrigated agriculture. The County Agricultural Commissioner's offices, for San Joaquin, Contra Costa, Alameda and Calaveras Counties, note that there are 520,172 acres, 22,000 acres, 3,695 acres and 2,495 acres of irrigated farm lands in the Coalition region respectively in their counties (San Joaquin acreage is from the 2002 Agricultural Report). Contra Costa, Alameda and Calaveras County acreages are estimates because not all of the county area is within the Coalition area.

The northern border of the Coalition area corresponds to the county line between San Joaquin and Sacramento Counties. The eastern portion of the Coalition area was expanded in April of 2004 and now includes portions of Calaveras County that are the upper Calaveras River, Bear Creek, and Mokelumne River subwatersheds. These subwatersheds extend from San Joaquin County into Calaveras County. Agricultural land use in this part of the Coalition area is primarily orchards and vineyards and includes a very small amount of irrigated agriculture. The southern border of the Coalition area is the Stanislaus River with the exception of the Del Puerto and West Stanislaus Irrigation Districts at the southern edge of the Coalition area, which are not covered by the Coalition. The Coalition boundary at the southwest corner of San Joaquin County is approximately that of the Delta Mendota Canal and California Aqueduct. The western boundary of the Coalition area has also been expanded and now lies along the western boundary of the CVRWQCB (Region 5) in Contra Costa County and Alameda County. There are several small subwatersheds in this portion of the Coalition region including the Kellogg Creek, Marsh Creek, Sand Creek, and Brushy Creek subwatersheds that drain from Mount Diablo. These water bodies flow east through urban areas on the western edge of the central Delta. Growers from these areas joined the Coalition at its inception and the expansion of the Coalition boundary is a formal recognition of their membership in the Coalition.

Within the Coalition area, the lower reaches of the San Joaquin River drain the California Central Valley (Valley). Drainage water is either exported to the San Francisco Bay through the Delta, or conveyed southward via the State Water Project and the Delta Mendota Canal. There are three major rivers in the Coalition area other than the San Joaquin River: Stanislaus River, Calaveras River, and Mokelumne River. These east side tributaries of the San Joaquin River drain a major portion of the Sierra Nevada Mountain range from east to west. The watershed of the Coalition area is the crest of the Sierra Nevada, and the drainage area is bounded by the San Joaquin River on the west, the Stanislaus River on the south, and the Mokelumne River on the north. Intermediate sized water bodies in the Coalition region (Littlejohns Creek, Duck Creek, Lone Tree Creek, Bear Creek, French Camp Slough, Dry Creek, Marsh Creek, Mormon Slough, Mosher Creek, and Pixley Slough) are tributaries to either one of the major rivers

or discharge to the San Joaquin Delta. Smaller water bodies found in the Coalition area are primarily canals and ditches that convey water to one of the larger rivers or intermediate creeks/sloughs, or are used to drain Delta islands (Figure 1).

The San Joaquin County Delta Water Quality Coalition topography varies greatly from the foothills of the Coast range to the delta islands up to the Sierras. Due to this large diversity in topography and weather, agriculture is only occurring in the flatter, more temperate valley and delta regions. The coastal range is too dry to farm and the Sierras are too cold and rocky, with a short growing season due the snow at higher elevations. The snow melt from the Sierras melts in the early spring to provide water to the Mokelumne and Calaveras Rivers. This snow pack helps provide runoff later into the spring and summer providing water for a longer irrigation season for corps in the valley.

#### 6.5 Photo monitoring

A minimum of four photos of each sampling site will be submitted to the CVRWQCB with the Annual Monitoring Report along with the target GPS coordinates. The photos will depict a general site overview, an upstream view, a downstream view, and the entrance to the location where the samples are collected.

#### 6.6 Constraints

Certain periods of high runoff volume, such as during intense storms, may completely flush contaminants through a water system before they can be captured and measured. Assessment of water quality for the Conditional Waiver is thus a best estimate based on discrete instantaneous measurements.

Water quality parameters may be expressed as instantaneous load ( $\mu\text{g}$  constituent/second). This method of expressing load is not always accurate for some reasons and not always possible for other reasons, including that the water body may flow intermittently and so may not be flowing during the sampling visit, or the sampler may be unable to measure discharge safely when a sample is collected.

## 7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

### 7.1. Data quality objectives.

Data quality objectives are listed below and in Tables 5-7.

<u>Measurement or Analyses Type</u>	<u>Applicable Data Quality Objective</u>
Field Measurements	Accuracy, Precision, Completeness
Physical Parameters	Accuracy, Precision, Completeness, Recovery
Toxicity	Precision, Completeness
Pathogens	Precision, Completeness, Contamination
Nutrients	Accuracy, Precision, Completeness, Recovery, Contamination
Metals	Accuracy, Precision, Completeness, Recovery, Contamination
Carbamates	Accuracy, Precision, Completeness, Recovery, Contamination
Organochlorines	Accuracy, Precision, Completeness, Recovery, Contamination
Organophosphates	Accuracy, Precision, Completeness, Recovery, Contamination
Pyrethroids	Accuracy, Precision, Completeness, Recovery, Contamination
Herbicides	Accuracy, Precision, Completeness, Recovery, Contamination

Data quality objectives for accuracy, precision, completeness, recovery, and contamination are determined through a combination of instrument calibration and the analysis of duplicates, blanks, and spikes. Completeness is assessed with each annual monitoring report based on the number of samples successfully obtained and validated for use and the proportion of quality control samples that are within acceptance criteria.

Field measurements are taken with a YSI 556 MPS multi-parameter system and a Marsh McBirney FloMate 2000; accuracy and precision are measured during calibration (if applicable), taking into account the manufacturers specifications. For all other types of analysis accuracy, precision, and recovery are assessed through use of QC samples, including lab spikes and matrix spikes to assess accuracy and recovery, and lab and field duplicates to assess precision.

### 7.2 Project action limits.

Project action limits, also referred to as WQTLs, are listed in Table 13 and Table 14 (Element 13).

### 7.3 Acceptance criteria of previously collected information.

All data used by this project must meet the accuracy, precision, and recovery criteria in Tables 5-7 (where applicable). Data that fails to meet the criteria will undergo a review following the guidelines established in Group D, Element 22 of this QAPP before being accepted for use.

**Table 5. (Element 7) Data quality objectives for field and laboratory accuracy, precision, and completeness measurements.**

Data quality objectives in measurements of accuracy, precision, and completeness.

Constituent	Matrix	Matrix Spike Frequency <sup>†</sup>	Lab Control Spike Frequency <sup>†</sup>	Accuracy/ Recovery	Lab Duplicate Frequency <sup>†</sup>	Precision	Completeness
Physical Parameters							
Flow	Fresh Water	N/A	N/A	±2%	1 per batch	±2%	90%
pH	Fresh Water	N/A	N/A	±0.5 units	1 per batch	±0.5 units	90%
Specific Conductivity	Fresh Water	N/A	N/A	±5%	1 per batch	±5%	90%
Dissolved oxygen	Fresh Water	N/A	N/A	±0.5 mg/L	1 per batch	±0.5 mg/L or ±10%	90%
Temperature	Fresh Water	N/A	N/A	±0.5°C	1 per batch	±0.5°C or 10%	90%
Turbidity	Fresh Water	N/A	N/A	N/A	1 per batch	RPD ≤ 20%	90%
Total Dissolved Solids	Fresh Water	N/A	N/A	N/A	1 per batch	RPD ≤ 20%	90%
Total Suspended Solids	Fresh Water	N/A	N/A	N/A	1 per batch	RPD ≤ 20%	90%
Hardness	Fresh Water	1 per batch	1 per batch	80-120%	1 per batch	RPD ≤ 20%	90%
Total Organic Carbon	Fresh Water	1 per batch	1 per batch	80-120%	1 per batch	RPD ≤ 20%	90%
Pathogens							
Escherichia coli	Fresh Water	1 per batch	1 per batch	N/A	1 per batch	R <sub>log</sub> ≤ 3.27*mean R <sub>log</sub>	90%
Toxicity							
Water Column Toxicity	Fresh Water	1 per batch	1 per batch	N/A	1 per batch	RPD ≤ 25%	90%
Sediment Toxicity	Sediment	1 per batch	1 per batch	N/A	1 per batch	RPD ≤ 25%	90%
Carbamates							
Aldicarb	Fresh Water	1 per batch	1 per batch	31-133%	1 per batch	RPD ≤ 25%	90%
Carbaryl	Fresh Water	1 per batch	1 per batch	44-133%	1 per batch	RPD ≤ 25%	90%
Carbofuran	Fresh Water	1 per batch	1 per batch	36-165%	1 per batch	RPD ≤ 25%	90%
Methiocarb	Fresh Water	1 per batch	1 per batch	35-142%	1 per batch	RPD ≤ 25%	90%
Methomyl	Fresh Water	1 per batch	1 per batch	23-152%	1 per batch	RPD ≤ 25%	90%
Oxamyl	Fresh Water	1 per batch	1 per batch	10-117%	1 per batch	RPD ≤ 25%	90%
Organochlorines							
DDD	Fresh Water	1 per batch	1 per batch	38-135%	1 per batch	RPD ≤ 25%	90%
DDE	Fresh Water	1 per batch	1 per batch	21-134%	1 per batch	RPD ≤ 25%	90%
DDT	Fresh Water	1 per batch	1 per batch	18-145%	1 per batch	RPD ≤ 25%	90%
Dicofol	Fresh Water	1 per batch	1 per batch	40-135%	1 per batch	RPD ≤ 25%	90%
Dieldrin	Fresh Water	1 per batch	1 per batch	48-121%	1 per batch	RPD ≤ 25%	90%
Endrin	Fresh Water	1 per batch	1 per batch	24-143%	1 per batch	RPD ≤ 25%	90%
Methoxychlor	Fresh Water	1 per batch	1 per batch	30-163%	1 per batch	RPD ≤ 25%	90%
Organophosphates							
Azinphos-methyl	Fresh Water	1 per batch	1 per batch	36-189%	1 per batch	RPD ≤ 25%	90%
Chlorpyrifos	Fresh Water	1 per batch	1 per batch	61-125%	1 per batch	RPD ≤ 25%	90%
Diazinon	Fresh Water	1 per batch	1 per batch	57-130%	1 per batch	RPD ≤ 25%	90%
Dichlorvos	Fresh Water	1 per batch	1 per batch	10-175%	1 per batch	RPD ≤ 25%	90%
Dimethoate	Fresh Water	1 per batch	1 per batch	68-202%	1 per batch	RPD ≤ 25%	90%
Dimeton-s	Fresh Water	1 per batch	1 per batch	40-125%	1 per batch	RPD ≤ 25%	90%
Disulfoton	Fresh Water	1 per batch	1 per batch	47-117%	1 per batch	RPD ≤ 25%	90%
Malathion	Fresh Water	1 per batch	1 per batch	47-125%	1 per batch	RPD ≤ 25%	90%
Methamidiphos	Fresh Water	1 per batch	1 per batch	25-136%	1 per batch	RPD ≤ 25%	90%
Methidathion	Fresh Water	1 per batch	1 per batch	50-150%	1 per batch	RPD ≤ 25%	90%
Parathion, methyl	Fresh Water	1 per batch	1 per batch	55-164%	1 per batch	RPD ≤ 25%	90%
Phorate	Fresh Water	1 per batch	1 per batch	44-117%	1 per batch	RPD ≤ 25%	90%
Phosmet	Fresh Water	1 per batch	1 per batch	50-150%	1 per batch	RPD ≤ 25%	90%
Herbicides							
Atrazine	Fresh Water	1 per batch	1 per batch	39-156%	1 per batch	RPD ≤ 25%	90%
Cyanazine	Fresh Water	1 per batch	1 per batch	22-172%	1 per batch	RPD ≤ 25%	90%
Diuron	Fresh Water	1 per batch	1 per batch	52-136%	1 per batch	RPD ≤ 25%	90%
Glyphosate	Fresh Water	1 per batch	1 per batch	85.7-121%	1 per batch	RPD ≤ 25%	90%
Linuron	Fresh Water	1 per batch	1 per batch	49-144%	1 per batch	RPD ≤ 25%	90%
Paraquat dichloride	Fresh Water	1 per batch	1 per batch	50-141%	1 per batch	RPD ≤ 25%	90%
Simazine	Fresh Water	1 per batch	1 per batch	21-179%	1 per batch	RPD ≤ 25%	90%
Trifluralin	Fresh Water	1 per batch	1 per batch	40-148%	1 per batch	RPD ≤ 25%	90%
Metals							

Constituent	Matrix	Matrix Spike Frequency <sup>†</sup>	Lab Control Spike Frequency <sup>†</sup>	Accuracy/ Recovery	Lab Duplicate Frequency <sup>†</sup>	Precision	Completeness
Arsenic	Fresh Water	1 per batch	1 per batch	85-115%	1 per batch	RPD ≤ 20%	90%
Boron	Fresh Water	1 per batch	1 per batch	85-115%	1 per batch	RPD ≤ 20%	90%
Cadmium	Fresh Water	1 per batch	1 per batch	85-115%	1 per batch	RPD ≤ 20%	90%
Copper	Fresh Water	1 per batch	1 per batch	85-115%	1 per batch	RPD ≤ 20%	90%
Lead	Fresh Water	1 per batch	1 per batch	85-115%	1 per batch	RPD ≤ 20%	90%
Molybdenum	Fresh Water	1 per batch	1 per batch	85-115%	1 per batch	RPD ≤ 20%	90%
Nickel	Fresh Water	1 per batch	1 per batch	85-115%	1 per batch	RPD ≤ 20%	90%
Selenium	Fresh Water	1 per batch	1 per batch	85-115%	1 per batch	RPD ≤ 20%	90%
Zinc	Fresh Water	1 per batch	1 per batch	85-115%	1 per batch	RPD ≤ 20%	90%
Nutrients							
Total Kjeldahl Nitrogen	Fresh Water	1 per batch	1 per batch	90-110%	1 per batch	RPD ≤ 20%	90%
Nitrate (as N)+ Nitrite (as N)	Fresh Water	1 per batch	1 per batch	90-110%	1 per batch	RPD ≤ 20%	90%
Total Ammonia	Fresh Water	1 per batch	1 per batch	90-110%	1 per batch	RPD ≤ 20%	90%
Total Phosphorus	Fresh Water	1 per batch	1 per batch	90-110%	1 per batch	RPD ≤ 20%	90%
Soluble Orthophosphate	Fresh Water	1 per batch	1 per batch	90-110%	1 per batch	RPD ≤ 20%	90%
Sediment Sampling							
Bifenthrin	Sediment	1 per batch	1 per batch	10-160%	1 per batch	RPD ≤ 25%	90%
Cyfluthrin	Sediment	1 per batch	1 per batch	10-160%	1 per batch	RPD ≤ 25%	90%
Cypermethrin	Sediment	1 per batch	1 per batch	10-160%	1 per batch	RPD ≤ 25%	90%
Deltamethrin:Tralomethrin	Sediment	1 per batch	1 per batch	10-160%	1 per batch	RPD ≤ 25%	90%
Esfenvalerate	Sediment	1 per batch	1 per batch	10-160%	1 per batch	RPD ≤ 25%	90%
Lambda-Cyhalothrin	Sediment	1 per batch	1 per batch	10-160%	1 per batch	RPD ≤ 25%	90%
Permethrin	Sediment	1 per batch	1 per batch	10-160%	1 per batch	RPD ≤ 25%	90%
Fenpropathin	Sediment	1 per batch	1 per batch	10-160%	1 per batch	RPD ≤ 25%	90%
Chlorpyrifos	Sediment	1 per batch	1 per batch	10-160%	1 per batch	RPD ≤ 25%	90%
Total Solids	Sediment	N/A	N/A	N/A	1 per batch	RPD ≤ 25%	90%
Total Organic Carbon	Sediment	N/A	1 per batch	75-125%	1 per batch	RPD ≤ 20%*	90%
Grain Size	Sediment	N/A	N/A	N/A	1 per batch	RPD ≤ 25%	90%

<sup>†</sup>Either a matrix spike duplicate or a lab control spike duplicate may function as the lab duplicate in any batch. A CRM may be used in place of a lab control spike.

\*if result > 10x MDL

**Table 6. (Element 7). Data quality objectives for field and laboratory accuracy and precision measurements of additional constituents monitored for CWA 303(d) compliance.**

Data quality objectives in measurements of accuracy, precision, and completeness of constituents monitored for CWA 303(d) compliance. Either a Matrix Spike duplicate or a Lab Control Spike duplicate may function as the lab duplicate in any batch.

Site Name	Constituent	Matrix	Matrix Spike/Lab Control Spike Frequency	Accuracy/Recovery	Lab Duplicate Frequency	Precision	Completeness
Mokelumne River @ Bruella Rd	Aldrin	Fresh Water	1 per batch	11-138%	1 per batch	RPD ≤ 25%	90%
	Chlordane	Fresh Water	1 per batch	44-152%	1 per batch	RPD ≤ 25%	90%
	Heptachlor	Fresh Water	1 per batch	24-124%	1 per batch	RPD ≤ 25%	90%
	Heptachlor epoxide	Fresh Water	1 per batch	58-109%	1 per batch	RPD ≤ 25%	90%
Duck Creek @ Highway 4	Hexachlorocyclohexane (alpha-BHC)	Fresh Water	1 per batch	33-111%	1 per batch	RPD ≤ 25%	90%
	Hexachlorocyclohexane (beta-BHC)	Fresh Water	1 per batch	49-119%	1 per batch	RPD ≤ 25%	90%
Drain @ Woodbridge Rd	Hexachlorocyclohexane (gamma-BHC; Lindane)	Fresh Water	1 per batch	40-114%	1 per batch	RPD ≤ 25%	90%
	Hexachlorocyclohexane (delta-BHC)	Fresh Water	1 per batch	12-97%	1 per batch	RPD ≤ 25%	90%
Roberts Island Drain @ Holt Rd	Endosulfan I	Fresh Water	1 per batch	50-131%	1 per batch	RPD ≤ 25%	90%
	Endosulfan II	Fresh Water	1 per batch	55-128%	1 per batch	RPD ≤ 25%	90%
	Toxaphene	Fresh Water	1 per batch	23-140%	1 per batch	RPD ≤ 25%	90%

**Table 7. (Element 7) Data quality objectives for field and laboratory contamination measurements.**

Includes additional constituents monitored for CWA 303(d) compliance.

Group	Field/Method Blank Criterion	Field Blank Frequency	Method Blank Frequency
Physical Parameters	FB < RL or < sample/5, MB < RL or if n≥3 avg ±2 s.d < RL	5%	1 per batch
Toxicity	NA	NA	NA
Pathogens	FB < RL or < sample/5, MB < RL or if n≥3 avg ±2 s.d < RL	5%	1 per batch
Nutrients	FB < RL or < sample/5, MB < RL or if n≥3 avg ±2 s.d < RL	5%	1 per batch
Metals	FB < RL or < sample/5, MB < RL or if n≥3 avg ±2 s.d < RL	5%	1 per batch
Carbamates	FB < RL or < environmental sample/5	5%	1 per batch
Organochlorines	FB < RL or < environmental sample/5	5%	1 per batch
Organophosphates	FB < RL or < environmental sample/5	5%	1 per batch
Pyrethroids	FB < RL or < environmental sample/5	5%	1 per batch
Herbicides	FB < RL or < environmental sample/5	5%	1 per batch

FB: Field Blank  
MB: Method Blank  
RL: Reporting Limit



#### 7.4. Precision and accuracy as pertains to this data set.

Data quality will be attained by maximizing the accuracy and precision of the methods used. Any changes in procedures due to equipment changes or to improved precision and accuracy will be documented. All analyses and determinations must be performed by qualified personnel in conformance with all current EPA standards and procedures. All laboratories under contract by MLJ-LLC will employ only methods and techniques which have been determined to produce measurement data of a known and verifiable quality and which are of quality sufficient to meet the overall objectives of the project.

#### 7.5. Representativeness and completeness.

Sampling locations are selected to represent agricultural discharges within a zone. Requirements for selecting sample sites are discussed in more detail in the MRPP. Only approved/documented sample collection methods, sample transport/holding methods, and analytical methods will be used to ensure that the measurement data represents the conditions at the sample site to the extent possible. The water bodies monitored are physically dynamic and may be altered by rate of flow, dredging, aquatic vegetation, rate of discharge/input, and many other factors. Locations and methodology are chosen to maximize representativeness, where possible and applicable; however, the samples collected can only represent the specific time and place where collected.

Completeness is defined as a measure of the amount of valid data obtained from a measurement system as compared to the planned amount. Project completeness is divided into two areas: field and transport completeness and laboratory completeness. The completeness goal of 90% is the combination of these two areas on an annual basis.

Field and transport completeness requires that samplers successfully visit each site, document the visit and collect the field information and samples as outlined in Elements 10-12. In addition, the samples must be successfully transported to the laboratories. A properly documented dry site does not reduce the completeness of the event.

Laboratory completeness refers to the process of sample reception, COC documentation, storage and in-house preservation, extraction, analysis, and laboratory QA/QC.

#### 7.6. Minimizing bias.

Bias in sample timing is minimized by using a predetermined sample schedule that rigidly defines the sample dates for each site months in advance. In this way sampling at any given site will not be subjectively influenced by temporal factors that risk introducing intentional or unintentional sampling bias, such as irrigation events or weather patterns.

Bias in field sampling quality control monitoring is minimized by randomly distributing QC samples among all sites throughout the year. Additionally, the samplers collecting the QC samples are randomly assigned to minimize the chances of a single site or single sampler exerting more influence on overall sample quality than randomness would predict.

Bias in analysis is minimized through the use of professional, private, objective third-party labs. Any potential bias that may be introduced by these labs is assessed with semi-blind QC samples; field QC samples are not overtly identified to the lab.

Sediment sample collection is intentionally biased towards the finest sediments available, which are most likely to have been most recently deposited and are also most likely contain high  $K_{OC}$  compounds. These samples may not thoroughly represent the area of sample collection, but are necessary to achieve the goals of the program.

## 8. SPECIAL TRAINING NEEDS/CERTIFICATION

### 8.1 Specialized training or certifications.

All personnel performing sampling are trained in proper sampling techniques under the supervision of the QA Officer at MLJ-LLC, Melissa Turner. Training includes a review of all Standard Operating Procedures (SOPs) and detailed information on filling sample bottles for the various types of analysis (some constituents have specific SOPs; see appendices), proper procedures for filling field QC samples, and measuring discharge with a Marsh McBirney FloMate 2000 and Rickly Hydrological wading rod. Other topics covered are sample transport, calibration use and maintenance of YSI meters, GPS use and sample site confirmation. To further safeguard against sampling error, all sampling by recently trained personnel is done under the supervision of more experienced personnel who accompany sampling crews each time they go in the field for reference at any time. The field and laboratory SOPs in the appendices to this document are available for all staff to familiarize themselves. In addition to sampling training all sampling staff attend a field safety course presented by the MLJ-LLC QA Officer, Melissa Turner. Field safety is supplemented by a brief course in office safety and ergonomics.

### 8.2 Training personnel.

Melissa Turner, MLJ-LLC QA Officer, is responsible for training all sampling personnel in field sampling and safety. Assistance is provided by the MLJ-LLC Sampling Coordinator, Frank Wulff.

**Table 8. (Element 8) Specialized personnel training or certification.**

Specialized Training Course Title or Description	Training Provider	Personnel Receiving Training/ Organizational Affiliation	Location of Records & Certificates
Field Sampling (4 hours)	Melissa Turner and Frank Wulff, MLJ-LLC	All MLJ-LLC Sampling Personnel	MLJ-LLC Office
Field Safety/Office Safety (4 hours)	Melissa Turner and Frank Wulff, MLJ-LLC	All MLJ-LLC Sampling Personnel	MLJ-LLC Office

### 8.3 Training and certification documentation.

All training of sampling personnel is done at or near the MLJ-LLC office in Davis, CA. Training courses and refresher courses are presented twice annually, approximately every six months; once before storm season and again before irrigation season. Training generally consists of a lecture and presentation, a variety of supporting literature, a field excursion, and occasionally a quiz. Attendance at each training event is documented with the date and trainer noted.

### 8.4. Training and certification oversight.

It is the responsibility of the QA officers to ensure that all employees achieve satisfactory training, including any necessary certifications. This includes the sampling QA Officer and the QA Officers of the contract laboratories. Signatures of participants are collected as evidence of attendance and this documentation is kept in the MLJ-LLC office.

### 8.5. Obtaining training and certification records.

To obtain copies of sampler training materials and documentation contact the MLJ-LLC QA Officer, Melissa Turner. Contract laboratory training and certification records can be obtained from the contract laboratory QA Officer identified in Element 1.6 of this QAPP.

## **9. DOCUMENTS AND RECORDS**

### **9.1. Report format.**

MLJ-LLC maintains field records, sample records, and data records for each sample collected. Many of these records are presented to the CVRWQCB in the Quarterly Monitoring Reports or the Annual Monitoring Report; originals and occasionally copies of all records are kept at the MLJ-LLC office. Any records not available within a Quarterly or Annual Monitoring Report may be requested from MLJ-LLC.

Reports from the laboratories are received both as hard copies and in a SWAMP comparable EDD which is uploaded into a SWAMP comparable ILRP database by the MLJ-LLC QA Officer Melissa Turner.

### **9.2. Additional documents and records.**

All samples collected are accompanied to the lab by a chain of custody (COC) form which identifies continuous sample custody from collection to login at the laboratory. Field data gathered at the time of sample collection is recorded on field sheets, along with positive confirmation of sampling location (latitude/longitude coordinates and photos), and entered into a SWAMP comparable database.

The exceedance reports will be submitted electronically to the CVRWQCB throughout the year following each sampling event as needed. Copies of each exceedance report will be retained at the MLJ-LLC office and incorporated into the Annual Monitoring Report, which is submitted to the CVRWQCB in both hard-copy and digital form.

### **9.3. Document and record archives.**

Melissa Turner, MLJ-LLC QA Officer, will maintain all sample collection, chain of custody, and field analyses forms at the MLJ-LLC office for a minimum of five years. The respective laboratories will maintain all records associated with the receipt and analysis of samples analyzed for pesticides for at least five years. All electronic data entered into a SWAMP comparable database will be permanently stored in the database. CVRWQCB coalition liaison Chris Jimmerson will oversee the actions of these persons and will arbitrate any issues relative to records retention and any decisions to discard records.

**Table 9. (Element 9) Document and record retention, archival, and disposition information.**

<b>Record Type</b>	<b>Record Needed</b>	<b>Retention</b>	<b>Archival</b>	<b>Disposition</b>
Sample Collection Records	COC forms	Original at lab or at MLJ-LLC Office	Copies at MLJ-LLC Office	Stored at lab or in MLJ-LLC office for at least 5 years
Field Records	Field Sheets	MLJ-LLC Office	MLJ-LLC Office	Stored in MLJ-LLC office for at least 5 years
Analytical Records	Hard Copy Lab Reports	MLJ-LLC Office	MLJ-LLC Office	Stored in MLJ-LLC office for at least 5 years
	Electronic Data Deliverables	MLJ-LLC office	MLJ-LLC Office	Stored in MLJ-LLC office for at least 5 years
Data Records	ILRP SWAMP Comparable Database	UCD AEAL Office	UCD AEAL Office	Permanent Storage at UCD AEAL
Assessment Records	Event Exceedance Reports	MLJ-LLC office	MLJ-LLC Office and CVRWQCB	Permanent Storage at CVRWQCB
	Quarterly Monitoring Reports	MLJ-LLC office	MLJ-LLC Office and CVRWQCB	Permanent Storage at CVRWQCB
	Annual Monitoring Reports	MLJ-LLC office	MLJ-LLC Office and CVRWQCB	Permanent Storage at CVRWQCB

9.4. Electronic record backups.

Melissa Turner, MLJ-LLC QA Officer, will maintain the database; data management procedures including back-up plans for data stored electronically are outlined in Element 19 of this QAPP.

9.5. QAPP distribution.

Copies of this QAPP will be distributed to all parties involved with the project. Hard copies will be sent to all labs for review and reference. Any future amended QAPPs will be held and distributed in the same fashion. All originals and subsequent amended QAPPs will be held at the CVRWQCB. Copies of versions, other than the most current, will be discarded.

## **GROUP B: DATA GENERATION AND ACQUISITION**

### **10. SAMPLING PROCESS DESIGN**

For full sampling process design, see the Monitoring and Reporting Program Plan (MRPP) submitted to the CVRWQCB. The MRPP can be requested from Melissa Turner, QA Officer at MLJ-LLC, or Chris Jimmerson, Coalition liaison at the CVRWQCB. A brief summary of the MRPP description is reproduced below.

The Coalition area has been divided into six zones based on hydrology, crop types, land use, soil types, and rainfall. For a description of each zone in regards to land use, hydrology, precipitation, soil types and crop patterns refer to the Description of Coalition Area section in the MRPP. The zone names are based on the Core site within that area and include: 1) Mokelumne River @ Bruella Zone, 2) French Camp @ Airport Way Zone, 3) Terminous Tract Drain @ Hwy 12 Zone, 4) Roberts Island Drain @ Holt Ave Zone, 5) Lower San Joaquin Zone, and 6) Contra Costa Zone. One Core site in each zone and a single Assessment site will be monitored monthly. The Assessment site will rotate between the Coalition zones yearly (Table 9 of the MRPP submitted on August 25, 2008 and amended October 20, 2010).

Core sites have been selected from water bodies that have a history of monitoring and are suitable to track water and sediment quality trends over extended periods of time. A list of criteria used to select these sites is discussed in more detail in the MRPP. Core sites will undergo Assessment Monitoring every three years in order to evaluate the effects of changes in land-use and management practices and provide information about long-term trends and effectiveness of the management practices. Management plan monitoring may also occur at Core sites. Core Monitoring is not limited to largest volume water bodies, but includes a diversity of water body sizes and flows. Data generated from the Core Monitoring sites will be used to establish trend information about the effectiveness of the Coalition's efforts to reduce or eliminate the impact of irrigated agriculture on surface waters.

Assessment Monitoring will focus on a diversity of monitoring sites that are representative of individual zones. Assessment sites were selected based on the sizes and flows of surface water bodies and land uses (e.g., agricultural activities, crops and pesticide use), and include water bodies that carry agricultural drainage into natural water bodies (see Tables 2 and 3 of the MRPP). Sites with known water quality impairments (such as, but not limited to those on the Clean Water Act 303(d) listing) and sites undergoing compliance monitoring for TMDLs will also be included in this monitoring. Assessment sites are selected in order to adequately characterize water quality for all waters of the State within the Coalition region. In conjunction with Core Monitoring for trends and Special Projects sampling focused on specific problems, Assessment Monitoring will help demonstrate the effectiveness of management practices and identify locations for implementation of new management practices, as needed.

To allow the Coalition to monitor a large number of waterbodies across the six zones, the Assessment site will be rotated every year. If an Assessment site experiences more than one water quality exceedance for the same constituent within the year, it will become part of the SJCDWQC Management Plan monitoring which requires additional monitoring beyond the initial year. For site subwatersheds that are currently under a management plan, the Coalition will continue to monitor at those locations for the constituents within the management plan.

Special project monitoring will occur for the purpose of constituent-specific monitoring or targeted source identification studies as needed. This supplementary monitoring may include, but is not limited to, specific targeted studies to source exceedances or monitoring to provide information about conditions of a water body that predate agricultural inputs that occurred prior to the formation of the Coalition. Pre-existing conditions may include legacy pesticides and metals use by agriculture in the past and which bind to sediments and settled into the bed of the water body. These compounds can result in current water contamination when sediment is mobilized into the water column. Additionally, there are natural background levels of salts and metals in the subwatershed that occur as a result of weathering of local

soils. Special Project Monitoring is considered supplemental to the MRPP's requirements and will occur in specific site subwatersheds based on the actions described in the Coalition's Management Plan.

10.3. Total number of samples.

The total number of samples anticipated to be collected once each month, December-September, is outlined in Table 10 and Table 11 below. Sediment samples will be collected at Assessment sites twice per year during assessment years.

**Table 10. (Element 10) Core site names, site IDs, and number of water samples collected each month.**

Site Name	Station Code	Lattitude	Longitude	Zone	Analytical Parameter	# Samples	Sampling SOP	Sample Volume	Containers
Mokelumne River @ Bruella Rd	531XMRABR	38.1601	-121.2051	1	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
French Camp Slough @ Airport Way	531SJC504	37.8817	-121.2493	2	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Terminus Tract Drain @ Hwy 12	544XTTHWT	38.1166	-121.4936	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Roberts Island Drain @ Holt Rd	544RIDAHT	37.9556	-121.4223	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Field Duplicate Samples	Random				All parameters	1 per event	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Field Blank Samples	Random				All parameters except water column toxicity	1 per event	Appendices I-IV	8 L (2.1 gallons)	See Table 12
Matrix Spike Samples	Random				Pesticides, nutrients, metals, TOC	1 per event	Appendices I-IV	15.8 L (4.2 gallons)	See Table 12

**Table 11. (Element 10) Assessment site names, site IDs, and number of samples collected each month.**

Site Name	Station Code	Latitude	Longitude	Zone	Analytical Parameter	# Samples	Sampling SOP	Sample Volume	Containers
Bear Creek @ North Alpine Rd	531BCANAR	38.0737	-121.2118	1	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Coyote Creek Drain @ Liberty Rd	531CCDALR	38.2345	-121.1747	1	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Jahant Slough @ Cherokee Ln	531XJSACL	38.2103	-121.2619	1	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Mokelumne River Drain @ North Lower Sacramento Rd	531MRDNLS	38.1952	-121.2950	1	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Mokelumne River Drain 2 @ Cherokee Ln	531MRD2CL	38.2107	-121.2630	1	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Mosher Creek @ North Alpine Rd	531MCANAR	38.0606	-121.2102	1	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Pixley Slough @ Fury Rd	531PSAFRXX	38.0824	-121.2425	1	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Duck Creek @ Hwy 4	531XDCAHF	37.9491	-121.1810	2	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Littlejohns Creek @ Jack Tone Rd	531XLCAJR	37.8896	-121.1461	2	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Lone Tree Creek @ Jack Tone Rd	531XLTCJR	37.8376	-121.1438	2	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Mormon Slough @ Jack Tone Rd	544MSAJTR	37.9647	-121.1488	2	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Unnamed Drain to Lone Tree Cr @ Jack Tone Rd	531UDLTAJ	37.8536	-121.1457	2	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Drain @ Woodbridge Rd	544DAWRXX	38.1525	-121.5022	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Drain to Bishop Cut @ North Rio Blanco Rd	544DBCRBR	38.0505	-121.4176	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Drain to Hog Slough	544DTHSXX	38.1667	-121.4781	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Empire Tract @ 8 Mile Rd	544ETAEMR	38.0596	-121.4849	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Empire Tract Pump	544ETPXXX	38.0418	-121.4891	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Bouldin Island Pump	544BIPXXX	38.1019	-121.5582	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
King Island Drain along 8 Mile Rd	544KIDAEM	38.0591	-121.4576	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
New Hope Tract Drain @ Walnut Grove Ct	544NHTDWG	38.2283	-121.4903	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Ridge Tract Drain	544RTDXXX	38.0455	-121.4705	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Staten Island Drain @ Staten Island Rd	544SIDASI	38.1330	-121.5232	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Venice Island Pump	544VIPXXX	38.0802	-121.5397	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Wright Tract Drain	544WTDXXX	38.0210	-121.3858	3	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
South Webb Tract Drain	544XXSWTD	38.0632	-121.6033	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Bacon Island Pump @ Old River	544BIPAOR	37.9792	-121.5708	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Byron Tract @ Discovery Bay	544BTADBX	37.9174	-121.5866	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Byron Tract Drain @ Old River	544BTDAOR	37.8853	-121.5771	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Drexler Drain	544DDXXXXX	37.8890	-121.4853	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
East Lower Jones Tract Pump	544ELJTPX	37.9640	-121.4738	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
East Palm Tract Drain	544EPTDXX	37.9410	-121.5659	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Holland Drain @ Old River	544HDAORX	37.9879	-121.5842	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Mandeville Island Pump @ Middle River	544MIPAMR	38.0485	-121.5373	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Mandeville Island Pump @ Old River	544MIPAOR	38.0065	-121.5336	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
McDonald Island Pump	544MDIPXX	38.0268	-121.4982	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Medford Island Drain	544MIDXXX	38.0399	-121.5226	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Medford Island Pump @ Middle River	544MDIPMR	38.0399	-121.5226	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
North Lower Jones Tract Pump	544NLJTPX	37.9705	-121.5007	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Orwood Tract Drain @ Old River	544OTDAOR	37.9290	-121.5607	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12



Site Name	Station Code	Latitude	Longitude	Zone	Analytical Parameter	# Samples	Sampling SOP	Sample Volume	Containers
South East Roberts Island Drain @ Howard Rd	544SERIDH	37.8768	-121.3765	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
South East Union Island Pump	544SEUIPX	37.8202	-121.4229	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
South McDonald Island Pump	544SMDIPX	37.9894	-121.4642	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
South West Roberts Island Drain @ Howard Rd	544SWRIDH	37.8770	-121.3738	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Union Island Drain @ Bonetti Rd	544UIDABR	37.8715	-121.5273	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Union Island Drain @ Klein Rd	544UIDAKR	37.8843	-121.4974	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Unnamed Drain along West Mahilla Rd	544UDAWMR	37.8516	-121.3212	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Upper Roberts Island Drain	544URIDXX	37.8189	-121.3593	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Victoria Drain along Hwy 4	544VDAHFX	37.8904	-121.5685	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Victoria Island Drain	544VIDXXX	37.9118	-121.5406	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
West McDonald Island Pump	544WMDIPX	37.9720	-121.4925	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
West Orwood Tract Drain	544WOTDXX	37.9294	-121.6075	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
West Palm Tract Drain	544WPTDXX	37.9481	-121.6080	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
West Victoria Island Drain	544WVIDXX	37.8758	-121.5765	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Grant Line Canal @ Clifton Court Rd	544XGLCAA	37.8414	-121.5288	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Grant Line Canal near Calpack Rd	544XGLCCR	37.8205	-121.4999	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Roberts Island Drain along House Rd	544RIDAHR	37.9702	-121.4074	4	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Walthall Slough Drain @ Woodward Ave	544WSAWAV	37.77046	-121.2927	5	See Table 5	1	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Field Duplicate Samples	Random				All parameters	5% of total #	Appendices I-IV	28 L (7.4 gallons)	See Table 12
Field Blank Samples	Random				All parameters except water column toxicity	5% of total #	Appendices I-IV	8 L (2.1 gallons)	See Table 12
Matrix Spike Samples	Random				Pesticides, nutrients, metals, TOC	5% of total #	Appendices I-IV	15.8 L (4.2 gallons)	See Table 12

It is the sampler's responsibility to positively locate each sampling site even when unfamiliar with the site. To facilitate a positive location, latitude/longitude coordinates, photographs and detailed notes are taken when the sites are initially scouted. A description that includes suggested driving directions, local landmarks, the latitude and longitude of the site, and photos for verification is provided to the samplers. Samplers should refer to the MLJ-LLC SOP presented in Appendix VIII. The sample should be collected from the location at the site identified in the description.

If a site becomes inaccessible for any reason, including personal danger due to high water, a failing bank, or aerial pesticide application, it is up to the discretion of the samplers whether a sample can be collected. The samplers may choose to leave and return later to collect samples and should notify the QA Officer Melissa Turner. The reason for not sampling a site must be documented in writing on the field sheet and if possible by photo; if it is determined that no sample can be collected samplers must notify the project QA Officer Melissa Turner.

Samples are collected according to a defined once-per-month schedule discussed in Element 6.1. After samples are collected the proper holding requirements of each sample, listed in Table 12, are met by employing separate couriers to deliver samples to each laboratory. The sample with the shortest holding time defines the time-frame within which all samples to a given lab are delivered. A general schedule for sampling that begins at time 00:00 is:

- 00:00-14:00 — sampling for all sites scheduled
- 14:00-15:00 — courier delivers samples to APPL
- 15:00-22:00 — samples are transferred to secure facility for overnight storage
- 22:00-23:00 — courier delivers samples to Caltest, 24-hr holding period pathogen tests are initiated
- 23:00-26:00 — samples remain in secure facility for storage
- 26:00-27:00 — courier delivers samples to AQUA-Science, 36 hr holding period toxicity tests are initiated
- 27:00 — samples to NCL packed and shipped via overnight UPS or FedEx

Because the SJCDWQC has planned to implement a long term monitoring program, data that are not successfully collected for a specific sample event or site can typically be recollected at a later sampling event. Therefore, no one specific measurement made is deemed critical (e.g., required to achieve project objectives). Each measurement will undergo close scrutiny during the data gathering and review process. The expected number of samples, specific analytical methods and procedures, and defined acceptance criteria for QC samples (as described in other sections of this QAPP) shall be included as part of the data review process.

Steps taken to minimize bias in sample collection and analysis are reviewed in Element 7.5 of this QAPP.

## 11. SAMPLING METHODS

All samples are collected according to detailed SOPs for collection of samples for trace metals analysis, pathogen analysis, water toxicity analysis, general chemistry analysis, or sediment toxicity analysis found in Appendices I-X to this QAPP. The SOPs contain instructions for collecting samples and cleaning equipment between samples. These methods are summarized below.

All bottles collected from a site are considered a single sample, so all bottles share a common site ID and sample time. All bottles are certified pre-cleaned and, with the exception of the bottle for trace metals analysis, are collected by one sampler who dons clean nitrile gloves, wades to mid-channel if it is safe to do so, uncaps the bottle and fills it approximately 0.1 m below the water surface. For trace metals analysis samples are collected using “clean hand-dirty hand” technique that minimizes sampler induced contamination. This method involves two samplers. One sampler opens the bottle wearing new clean gloves; this sampler touches nothing but the bottle cap with clean gloves. The other sampler fills the bottle wearing gloves which are immersed in native water during the filling process, taking care not to touch the bottle near the open mouth. Trace metals samples are preserved with HNO<sub>3</sub> to less than pH 2 and chilled to 4°C. Toxicity samples are collected in new certified pre-cleaned 1-gallon amber glass bottles which are triple rinsed with native water before being filled with sample water. All other samples for general chemistry analysis are collected into analysis-specific containers, both glass and plastic. Where appropriate bottles are amber or brown to block light and prevent UV decay of analytes. Samples collected in pre-preserved bottles are filled to within 1 cm of the top to avoid preservative loss; all other samples are collected into a bottle with zero headspace.

After each bottle is full the sampler returns it to the bank. Another sampler immediately rinses the outside of the bottle with deionized water and places it into a cooler of ice away from direct sunlight. Field parameters are measured simultaneous to sample collection. After all bottles have been placed on ice, discharge is measured using a Marsh McBirney FloMate 2000. Samples are kept away from sunlight at 4°C until extraction or analysis. Although all bottles are considered a single sample, to prevent unnecessary contamination of the sample no volumes are homogenized. All are potentially subject to rare minor inter-bottle variations as a result.

Field duplicates and samples for matrix spike analysis are collected by both samplers donning nitrile gloves and filling bottles as simultaneously as possible. Field blanks are collected in an identical bottle to the environmental sample using an identical process, but bottles are filled with DI water and capped. Field QC samples are stored at 4°C alongside environmental samples until extraction or analysis.

Sediment samples are collected by a sampler wearing clean nitrile gloves using clean and acetone rinsed stainless steel scoops. Sediment from the topmost 2 cm of bed substrate is scooped from the bed, some natant liquid is carefully decanted, and the sample is placed into the appropriate containers for toxicity testing, grain size and TOC analyses, and any chemistry that may be necessary in case of toxicity. Containers are rinsed with DI water and stored away from sunlight and chilled to 4°C. Sediment chemistry and TOC samples are frozen within 48 hours; sediment toxicity and grain size samples are held at 4°C until analysis.

An acceptable water sample will meet the following criteria:

- Water samples in correct container and correct volume
- Water samples free of sampler induced contamination (no touching the inside of cap or open bottle, collected upstream of sampler)
- Water samples without sediments stirred up from water body bed
- Water samples collected below water surface
- Water samples representative of greater sample area (from a segment where water is well mixed)
- Water samples in multiple bottles apparently identical
- Water samples without headspace (unless in an acid-preserved bottle)
- Water samples in acid preserved bottles reduced to pH<2 (no preservative lost)

- Water samples immediately moved to a cooler with ice to prevent target constituent breakdown
- Water samples clearly identifiable with proper/unique sample ID noted on bottle, COC, and field sheet
- Water samples delivered to laboratories with sufficient time for analysis or extraction within hold time
- Water samples collected along with complete field data consisting of ambient environmental notes, water parameters, photo documentation, and latitude and longitude recorded.

An acceptable sediment sample will meet the following criteria:

- Sediment sampled from beneath overlying water or at the minimum moist sediment
- Sediment samples in correct containers and correct volume
- Sediment samples free of sampler induced contamination (no touching the inside of cap or open bottle, samples collected as sampler moves downstream to upstream)
- Sediment samples consisting of top 2 cm of recently deposited silt/clay, not gravel or sand
- Sediment samples representative of greater sample area (from multiple areas around sampling location)
- Sediment samples in multiple bottles apparently identical
- Sediment samples immediately moved to a cooler with ice to prevent target constituent breakdown
- Sediment samples clearly identifiable with proper/unique sample ID noted on bottle, COC, and field sheet
- Sediment samples properly frozen within hold time, if required
- Sediment samples delivered to laboratories with sufficient time for analysis or extraction within hold time and hold temperature
- Sediment samples collected along with complete field data consisting of ambient environmental notes, water parameters, photo documentation, and latitude and longitude.

Any samples that do not meet the above criteria are considered unacceptable and will not be analyzed. Samples collected in multiple bottles are not homogenized by the samplers and are only homogenized by the lab if the method specifically requires it. Samples are unfiltered unless the method specifically requires it.

Any deviation from the written SOP requires notification of the project QA Officer Melissa Turner. All deviation or problems will be noted both on the field sheet and subsequently in the SWAMP comparable database. Corrective action will be determined by the project QA Officer Melissa Turner.

## 12. SAMPLE HANDLING AND CUSTODY

All sample bottles are labeled with indelible marker clearly stating sample ID (composed of region code, hydrologic unit code and site ID), collection date and time, and collector. Immediately after collection, sample bottle caps are checked for tightness and bottles are placed into padded sleeves (if necessary) and packed in wet ice within an insulated cooler and kept out of direct sunlight. All samples are kept in wet ice to maintain a temperature of 4°C until delivered into lab custody. Transfer of custody by MLJ-LLC staff is outlined in an SOP located in Appendix V of this QAPP. Samples are delivered to labs or shipped by courier on wet ice within insulated coolers; if the sample is shipped, the COC is placed in a plastic bag taped to the inside of the lid and the ice chest is sealed with tape. A custodian at the receiving laboratory examines the samples for correct documentation and proper preservation while adhering to proper holding times. Method of preservation and duration of holding time varies by target analyte; these details are provided in Table 12 below. Contract laboratories follow sample custody procedures outlined in their QA plans; contract laboratory QA plans are on file with the respective laboratories. It is the responsibility of the personnel of each analytical laboratory to ensure that all applicable regulations are followed in the disposal of samples or related chemicals remaining after successful completion of analyses.

Custody of all samples is documented and traceable from collection time to submittal for analysis on a COC form. A COC form is provided as Figure 2. The COC accompanies the samples at all times.

Samples are considered under custody if:

- it is in actual possession;
- it is in view after being in physical possession;
- it is placed in a secure area (accessible by or under the scrutiny of authorized personnel only after in possession).

All transfer of custody will proceed according to the appropriate SOP located in Appendix V of this QAPP.

All samples and accompanying COCs are submitted to analyzing laboratories by the samplers, by private overnight courier, or by overnight common parcel service. Once in the lab's possession it is the responsibility of the analyzing laboratory to maintain custody logs sufficient to track each sample submitted and to analyze or preserve each sample within specified holding times.

Field crews are required to fill out standardized field sheets for each sampling event. A standardized field sheet is provided as Figure 3.

**Table 12. (Element 12). Sample handling and custody.**

Analytical Parameter	Sample Volume	Containers # size type	Initial Preservation/Holding Requirements	Maximum Holding Time:
Total Dissolved Solids	500 mL	1x 2000 mL Polyethylene	Store at 4°C	7 Days
Total Suspended Solids	500 mL			7 Days
Turbidity	150 mL			48 Hours
Soluble Orthophosphate	1 L			
TKN, Ammonia, Total Phosphorus, Nitrate-Nitrite as N	500 mL	1x 500 mL Polyethylene	Preserve to $\leq$ pH 2 with H <sub>2</sub> SO <sub>4</sub> , store at 4°C	28 Days
Metals/Trace Elements, Hardness	500 mL	1x 500 mL Polyethylene	Filter as necessary; preserve to $\leq$ pH 2 with HNO <sub>3</sub> , store at 4°C	180 Days
<i>E. coli</i> (pathogens)	100 mL	1x 100 mL Polyethylene	Store at 4°C	24 Hours
Fecal coliform (pathogens)	100 mL	1x 100 mL Polyethylene	Store at 4°C	24 Hours
Total Organic Carbon	120 mL	3x 40 mL Glass VOA with PTFE-lined cap	Preserve with HCl, store at 4°C	28 Days
Carbamates	1 L	4x 1 L Amber Glass	Store at 4°C; extract within 7 days	40 Days
Organochlorines	1 L			
Organophosphates	1 L			
Herbicides (general)	1 L			
Herbicides (paraquat dichloride)	1 L	1x 1 L brown Polyethylene	Store at 4°C; extract within 7 days	21 days
Herbicides (glyphosate)	80 mL	2x 40 mL Glass VOA	Store at 4°C; freeze (-20°C) within 2 weeks	6 Months
Aquatic Toxicity	5 Gallons	5x 1 Gallon Amber Glass	Store at 4°C	36 Hours
Sediment Toxicity	2 L	2x 1 L Glass	Store at 4°C, do not freeze	14 Days
Sediment Grain Size	250 mL	1x 250 mL Glass	Store at 4°C, do not freeze	28 days
Sediment Total Organic Carbon	250 mL	1x 250 mL Glass	Store at 4°C, freeze (-20°C) within 48 hours	12 Months
Sediment Chemistry	1 L	4x 250 mL Amber Glass	Store at 4°C, freeze (-20°C) within 48 hours	12 Months
Sediment Total Solids	250 mL	1x 250 mL Glass	Store at 4°C	7 Days

Figure 2. Sample COC form



**MICHAEL L. JOHNSON LLC**  
 ECOSYSTEMS CONSULTING  
 1490 DREW AVE., SUITE 175, DAVIS, CA 95618  
 Office: (530) 756-5225 Fax: (530) 756-5225

**APPL CHAIN-OF-CUSTODY RECORD**

Client Name: MJ-LLC  
 Address: 1490 Drew Ave, Suite 175, Davis, CA 95618  
 Sampled By:  
 Phone: (530) 756-5200  
 Fax: (530) 756-5225  
 Project Manager: Michael Johnson  
 Project Name: San Joaquin County & Delta Water Quality Coalition

<input checked="" type="checkbox"/>	Carbamate pesticides by EPA 8321 or EPA 632*
<input checked="" type="checkbox"/>	Organochlorine pesticides by EPA 8081A or EPA 608*
<input checked="" type="checkbox"/>	Herbicides by EPA 619, EPA 8321, EPA 8141A*
<input checked="" type="checkbox"/>	Organophosphorus pesticides by EPA 8141A or EPA 614*
<input checked="" type="checkbox"/>	Paraquat dichloride by EPA 549.1

Sample Identification	Sample Date	Sample Time	Sample Matrix	Number	Type	Preservative	SAMPLE COMMENTS				
							Carbamate pesticides by EPA 8321 or EPA 632*	Organochlorine pesticides by EPA 8081A or EPA 608*	Herbicides by EPA 619, EPA 8321, EPA 8141A*	Organophosphorus pesticides by EPA 8141A or EPA 614*	Paraquat dichloride by EPA 549.1
1			FW	4	1-L Amber Glass	Ice	X	X	X	X	
2			FW	1	1-L Brown Poly	Ice					
3			FW	4	1-L Amber Glass	Ice	X	X	X		
4			FW	4	1-L Brown Poly	Ice					
5			FW	4	1-L Amber Glass	Ice	X	X	X		
6			FW	1	1-L Brown Poly	Ice					
7			FW	4	1-6oz Amber Glass	Ice	X	X	X		
8			FW	1	1-L Brown Poly	Ice					
9			FW	4	1-L Amber Glass	Ice	X	X	X		
10			FW	1	1-L Brown Poly	Ice					
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21											
22											

Comments:  
 Please fax signed and completed COC to MJ LLC:  
 (530) 756-5225, or email to jkatz@mjl-llc.com  
 \* See project-specific guidelines for exact analyte list

Relinquished By		Relinquished By	
Signature		Signature	
Print Name		Print Name	
Organization		Organization	
Date	Time	Date	Time
<b>Received By</b>		<b>Received By</b>	
Signature		Signature	
Print Name		Print Name	
Organization		Organization	
Date	Time	Date	Time

Temperature at Log In: \_\_\_\_\_ (°C)

Matrix codes: SED = sediment, FW = freshwater, WW = wastewater, STRMW = stormwater

Figure 3. Sample Field Sheet

<b>SJCDWQC Field Data Sheet: Water Sampling (Event Type = WQ)</b>		Entered in d-base (initial/date)		double checker:																												
<b>Station Name: French Camp Slough @ Airport Way</b>		DATE (mm/dd/yyyy):		Pg _____ of _____ Pgs																												
<b>Station ID: 531SJCS04</b>		Arrival Time:		Agency: MLJ-LLC																												
<b>Funding: 04S15001</b>		SAMPLE TIME: <span style="border: 1px solid black; padding: 2px;">                    </span>		Protocol: MLJ-LLC FieldSOP 09/17/07																												
<b>Project ID: ILRP_SJCDWQC</b>		Departure Time:																														
<b>Group: Irrigation 4 2009</b>		Purpose (Circle all that apply):		Purpose/ature:																												
Occupation Method: Walk-in, Bridge, Other Collection Equipment: Inev. bottle by hand, By pole, UCCO 3L PTFE, Other Sample Type: Grab, Integrated Sample Location: Bank, Near Bank, Thawing, Mudchannel, Open Water Hydro-Morphology: None, Bridge Piles, Concrete Channel, Grade Control, Culvert, Other Hydro-MoDLOC: US / DS / NA Starting Bank: LB / RB / NA		Precipitation: None, Foggy, Drizzle, Rain, Snow Observed Flow: NA, Dry/Waterbody Bed, No Observed Flow, Isolated Pool, 0.1 - 1 cfs, 1 - 5 cfs, 5 - 20 cfs, 20 - 50 cfs, 50 - 200 cfs, >200 cfs Wind: Calm, Light Breeze, Gusty Wind Direction (From): circle elevation in compass at right Water Color: Colorless, Green, Yellow, Brown, Other Water Clarity: Clear (see bottom), Cloudy (>2" vis), Murky (<2" vis) Water Odor: None, Sulfides, Sewage, Petroleum, Mixed, Other Wadable: YES / NO Other Presence: Vascular, Nonvascular, OM/Sherm, Fern, Trash, None, Other Sky Code: Clear, Partly Cloudy, Overcast, Fog, Hazy Site Odor: None, Sulfides, Sewage, Petroleum, Mixed, Other Dominant Substrate: Concrete, Cobble, Gravel, Sand, Mud, Urk., Other		Picture Number: Picture Name: Field Dup: Yes / No Position Water Column: Subsurface (Depth = 0.1 m, Field/Water): Not Applicable (Depth = 2 cm, Sediment)																												
Samples Taken (# of Containers Filled) Method = Water, Grab		GPS: Target: 37.8817, -121.2493 Actual: - Difference: GPS Model: MLJ-LLC Garmin eTrex Datum: WAD83 Accuracy (ft./m):		Field Measurements Air Temp (Celsius) Water Temp (Celsius) EC (uS/cm) DO (mg/L) pH TDS ORP YSI Water ID Midchannel depth (ft./m) Wet Channel Width (ft./m) Stage Calculated Site Discharge																												
<table border="1" style="width:100%; border-collapse: collapse;"> <thead> <tr> <th>Container</th> <th>Number</th> <th>Notes</th> </tr> </thead> <tbody> <tr> <td>531SJCS04-GR Total Hardhat Nitrogen, Total Ammonia, Total Phosphorus (as P)</td> <td>1</td> <td>1.0L Amber Glass</td> </tr> <tr> <td>531SJCS04-GR TOC</td> <td>1</td> <td>500-ml Plastic (W-CO-0)</td> </tr> <tr> <td>531SJCS04-GR Cadmium, OCS, Penthons, OCS, Benzides</td> <td>5</td> <td>45-ml Glass Amvial, set of 3</td> </tr> <tr> <td>531SJCS04-GR Parasit</td> <td>1</td> <td>1L Plastic</td> </tr> <tr> <td>531SJCS04-GR Metals: Barides (as CrCo3)</td> <td>1</td> <td>500-ml Plastic (W-HNO3)</td> </tr> <tr> <td>531SJCS04-GR Ophospha</td> <td>2</td> <td>40-ml Glass Amvial</td> </tr> <tr> <td>531SJCS04-GR E coli</td> <td>1</td> <td>100-ml Polytene</td> </tr> <tr> <td>531SJCS04-GR Total dfn, TDS, TSS, Nitrate + Nitrite (as N), Sulfate, Orthophosphate (as P)</td> <td>1</td> <td>2L Plastic Jug</td> </tr> </tbody> </table>		Container	Number	Notes	531SJCS04-GR Total Hardhat Nitrogen, Total Ammonia, Total Phosphorus (as P)	1	1.0L Amber Glass	531SJCS04-GR TOC	1	500-ml Plastic (W-CO-0)	531SJCS04-GR Cadmium, OCS, Penthons, OCS, Benzides	5	45-ml Glass Amvial, set of 3	531SJCS04-GR Parasit	1	1L Plastic	531SJCS04-GR Metals: Barides (as CrCo3)	1	500-ml Plastic (W-HNO3)	531SJCS04-GR Ophospha	2	40-ml Glass Amvial	531SJCS04-GR E coli	1	100-ml Polytene	531SJCS04-GR Total dfn, TDS, TSS, Nitrate + Nitrite (as N), Sulfate, Orthophosphate (as P)	1	2L Plastic Jug				
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### **13. ANALYTICAL METHODS**

Field and laboratory analyses will require the equipment listed in Table 17 and Table 18; analytical methods are listed in Table 13 below. In the event of equipment failure, the laboratory QA officer or Project manager should notify the project QA Officer Melissa Turner as soon as possible and appropriate documentation and corrective action can be initiated. This documentation will include shall be appended to the appropriate report from MLJ-LLC to the CVRWQCB. Corrective action must be determined on a case-by-case basis but may include re-extraction, re-analysis, resampling or data rejection if the sample cannot be salvaged. If the failure necessitates a qualifier or flag in the database it is the project QA Officer's responsibility to ensure that the correct qualifier or flag is applied.

A laboratory may store surplus volume for as long as it sees fit for re-extraction if necessary. The laboratory shall dispose of all samples in accordance with state and federal regulations.

**Table 13. (Element 13) Field and laboratory analytical methods.**

See Table 2 for a description of measurement principles for each analysis. Requirements of field measurements include, but are not limited to clean/calibrated sensors which are not buried in the bed of the river.

Constituent	Matrix	Analyzing Lab	WQTL	RL	MDL	Analytical Method		
						Method	SOP/Appendix	Modified for Method
Physical Parameters								
Flow	Fresh Water	Field Measure	NA <sup>1</sup>	1 cfs	NA	USGS R2Cross streamflow Method	Appendix IV	Yes
pH	Fresh Water	Field Measure	6.5-8.5	0.1 pH units	NA	EPA 150.1	Appendix IX	No
Electrical Conductivity	Fresh Water	Field Measure	700 µmhos/cm	100 µmhos/cm	NA	EPA 120.1	Appendix IX	No
Dissolved oxygen	Fresh Water	Field Measure	7 mg/L	0.1 mg/L	NA	SM 4500-O	Appendix IX	No
Temperature	Fresh Water	Field Measure	NA <sup>1</sup>	0.1 °C	NA	SM 2550	Appendix IX	No
Turbidity	Fresh Water	Caltest	variable	0.05 NTU	0.020 NTU	EPA 180.1	SOPW-TURB-rev7, Appendix XXIX	No
Total Dissolved Solids	Fresh Water	Caltest	450 mg/L	10 mg/L	4.0 mg/L	SM 2540C	SOP W-TDS-rev8, Appendix XXVI	No
Total Suspended Solids	Fresh Water	Caltest	NA <sup>2</sup>	3 mg/L	2.0 mg/L	SM2540D	SOP B-TSS-rev7, Appendix XXX	No
Hardness	Fresh Water	Caltest	NA <sup>1</sup>	5 mg/L	3.0 mg/L	SM2340C	SOP W-HARD-rev8, Appendix XXII	No
Total Organic Carbon	Fresh Water	Caltest	NA <sup>1</sup>	0.5 mg/L	0.30 mg/L	SM5310B	SOP W-TOC/DOC-rev10, Appendix XXVIII	No
Pathogens								
Escherichia coli	Fresh Water	Caltest	235 MPN/100 mL	1 MPN/100 mL	1.0 MPN/100 mL	SM 9223	SOP B-MMOMUG-REV11, Appendix XXI	No
Toxicity								
Water Column Toxicity	Fresh Water	AQUA-Science	No Toxicity	NA	NA	EPA 821-R-02-012	SOP 6.1A-5/Appendix XV, SOP 6.2A-5/Appendix XVI	No
	Fresh Water	AQUA-Science	No Toxicity	NA	NA	EPA 821-R-02-013	SOP 6.3C-4/ Appendix XVII	No
Sediment Toxicity	Sediment	AQUA-Science	No Toxicity	NA	NA	EPA 600/R-99-064	Appendix XVIII	No
Carbamates								
Aldicarb	Fresh Water	APPL Inc	3 µg/L	0.4 µg/L	0.20 µg/L	EPA 8321	SOP HPL8321A/ Appendix XIV	No
Carbaryl	Fresh Water	APPL Inc	2.53 µg/L	0.07 µg/L	0.050 µg/L	EPA 8321	SOP HPL8321A/ Appendix XIV	No
Carbofuran	Fresh Water	APPL Inc	ND	0.07 µg/L	0.050 µg/L	EPA 8321	SOP HPL8321A/ Appendix XIV	No
Methiocarb	Fresh Water	APPL Inc	0.5 µg/L	0.4 µg/L	0.20 µg/L	EPA 8321	SOP HPL8321A/ Appendix XIV	No
Methomyl	Fresh Water	APPL Inc	0.52 µg/L	0.07 µg/L	0.050 µg/L	EPA 8321	SOP HPL8321A/ Appendix XIV	No
Oxamyl	Fresh Water	APPL Inc	50 µg/L	0.4 µg/L	0.20 µg/L	EPA 8321	SOP HPL8321A/ Appendix XIV	No
Organochlorines								
DDD	Fresh Water	APPL Inc	0.00083 µg/L	0.01 µg/L	0.003 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
DDE	Fresh Water	APPL Inc	0.00059 µg/L	0.01 µg/L	0.004 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
DDT	Fresh Water	APPL Inc	0.00059 µg/L	0.01 µg/L	0.007 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
Dicofol	Fresh Water	APPL Inc	NA <sup>1</sup>	0.1 µg/L	0.01 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
Dieldrin	Fresh Water	APPL Inc	0.00014 µg/L	0.01 µg/L	0.005 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
Endrin	Fresh Water	APPL Inc	0.036 µg/L	0.01 µg/L	0.007 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
Methoxychlor	Fresh Water	APPL Inc	0.03 µg/L	0.01 µg/L	0.008 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
Organophosphates								
Azinphos-methyl	Fresh Water	APPL Inc	0.01 µg/L	0.1 µg/L	0.02 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No

Constituent	Matrix	Analyzing Lab	WQTL	RL	MDL	Analytical Method		
						Method	SOP/Appendix	Modified for Method
Chlorpyrifos	Fresh Water	APPL Inc	0.015 µg/L	0.015 µg/L	0.003 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Diazinon	Fresh Water	APPL Inc	0.1 µg/L	0.02 µg/L	0.004 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Dichlorvos	Fresh Water	APPL Inc	0.085 µg/L	0.1 µg/L	0.02 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Dimethoate	Fresh Water	APPL Inc	1.0 µg/L	0.1 µg/L	0.08 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Demeton-s	Fresh Water	APPL Inc	NA <sup>2</sup>	0.1 µg/L	0.01 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Disulfoton	Fresh Water	APPL Inc	0.05 µg/L	0.05 µg/L	0.02 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Malathion	Fresh Water	APPL Inc	ND	0.1 µg/L	0.05 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Methamidiphos	Fresh Water	APPL Inc	0.35 µg/L	0.2 µg/L	0.08 µg/L	EPA 8321	SOP HPL8321A/ Appendix XIV	No
Methidathion	Fresh Water	APPL Inc	0.7 µg/L	0.1 µg/L	0.04 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Parathion, methyl	Fresh Water	APPL Inc	ND	0.1 µg/L	0.075 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Phorate	Fresh Water	APPL Inc	0.7 µg/L	0.1 µg/L	0.07 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Phosmet	Fresh Water	APPL Inc	140 µg/L	0.2 µg/L	0.06 µg/L	EPA 8141A	SOP ANA8141A/Appendix XIII	No
Herbicides								
Atrazine	Fresh Water	APPL Inc	1.0 µg/L	0.5 µg/L	0.07 µg/L	EPA 619	SOP ANA619/Appendix XI	No
Cyanazine	Fresh Water	APPL Inc	1.0 µg/L	0.5 µg/L	0.09 µg/L	EPA 619	SOP ANA619/Appendix XI	No
Diuron	Fresh Water	APPL Inc	2 µg/L	0.4 µg/L	0.2 µg/L	EPA 8321	SOP HPL8321A/ Appendix XIV	No
Glyphosate	Fresh Water	NCL Ltd	700 µg/L	5 µg/L	2.77 µg/L	EPA 547	SOP ME075v08/Appendix XIX	No
Linuron	Fresh Water	APPL Inc	1.4 µg/L	0.4 µg/L	0.2 µg/L	EPA 8321	SOP HPL8321A/ Appendix XIV	No
Paraquat dichloride	Fresh Water	APPL Inc	3.2 µg/L	0.5 µg/L	0.08 µg/L	EPA 549.1	SOP ME019v10/Appendix XX	No
Simazine	Fresh Water	APPL Inc	4.0 µg/L	0.5 µg/L	0.08 µg/L	EPA 619	SOP ANA619/Appendix XI	No
Trifluralin	Fresh Water	APPL Inc	5 µg/L	0.05 µg/L	0.036 µg/L	EPA 8141	SOP ANA8141A/Appendix XIII	No
Metals								
Arsenic	Fresh Water	Caltest	10 µg/L	0.5 µg/L	0.01 µg/L	EPA 200.8 (ICPMS Collision Cell)	SOP M-2008-3MODErev2, Appendix XXIII	No
Boron	Fresh Water	Caltest	700 µg/L	10 µg/L	0.47 µg/L	EPA 200.8 (ICPMS Collision Cell)	SOP M-2008-3MODErev2, Appendix XXIII	No
Cadmium	Fresh Water	Caltest	Variable <sup>3</sup> (MUN=2.0 µg/L)	0.1 µg/L	0.011 µg/L	EPA 200.8 (ICPMS Collision Cell)	SOP M-2008-3MODErev2, Appendix XXIII	No
Copper	Fresh Water	Caltest	Variable <sup>3</sup> (MUN=170 µg/L)	0.5 µg/L	0.06 µg/L	EPA 200.8 (ICPMS Collision Cell)	SOP M-2008-3MODErev2, Appendix XXIII	No
Lead	Fresh Water	Caltest	Variable <sup>3</sup> (MUN=2.0 µg/L)	0.25 µg/L	0.071 µg/L	EPA 200.8 (ICPMS Collision Cell)	SOP M-2008-3MODErev2, Appendix XXIII	No
Molybdenum	Fresh Water	Caltest	10 µg/L	0.25 µg/L	0.016 µg/L	EPA 200.8 (ICPMS Collision Cell)	SOP M-2008-3MODErev2, Appendix XXIII	No
Nickel	Fresh Water	Caltest	Variable <sup>3</sup> (MUN=12 µg/L)	0.5 µg/L	0.01 µg/L	EPA 200.8 (ICPMS Collision Cell)	SOP M-2008-3MODErev2, Appendix XXIII	No
Selenium	Fresh Water	Caltest	50 µg/L (5 µg/L 4 day average)	1 µg/L	0.06 µg/L	EPA 200.8 (ICPMS Reaction Cell)	SOP M-2008-3MODErev2, Appendix XXIII	No
Zinc	Fresh Water	Caltest	Variable <sup>3</sup> (MUN=5000 µg/L)	1 µg/L	0.8 µg/L	EPA 200.8 (ICPMS Collision Cell)	SOP M-2008-3MODErev2, Appendix XXIII	No

Constituent	Matrix	Analyzing Lab	WQTL	RL	MDL	Analytical Method		
						Method	SOP/Appendix	Modified for Method
Nutrients								
Total Kjeldahl Nitrogen	Fresh Water	Caltest	NA <sup>1</sup>	0.1 mg/L	0.07 mg/L	SM4500NH3 C	SOP W-NH3-TKN-rev10, Appendix XXVII	No
Nitrate (as N)+ Nitrite (as N)	Fresh Water	Caltest	10,000 µg/L	0.05 mg/L	0.05 mg/L	EPA 353.2	SOP W-NNO3-rev2, Appendix XXIV	No
Total Ammonia	Fresh Water	Caltest	1.5 mg/L or variable <sup>4</sup>	0.1 mg/L	0.060 mg/L	SM4500NH3 C	SOP W-NH3-TKN-rev10, Appendix XXVII	No
Total Phosphorus	Fresh Water	Caltest	NA <sup>1</sup>	0.01 mg/L	0.040 mg/L	SM4500P E	SOP W-PHOS-rev8, Appendix XXV	No
Soluble Orthophosphate	Fresh Water	Caltest	NA <sup>1</sup>	0.01 mg/L	0.010 mg/L	SM4500P E	SOP W-PHOS-rev8, Appendix XXV	No
Sediment								
Bifenthrin	Sediment	Caltest	NA <sup>5</sup>	0.33 µg/kg	0.1 µg/kg	GCMS-NCI-SIM	SOP O-Pyrethroidsncirev1, APPENDIX XXXII	No
Cyfluthrin	Sediment	Caltest	NA <sup>5</sup>	0.33 µg/kg	0.11 µg/kg	GCMS-NCI-SIM	SOP O-Pyrethroidsncirev1, APPENDIX XXXII	No
Cypermethrin	Sediment	Caltest	NA <sup>5</sup>	0.33 µg/kg	0.1 µg/kg	GCMS-NCI-SIM	SOP O-Pyrethroidsncirev1, APPENDIX XXXII	No
Deltamethrin: Tralomethrin	Sediment	Caltest	NA <sup>5</sup>	0.33 µg/kg	0.12 µg/kg	GCMS-NCI-SIM	SOP O-Pyrethroidsncirev1, APPENDIX XXXII	No
Esfenvalerate	Sediment	Caltest	NA <sup>5</sup>	0.33 µg/kg	0.13 µg/kg	GCMS-NCI-SIM	SOP O-Pyrethroidsncirev1, APPENDIX XXXII	No
Lambda-Cyhalothrin	Sediment	Caltest	NA <sup>5</sup>	0.33 µg/kg	0.06 µg/kg	GCMS-NCI-SIM	SOP O-Pyrethroidsncirev1, APPENDIX XXXII	No
Permethrin	Sediment	Caltest	NA <sup>5</sup>	0.33 µg/kg	0.11 µg/kg	GCMS-NCI-SIM	SOP O-Pyrethroidsncirev1, APPENDIX XXXII	No
Fenpropathrin	Sediment	Caltest	NA <sup>5</sup>	0.33 µg/kg	0.07 µg/kg	GCMS-NCI-SIM	SOP O-Pyrethroidsncirev1, APPENDIX XXXII	No
Chlorpyrifos	Sediment	Caltest	NA <sup>5</sup>	0.33 µg/kg	0.12 µg/kg	GCMS-NCI-SIM	SOP O-Pyrethroidsncirev1, APPENDIX XXXII	No
Total Solids	Sediment	Caltest	NA	0.1%	0.1%	SM2540B	SOP W-RESIDUE-rev7, APPENDIX XXXI	No
Total Organic Carbon	Sediment	Caltest <sup>6</sup>	NA <sup>1</sup>	200 mg/kg	100 mg/kg	Walkley Black	PTS SOP #4, Appendix XXXIV	No
Grain Size	Sediment	Caltest <sup>6</sup>	NA <sup>1</sup>	1% sand, silt, clay, gravel	0.4 µm	ASTM D-422-63, ASTM D4464M-85	PTS SOP #3, Appendix XXXIII	No

<sup>1</sup> Not available until completion of evaluation studies or no Water Quality Trigger Limit applicable.

<sup>2</sup> Currently these constituents do not have a WQTL designated by the Regional Board however this may change in the future.

<sup>3</sup> Variable WQTLs based on hardness. Municipal and domestic supply WQTLs in parenthesis are regardless of hardness.

<sup>4</sup> Variable WQTLs based on pH and temperature. Municipal and domestic supply WQTLs in parenthesis are regardless of pH and temperature.

<sup>5</sup> Sediment chemistry result reported if positive sediment toxicity is measured.

<sup>6</sup> Subcontracted to PTS Laboratories.

**Table 14. (Element 13). Laboratory analytical methods of constituents monitored for CWA 303(d) compliance.**

Site Name	Constituent	Matrix	Analyzing Lab	WQTL	RL	MDL	Analytical Method		
							Method	SOP/Appendix	Modified for Method
Mokelumne River @ Bruella Rd	Aldrin	Fresh Water	APPL Inc	0.00013 µg/L <sup>1</sup> 3 µg/L <sup>2</sup>	0.01 µg/L	0.009 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
	Chlordane	Fresh Water	APPL Inc	0.00057 µg/L <sup>1</sup> 0.0043 µg/L <sup>2</sup>	0.01 µg/L	0.007 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
	Heptachlor	Fresh Water	APPL Inc	0.00021 µg/L <sup>1</sup> 0.0038 µg/L <sup>2</sup>	0.01 µg/L	0.008 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
Duck Creek @ Highway 4	Heptachlor epoxide	Fresh Water	APPL Inc	0.0001 µg/L <sup>1</sup> 0.0038 µg/L <sup>2</sup>	0.01 µg/L	0.007 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
	Hexachlorocyclohexane (alpha-BHC)	Fresh Water	APPL Inc	0.0039 µg/L <sup>1,3</sup> 0.95 µg/L <sup>2,3</sup>	0.01 µg/L	0.005 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
Drain @ Woodbridge Rd	Hexachlorocyclohexane (beta-BHC)	Fresh Water	APPL Inc	0.0039 µg/L <sup>1,3</sup> 0.95 µg/L <sup>2,3</sup>	0.01 µg/L	0.008 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
	Hexachlorocyclohexane (gamma-BHC; Lindane)	Fresh Water	APPL Inc	0.0039 µg/L <sup>1,3</sup> 0.95 µg/L <sup>2,3</sup>	0.01 µg/L	0.005 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
	Hexachlorocyclohexane (delta-BHC)	Fresh Water	APPL Inc	0.0039 µg/L <sup>1,3</sup> 0.95 µg/L <sup>2,3</sup>	0.01 µg/L	0.005 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
Roberts Island Drain @ Holt Rd	Endosulfan I	Fresh Water	APPL Inc	110 µg/L <sup>1,4</sup> 0.056 µg/L <sup>2,4</sup>	0.01 µg/L	0.005 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
	Endosulfan II	Fresh Water	APPL Inc	110 µg/L <sup>1,4</sup> 0.056 µg/L <sup>2,4</sup>	0.01 µg/L	0.004 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No
	Toxaphene	Fresh Water	APPL Inc	0.00073 µg/L <sup>1</sup> 0.0002 µg/L <sup>2</sup>	0.5 µg/L	0.380 µg/L	EPA 8081A	SOP ANA8081A/Appendix XII	No

<sup>1</sup> Municipal and domestic supply

<sup>2</sup> Cold freshwater habitat, spawning

<sup>3</sup> WQTL is total Hexachlorocyclohexane

<sup>4</sup> WQTL is total Endosulfan

## 14. QUALITY CONTROL

This project will comply with all current SWAMP QC guidelines to maintain comparability of data quality throughout the ILRP SWAMP Comparable database. Field QC frequencies are calculated to ensure that a minimum of 5% all analyses are for QC purposes. All analytical QCs must be analyzed at a frequency of 5% and 1 per batch. QC activities for this project are listed in the tables below.

**Table 15. (Element 14) Field Sampling QC.**

Sample Type	Frequency	Acceptable Limits	Corrective Action	Sampling SOP	Analytical SOP & Method
Water Column Toxicity					
Field Duplicate	5% annual total, minimum 5% per event	RPD $\leq$ 25%	Determine cause, take appropriate corrective action.	Appendix I	Appendix XV; EPA821-R02-12
Organic and Inorganic Chemistry Parameters					
Field Blank	5% annual total	Detectable substance contamination <RL or < sample/5	Determine cause of problem, remove sources of contamination.	Appendix II	See Table 16
Field Duplicate	5% annual total	RPD $\leq$ 25%	Determine cause, take appropriate corrective action.		
Sediment Toxicity					
Field Duplicate	5% annual total, minimum 5% per event	RPD $\leq$ 25%	Determine cause, take appropriate corrective action.	Appendix IV	Appendix XVIII, EPA 600/R-99-064
Sediment Chemistry					
Field Blank	5% annual total	Detectable substance contamination <MDL or <30% of lowest sample	Determine cause of problem, remove sources of contamination.	Appendix IV	Appendix XXXII; GCMS-NCI-SIM
Field Duplicate	5% annual total	RPD $\leq$ 25%	Determine cause, take appropriate corrective action.		
Sediment TOC					
Field Duplicate	5% annual total	RSD $\leq$ 20%	Determine cause, take appropriate corrective action.	Appendix IV	Appendix XXXIV; Walkley Black Method
Sediment Grain Size					
Field Duplicate	5% annual total	RSD $\leq$ 20%	Determine cause, take appropriate corrective action.	Appendix IV	Appendix XXXIII; ASTM D422-63

**Table 16. (Element 14) Analytical QC.**

Sample Type	Frequency	Acceptable Limits	Corrective Action	Sampling SOP	Analytical SOP & Method
Water Column Toxicity					
Lab Control Sample, <i>Ceriodaphnia dubia</i>	1 per 20 samples, minimum 1 per batch	Survival in control samples $\geq 90\%$ ; all performance criteria outlined in SOP are met.	Determine cause, take appropriate corrective action. Reanalyze all suspect samples.	Appendix I	Appendix XV; EPA821-R02-12
Lab Control Sample, <i>Pimephales promelas</i>	1 per 20 samples, minimum 1 per batch	Survival in control samples $\geq 80\%$ , all performance criteria outlined in SOP are met.	Determine cause, take appropriate corrective action. Reanalyze all suspect samples.		
Lab Control Sample, <i>Selenastrum capricornutum</i>	1 per 20 samples, minimum 1 per batch	> 200,000 cells/mL, variability of controls <20%, all performance criteria outlines in SOP are met.	Determine cause, take appropriate corrective action. Reanalyze all suspect samples.	Appendix I	Appendix XVII; EPA821-R02-13
Organic Parameters: Organophosphates, Organochlorines, Carbamates, and Additional Herbicides					
Lab Blanks (method, reagent, instrument)	1 per 20 samples, minimum 1 per batch	Detectable substance contamination <RL	Determine cause of problem, remove sources of contamination, reanalyze suspect samples or flag all suspect data.	Appendix II	Appendices XI-XIV, XIX, XX; ANA 619, EPA 8081A, EPA 8141A, EPA 8321A, EPA 547, EPA 549.2
Lab Duplicate*	1 per 20 samples, minimum 1 per batch	RPD $\leq 25\%$	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Matrix Spike*	1 per 20 samples, minimum 1 per batch	% Recovery =50-150% or control limits based on 3x the standard deviation of the labs actual method recoveries	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data. Zero percent recovery requires rejection of all suspect data.		
Matrix Spike Duplicate*	1 per 20 samples, minimum 1 per batch	RPD $\leq 25\%$	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Lab Control Spike, CRM, or SRM	1 per 20 samples, minimum 1 per batch	Measured value <95% confidence intervals, if certified. Otherwise % recovery =50-150%	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Surrogates	In every calibration standard, sample, and blank analyzed for organics by GC or isotope dilution GC-MS; added to samples prior to extraction	Based on 3x the standard deviation of the lab's actual method recoveries	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Inorganic Parameters: Nutrients, Metals, Total Organic Carbon					

Sample Type	Frequency	Acceptable Limits	Corrective Action	Sampling SOP	Analytical SOP & Method
Lab Blanks (method, reagent, instrument)	1 per 20 samples, minimum 1 per batch	Detectable substance contamination <RL	Determine cause of problem, remove sources of contamination, reanalyze suspect samples or flag all suspect data.	Appendix II, Appendix III	Appendices XXVII, XXIII, XXVIII; EPA 353.2, EPA 200.8, EPA 415.1
Lab Duplicate*	1 per 20 samples, minimum 1 per batch	RPD ≤25%	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Matrix Spike*	1 per 20 samples, minimum 1 per batch	% Recovery =75-125%	If SRMs are in control then proceed. If not, determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Matrix Spike Duplicate*	1 per 20 samples, minimum 1 per batch	RPD ≤25%	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Lab Control Spike, CRM, or SRM	1 per 20 samples, minimum 1 per batch	% Recovery =75-125%	Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Internal Standards	EPA 200.8 - Must be present on all samples. Standards and blanks at identical levels	EPA 200.8 – Absolute response of any one internal standard must not deviate outside of 70-125% of the original response in the calibration blank	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
<b>Inorganic Parameters: Turbidity, Total Dissolved Solids, Total Suspended Solids</b>					
Lab Blanks (method, reagent, instrument)	1 per 20 samples, minimum 1 per batch	Detectable substance contamination <RL	Determine cause of problem, remove sources of contamination, reanalyze suspect samples or flag all suspect data.	Appendix II	Appendices XXVI , XXIX, XXX; SM 2540C/EPA 160.1, EPA 180.1/SM 2130B, EPA 160.2/SM 2540D
Lab Duplicate*	1 per 20 samples, minimum 1 per batch	RPD ≤25%	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Lab Control Spike, CRM, or SRM	1 per 20 samples, minimum 1 per batch	Measured value <95% confidence intervals, if certified. Otherwise % recovery =80-120%	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
<b>Pathogens</b>					



Sample Type	Frequency	Acceptable Limits	Corrective Action	Sampling SOP	Analytical SOP & Method
Lab Blanks (method)	1 per 20 samples, minimum 1 per batch	Detectable substance contamination <RL	Identify contamination source. Clean equipment and prepare new media, check reagents, reanalyze samples.	Appendix II	Appendix XXI; SM 9223
Lab Negative Control	1 per culture medium or reagent lot	Detectable substance contamination <RL	Identify contamination source. Clean equipment and prepare new media, reanalyze samples.		
Lab Positive Control	1 per culture medium or reagent lot	Detectable substance contamination <RL	Identify and correct problem. Re-examine positive control.		
Lab Duplicates	1 per 10 samples, minimum 1 per batch	$R_{log} \leq 3.27 \times \text{mean } R_{log}$	Recalibrate and reanalyze.		
<b>Sediment Toxicity</b>					
Lab Control Sample, <i>Hyalella azteca</i>	1 per 20 samples, minimum 1 per batch	Survival in control samples $\geq 80\%$ ; measurable growth in the controls, all performance criteria outlined in SOP are met.	Determine cause, take appropriate corrective action. Reanalyze all suspect samples.	Appendix IV	Appendix XVIII, EPA 600/R-99-064
<b>Sediment Organics</b>					
Lab Blanks (method, reagent, instrument)	1 per 20 samples, minimum 1 per batch	Detectable substance contamination <MDL	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.	Appendix IV	Appendix XXXII; GCMS-NCI-SIM
Lab Duplicate*	1 per 20 samples, minimum 1 per batch	RPD $\leq 25\%$	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Matrix Spike*	1 per 20 samples, minimum 1 per batch	% Recovery =50-150% or control limits based on 3x the standard deviation of the labs actual method recoveries	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data. Zero percent recovery requires rejection of all suspect data.		
Matrix Spike Duplicate*	1 per 20 samples, minimum 1 per batch	RPD $\leq 25\%$	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Lab Control Spike, CRM, or SRM	1 per 20 samples, minimum 1 per batch	Measured value 70-130% of the 95% confidence intervals, if certified. Otherwise %Recovery =50-150%	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		

Sample Type	Frequency	Acceptable Limits	Corrective Action	Sampling SOP	Analytical SOP & Method
Surrogates	In every calibration standard, sample, and blank analyzed for organics by GC or isotope dilution GC-MS; added to samples prior to extraction	Determined by Lab Manager	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
Internal Standards	According to frequency in lab SOP	Linear regression, $r > 0.995$	Determine cause, take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.		
<b>Sediment TOC</b>					
Lab Blanks (method, reagent, instrument)	1 per 20 samples, minimum 1 per batch	Detectable substance contamination <MDL or <30% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.	Appendix IV	Appendix XXXIV; Walkley Black Method
Lab Control Spike, CRM, or SRM	1 per 15 samples,	Within 95% confidence interval of the certified value; if not certified within 20-25% consensus value	Review raw data quantification reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat until control limits are met.		
Lab Duplicates	1 per 20 samples, minimum 1 per batch	RSD $\leq 20\%$	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.		
<b>Sediment Grain Size</b>					
Lab Duplicates	1 per 12 samples,	RSD $\leq 20\%$	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.	Appendix IV	Appendix XXXIII; ASTM D422-63

\*For the purposes of this project it is acceptable for the matrix spike duplicate or the laboratory control duplicate to stand in for the lab duplicate as a measure of the precision of the analytical method.

When control limits are exceeded the lab QA officer and Project QA Officer must agree on a potential cause and develop a response that ensures it will not happen again. Detections in blanks must be sourced and field, analytical, or cleaning practices must be modified to reduce the risk of further contamination. Excessive RPD values or recovery rates outside of criteria may also require a change of field or laboratory practices. Exceedances of analytical control limits must be reported in the appropriate lab report. Precision in this project is assessed through a combination of field duplicate samples and laboratory duplicate samples. Precision of a pair of samples is measured as the relative percent difference (RPD) between a sample and its duplicate—a laboratory control sample (LCS) and its duplicate (LCSD), a matrix spike (MS) and matrix spike duplicate (MSD), an environmental sample (E) and field duplicate (FD), or an environmental sample and its associated lab duplicate. It is calculated as follows:

$$RPD(\%) = \left| \frac{2(V_i - V_D)}{V_i + V_D} \right| \times 100$$

$V_i$  = The measured concentration of the initial sample

$V_D$  = The measured concentration of the sample duplicate

This same calculation is done for field duplicates and the associated environmental sample.

For precision assessment purposes any lab duplicate, including a matrix spike duplicate or a lab control spike duplicate, may function as the lab duplicate in any batch.

For sediment grain size samples, individual grain size classes are reported as a percentage based on the composition of the entire sample and therefore are not values that can be evaluated individually (they are not independent variables). Precision for sediment grain size is evaluated by the relative percent difference between grain size standard deviations of the environmental sample and the duplicate. The grain size standard deviation (SD) for all classes of a single sample is calculated using the following Folk and Ward 1957 Logarithmic equation:

$$SD = \sigma_1 = \frac{\Phi_{84} - \Phi_{16}}{4} + \frac{\Phi_{95} - \Phi_5}{6.6}$$

Where  $\Phi_{84}$  = phi value of the 84<sup>th</sup> percentile sediment grain size category  
 $\Phi_{16}$  = phi value of the 16<sup>th</sup> percentile sediment grain size category  
 $\Phi_{95}$  = phi value of the 95<sup>th</sup> percentile sediment grain size category  
 $\Phi_5$  = phi value of the 5<sup>th</sup> percentile sediment grain size category

Precision is calculated based on the relative percent difference between the standard deviation of the environmental sample and the standard deviation of a duplicate sample using the following formula:

$$RPD_{SD} = \left| \frac{2(SD_i - SD_D)}{SD_i + SD_D} \right| \times 100$$

$SD_i$  = standard deviation of the initial or environmental sample based on the Folk and War Logarithmic equation

$SD_D$  = standard deviation of the field or laboratory duplicate sample based on the Folk and War Logarithmic equation

Accuracy in this project is assessed using either an LCS or MS. For an LCS lab water is spiked with a known concentration of a target analyte and the percent recovery (PR) is reported. PR in an LCS is calculated as follows:

$$\% \text{ Recovery} = \left( \frac{V_{LCS}}{V_{Spike}} \right) \times 100$$

$V_{LCS}$  = The measured concentration of the spiked control sample

$V_{Spike}$  = The expected spike concentration

A MS can also be used to assess accuracy. For a MS, environmental water is spiked with a known concentration of a target analyte and the PR is reported. PR in and MS is calculated as follows:

$$\% Recovery = \left( \frac{V_{MS} - V_E}{V_{Spike}} \right) \times 100$$

$V_{MS}$  = The measured concentration of the spiked matrix sample

$V_{Spike}$  = The concentration of the spike added

$V_E$  = The measured concentration of the original (unspiked) matrix sample

The MS should not be used solely to assess accuracy due the likelihood of matrix interference however if an LCS does not fall within acceptance criteria an MS may be used to validate a batch if the MS is within acceptance criteria. Some constituents are difficult to spike (e.g. turbidity) and therefore a laboratory may chose to analyze a certified reference material (CRM). A CRM analysis may be used in place of an LCS analysis.

If results for any precision or accuracy samples do not meet the data quality objectives provided in this QAPP, the laboratory must implement corrective measures as outlined in Table 16. If corrective measures require reanalysis of the sample, and the results repeatedly fail to meet the objectives, then the lab is obligated to halt the analysis of samples, identify the source of the imprecision, and make corrections where appropriate before proceeding. If results for any field duplicates and associated environmental samples do not meet the data quality objectives listed in the above tables then the samplers must assess sampling practices and make corrections to their field procedures which will ensure homogeneity in the samples before proceeding.

## 15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Laboratory equipment is maintained by a qualified technician at the frequency listed in Table 17. MLJ-LLC field meters are maintained according to the owner's manual specifications at the frequency listed in Table 18. Laboratories are responsible for maintaining all laboratory equipment according to manufacturer specifications or SWAMP requirements, whichever are more stringent. Frequency and procedures for maintenance of analytical equipment used by each laboratory are documented in the Quality Assurance Manual for each laboratory, which is available from the laboratory on request. Laboratories are responsible for testing, inspecting, and maintaining all analytical equipment. In the event of equipment failure, the source of the failure must be identified and rectified, the equipment must be recalibrated, and any samples analyzed outside of calibration limits must be reanalyzed.

**Table 17. (Element 15) Testing, inspection, maintenance of field and analytical instruments.**

Due to the complexity and sensitivity of most laboratory instruments the testing, inspection, and maintenance procedures are difficult to summarize. A brief and general summary for each instrument follows; however, this table is not intended to describe all testing, inspection, and maintenance procedures for all tests, nor will this QAPP attempt to report SOPs for all such procedures. It is expected that laboratories will employ knowledgeable staff capable of testing, inspecting, and maintaining analytical instruments to ensure a level of data quality that matches or exceeds that demanded in this QAPP.

Equipment / Instrument	Maintenance Activity, Testing Activity or Inspection Activity	Responsible Person	Frequency	SOP Reference
YSI 556MPS with Glass Electrode pH	Clean glass bulb and visually inspect	F. Wulff (MLJ-LLC)	<24 hours before sampling	Appendix IX
YSI 556MPS with Steady State Polarographic DO Sensor	Change membrane and KCl solution	F. Wulff (MLJ-LLC)	Every 30 days	Appendix IX
YSI 556MPS with Electrode Cell EC and Thermistor Temperature Probe	Clean electrodes	F. Wulff (MLJ-LLC)	<24 hours before sampling	Appendix IX
Tecator auto analyzer (Model 2400)	Clean manifold	Sonya Babcock (Caltest)	According to manufacturers specifications	Retained in laboratory
Turbidimeter	Periodic meter zero, calibration in each range	Sonya Babcock (Caltest)	When switching ranges	W-TURB-rev4 Appendix XXXI
ICP-MS	Check and replace water filter, replace pump gaskets, check source filament, check multiplier gain, clean ion source, replace lamp	Sonya Babcock (Caltest)	According to manufacturers specifications	Retained in laboratory
Shimadzu TOC-Vcsh Analyzer Shimadzu 68 place auto analyzer Model ASI-V	Change: catalyst, sample pump tubing, permcation tube, halide scrubber, acid reagent bottle, rinse bottle, humidifier water	Sonya Babcock (Caltest)	According to manufacturers specifications	W-TOC/DOC-rev9 Appendix XXX

<b>Equipment / Instrument</b>	<b>Maintenance Activity, Testing Activity or Inspection Activity</b>	<b>Responsible Person</b>	<b>Frequency</b>	<b>SOP Reference</b>
Ion Chromatograph (DX 320)	Inspect pump and injector seals for leaks, inspect tubing for clogs, inspect or replace precolumn filter, inspect detector for leaks and air bubbles, replace old lamps	Sonya Babcock (Caltest)	According to manufacturers specifications	Retained in laboratory
Spectrophotometer	Check/replace lamp	Sonya Babcock (Caltest)	According to manufacturers specifications	Retained in laboratory
Hewlett Packard 1090L HPLC; Agilent 100 Liquid Chromatograph	Inspect pump and injector seals for leaks, inspect tubing for clogs, inspect or replace precolumn filter, inspect detector for leaks and air bubbles, replace old lamps	Leonard Fong (APPL)	According to manufacturers specifications	Retained in laboratory
Finnigan LCQ Ion Trap Mass Spectrometer; Agilent 1100 G1946D SL Mass Spectrometer	Check and replace water filter, replace pump gaskets, check source filament, check multiplier gain, clean ion source, replace lamp	Leonard Fong (APPL)	According to manufacturers specifications	Retained in laboratory
Hewlett Packard 6890 Gas Chromatograph, Agilent Technologies 6890 Gas Chromatograph, Hewlett Packard 5890 Gas Chromatograph	Check and clean detector and injector, check syringe and column for integrity and installation, rinse column with solvent, check column for leaks,	Leonard Fong (APPL)	According to manufacturers specifications	Retained in laboratory
Perkin Elmer Series 200 Pump, post column pump, and Perkin Elmer LC 240 Fluorescence Detector	Inspect pump and injector seals for leaks, inspect tubing for clogs, inspect or replace precolumn filter, inspect detector for leaks and air bubbles, replace old lamps	Theresa Sherman (NCL)	Every analytical analysis	Retained in laboratory

## 16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

MLJ-LLC field meters are calibrated according to the owner's manual specifications at the frequency listed in Table 18. Laboratories are responsible for calibrating all laboratory equipment according to manufacturer specifications or SWAMP requirements, whichever are more stringent. Frequency and procedures for calibration of analytical equipment used by each laboratory are documented in the Quality Assurance Manual for each laboratory, which is available from the laboratory on request. All equipment capable of being calibrated must be successfully calibrated before analysis. If calibration fails, all affected samples must be re-analyzed or the data flagged and the equipment must be repaired before further analysis.

**Table 18. (Element 16) Calibration of field and analytical equipment.**

Equipment / Instrument	SOP Reference	Calibration Description and Criteria	Frequency of Calibration	Responsible Person
YSI 556MPS with Glass Electrode pH	Appendix IX	3 Point calibration at pH 4, 7, and 10; calibration must be accepted by YSI meter	<24 hours before sampling	F. Wulff (MLJ-LLC)
YSI 556MPS with Steady State Polarographic DO Sensor	Appendix IX	H <sub>2</sub> O Saturated air calibration (%O <sub>2</sub> ) at default 760mm Hg	Before every measurement	F. Wulff (MLJ-LLC)
YSI 556MPS with Electrode Cell EC and Thermistor Temperature Probe	Appendix IX	Calibration to 1413 µS/cm; calibration must be accepted by YSI meter. Temperature calibration is factory set and does not require user calibration	<24 hours before sampling	F. Wulff (MLJ-LLC)
Tecator auto analyzer (Model 2400)	W-TKN-rev9 Appendix XXIX	For TKN calibrate with TKN digestion tablet. For NH <sub>3</sub> standardize with 100mL sample with 5mL borate buffer all adjusted to pH 9.5 with NaOH	Every analytical analysis	Sonya Babcock (Caltest)
Turbidimeter	W-TURB-rev6 Appendix XXXI	Periodic meter zero, calibration in each range	When switching ranges	Sonya Babcock (Caltest)
ICP-MS	M-200.8-rev5E Appendix XXIV	Three calibration standards per linear range, MDL determination, ICV, CCV	When analyst observes calibration is necessary, MDL determined annually, ICV immediately after calibration, CCV after every 10 samples and at end of sample run	Sonya Babcock (Caltest)
Shimadzu TOC-Vcsh Analyzer Shimadzu 68 place auto analyzer Model ASI-V	W-TOC/DOC-rev9 Appendix XXX	a. 2 calibration curves: curve 10 – 6 points, curve 200 – 5 points. $r^2 = 0.995$ b. Analyze blank & LCS, ICV for every 20 samples, CCV, spike and spike duplicate, every 10 samples	a. Every month b. Every 20 or 10 samples respectively	Sonya Babcock (Caltest)
Ion Chromatograph (DX 320)	W-DIONEXrev5 Appendix XXVI	Mixed-standard curve calibration	Every analytical analysis	Sonya Babcock (Caltest)

<b>Equipment / Instrument</b>	<b>SOP Reference</b>	<b>Calibration Description and Criteria</b>	<b>Frequency of Calibration</b>	<b>Responsible Person</b>
Spectrophotometer	W-NO2-rev5 Appendix XXV	Four standard calibration curve, reagent blank, QC blanks, spikes, control samples, and duplicates	Every batch of every analytical analysis	Sonya Babcock (Caltest)
Hewlett Packard 1090L HPLC	HPL8321A Appendix XIV	Calibration with minimum of five stock standard concentrations	Every analytical sequence	Leonard Fong (APPL)
Agilent 100 Liquid Chromatograph	HPL8321A Appendix XIV	Calibration with minimum of five stock standard concentrations. Calibration check after every 20 samples.	Every analytical sequence	Leonard Fong (APPL)
Finnigan LCQ Ion Trap Mass Spectrometer	HPL8321A Appendix XIV	Calibration with minimum of five stock standard concentrations. Calibration check after every 20 samples.	Every analytical sequence	Leonard Fong (APPL)
Agilent 1100 G1946D SL Mass Spectrometer	HPL8321A Appendix XIV	Calibration with minimum of five stock standard concentrations. Calibration check after every 20 samples.	Every analytical sequence	Leonard Fong (APPL)
Hewlett Packard 6890 Gas Chromatograph, Agilent Technologies 6890 Gas Chromatograph	ANA8081A ANA8141B Appendix XII Appendix XIII	Calibration with minimum of five stock standard concentrations. Calibration check after every 20 samples.	Every analytical sequence	Leonard Fong (APPL)
Hewlett Packard 5890 Gas Chromatograph, Hewlett Packard 6890 Gas Chromatograph	ANA619 Appendix XI	Three point calibration. Calibration verification check standard analyzed after every 20 samples	Every analytical sequence	Leonard Fong (APPL)
Perkin Elmer Series 200 Pump, post column pump, and Perkin Elmer LC 240 Fluorescence Detector	NCL ME 075 Appendix XIX	Five calibration standard levels. Calibration verification check standard analyzed after every 20 samples	Every analytical analysis	Theresa Sherman (NCL)



## 17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

MLJ-LLC project consumables are listed in Table 19. Consumables are rejected for use if obvious signs of contamination or tampering exist. Calibrating standard solution acceptance records are maintained alongside calibration records. Bottle integrity records are maintained alongside receiving records. All records are available upon request at the MLJ-LLC office. All laboratories are responsible for inspecting and testing all consumables against a laboratory-specific acceptance criteria and maintaining adequate records.

**Table 19. (Element 17) Inspection/acceptance testing requirements for consumables and supplies.**

<b>Project-Related Supplies (source)</b>	<b>Inspection / Testing Specifications</b>	<b>Acceptance Criteria</b>	<b>Frequency</b>	<b>Responsible Individual</b>
pH standard calibrating solutions (Fisher Scientific)	Solution bottles are inspected to verify factory seal; initial measurements are compared to prior standard measurement	Manufacturer's seal intact, measurements within $\pm 0.2$	Upon opening a fresh standard solution	F. Wulff (MLJ-LLC)
EC standard calibrating solutions (Fisher Scientific)	Solution bottles are inspected to verify factory seal; initial measurements are compared to prior standard measurement	Manufacturer's seal intact, measurements within $\pm 0.5\%$ or $1\mu\text{S/cm}$	Upon opening a fresh standard solution	F. Wulff (MLJ-LLC)
Certified pre-cleaned glass bottles for toxicity (I-Chem/Fisher Scientific)	Carton custody seal is inspected	Carton custody seal intact	At receipt date of shipment	F. Wulff (MLJ-LLC)
Certified pre-cleaned bottles (from laboratory)	Individual bottles are inspected for physical integrity	Bottles and caps intact	At receipt date of shipment	F. Wulff (MLJ-LLC)
Pre-preserved containers (from laboratory)	Preservative volume is visually verified, individual bottles are inspected for physical integrity	Proper preservative volume present, bottles and caps intact	At receipt date of shipment	F. Wulff (MLJ-LLC)
Deionized water	Analysis for target constituent contamination	Detectable substance contamination < RL	Once annually	M. Turner (MLJ-LLC)
Nitrile Gloves (Fisher Scientific)	Carton seal is visually inspected for damage or tampering	Carton is intact and gloves within are clean and intact	At receipt date of shipment	F. Wulff (MLJ-LLC)

## **18. NON-DIRECT MEASUREMENTS (EXISTING DATA)**

It may also be necessary to use preexisting data residing in the ILRP SWAMP Comparable Database housed at the Central Valley Regional Data Center (RDC), to which MLJ-LLC has access. Since this database receives data from a number of sources including MLJ-LLC, it is possible that relevant data may be produced by another project working within the Coalition region. It is assumed that all data within this database has passed SWAMP Comparability QA/QC requirements; however, all third party data considered for use will be reviewed against the data quality objectives stated in Element 7 and only those data meeting all criteria will be used in this project. Third party data may be used to extend the monitoring history of specific locations or more completely characterize zones within the Coalition region.

## **19. DATA MANAGEMENT**

As established in Element 9 above, MLJ-LLC will maintain an inventory of data and will periodically check the inventory against the records in their possession.

All field data is entered into the ILRP SWAMP comparable database after being reviewed and qualified. All data transcribed or transformed, electronically and otherwise, is double checked for accuracy by MLJ-LLC staff and records of this double-checking are maintained at the MLJ-LLC office. After entry into the database, field sheets are scanned and an electronic copy is filed on the MLJ-LLC server. An additional hard copy is printed and archived in the MLJ-LLC office in a separate location from the original. All completed COCs are archived in the same manner.

Transfer of data from laboratories to MLJ-LLC is accomplished by a combination of overnight mail, hand delivery, and electronic submittal. Lab reports are received as electronic PDFs and in SWAMP comparable EDD format, both of which are filed on the MLJ-LLC server and simultaneously copied to CD-ROM format. Hard copies of the reports are filed in the MLJ-LLC office. EDDs are uploaded according to the procedures outlined in Appendices XXXV, XXXVI, and XXVII.

All data residing on the MLJ-LLC server is automatically backed up onto magnetic tape media. Complete backup takes place once per week, with incremental backups every night. Digital tape backups are kept for seven days before being completely written over by the next complete backup. MLJ-LLC adds data to a replica of the ILRP SWAMP Comparable Microsoft Access database housed at the Central Valley Regional Data Center; the MLJ-LLC replica is periodically synchronized with the Design Master. The Design Master is automatically backed up to magnetic tape according to the same schedule as the MLJ-LLC server. The MLJ-LLC Database Management Team (DMT), consisting of Melissa Turner, project QA Officer and the MLJ-LLC database manager, is responsible for database maintenance, synchronization and backup. In the event of hardware failure MLJ-LLC server data is restored from the tape backup and the ILRP Design Master is restored from the Central Valley RDC tape backup.

A copy of the database is delivered to the CVRWQCB staff quarterly. Monitoring reports which summarize the monitoring data are submitted to the CVRWQCB following the schedule outlined in section 21.

## GROUP C: ASSESSMENT AND OVERSIGHT

### 20. ASSESSMENTS & RESPONSE ACTIONS

All reviews of QA data will be made by the MLJ-LLC QA Officer and may include the CVRWQCB QA Officer. Reviews of the sampling procedures will be made bimonthly. Reviews involve comparing observed sampling procedures against those established in the MLJ-LLC SOPs. Additional reviews will be made as SOPs are updated and refined. Contract laboratories are responsible for self assessment and oversight, although each data report is audited for compliance with MLJ-LLC’s QA/QC program. The MLJ-LLC QA Officer Melissa Turner is responsible for flagging all data that does not meet established QA/QC criteria.

If a review discovers any discrepancy, MLJ-LLC’s QA Officer Melissa Turner will discuss the observed discrepancy with the personnel responsible for the activity. The discussion will include the accuracy of the information, potential cause(s) leading to the deviation, how the deviation might impact data quality and the corrective actions that might be considered.

The MLJ-LLC QA Officer Melissa Turner has the power to halt all sampling and analytical work by both MLJ-LLC and the contract laboratories if the deviation(s) noted are considered detrimental to data quality.

Assessments will be oral; if no discrepancies are noted and corrective action is not required additional records are neither maintained nor reported. If discrepancies are observed the details of the discrepancy and any corrective action will be reported in the quarterly and annual monitoring report.

Corrective action will be determined from Monitoring and Reporting Program Order No. R5-2008-0005 Appendix F Attachment C based on analysis of the type of discrepancy. Corrective action may correct an unauthorized deviation from the QA/QC procedures or SOPs, or it may remedy a systematic failure in the established QA/QC procedures or SOPs. The MLJ-LLC QA Officer will be responsible for addressing all corrective action. All correspondence will be documented in print, and all correspondence will be filed at the MLJ-LLC office which is available upon request.

### 21. REPORTS TO MANAGEMENT

Data summary and other reports will be written by MLJ-LLC according to the following table. The table provides dates for the first year this QAPP is active. In subsequent years if the deliverable due date is not a weekday, the deliverable will be provided on the first business day following the due date.

**Table 20. (Element 21) QA management reports.**

Type of Report	Frequency	Projected Delivery Dates(s)	Person(s) Responsible for Report Preparation	Report Recipients
Monitoring Report	Quarterly	June 1, 2009 September 1, 2009 December 1, 2009	Michael Johnson	Chris Jimmerson Mike Wackman John Brodie
Monitoring Report	Annually	March 1, 2009	Michael Johnson	Chris Jimmerson Mike Wackman John Brodie
Management Plan Report	Annually	April 1, 2009	Michael Johnson	Chris Jimmerson Mike Wackman John Brodie

## **GROUP D: DATA VALIDATION AND USABILITY**

### **22. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS**

Data generated by project activities will be reviewed against the data quality objectives cited in Element 7 and the QA/QC practices cited in Elements 14, 15, 16, and 17. The MLJ-LLC QA Officer will review any data that fails any stated quality objectives to decide whether to accept or reject the data. The decision to accept or reject the data will be based on an assessment of the impact of the data quality failure and will be made according to the following process.

Data will be separated into three categories: data meeting all data quality objectives, data failing to meet precision or recovery criteria, and data failing to meet accuracy criteria. Data meeting all data quality objectives, but with failures of quality assurance/quality control practices will be set aside until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the last category.

Data falling in the first category is considered usable by the project. Data falling in the last category is considered not usable. Data falling in the second category will have all aspects assessed. If sufficient evidence is found supporting data quality for use in this project, the data will be moved to the first category, but will be flagged with the appropriate SWAMP data qualifier code by the MLJ-LLC QA Officer.

### **23. VERIFICATION AND VALIDATION METHODS**

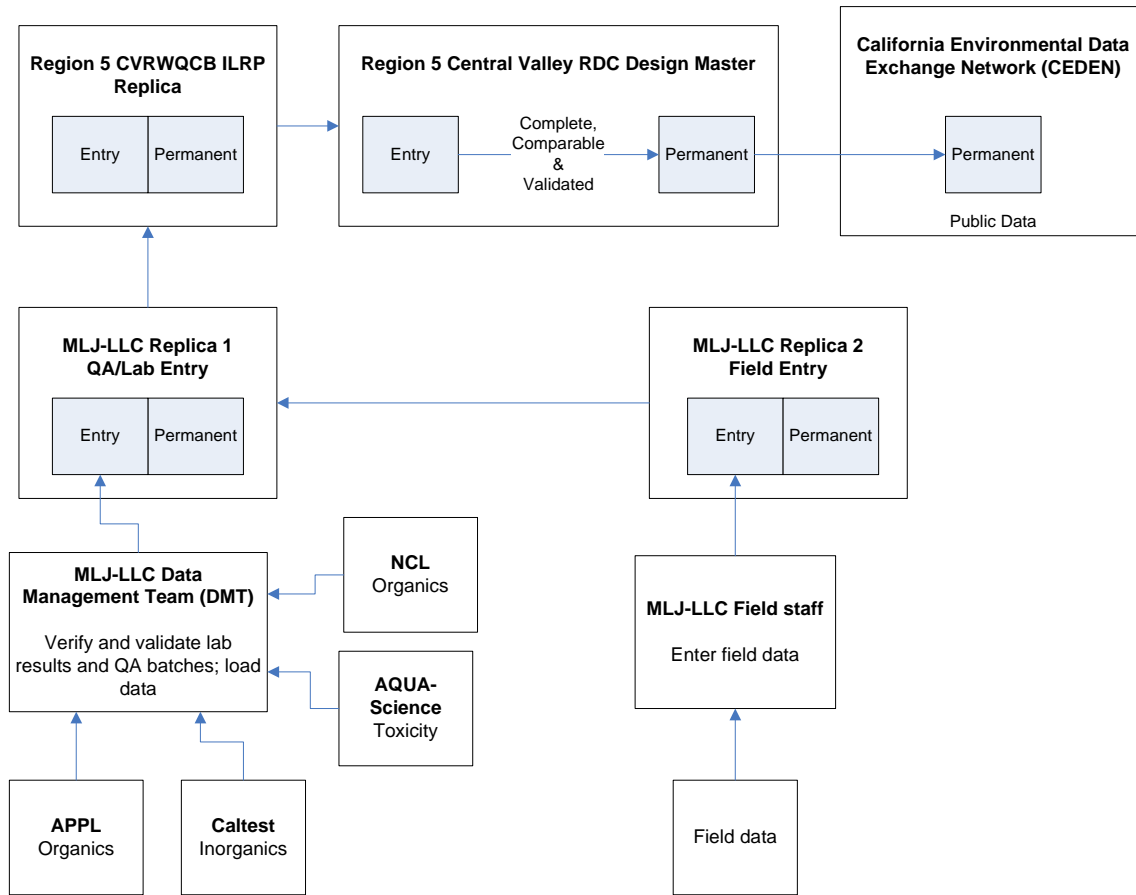
Data will be QC'd visually and recorded as checked by initials and dates directly on the record or on a specialized record tracking document. MLJ-LLC's QA Officer or a delegate of the QA Officer will do all reviews of 100% of the reports. Each contract laboratory's QA Officer will perform checks of all of its records at a frequency that the lab determines sufficient.

The contract laboratories will be responsible for the reduction of the raw data generated at the laboratory bench to a format determined by agreement between the laboratory and the MLJ-LLC QA Officer. The analytical process includes verification or a quality assurance review of the data, which includes:

- Verifying the calibration samples for compliance with the laboratory and project criteria;
- Verifying that the batch QCs were analyzed at a proper frequency and the results were within specifications;
- Comparing the raw data (e.g. chromatogram) with reported concentration for accuracy and consistency;
- Verifying that the holding times were met and that the reporting units and quantitation limits are correct;
- Determining whether corrective action was performed and control was re-established and documented prior to reanalysis of QC or project samples;
- Verifying that all project and QC sample results were properly reported and flagged; and
- Preparing batch narratives that adequately identify and discuss any problems encountered.

All QA issues will be noted. Reconciliation and correction of these issues will be done by a committee composed of MLJ-LLC's QA Officer, Field Supervisor, and Project Manager, and the contracting laboratory's QA Officer and Laboratory Director. Any corrections require a unanimous agreement that the correction is appropriate. Contract laboratories submit in their data report the batch narrative that identifies and discusses any problems encountered. If the report is accepted with or without correction pertinent portions of this narrative will be transferred to the ILRP SWAMP Comparable database as the MLJ-LLC QA Officer deems necessary.

**Figure 4. Flowchart of MLJ-LLC Data Progression**



## **24. Reconciliation with User Requirements**

Procedures to review, verify and validate data are included in Appendix XXXV (SOP for Data Verification, Validation and Loading to the ILRP SWAMP Comparable Database) and Appendix XXXVII (SOP for Toxicity Data Verification, Validation and Loading to the ILRP SWAMP Comparable Database). This process ensures that all data uploaded into the ILRP SWAMP Comparable database has been qualified on a result, batch and project level with each deviation being coded and comments provided.

Data is reported to the CVRWQCB in a variety of formats including raw data, narrative data summaries including data compiled into tables and charts, and data contained within the ILRP SWAMP Comparable database. Limitations in data use will be reported to the CVRWQCB in the Annual Monitoring Report as well as through codes and comments in the database. Non-primary data users beyond the CVRWQCB will be able to access the data generated by this project deposited in the ILRP SWAMP Comparable database and should heed the qualifier flags applied to the data by the MLJ-LLC QA Officer to alert them of limitations to the data. Non-primary data users will be able to access the narrative reports by request to the CVRWQCB, the Coalition, or MLJ-LLC.

**APPENDIX I. Standard Operating Procedure (SOP) for Water Toxicity Sampling (Revision 1.0, 07/19/07)**

# Standard Operating Procedure (SOP) for Water Toxicity Sampling (Revision 1.0, 07/19/07)

MLJ-LLC  
Updated 07/19/07  
Revision 1.0

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## 1. Purpose

This SOP describes procedures for collecting toxicity testing water samples from main stems, tributaries and drainages in the East San Joaquin Water Quality Coalition and San Joaquin and Delta County Water Quality Coalition areas. A standard method may be used to collect the samples. This SOP describes the planning, sample collection and quality control (QC) procedures for toxicity testing water sampling.

## 2. Terms and Definitions

**Grab Sample** A sample collected from one location and depth

**Bucket sampler** Specially designed sampler that fits a 3-L Teflon lined jug and is attached on a rope and carabiner

**QC** Quality control

**COC** Chain of Custody

## 3. Equipment and Supplies

- Field sheets, COC sheets, maps, Avery Weatherproof labels, sharpie permanent markers, clear tape and dispenser, clip board
- Five** 1-Gal pre-cleaned Amber Glass Jugs w/ Teflon-lined caps per sample and reserve bottles
- Coolers with ice
- Field parameter multi-meter
- Gloves (Nitrile) for safety and to eliminate cross contamination
- Bucket sampler with work gloves
- Safety equipment: Orange Safety Vest, Road Cones, first aid kit, cell phone, head lamp
- Waders

## 4. Procedures

Toxicity testing water sampling involves the following steps:

### 4.1. Labeling the Sample Bottle

- Use pre-printed labels for each site. The label should include the site name, site ID number, date, sample time, and your initials. Labels are supplied with the sampling plan prepared and sent by PER.
- Complete the printed label with an extra-fine-point Sharpie. Attach it to the jug and cover the entire label with a piece of clear tape and wrap it all around the bottle to prevent peeling. Do this before the bottle gets submerged
- Use 24-hour military time for the sample time; round to the nearest 10 minutes. For example: a sample collected at 09:52 would have the sample time on the label and Chain of Custody (COC) form rounded off to 09:50; a sample collected at 09:57 would be rounded up to 10:00; 09:55 would also be rounded up to 10:00. Use the following format for the date: mm/dd/yy

### 4.2. Completing the Field Sheet

See SOP for surface water sampling for details.

### 4.3. Collecting an Environmental Sample

*Always wear clean gloves during the sampling procedure!*

## SAMPLE COLLECTED BY WADING INTO THE STREAM:

When collecting by wading, choose a site that has the most well-mixed flow. If a dock or other safe structure would allow you to collect the sample closer to the middle of the stream you should utilize it. If sampling from a structure, be sure to collect the sample on the upstream side of the structure (to minimize contamination of the sample).

When collecting from the bank, bottles can be rinsed from the bank but you should wade out as far as is safe to collect the sample. Simply hold the sample container as far under the surface of the water as possible (but not on the bottom) until it is full. Tilting the bottle at a 45° angle works best. Avoid collecting sediment in the water stirred up by your feet.

At each site, **rinse every sample bottle three times with site water**. When rinsing each jug, be sure the cap is on the bottle so that the cap gets rinsed as well.

Once every jug is rinsed three times, they can be filled with site water. *Note: The rinsing process can stir up sediment near the bank, so samples should be collected upstream of where you were rinsing in order to get a representative sample.*

Be sure to fill bottles all the way to the top, making sure to leave no head space, which decreases the chance of losing any volatile organic compounds present. This can be done by capping the bottles under the water surface.

Once all jugs are filled to the top, load them into the white 120 qt coolers. Use either bubble wrap or Styrofoam blocks to insure no glass to glass contact. Cover bottles with ice to ensure that the samples are at 4°C.

## BRIDGE SAMPLE

When collecting water samples from a bridge be sure to wear the orange vests and to put out the orange cones (approximately 50-100 feet before the place you are sampling from) so that anyone driving by can readily see you and has time to slow down as they approach the bridge.

If it is safe you should collect the sample on the **upstream side of the bridge** in the middle of the waterway.

An attempt should be made to retrieve the sample from 1/3 of the total depth of the river.

To rinse the bottles with site water, secure a bottle into the bucket sampler with the surgical tubing and a weight. Lower the sampler down into the water until it reaches the bottom (the rope slacks off). Gradually pull the sampler off the bottom to 1/3 of the total depth of the river to get a representative of the water column. When the bottle is partly full, pull the sampler up being careful not to allow it to swing too much as it may hit the side of the bridge and cause the bottle to break. Rinse one jug three times, after that, use this jug to rinse the other bottles. Do so by pouring a little water into the other jugs and rinse each jug with cap on also three times. *Note: Wear heavy-duty gloves when lowering the sampler to avoid rope burn.*

Once every bottle is rinsed three times, they can be filled with site water by placing them in the bucket sampler and lowering them from the bridge. Be sure to fill bottles all the way to the top, making sure to leave no head space, which decreases the chance of losing any volatile organic compounds present.

The last thing to do before filling any amber glass sample bottle, regardless of method, is to remove the lid. The first thing to do after filling any bottle, regardless of the method, is to replace the lid. If you have more than one sample bottle to fill, remove each lid prior to filling the bottle. The person that opens and closes the 1-Gal amber glass bottle always wears new, clean gloves for this procedure and does not touch anything but the cap.

#### 4.4. Collecting a Quality Control Sample (5% of overall samples)

View the QC Schedule to find out at which site you should collect a QC sample.

##### FIELD DUPLICATE

The sampling time for the duplicate will be the same as the environmental sample. Field duplicates will be designated by the prepared sampling plans and labels will have a Station ID that ends with FD.

##### BRIDGE SAMPLE

Fill ten 4-L jugs with the bucket sampler; five for the environmental sample and five for duplicate sample.

##### SAMPLE COLLECTED BY WADING

Fill ten 4-L jugs from the bank or by wading; five for the environmental sample and five for the duplicate. Both samplers should fill bottles at the same time and bottles should be filled sequentially.

#### 4.5. Check all field data

A second person, not the one who filled out the field sheets and COCs, should double-check all of the recorded times for completeness and error at the end of the sampling day!

#### 4.6. Check ice level

The temperature of the ice chest should be around 4°C. Make sure to add ice if necessary.

If you can't deliver the samples to the designated lab on time, make sure that there is enough ice in the cooler until the samples are delivered the following day.

### 5. Sample Delivery

Samples need to be delivered within 36 hours (by 09:00 next day) to:

AQUA-Science

17 Arboretum Drive

Davis, CA 95616-7011

(530) 756-5456

### 6. Completing a Chain of Custody form

Complete a Chain of Custody form for each sampling day.

The original COC's will stay in the respective labs. Be sure to have lab personnel give you a copy of the COC.

Sample transfer between field staff and laboratory is documented by **signing and dating** "relinquished by" and "received by" blocks whenever sample possession changes. The document must have both yours **and** the recipient lab's signature.

**APPENDIX II. Standard Operating Procedure (SOP) for Surface Water Sampling (Revision 1.0, 09/17/07)**

# Standard Operating Procedure (SOP) for Surface Water Sampling (Revision 1.0, 09/17/07)

MLJ-LLC  
Updated 09/17/07  
Revision 1.0

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## 1. Purpose

This SOP describes procedures for collecting surface water samples from main stems, tributaries and drainages in the East San Joaquin Water Quality Coalition and San Joaquin and Delta County Water Quality Coalition areas. A standard multi-vertical depth integrating method may be used to collect the samples although most samples are collected direct to container. This SOP describes the planning, decontamination, sample collection and quality control (QC) procedures for surface water sampling.

## 2. Terms and Definitions

Grab sample	a sample collected from one location/depth
Integrated sample	a sample comprised of a designated number of sub-samples that have been combined. An integrated or composite sample represents the waters overall composition.
Techma	Specially designed cage sampler that fits a 3L Teflon bottle and is generally attached on a rope and karabiner
QC	Quality control
COC	Chain of Custody
DI	De-ionized water

## 3. Equipment and Supplies

- Field sheets, COC sheet, maps, Avery Weatherproof labels, sharpie permanent markers, clear tape and dispenser
- Sampling bottles supplied by laboratories for specific analyses
- Coolers with ice
- Field parameter meter (pH, temperature, Electrical Conductivity, DO)
- Decontamination supplies: 5-gallon carboy with DI water, Methanol\*, Liquinox soap\*, Methanol waste container\* (\*=using Techma)
- Gloves (nitrile) for safety and to eliminate cross contamination
- Waders
- Techma cage sampler with rope, bungee cord and karabiner; 3L Teflon bottle
- Safety equipment: Orange Safety Vest, Road Cones


**For the collection of Water Column Toxicity and Trace Metals samples please view separate SOP's.**

## 4. Procedures

Surface water sampling involves the following steps:

### 4.1. Labeling the Sample Bottle

Use pre-printed labels for each site. The label should include the site name and the site ID; the sampler will fill in the **date, sample time** and **their initials**. Complete the printed label with an extra-fine-point Sharpie before you collect the sample and cover the entire label with a piece of clear tape to prevent peeling. Use 24-hour military time for the sample time; round to the nearest 10 minutes. For example: a sample collected at 09:52 would have the sample time on the label and Chain of Custody (COC) form rounded off to 09:50; a sample collected at 09:57 would be rounded up to 10:00; 09:55 would also be rounded up to 10:00. Use the following format for the date: mm/dd/yy

Sample ID: <b>535XSSAQR-GR</b>		
Lab: <b>APPL</b>	Sample Matrix: <b>Site Water</b>	
Sample Analyses: <i>Carbamates, OCs, OPs, Herbicides</i>		
Methods: EPA 8321, EPA 8081, EPA 8141/619		<div style="border: 1px solid black; padding: 5px; text-align: center;">           Container:            1-L Amber Glass            1 of 4         </div>
Sample Date	Time	

4.2. Completing the Field Sheet  
(See example in Element 12 Figure 3)

Field sampling plans are created and printed at the MLJ-LLC office.

The Field Sheet already shows the Station ID, Date, Project ID, Station Name, Site Code and Season, the Target Latitude and Longitude. The sampling team has to fill in the rest of the requested information.

Either add the needed information or circle the applicable answer. Please complete all fields!!

Event Type: *WaterTox\_Chem* means sampling everything including, Water Column Toxicity, but not Sediment. *WaterChem* means no Water Column Toxicity, or pesticide screening only. *WaterTox* means only Water Column Toxicity. *SedTox\_Chem* means sediment only.

Field parameter meter(s): use the equipment calibration SOP to calibrate the field equipment prior to sampling event. Allow the probe to soak in native water for a few minutes until the reading stabilizes.

**BANK SAMPLE:** measure directly from river edge

**BRIDGE SAMPLE:** If possible measure field parameters directly from the water body. Otherwise after filling sample containers from 3L Teflon bottle use excess water from the 3L Teflon bottle for the field measurements. First, rinse the probe and plastic container used to measure parameters with water from the 3L bottle before pouring portion into the measuring container. Measure water parameters soon after pouring off the sample so that conditions (i.e. temperature) do not change.

At the end of the day rinse the probe with tap water and moisten the storage cap with tap water before placing the meter in its case.

Record the meter number (for example YSI #1, shown on outside of meter case or serial # on the back side of the meter) used on the bottom of the field sheet.

Record recalibration date on the calibration logbook in the MLJ-LLC office and the cover sheet of the field sheets.

Original field sheets stay with MLJ-LLC in a prepared folder at the office. Field sheets are scanned and electronic copies are kept on the MLJ-LLC server.

4.3. Collecting an Environmental Sample

Always wear clean nitrile gloves during the sampling procedure!

A full range of samples will only be collected if you have normal water conditions.

If the water level is very low or there is no flow and the situation seems more puddle-like with standing water, samples will not be collected. No other samples or QC's will be collected. On the field sheet and COC (if pre-filled out) record why the samples were not collected (i.e. dry site).

Notify your project supervisor about these conditions since the QC schedule will have to be changed accordingly.

If you are not sure about collecting water samples at a particular site for whatever reason, try calling your senior sampler, Jon Katz (530 902 1622), your QA Officer, Melissa Turner (530 297 4684 or cell: 916 607 5602) or Michael Johnson (530 400 6725).

If the water has a bad odor, please make a note on the label and on the COC. The lab will use a different handling procedure for those bottles.

#### GRAB SAMPLE (individual bottle by hand)

Most sampling will be performed by wading into the midchannel and filling each pre-labeled bottle with native water and capping with clean gloves under the water surface, so that no headspace is left in the bottle. All bottles should be rinsed with DI water after filling and wrapped in protective sleeves before putting on ice.

If wading into the water is unsafe or impossible, either sample from a bank or bridge using the following procedures:

#### BANK SAMPLE (using pole sampler, which we don't carry to sites)

- a) Using bungee cord, affix the sample bottle (already labeled and taped) to the sampling pole
- b) Check to insure the bottle is secure
- c) Remove the cap (wear clean glove!)
- d) Immerse the bottle until bubbles stop. Fill completely and do not leave any headspace
- e) Replace the cap (still wearing the clean glove!)
- f) Rinse the outside of the bottle with DI water
- g) Slip the bottle into a protective sleeve
- h) Place sample directly into a cooler. Make sure there is no glass-to-glass contact

#### INTEGRATED GRAB SAMPLE (bridge sample)

Set out orange traffic cones. Put on your orange safety vest. Always be aware of traffic and use caution while sampling from a bridge. At the van, put the **clean** 3L Teflon bottle into the TECHMA cage, secure it with the bungee cord (***you will lose the bottle if the bungee cord is not strapped around the bottle!***) and remove the cap (have the "clean hands" person remove this with gloves on). Wearing leather work gloves carefully lower the bottle from the bridge railing to the water surface. Do not lower too fast or the bottle may be propelled from the cage upon impact. Perform a triple rinse with native water. Fill the bottle at least ¼ full for each rinse. To collect the sample, fill the bottle 1/3 at each of three equally spaced verticals (submerge for about 3-5 seconds), being careful to avoid contact between the bottle and anything but river water, especially when moving between verticals. Return to the van. Remove the 3L bottle from the TECHMA cage and swirl the water until completely mixed. The second person has already labeled the sample bottles. While wearing clean gloves the second person removes the sample bottle cap and holds the bottle as the sampler pours from the 3L Teflon bottle into the sample bottle. After the sample bottle is completely filled the second person then recaps the sample bottle. Rinse the outside of the sample bottle with de-ionized water, place the bottle in a protective sleeve and store it in the cooler.

The last thing to do before filling any sample bottle, regardless of method, is to remove the cap. The first thing to do after filling any sample bottle, regardless of method, is to replace the cap. If you have more than one sample bottle to fill, remove each cap just prior to filling the bottle. If using the clean hands-dirty hands method the person that opens and closes the sample container always wears clean gloves for this procedure and does not touch anything but the cap. In all other cases the sample bottle is opened by the sampler using a glove that has touched nothing but the bottle and native water.



#### 4.4. Cleaning the Sampling Equipment

Clean the 3L bottle after sampling with the following procedure:

While wearing gloves, add 10% liquinox soap mixture (2-3 squeezes) and approximately 50ml of deionized water to the Teflon bottle. Place the cap on the bottle and swirl the soap around inside the bottle until the entire inside surface has been covered with suds. Un-cap the bottle and pour the soap onto the ground. Rinse the bottle and cap using deionized water until no suds remain inside the bottle or on the cap

Pour 5-10ml of Methanol into the bottle and swirl, with the cap on, until Methanol has covered the entire inside surface of the bottle. Carefully pour the waste Methanol into the Methanol waste container. Seal the Methanol bottle and waste container with Parafilm to prevent fume leakage.

*Methanol is dangerous—do not inhale or touch! Know your MSDS!*

The 3L bottle is ready for the next sampling and should be stored, with the cap on, inside the TECHMA cage

#### 4.5. Collecting a Quality Control Sample

One site will be designated for QC collection. This will be listed in the sampling plan previously prepared.

##### **Field duplicate:**

Collect the environmental sample and the field duplicate sample at the same time. For toxicity sampling this requires two people to sample at the same time. The sample time for the duplicate will be the same time as the environmental sample (rounded to the nearest 10). Field duplicates are noted in the sample ID by following the site ID with “-FD”.

##### BRIDGE SAMPLE

From the single 3L Teflon filled using the procedure above pour the collected water into two equal bottles; one for the environmental sample and one for duplicate sample

##### WADING OR BANK SAMPLE

Fill two equal bottles in the stream or with one reach of the pole sampler; one for the environmental sample and one for the duplicate.

##### **Matrix Spike:**

An extra bottle for a matrix spike should be collected at the same time as the environmental sample following the same procedures. For pesticides, the bottle will be a 1-gallon glass amber jug that will be used for a matrix spike and matrix spike duplicate sample. Be sure to use the label that says matrix spike or MS for that site and that the COC notes which sample is the matrix spike (written in the notes section of the COC). Matrix spikes are noted in the sample ID by following the site ID with “-MS”.

##### **Blank sample:**

Wearing clean nitrile gloves, open the sample bottle and fill with DI water. Do not allow anything into the bottle or cap that is not DI water. Fill bottles to the top and cap without leaving any headspace. Blank samples are noted in the sample ID by following the Site ID with “-FB”. The sample time will be the same as the corresponding environmental sample.

##### BRIDGE SAMPLE

##### ***BEFORE TAKING ENVIRONMENTAL SAMPLE:***

Rinse the clean 3L Teflon bottle three times with deionized water (approximately 50ml for each rinse)

Fill the 3L bottle 2/3 full with deionized water and pour into the sample bottle for the blank

##### WADING OR BANK SAMPLE

Fill sample bottle with deionized water for the blank sample.

4.6. A second person, other than the one who filled out the field sheets and COC's, should double-check all of the recorded times for completeness and error at the end of the sampling day!

4.7. Check ice level

The temperature of the ice chest should be around 4°C. Make sure to add ice if necessary. Drain melted water, since it is a possible source of contamination and will also take up valuable cooling volume.

## 5. Sample Delivery

Samples for Caltest and APPL laboratories will be delivered by Extra Mile Courier or other lab-designated courier the same day as sampling or as soon as possible thereafter. Both sampler and courier sign the COC, the sampler should make a copy and the original stays with the samples.

## 6. Completing a Chain of Custody form

(See example in Element 12 Figure 2)

Complete Chain of Custody forms for each sampling day and for each lab receiving samples. These will be printed on Rite-n-Rain paper and included with the prepared sampling plans.

The original COC's will stay with the samples in the respective labs. Be sure to have lab personnel give you a copy of the COC or, if using a courier, that the COC is signed and copied prior to sending the samples. All copies should be stamped or handwritten "COPY" to prevent confusion.

Sample transfer between field staff and laboratory is documented by **signing and dating** "relinquished by" and "received by" blocks whenever sample possession changes. The document must have both yours **and** the lab's signature.

**APPENDIX III. Standard Operating Procedure (SOP) for Total Metals Sampling (Revision 1.0, 07/19/07)**

Standard Operating Procedure (SOP) for Total Metals Sampling (Revision 1.0, 07/19/07)

MLJ-LLC  
Updated 07/19/07  
Revision 1.0

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Modified by Melissa Turner to reflect Caltest Laboratory specific procedures on August 11, 2006 based on MLML SWAMP SOP 001-B: Field Water Sampling for Trace Metal Analysis Based Upon Modified Frontier Geoscience’s SOP 008 and Modified EPA Method 1669.

## 1. Scope and Application

This SOP describes the techniques used to collect and preserve water samples for Trace Metal Analysis in a way that neither contaminates, loses or changes the chemical form of the analytes of interest.

The samples are collected in the field into previously cleaned and tested sample bottles of a material appropriate to the analysis to be conducted.

Appropriate sampling technique may vary depending on the location, sample type, sampling objective, and weather.

## 2. Summary of Method

The sample bottles that are used have been tested and found to have low levels for trace metals after the cleaning procedure. At the site the bottles are filled with the sample water using the “clean hands-dirty hands” technique. Bottles are resealed tightly. The bottles contain  $\text{HNO}_3$  which acidifies the sample and is kept at  $4^\circ\text{C}$  until analysis.

## 3. Equipment

Clean box for gloves. A Rubbermaid storage box is used to keep the sampling gloves clean. Gloves should be packed in zip lock bags and handled with care to avoid contamination. Reseal zip lock bags after use. Try to take out clean gloves touching the wrist part of the glove and not finger part. “Dirty hand”-person hands out the clean gloves to the “clean hand”-person.

Plastic Sample Bottles. 500 ml plastic bottles containing  $\text{HNO}_3$  are used for sample collection. Bottles are stored zipped in two Ziploc bags to minimize exposure to the ambient atmosphere prior to sampling.

## 4. Procedures

### 4.1. Pre-sampling preparations

Obtain the proper equipment and supplies such as: 500ml bottles with  $\text{HNO}_3$ , nitrile gloves, Milli-Q or metal-free DI water from Caltest Laboratories for field blanks. Check the need for special supplies including safety equipment, boots, first-aid kit, traffic control devices, coolers and ice. Pre-label all environmental sample bottles with a label and finish with clear tape. The preprinted and filled out label is securely attached to the outer bag. Clear tape is put over the label.

### 4.2. Collection of unfiltered samples for total Trace Metal Analysis

The sample can be collected by dipping the bottle into the stream or river by hand using the “clean hands–dirty hands” technique using nitrile gloves.

Two people are required for sample collection; determine which person is designated as “clean hands” and which person is designated as “dirty hands” for the duration of the sampling event. The personnel should all wear nitrile gloves. Gloves can be discarded during sampling if anything happens which may compromise their cleanliness. The “dirty hands” person opens the bag with the gloves and hands the “clean hands” person a pair of clean gloves and then also puts on clean gloves and closes the glove bag. The “clean hands” person executes the sampling process. The bottle is opened and filled with sample water. Be sure not to overflow the bottle with water as the  $\text{HNO}_3$  will be lost. The cap is placed back on the bottle and fastened tight.

The sampling process is to be executed as quickly as possible to minimize the chance for contamination by ambient particles, etc.

### 4.3. Preservation

All samples are preserved with the  $\text{HNO}_3$  already present in the bottle.

### 4.4. Blanks and Duplicates

Blanks for Metals

Field Blanks will be filled with DI water obtained from Caltest Laboratories in the field following normal sample procedures.

Duplicates for Metals

Sample duplicates for QA purposes are obtained by filling two sample bottles with sample water from one location using identical methods.

**5. Sample tracking**

Sample tracking: Field samples are checked for proper labeling including site ID, date, and type of sample. Field data sheets are filled out with information on sample collectors, processing and other relevant information. Chain of Custody forms are prepared for all samples.

**6. Shipping or sample delivery**

Acidified samples will be brought to the MLJ-LLC office in Davis, CA with the signed COC's and will be picked up by a Caltest courier the following morning.

**APPENDIX IV. Standard Operating Procedure (SOP) for Sediment Sampling (Revision 1.0, 02/08/08)**

Standard Operating Procedure (SOP) for Sediment Sampling (Revision 1.0, 02/08/08)

MLJ-LLC  
Adapted from UCD AEAL; Updated 02/08/08  
Revision 1.0

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## 1. Field gear needed

- I-Chem 1000 ml tall clear 200 series glass jars (2 per sample plus extras) (Fisher Catalog No. 05-719-476)
- Pre-cleaned scoops (1 per sample plus extras)
- Ekman bottom grab, rope, and messenger
- 5-Gal bucket
- Ice chests with sufficient capacity to hold I-Chem jars
- Ice for ice chests
- Disposable gloves – nitrile
- Markers, labels, sampling field sheets and 2" plastic tape
- Hip boots or waders
- Liquinox soap (10% mix)
- Acetone container, acetone waste container, and parafilm to seal them
- Pasteur pipettes and bulbs

## 2. Sampling procedure

### SCOOP METHOD

The following sampling protocol assumes sampling will generally be done in small wadeable creeks or agricultural drains. Occasional samples may be collected from larger rivers, but collection is presumed to occur from shore, without use of a boat. The protocol is limited to water depths of <24 inches and preferably <12 inches.

Sediment to be collected should be soft silt and clays. Avoid hard clay, rock, sand and gravel; though in areas dominated by these unacceptable substrates, suitable sediments may be sometimes be found in depositional areas (e.g., inside of bends or downstream of obstructions). Current should be slow, both for the sake of safety and to avoid scouring of sediment from the sampling tool during collection. If there is a risk of the sampling person being swept of his/her feet, then do not sample. Conversely, if the Ag drain contains no water, then do not sample. As with water sampling, if the waterway is in discreet sections separated by patches of dry ground and water doesn't flow between the discreet sections do not sample.

Prior to sampling, fill out the prepared label sampling date and sampling time. Cover label with clear tape. Collect and record other ancillary information routinely collected under the Ag drain sampling protocol on the field sheet. Put on a fresh pair of disposable gloves before sampling.

Depending on site characteristics, sampling may be possible from the bank or, if necessary, by wading into shallow water. In most cases, when water depth is less than 12 inches, sampling will be possible with a hand scoop. Using a pre-cleaned scoop (a fresh one for each sample location) skim the upper 1-2 cm of the sediment column, until the scoop is 1/2 to 3/4 full. The intent is to collect freshly deposited material on the sediment surface with which most biota would interact. Do not dig deeply into the substrate, but limit penetration into the sediment to 1-2 cm. Raise the scoop out of the water slowly to avoid winnowing of its contents and slowly pour excess water off a back corner of the scoop. Do not pour off fine sediments, only clear water, and do not lose the fine flocculent material that is often found on the sediment surface. After removal of excess water, the sediment is placed into the I-Chem jar.

Many scoops of sediment (perhaps 20-30) will be needed to fill both jars. When collecting, work in an upstream direction, both for improved water clarity and to avoid sampling material that you may have disturbed and was re-deposited further downstream.

The jar should not be filled to the point of overflowing and headspace is permissible. You can either sample a continuous stretch of the water body (note the distance you sample, for example "over 30m stretch") or sample at 3-5 different locations along a certain stretch. Sediments from each location comprising 1/3 to 1/5 of the total sample volume. If you do that, please note the # of composites. (For example 4 composites) Do not worry about homogenizing the sediment while in the sample jar; this will be done back in the laboratory. Take large debris out. It is recognized that compositing of multiple

sites may frequently not be possible because of, for example, steep banks or dense vegetation providing few access points. In such instances, collection of all sediment from a single point is acceptable.

#### **EKMAN BOTTOM GRAB METHOD**

When it is not possible to collect a sample by wading but it is possible to drop a dredge from a bridge the Ekman bottom grab kit may be employed.

Before use, inspect the stainless dredge for cleanliness and clean if necessary according to the instructions below. Check the knot attaching the dredge to the rope, and check the rope for fraying or weakness. Place the spring on each side of the dredge around the posts on the jaws. Wearing nitrile gloves, carry the Ekman kit, a scoop, and a set of bottles out to the sampling location. Sampling downstream of the bridge is recommended to prevent the Ekman from being pulled out of sight when it enters the current. Tie the free end of the rope to the bridge railing (do not tie it to your body) and open the jaws of the Ekman one side at a time by pulling the cable with the white ball back and slipping the loop around the trigger posts. Observe that one jaws must be opened in sequence. When the jaws of the Ekman are armed NEVER reach into the body of the dredge with your hands; if the jaws snap shut severe injury may occur. Attach the messenger to the rope by affixing the karabiner and twisting open the slot to allow the body of the messenger over the rope. While holding the messenger, lower the Ekman into the water until it reaches the bottom, pull the rope taut, and allow the messenger to slide down the rope to the Ekman. Gently pull the Ekman from the water and open the top flaps. With the scoop remove the top 2 cm of sediment from the inside of the container and transfer it to a sample jar. Repeat the above process until the requisite sample volume has been collected. After sampling, rinse the dredge in native water to remove mud, then rinse again in DI water. Clean the dredge as described in section 3 below; collect acetone in the 5-Gal bucket and transfer it to the acetone waste container. Allow the Ekman to air dry several minutes, and then place the entire kit back in the carrying case.

#### **FIELD DUPLICATES**

Sample duplicates for QA purposes are obtained by filling and additional two sample bottles with sediment from one site using identical methods.

Rinse the outside of the jar with DI water, slip it into a bubble wrap sleeve, and place the sample in the ice chest containing ice. As the ice melts, excess water should be drained from the chest and replaced with fresh ice. Upon return to the office be sure to drain the water again and top off the ice as needed so the samples remain cold until delivery to the lab. Holding time for the toxicity samples is 14 days.

### **3. Sample gear cleaning**

Depending on the # of sites sampled per day, do this either in the field or back in the office. Between sampling events scoops should be cleaned as follows:

1. Wash in a laboratory-grade detergent (e.g., LiquiNox).
2. Rinse with tap water (not in the field)
3. Rinse with deionized water
4. Double-rinse with acetone using pasteur pipette and collect Acetone in waste container
6. Allow drying, put in clean zip lock bag and mark "Cleaned and the date".

### **4. Preservation**

Toxicity samples are held at 4°C until analysis.

### **5. Sample tracking**

Sample tracking: Samples are checked for proper labeling including site ID, date, and type of sample. Field data sheets are filled out with information on sample collectors, processing and other relevant information. Chain of Custody forms are prepared for all samples.

### **6. Shipping or sample delivery**

Samples will be brought to the MLJ-LLC office in Davis, CA with the signed COC's. Toxicity samples are packed in coolers of wet ice and bubble wrap to prepare them for shipping. Samples are delivered to:

AQUA-Science  
17 Arboretum Drive  
Davis, CA 95616-7011  
(530) 756-5456

**APPENDIX V. Standard Operating Procedure (SOP) for Transferring Custody of Samples  
(Revision 1.0, 08/29/07)**

# Standard Operating Procedure (SOP) for Transferring Custody of Samples (Revision 1.0, 08/29/07)

MLJ-LLC  
08/29/07  
Revision 1.0

Follow these six steps (in order) each time samples change custody.

1. **Inspect all bottle labels for accuracy.** Compare the Sample ID on the bottle to the sample ID on the label. Compare the sample time on the label to the sample time on the COC. If a discrepancy is found refer to the field sheet to resolve it. Both parties should be sure that the COC agrees with the bottles 100% when the bottles leave sampler custody or enter laboratory custody.
2. **Protect the samples from breakage.** Make sure that all bottles are upright in the cooler and glass bottles do not touch each other. Pad glass bottles with bubble wrap sleeves or sheets of bubble wrap. There should be room around each bottle for ice, but do not rely on ice to keep bottles spaced apart.
3. **Add additional ice to the coolers.** Add enough to maintain a temperature between 0.5°C and 4°C for the remainder of the time the coolers will be in transit to the lab, if possible. If samples will be stored outside of a refrigerator discuss who will be responsible for ensuring they remain within their holding temperature; this may mean adding ice and draining melt water once a day (more or less depending on ambient temperature).
4. **Drain water from coolers.** Remove drain plug. Be sure to put the plug back in when you are done. If there is no drain plug, hold the cooler lid closed and raise one side of the cooler, then carefully open the lid a crack to let the water drain out. If using this method be sure to first fill the cooler with ice to minimize bottle movement as the cooler tilts, and be sure to keep one hand on the lid to prevent your samples from dumping onto the pavement and potentially breaking.
5. **Transfer samples, sign Chain of Custody (COC).** Both parties should sign the COC; the initial custodian relinquishes, and the new custodian receives. The COC should represent an unbroken timeline from the time of sampling to the time of extraction/test initiation at the laboratory.
6. **Photocopy the COC.** The original stays with the samples and we bring the copy back to the office. Set the copier to darken by one unit for a more legible copy.

**APPENDIX VI. Standard Operating Procedure (SOP) for Velocity Measurement and Discharge Calculation (Revision 1.0, 07/29/07)**

Standard Operating Procedure (SOP) for Velocity Measurement and  
Discharge Calculation (Revision 1.0, 07/29/07)

MLJ-LLC  
07/29/07  
Revision 1.0

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## 1. Background

Stream discharge is the volume of water passing a cross-section per unit of time and is generally measured in cubic feet per second (cfs) or cubic meters per second (cms). The cross-sectional area is measured by stretching a tape across the stream to determine width, and recording depths using a wading rod or bridgeboard and sounding reel. For accuracy to US Geological Survey standards there should be a minimum of 20-30 verticals, or points, at which the velocity is measured in any particular stream, with no more than 10% of the total discharge in any rectangular subsection to ensure that a valid average discharge is measured. To work within time constraints and to take discharge in small, low-volume canals we seldom use more than five verticals and consider our calculations really good estimates with a measured accuracy within 5% of USGS standard protocol. For measuring discharge, follow the steps below.

## 2. Procedures

### WADING ROD METHOD

1. Select a cross section that best meets the following criteria:
  - Converging flow (i.e., cross-sectional area decreasing downstream) without areas of near-zero velocity or eddies
  - Absence of backwater conditions
  - Smooth cross section with minimal flow obstructions upstream or downstream.
  - Depth shallow enough to provide safe wading conditions.Remove any large stones, sticks, vegetation and other objects immediately upstream and downstream of the measurement section.
2. Stretch a tape between the endpoints (width) of the channel making sure that the tape is perpendicular to the banks of the stream. To obtain a rough discharge measure at least 5 verticals; for larger channel widths measure more verticals. Equal widths of partial sections across the entire cross section are not recommended unless the discharge is well distributed. Make the width of the partial sections less as depths and velocities becomes greater.
3. Note the value shown on the tape at each edge of the water. Decide how many verticals you plan to do and where in the channel you will do them. If verticals are to be evenly spaced, divide stream width by at least six to obtain at least five verticals.
4. Slip the velocity probe of the Marsh-McBirney Meter (MMB) onto the wading rod with the data cable pointed upwards and gently tighten the thumbscrew. Turn on the meter by pressing and releasing the "ON/C" button. The first number to appear on the screen is the battery voltage; if battery voltage is adequate the meter will begin measuring flow when placed in the water.
5. To ensure an accurate reading, the meter must be completely submerged under water and free of interference. Make notes about boulders, snags, pier influences or other obstructions that may bias the actual flow. Estimate the area influenced by these obstructions.
6. Record on the discharge field sheet which bank you begin your measurements from by writing the abbreviations LEW (left edge water) or REW (right edge water) next to that vertical. Left and right banks are denoted facing downstream. The measuring tape doesn't have to show zero at the edge of the water. and go from there recording the value at your next increment and so on. Record on the field sheet the units of the tape (default: meters), units of the MMB meter (default: ft/s), the method (default: wading)
7. Record your start time.
8. Stand downstream from the flow meter, in a position that least affects the velocity of the water passing through the meter. Hold the rod with the meter directly facing the flow; ensure that the rod is plumb.
  - If the depth is  $\leq 2.5$ ft, measure velocity (V) once for each subsection at 0.6 times the total depth measured down from the water surface (e.g. if the depth = 2ft, position the sensor at 1.2ft from the water's surface or 0.8ft from the bottom). Note that the staff is divided into tenths of a foot for easy calculation. If the depth is  $> 2.5$ ft, measure V two times: at 0.2 and 0.8 times the total depth (e.g. if the depth = 3ft, measure at 0.6ft and 2.4ft from the water's surface). The average of these



two readings is the V of the subsection. See below for further details on the two-point and six-tenths methods.

The wading rod has a scale on the top of the rod that allows you set the velocity probe to 0.6 of the depth from the water surface down for a depth that is  $\leq 2.5$  ft.

For example, if you have a depth of 2 feet, put the 2 of the movable rod next to the 0 of the scale and that moves the velocity probe automatically at 1.2ft (0.6) from the surface.

For depth greater than 2.5 ft, please proceed as follows: for a depth of for example 3 ft, multiply 3 by two (=6) and move the 6 to the 0 on the scale, which puts your velocity probe to 0.2 of the depth. Then divide 3 by two (1.5) and move the 1 to 5 of the scale, which puts the velocity probe to 0.8 of the depth.

If you don't want to use the scale, you and your partner can hold math quiz competitions to see who can calculate the correct values in your head the fastest. Be sure you both agree on the correct value before taking a reading. Just kidding. Use the scale.

9. Allow enough time between each reading (a minimum of 30 seconds) to obtain an accurate velocity. The MMB should be set to Fixed Point Averaging (FPA) by default. Pressing the up/down arrow keys simultaneously toggles meter between FPA and Time Constant modes. In FPA mode the time interval can be adjusted by pressing the up/down arrows one at a time. The operator calls out the number on the tape, the depth and the velocity at each vertical. The note taker repeats back as it is recorded, as a verification system. For each vertical record number on the tape, depth, observation depth (i.e. 0.2, 0.6, 0.8), velocity and time. Continue this process as you move along the cross-section.
10. Record your end time.

#### The two-point method:

- The two-point method is the one generally used by the US Geological Survey. This is the method we will be using for all of our verticals where the depth is greater than 0.76 m (2.5 feet). The two-point method is not used at depths less than 0.76 m (2.5 feet) because the current meter would be too close to both the water surface and the streambed to give dependable results. With the two-point method, observations of velocity are made at 0.2 and 0.8 of the depth below the water surface. The average of these two readings is the V of the subsection.

#### Six-tenths-depth method:

- With the 0.6-depth method, an observation of velocity made at 0.6 of the depth below the surface in the vertical is used as a mean velocity in the vertical. Actual observation and mathematical theory has shown that the 0.6-depth method provides reliable results and is used by the US Geological Survey whenever the depth is between 0.1 m (0.3 foot) and 0.76 m (2.5 feet).

### CULVERT METHOD

If your site is at a perfectly round culvert, discharge can be measured in the culvert.

In this case you only need to get the diameter of the culvert, the depth in the deepest section of the water, the distance from the sediment surface to the top of the culvert in the deepest section of the culvert and the discharge measured at 0.2, 0.6, 0.8 of the deepest depth of the culvert.

The discharge can be calculated with the Excel spreadsheet culvert calculator.

### 3. Discharge Calculations

Use the prepared Excel spreadsheet on the common folder to calculate the discharge at each site. The spreadsheet works by multiplying each depth (ft or m) by the width (ft or m) of each interval to yield the subsection area ( $\text{ft}^2$  or  $\text{m}^2$ ). It then multiplies the area by the velocity to obtain the discharge (cfs or cms) for the interval. Finally, it sums all the discharge measurements across the width of the river, yielding the

total discharge of the river. If the subsection depth was >2.5ft (0.76m), then the V was taken at 0.2 and 0.8 times the total depth. Therefore, the V at 0.2 and 0.8 times the subsection depth are averaged to yield a single V measurement before multiplying the V by the area of the subsection. See the separate SOP for discharge calculation details.

#### **4. Appendix A: Mostly for Using a Bridgeboard (and we don't)**

Bridges are often used for making discharge measurements of streams that cannot be waded. Measurement cross sections under bridges are often satisfactory for current-meter measurements. No set rule can be given for choosing between the upstream or downstream side of the bridge for making a discharge measurement. The advantages of using the upstream side of the bridge are:

- Hydraulic characteristics at the upstream side of bridge openings usually are more favorable.
- Approaching drift can be seen and thus can be more easily avoided.
- The streambed at the upstream side of the bridge is not likely to be scoured as badly as the downstream side.

The advantages of using the downstream side of the bridge are:

- Vertical angles are more easily measured because the sounding line will move away from the bridge.
- The flow lines of the stream may be straightened by passing through a bridge opening with piers.

Whether to use the upstream side or the downstream side of a bridge for a current-meter measurement should be decided individually for each bridge after considering the above factors. Other pertinent factors relate to physical conditions at the bridge, such as location of the walkway, traffic hazards, and accumulation of trash on pilings and piers.

Where piers are in the measuring section, it is usually necessary to use more than 25-30 subsections to obtain results as reliable as those obtained with a similar measuring section that has no piers. Piers not only affect the horizontal distribution of velocities, but they frequently affect the direction of the current, causing horizontal angles that must be carefully measured.

Whether or not to exclude the area of a bridge pier from the area of the measurement cross section depends primarily on the relative locations of the measurement section and the end of the pier. If measurements are made from the upstream side of the bridge, it is the relative location of the upstream end (nose) of the pier that is relevant; for measurements made from the downstream side it is the location of the downstream end (tail) of the pier that is relevant. If any part of the pier extends into the measurement cross-section, the area of the pier is excluded. However, bridges quite commonly have cantilevered walkways from which discharge measurements are made. In that case the measurement cross-section lies beyond the end of the pier-upstream from the nose or downstream from the tail, depending on which side of the bridge is used. In that situation it is the position and direction of the streamlines that determines whether or not the pier area is to be excluded. The hydrographer, if he had not previously noted the stationing of the sides of the pier when projected to the measurement cross section, does so now. If there is negligible or no downstream flow in that width interval (pier subsection)-that is, if only stagnation and (or) eddying exists upstream from the nose or downstream from the tail, whichever is relevant-the area of the pier is excluded. If there is significant downstream flow in the pier subsection, the area of the pier is included in the area of the measurement cross section. The horizontal angles of the streamlines in and near the pier subsection will usually be quite large in that circumstance.

#### **5. Appendix B: Current Meter Care and Transport**

- Rinse probe in clear water as soon as possible after use and dry using a soft cloth
- Always transport current meter in its protective case.
- Meter is fully sealed and waterproof, but try to avoid complete submersion. If submerged, remove meter from case and air dry after use.

**APPENDIX VII. Standard Operating Procedure (SOP) for Discharge Calculation from Stream or Culvert Data (Revision 1.0, 11/19/07)**

Standard Operating Procedure (SOP) for Discharge Calculation from  
Stream or Culvert Data (Revision 1.0, 11/19/07)

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## 1. Procedure for Stream Data

### A. Finding the discharge calculation spreadsheet:

- i. Open the 'Common' drive from My Computer.
- ii. Open the 'Sampling' folder.
- iii. Open the 'Discharge' folder.
- iv. Open the 'STREAMFLOW\_CALCULATOR' Excel file.

### B. Entering your data:

- i. Begin by filling out the information at the top left of the spreadsheet (your name, the date, sampling start and end times, etc.).
- ii. Enter the LEW and REW values. The spaces for this data are located below the information that you just filled out. Be sure to enter your values in the correct column for the units that you measured in. Blue is for meters and yellow is for feet. Typically LEW and REW are in units of meters (blue column).
- iii. Enter the values for midpoint distances in descending order. The spaces for these values are located in the first two columns immediately to the right of the points column. Note the message to the left of the points column—begin with your lowest value. Be sure to enter your values in the correct column for the units that you measured in. Typically midpoint distances are in units of meters (blue column).
- iv. Enter the values for midpoint depths measured. The spaces for these values are located in the fifth and sixth columns to the right of the points column. Be sure to enter your values in the correct column for the units that you measured in. Also, be sure that your depths have been entered in the same order as your interval midpoint distances. Typically midpoint depths are in units of feet (yellow column).
- v. Enter the values for velocity measured. The spaces for these values are located in the ninth and tenth columns to the right of the points column. If water depth at a given point was less than or equal to 2.5ft and only one velocity measurement was taken, enter this single value in the top section of each split cell. If water depth at a given point was greater than 2.5 ft and two velocity measurements were taken, enter the value for the 20% depth in the top section of the split cell and enter the value for the 80% depth in the bottom section of the split cell. Be sure to enter your values in the correct column for the units that you measured in. Typically velocity measurements are in units of feet second<sup>-1</sup> (yellow column).
- vi. CHECK YOUR ENTRIES. Make sure that velocity and depth measurements correspond with each other and with the correct midpoint. Make sure that you have entered all of your data in the correct columns for the units used. Altering units in a single column (midpoint distance, depth, or velocity) will change your final discharge value by a multiple of either 3.28 or 0.305 (both approx.). Altering units in two columns in the same direction (both feet to meters or meters to feet) will change the final discharge value by a multiple of either 10.76 or 0.093 (both approx.). Obviously, it is important to get this part correct.

### C. Transcribing the calculated total discharge and wet channel width:

- i. Calculated wet channel width is found directly underneath where you entered your values for LEW and REW. Write this value on the Field Data Sheet in the designated space.
- ii. Calculated total discharge is found three spaces below the channel width cell. Use the discharge that has been calculated in cubic feet per second. Write this value on the Field Data Sheet in the designated space.

D. Saving the filled-in spreadsheet:

- i. Navigate to the File menu, then to Save As.
- ii. Open the 'Discharge files by site' folder.
- iii. Open the folder corresponding to the coalition of the site that you measured (either ESJWQC or SJCDWQC).
- iv. Open the folder corresponding to the site ID entered in the spreadsheet.
- v. Save the file using the format of the other files saved in this folder. Format should have the site ID (example, PFDCL), followed by the event type and number (example, IS 3 for an irrigation sampling event or storm2 for a storm sampling event), followed by the date, followed by your initials. An example: PFDCL IS 3 111907 BJ

**2. Instructions for Culvert Data**

A. Finding the culvert discharge calculation spreadsheet:

- i. Open the 'Common' drive from My Computer.
- ii. Open the 'Sampling' folder.
- iii. Open the 'Discharge' folder.
- iv. Open the 'Culvert\_flow\_calculator' Excel file.

B. Entering your data:

- i. Enter the value of the pipe diameter in the first cell in the yellow column. Use units of feet.
- ii. Enter the depth of the water in the second cell in the yellow column. Use units of feet.
- iii. Enter the depth of sediment or debris obstruction in the third cell of the yellow column. Use units of feet.
- iv. Enter the velocity measured at a depth of 80% in the fourth cell of the yellow column. Use units of feet second<sup>-1</sup>.
- v. Enter the velocity measured at a depth of 60% in the fifth cell of the yellow column. Use units of feet second<sup>-1</sup>.
- vi. Enter the velocity measured at a depth of 20% in the sixth cell of the yellow column. Use units of feet second<sup>-1</sup>.
- vii. Ignore the columns for converting from revolutions second<sup>-1</sup> to meters second<sup>-1</sup> and feet second<sup>-1</sup> if you already have data in feet second<sup>-1</sup>. If you used a Price AA meter, use this feature. Enter your data (revolutions and seconds) for each depth (80%, 60%, and 20%). Transcribe the resulting value in feet second<sup>-1</sup> to the corresponding space above after each calculation.
- viii. CHECK YOUR ENTRIES. Make sure all of the data you have entered is in units of feet and feet second<sup>-1</sup>. Check that you have entered the velocity values in the correct cells for each depth. Compare the calculated value for total flow with the calculated check value (next red cell below the total flow value). Are these two values fairly close? If not, you may want to check your entries again.

C. Transcribing the calculated total discharge:

- i. Find the calculated value for total flow in cubic feet per second. This is in the red cell under the heading 'FLOW RESULTS.' Write this value on the Field Data Sheet in the designated space.

D. Saving the filled-in spreadsheet:

- i. Navigate to the File menu, then to Save As.
- ii. Open the 'Discharge files by site' folder.
- iii. Open the folder corresponding to the coalition of the site that you measured (either ESJWQC or SJCDWQC).
- iv. Open the folder corresponding to the site ID.
- v. Save the file using the format of the other files saved in this folder. Format should have the site ID (example, PFDCL), followed by the event type and number (example, IS 3 for an irrigation sampling event or storm2 for a storm sampling event), followed by the date, followed by your initials. An example: PFDCL IS 3 111907 BJ

**APPENDIX VIII. Standard Operating Procedure (SOP) for Sampling Site Location (Revision 1.0, 08/20/07)**



# Standard Operating Procedure (SOP) for Sampling Site Location (Revision 1.0, 08/20/07)

MLJ-LLC  
08/20/07  
Revision 1.0

## Before leaving the office:

- Ensure that the batteries in the GPS are charged and that you can find all of your sites on the map. Carry spare batteries.
- If you are unsure of how to get to a site, ask your sampling coordinator for additional resources, (I.E. directions).
- Determine your itinerary before arriving in the field area.

## Once in the Field Area:

- Proceed to the first sampling site in accordance with any directions or advisories issued by the office.
- Upon arrival at the site, verify its authenticity by referring to the photo album.
- Check the GPS. Remember that at our general Latitude (Northing)  $0.014^{\circ}$  is roughly equal to a mile, whereas every  $0.01^{\circ}$  Longitude (Westing) is about a mile.

Example: The site is 535XHDACA at N37.3906 W120.9582 and you've located a site that could be it. The GPS shows you to be at N37.3956 W120.9583. The difference in the coordinates is N.005 W.0001. To find how far off you are, divide the difference by the conversion factor:  $N.005 \div .014 = 0.36$  miles or 628 yards (1885') too far north (too far to be GPS error). The Westing difference of  $.0001 \div .01 = .01$  mi, or 53ft, is probably insignificant especially if the GPS is not getting decent accuracy. If you get to a site and the difference in the coordinates is N.0003 W.0002 (113 ft North and 106 ft West) and there are no other streams within a 200ft (+ GPS accuracy) radius, then you're there and it's time to take better pictures.

NOTE: 1 mile = 5280' = 1760 yards

To make this process easier simply refer to the chart on the back of this sheet.

- Record the difference in the "Difference" box beneath the respective Lat or Long.
- Remember that for our purposes the coordinate values after the hundredths place (0.00) are very important because we have used our maps and directions to get us within ~1000 ft of the site and we are using the coordinates to locate the precise site.

Latitude									
Difference	MILES	Difference	Feet	Difference	Feet	Difference	Feet	Difference	Feet
0.01	1.0	0.001	528	0.0001	53	0.00001	5	0.000001	1
0.02	2.0	0.002	1056	0.0002	106	0.00002	11	0.000002	1
0.03	3.0	0.003	1584	0.0003	158	0.00003	16	0.000003	2
0.04	4.0	0.004	2112	0.0004	211	0.00004	21	0.000004	2
0.05	5.0	0.005	2640	0.0005	264	0.00005	26	0.000005	3
0.06	6.0	0.006	3168	0.0006	317	0.00006	32	0.000006	3
0.07	7.0	0.007	3696	0.0007	370	0.00007	37	0.000007	4
0.08	8.0	0.008	4224	0.0008	422	0.00008	42	0.000008	4
0.09	9.0	0.009	4752	0.0009	475	0.00009	48	0.000009	5

Longitude									
Difference	MILES	Difference	Feet	Difference	Feet	Difference	Feet	Difference	Feet
0.01	0.7	0.001	377	0.0001	38	0.00001	4	0.000001	0
0.02	1.4	0.002	754	0.0002	75	0.00002	8	0.000002	1
0.03	2.1	0.003	1131	0.0003	113	0.00003	11	0.000003	1
0.04	2.9	0.004	1509	0.0004	151	0.00004	15	0.000004	2
0.05	3.6	0.005	1886	0.0005	189	0.00005	19	0.000005	2
0.06	4.3	0.006	2263	0.0006	226	0.00006	23	0.000006	2
0.07	5.0	0.007	2640	0.0007	264	0.00007	26	0.000007	3
0.08	5.7	0.008	3017	0.0008	302	0.00008	30	0.000008	3
0.09	6.4	0.009	3394	0.0009	339	0.00009	34	0.000009	3

**APPENDIX IX. Standard Operating Procedure (SOP) for Use, Maintenance, and Storage of the YSI 556 MPS (Revision 1.0, 11/14/07)**

Standard Operating Procedure (SOP) for Use, Maintenance,  
and Storage of the YSI 556 MPS (Revision 1.0, 11/14/07)

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## 1. Field Operation

- I. Connect probe module cord to base of instrument. Align grooves on female connection with corresponding ridges on male connection. Turn outer ring clockwise until it locks into place (silver pegs visible through holes in outer ring).
- II. Ensure cleanliness of sensors. Remove transport/calibration cup by unscrewing from probe module. Visually inspect individual sensors for any signs of contamination. If visually contaminated, see cleaning instructions (Section 4).
- III. Turn instrument on. Press green on/off button located on top left of instrument keyboard. The 'Run' screen will be displayed.
- IV. Calibrate DO sensor. This calibration is performed at every sampling site. Calibration is optimal when the sample (water body) temperature is within 10°C of the ambient air temperature. Move into the shade if the air is too hot or into the sun if the air is too cool.
  - a. Make sure approximately 1/8" of water is present in the transport/calibration cup. DO calibration is based on water-saturated air.
  - b. Lightly attach cup to probe module to allow gas exchange between cup interior and atmosphere (you want interior and atmospheric pressures to be equal).
  - c. Press 'Esc' key on keyboard to navigate to the main menu.
  - d. Navigate to the 'Calibrate' heading and press the enter key (directly across from Esc key).
  - e. Navigate to the 'DO' heading and press enter.
  - f. Select 'DO %'
  - g. Enter 760 mmHg for the barometric pressure—this should be the default—and press enter.
  - h. Wait approximately 10 minutes for temperature and pressure to stabilize. When the DO value on the display screen has stabilized, press enter to complete calibration.
  - i. Press enter again to accept this calibration and return to the calibration menu.
- V. Attach probe sensor guard to probe module. Remove the transport/calibration cup by unscrewing. Attach the probe sensor guard by screwing onto the probe module.
- VI. Place probe module in water body. Place probe module in the water, allowing module to come to rest on or near the stream bottom but ensuring that sensors are not impeded by or inserted into bottom sediments. *NOTE: The DO sensor is oxygen consuming. A flow of at least 1 ft/s is needed for accurate measurement. If flow at the point of measurement is less than 1 ft/s, manually stir the probe module to ensure adequate flow before recording a DO value.*
- VII. Record measured parameters. Once necessary readings have stabilized, record them in the default units displayed on the screen.
- VIII. Turn off instrument. Press green on/off button.
- IX. Disassemble and replace in carrying case. Remove the probe module from the stream. Unscrew probe sensor guard, ensure its cleanliness by briefly rinsing, and place it back in carrying case. Visually inspect individual sensors for contaminants and rinse as needed. Replace the transport/calibration cup, making sure that approximately 1/2" water (not DI water) is in the cup. Detach the probe module cord from the instrument base by turning ring counterclockwise. Place probe module and instrument in carrying case.

## 2. Calibration of sensors

Calibration of DO measurement for the YSI 556 MPS takes place before each reading in the field and is covered in Section I. This section covers the as-needed calibration of conductivity

and pH measurements. Calibration should be performed whenever suspect readings are being observed, when sensors are being reconnected to the probe module following storage, or after the MPS has not been used for an extended period. The transport/calibration cup should be used for these procedures. Make sure that all probes are submersed in the calibration liquids when performing these procedures, as some calibrations are dependent on multiple readings (for example, temperature is needed to calibrate conductivity). If any sensors are not installed on the probe module, make sure probe plugs are installed to prevent the electrical connectors from becoming wet. Thoroughly clean the sensors of any contaminants prior to calibration (see Section 4).

#### 2a. Calibrating for Conductivity

- I. Navigate to the 'Calibrate' menu. With probe module attached to instrument, turn instrument on, press the Esc key, and navigate to 'Calibrate.' Press the enter key.
- II. Navigate to 'Conductivity' and press enter.
- III. Navigate to 'Specific Conductance' and press enter.
- IV. Place standard solution in transport/calibration cup. Ensure that the transport/calibration cup is completely clean and dry before filling. Use at least 55mL of Oaklon 1413  $\mu\text{S}$  (1.413 mS) at 25°C standard solution.
- V. Place the sensors of the probe module into the solution. Before carrying out this step, ensure that the conductivity sensor is clean and dry. If possible, pre-rinse sensor with standard solution before insertion into the transport/calibration cup. Rotate and move the probe module to ensure no bubbles are trapped in the conductivity sensor cell. If the sensor is completely submerged past its vent hole, screw the cup onto the probe and securely tighten. If not submerged, add more solution to the cup.
- VI. Enter the conductivity of the standard at 25°C. This value for the provided Oaklon solution will be 1.413 mS/cm. Press enter.
- VII. Allow at least one minute for temperature and specific conductance equilibration. Once both of these measurements are no longer changing significantly, press enter to complete calibration.
- VIII. Press enter again to return to the conductivity calibration menu. You can return to the main menu by pressing the Esc key.
- IX. Rinse the probe module and sensors in tap or purified water and dry.

#### 2b. Calibrating for pH

- I. Navigate to the 'Calibrate' menu. With probe module attached to instrument, turn instrument on, press the 'Esc' key, and navigate to 'Calibrate.' Press the enter key.
- II. Navigate to 'pH' and press enter.
- III. Select either '3 point' or '1 point' calibration and press enter. The '3 point' calibration should be used when no previous calibration exists or when the sensor has not been calibrated for an extended period. The '1 point' calibration is a convenient field alternative to the '3 point' calibration that can be used to adjust a previous '3 point' calibration. Use pH 7 buffer solution for a '1 point' calibration.
- IV. Place buffer solution in transport/calibration cup. Ensure that the transport/calibration cup is completely clean and dry before filling. Use at least 30mL of Fisher Scientific Buffer Solution. Use pH 7 solution for the first point. *NOTE: If performing a field calibration, immerse the*

*clean sensors with the attached probe sensor guard directly into the provided buffer solution packets (do not pour packet contents into transport/calibration cup).*

- V. Place the sensors of the probe module into the solution. Before carrying out this step, ensure that the pH sensor is clean and dry. If possible, pre-rinse sensor with buffer solution being used before insertion into the transport/calibration cup. Rotate and move the probe module to ensure no bubbles are trapped in the pH sensor. If the sensor is completely submerged, screw the cup onto the probe and securely tighten. If not submerged, add more solution to the cup.
- VI. Enter the pH of the buffer solution at the current temperature. A temperature-pH conversion chart is located on each buffer container. Press enter.
- VII. Allow at least one minute for temperature and pH equilibration. Once both of these measurements are no longer changing significantly, press enter to complete the first calibration point.
- VIII. Press enter again to return to the pH entry screen or the pH calibration menu. If performing a '1 point' calibration, proceed to step XII. If performing a '3 point' calibration, continue to step 9.
- IX. Rinse the probe module, transport/calibration cup and sensors in tap or purified water and dry.
- X. Repeat steps 4 through 9 using pH 4 and pH 10 buffer solutions. Proceed to step XI after calibrating at all 3 pH points.
- XI. Press enter again to return to the pH calibration menu. You can return to the main menu by pressing the 'Esc' key.

### **3. Long Term Storage of YSI 556 Multi-Probe System Sensors**

Short term storage can be accomplished by adding approximately ½" of tap water to the transportation/calibration cup when not in use. This water should keep the sensors moist without actually immersing them in water—make sure that the sensors are not submerged, as this will cause sensor calibrations to drift! Long term storage procedures are outlined below.

- I. Thoroughly clean all sensors. Follow cleaning procedures in Section IV.
- II. Remove the pH sensor from the probe module and replace with the provided port plug. The sensors still attached to the probe module can be stored for long term in the same way they are typically stored for short term. Add ½" water to the transportation/calibration cup. Make sure the cup is tightly sealed to the probe module to prevent evaporation of the storage liquid.
- III. Place the pH sensor in the storage vessel which was on the sensor upon delivery. The provided vessel should contain a solution of 2 M KCl. Fasten the vessel securely to prevent evaporation. Should the sensor dry out during storage, see section 12.2.2 of the official YSI 556 MPS Operations Manual.

### **4. Cleaning of YSI 556 Multi-Probe System Sensors**

Frequent cleaning is required to maintain sensor function and accuracy. If the steps outlined below for sensor cleaning are insufficient for restoring a sensor's function or accuracy, see the additional cleaning methods detailed in section 11.1 of the official YSI 556 MPS Operations Manual.

#### 4a. DO Sensor

- I. Replace KCl solution and membrane at least once per month. Average replacement interval is 2 to 4 weeks. Erratic readings can be caused by incorrectly installed, damaged, or faulty membranes, or by bubbles in the electrolyte solution, all of which can be remedied by changing the membrane and the solution.
- II. Rinse the sensor as needed. Try to remove any oxygen producing or oxygen consuming organisms from the membrane.
- III. To clean the silver anode or the gold anode, see the Operations Manual.

#### 4b. pH Sensor

- I. Remove the sensor from the probe module.
- II. Use clean water and a soft clean cloth, lens cleaning tissue, or cotton swab to remove all foreign material from the glass bulb and platinum button.
- III. Use a moistened cotton swab to carefully remove any material that may be blocking the reference electrode junction of the sensor. Be careful not to wedge the swab tip between the guard and the glass sensor. This stress could damage the sensor.
- IV. If performance not restored, see the Operations Manual.

#### 4c. Temperature/Conductivity Sensor

- I. Dip the small brush included in the Maintenance Kit in clean water.
- II. Insert brush into each hole 15-20 times.
- III. Rinse the sensor thoroughly in deionized or clean tap water.
- IV. If performance not restored, see the Operations Manual.



**APPENDIX X. Standard Operating Procedure (SOP) for Filling Out Field Sheets (Revision 1.0, 01/06/08)**

# Standard Operating Procedure (SOP) for Filling Out Field Sheets (Revision 1.0, 01/06/08)

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Begin filling out the field sheet by starting at the top of the page. The following fields should be preprinted on the field sheet: Coalition, Station ID, Project ID, Station Name, Season, & Agency. If they are not preprinted, fill them in. If you don't know what to write in a field, call the sampling coordinator for advice on how to proceed.

## Sample time and crew:

- Arrival time: use actual time to the nearest minute in 24 hour time.
- Sample time: always round to the nearest 10 minutes in 24 hour time. Estimate the time you will actually start to fill bottles, round to the nearest 10 minutes, then write that as the sample time. Write this same time on the labels and the C.O.C.
- Sampling crew: write first initial and full last name of all team members sampling at the site.
- Departure time: use actual time to the nearest minute in 24 hour time.

## Location verification:

- Turn on the GPS unit at let sit with a clear view of the sky to acquire satellites. Our GPS units (Garmin eTrex Legend) are accurate within 14 ft on a clear morning. An accuracy value higher than 40 ft should be given more time to drop before recording the coordinates on the field sheet.
- Target coordinates should be preprinted at the office along with the GPS model and Datum.
- Record actual coordinates. Subtract them from target coordinates to find the difference, and then refer to the SOP on site location to find out how far you are from your target site in American units.
- Record the accuracy of the GPS at the time the coordinates were recorded. This will be displayed in the GPS unit at the top of the screen.

## Picture:

- Take at least one picture of the site/area. A good photo includes the actual sample site and its surroundings; multiple photos may be necessary to properly document both aspects. A picture must be taken even if site is dry.
- Record how many pictures you took in Picture Number, and the direction depicted in the picture.

## Field Description:

- Event Type and Sample type should already be preprinted in the office.
- Wadeable: circle Yes if you can wade into the water to collect a sample, and No if you cannot enter the water for any reason.
- Dominate Substrate: circle what the bottom is composed of, more than one may be circled if multiple substrate types co-dominate.
- Site odor: what does the site smell like? Try to distinguish between site odor and water odor. Circle one or several options.
- Other presence: anything on or around the water or site that could be important, like trash, animal waste, etc. Circle one or several options.

- Water odor: what does the water smell like? Again, try to distinguish from site odor. Circle one or several options.
- Water clarity: Clear (means you can see the bottom), Cloudy (>4" visibility), Murky (<4" visibility)
- Observed flow: circle your best estimate of the flow. Remember that flow = cross sectional area x velocity.
- Wind: circle the option that best describes the wind at the site.
- Wind direction: The direction the wind is blowing from
- Sky code: Circle the option that best describes the sky at the site
- Precipitation: circle the option that best describes the precip. during sampling.
- Precipitation (last 24 hours): circle one
- Water color: circle one or several
- Comments: If site is dry write "dry site" in comments section. Add any other information to comments section.

**Sample location description/method:**

- Event type: should be pre printed at the office
- Sample depth: circle one. Samples are collected by hand and filled continuously are 0.1 subsurface grabs. Samples transferred from another piece of equipment discontinuously are -88 integrated (sediment, 3-L Teflon and Techma)
- Occupation method: Circle the one that best describes access to the water
- Starting bank: The side you start from( facing downstream)
- Sampling equipment: circle one (most are individual bottle by hand)
- Sample location: circle one
- Hydro-modification: circle the most appropriate option or circle other and write something in, with "something" being anything that modifies the flow of the water: a bridge, a culvert, a pump, etc.
- Hydromodloc: Where the Hydro-modification was relative to the sample site. If water was not flowing but you know which way is upstream, mark it as if water was flowing.
- # of samples in composite: how many samples did you take to fill one bottle/ jar (mostly applies to sediment samples and bucket samples)
- Starting bank: again, if water was not flowing but you know which way is upstream, mark it as if water was flowing.

**Note:** If you circle "other", you must write in what you consider an appropriate descriptor.

**Physical Parameters: From the YSI meter**

- Calibrate the DO according to the YSI Use, Maintenance, and Storage SOP.
- Record the air temperature in Celsius before taking off the cap.
- Put the perforated protective cap on the probes. Place the YSI meter in the water so it is not buried in the mud, preferably where there is a flow of at least 1 fps around the probes. Allow sufficient time for the readings to stabilize before recording any values.
- Record water temp, pH, EC(uS/cm), DO, TDS, & ORP. Double check each value to be sure the correct parameter was recorded in the correct box.
- Record the YSI meter number. It is written on the top of the meter.
- Stretch the tape across the creek and write down the Wet Channel Width (circle the units used; if you can, write it in meters)
- While you are taking discharge write down the Midchannel depth (circle the units used)

**Note:** Be sure recap the YSI probes with enough water from the creek to keep the DO probe in a 100% humidity environment. It should only require a few drops.

**Samples collected:**

- Make sure that the correct number of bottles were filled and that volume for all analytes was collected.
- Check off all bottles in the square to the left of the sample ID as they are put on ice. Add any sample specific notes in the box to the right of the number of bottles filled.

**Comments:** Add any general comments about the site in the comments section at the bottom of the page.

**Discharge: On the flip side of the field sheet**

- Fill in the samplers name, date, site ID, and site name.
- Circle the method used, meter type, & meter units.
- Fill in the data sheet as you measure discharge.
- Make sure to fill in start and stop time.

**Before you leave the site:**

- Write down the departure time round to the nearest minute in 24 time
- Make sure all the fields are filled in correctly in on the field sheet
- Have your team member double check the field sheet to make sure that everything is filled in correctly. This means actually giving them the field sheet or asking for the field sheet and looking at it.  
**DO THIS!** (It is easier to fix problems in the field, and a person who did not fill out the field sheet will find more problems than the one who filled it out.)
- Lastly make sure you have all the samples secure and in ice, and make sure all the sampling equipment is secure in the van before leaving for the next site.

**APPENDIX XI. SOP ANA619. Triazine Compounds By Gas Chromatography By EPA Method 619  
(Revision 9, 06/25/10)**



## Standard Operating Procedure

### TRIAZINE COMPOUNDS BY GAS CHROMATOGRAPHY BY EPA METHOD 619<sup>1</sup>

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#### STATEMENT OF PURPOSE

This procedure describes the extraction and analysis of Triazine pesticide compounds in water, groundwater, hazardous wastes, and solid samples.

#### INSTRUCTIONS

##### 1.0 Scope and Application

EPA Method 619<sup>1</sup> is a gas chromatographic (GC) method used to determine the concentration of various Triazine pesticides. Table 1 indicates compounds that may be determined by this method and lists the quantitation limit for each compound in reagent water.

When EPA Method 619<sup>1</sup> is used to analyze unfamiliar samples, at least one additional qualitative technique or mass spectroscopy should support compound identifications.

When EPA Method 619<sup>1</sup> is used to analyze unfamiliar samples, compound identifications are supported by confirmatory analysis (secondary column). Also, gas chromatograph/mass spectrometer (GC/MS) can be used for qualitative confirmation of compound identifications.

If an individual project has its own QAPP with client specific requirements that are different than the SOP, the QAPP overrides the SOP.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method. If an individual project has its own QAPP with client specific requirements that are different than the SOP, the QAPP overrides the SOP. This information will be specified in the comment section of the ARF.

##### 2.0 Method Summary

EPA Method 619<sup>1</sup> provides gas chromatographic conditions for the detection of parts per billion levels of Triazine pesticides. Prior to analysis, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids may be analyzed by direct injection. A 1-5 $\mu$ L aliquot of the extract is injected into a gas chromatograph, and compounds in the GC effluent are detected with a nitrogen phosphorus detector.

If interferences are encountered in the analysis, EPA Method 619<sup>1</sup> may also be performed on extracts that have undergone cleanup using EPA Method 3620B<sup>2</sup> and/or Method 3660B<sup>3</sup>.

##### 3.0 Sample Preservation, Containers, Handling and Storage

Containers used to collect samples for the determination of semivolatiles organic compounds are purchased precleaned. The sample containers for soils are brass or steel sleeves with Teflon caps or glass jars with Teflon lined screw caps. The sample containers for waters are 1 liter amber glass bottles with Teflon lined screw caps.

All samples will be taken and held at a temperature of 4°C  $\pm$  2°C until delivery to the laboratory. When the samples are delivered to the laboratory they are placed into a refrigerator



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that is kept at  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  until extraction. No additional preservative is required. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

Upon completion of extraction, any remaining sample is returned to the refrigerator in the receiving area. Sample extracts are stored until removed by either the receiving or extraction lab personnel.

### 4.0 Interferences and Potential Problems

The use of Florisil cleanup materials for some of the compounds in this method has been demonstrated to yield recoveries less than 85% and is therefore not recommended for all compounds. Use of phosphorus- or halogen-specific detectors, however, often obviates the necessity for cleanup for relatively clean sample matrices. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is no less than 85%.

### 5.0 Equipment/Apparatus

#### 5.1 Gas chromatograph

5.1.1 Hewlett Packard 5890 gas chromatograph equipped with 7673A Autosamplers

5.1.2 Hewlett Packard 6890 gas chromatograph equipped with 6890 Autosamplers

#### 5.2 Columns

5.2.1 Column 1 – DB-35MS - 30m x 0.32mm wide bore capillary column, 0.25 $\mu\text{m}$  film thickness, chemically bonded with 35% phenyl methyl polysiloxane

5.2.2 Column 2 - DB-5MS - 30m x 0.32mm wide bore capillary column, 0.5 $\mu\text{m}$  film thickness, chemically bonded with 5% phenyl polysiloxane, 95% methyl polysiloxane

5.3 Detectors: Nitrogen-Phosphorus Detector (NPD)

5.4 Hewlett Packard EnviroQuant Data System

5.5 Volumetric flasks, Class A: sizes as appropriate with ground-glass stoppers

5.6 Microsyringe

5.7 Syringes

5.8 Injection vials with crimp tops

5.9 Balances, Analytical, 0.0001g

### 6.0 Reagents

Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents used will be traceable at all steps of the procedure.

6.1 Hexane - Pesticide quality

6.2 Acetone - Pesticide quality

6.3 Methylene chloride - Pesticide quality

6.4 Methanol - Pesticide quality

6.5 Standards:

The certified solutions must be accompanied by a certificate of analysis that states balances used in the manufacture of this standard are calibrated with weights traceable to NIST in compliance with ANSI/NCSL Z-540-1 and ISO 9001. Standards formulated in house are prepared with balances that are calibrated with weights traceable to NIST.

One of the concentrations will be at the quantitation limit. Refer to Table 1 for list of quantitation limits. This list may be superseded by client specific requirements. The



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analyst must refer to the incoming sample notice for the lab works code and look at the detection limits listed on the appropriate form 1 to determine the quantitation limit standard.

- 6.6 Stock standard solutions:
- 6.6.1 Triazine stock standards (calibration and surrogate) are purchased in two mixes, TZA and TZB. See ROU006.
  - 6.6.2 Secondary source stock standards are purchased from a separate supplier.
  - 6.6.3 The stock standard solutions are stored in the sealed ampules and are kept at  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and protected from light. Stock standards are be checked for evaporation, especially just prior to preparing calibration standards from them.
  - 6.6.4 Stock standard solutions must be replaced after six months or sooner if comparison with check standards indicates a problem.
- 6.7 Calibration standards: Calibration standards at a minimum of 3 concentrations for each parameter of interest are prepared through dilution of the stock standards with hexane. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.
- 6.8 Second source calibration:  
The working calibration is verified once by the injection of a second source standard. This standard must be obtained from a vendor different from that of the initial calibration standard. If the second source calibration response varies from the predicted response by more than 15%D, inspect the GC system to determine the cause and perform the necessary maintenance before injecting a new calibration curve. If the laboratory control spike is obtained from a different vendor and is less than  $\pm 15\%D$  from the initial calibration, it may be used to satisfy this requirement.
- 6.9 Surrogate standards: Tributylphosphate and Triphenylphosphate are purchased as mixes. See SOP# ROU006. This solution is added to each sample, blank and all QC samples. Proceed with corrective action when surrogates are out of limits for a sample.

### 7.0 Procedure

#### Extraction:

Refer to APPL, Inc.'s SOPs for the following extraction procedures: The extract will be transferred to a scintillation vial with a Teflon-lined screw cap. Proceed with gas chromatographic analysis if further cleanup is not required.

#### Water:

- SOP# SEP001- Proper Use of Separatory Funnels
- SOP# SEP009- OCL/OP/Triazines Separatory Funnel Extraction
- SOP# LIQ001 - Continuous Liquid-Liquid OCL/OP/Triazine/Carbamate Extraction

#### Soil:

- SOP# SOX005- Soxhlet Extraction
- SOP# SON009- Sonication

#### 7.1 Gas chromatography column conditions:

- 7.1.1 Column 1: Carrier gas (5% methane/95% argon) flow rate: 5-8 mL/min
- 7.1.2 Column 2: Carrier gas (5% methane/95% argon) flow rate: 5-8 mL/min

#### 7.2 Operating Conditions

- 7.2.1 GC Conditions





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Oven Temperature: 80°C  
Equip Time: 1.00 min  
Oven Maximum: 290°C  
Initial Temp: 80°C  
Initial Time: 0.00 min

### 7.2.2 Temperature Program:

Rate: 10.0°C  
Final Temp: 290°C  
Final Time: 9.0 min  
Injection Temp: 225°C  
Detector Temp: 290°C

7.3 Calibration: Prior to using this introduction technique for any GC method, the system is calibrated. One of the concentrations will be at the quantitation limit. Refer to Table 1 for list of quantitation limits. This list may be superseded by client specific requirements. The analyst must refer to the incoming sample notice for the lab works code and look at the detection limits listed on the appropriate form 1 to determine the quantitation limit standard.

7.3.1 Analyze each calibration standard. Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph. For samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

7.3.2 The initial calibration curve is a reflection of the performance of the instrument at any given time. Individual compounds react to the changing dynamic of the instrument. Therefore it is sometimes necessary to delete points for individual compounds in an initial calibration curve. When this occurs the following rules are used to ensure integrity of the data.

7.3.2.1 A standard must be included in the curve for each compound, which is less than or equal to the reporting limit.

7.3.2.2 The deletion of discrete points must never result in a calibration curve consisting of less than three points for each analyte of interest.

7.3.2.3 Points for an individual analyte in the middle of the curve may not be deleted, however unforeseen circumstances may occur such as a misinjection by the autosampler, a loose cap on an injection vial, etc. In this situation the entire level is deleted for all compounds and the reason for deletion is noted on the multilevel form. If this results in a calibration curve that consists of less than five points another level may be run before the analysis of samples begin.

7.3.2.4 Points at the low end and high end of the curve may be deleted if it is determined the compound ceases to be linear at either end. Any positive findings in the samples will be analyzed so as to fall within the linear range of that particular compound.

7.3.2.5 When the initial calibration curve has been established, no changes are



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made to it after the processing of samples has begun.

- 7.3.3 Second source calibration - The working calibration is verified once by the injection of a second source standard. This standard must be obtained from a vendor different from that of the initial calibration standard. If the second source calibration response varies from the predicted response by more than 15%D, inspect the GC system to determine the cause and perform the necessary maintenance before injecting a new calibration curve. If the laboratory control spike is obtained from a different vendor and is less than  $\pm 15\%D$  from the initial calibration, it may be used to satisfy this requirement.
- 7.3.4 Calculate response factors or calibration factors and percent RSD for each analyte of interest as follows:

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}}{\text{Mass injected (in nanograms)}}$$

The percent RSD is calculated as follows:

$$\%RSD = (SD)(100\%)/(RF_{x1})$$

Where:

%RSD = Percent relative standard deviation.

$RF_{x1}$  = Mean of the initial RF for a compound.

SD = Standard deviation of the average RRF for a compound.

- 7.4 The working calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is every 10 injections. If the response for any analyte varies from the predicted response by more than  $\pm 15\%$ , a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{|R_1 - R_2|}{R_1} \times 100$$

Where:

$R_1$  = Average calibration factor from first analysis

$R_2$  = Calibration factor from continuing analysis

- 7.5 Gas chromatographic analysis:
- 7.5.1 Triazine compounds are introduced by direct injection using HP Autosamplers.
- 7.5.2 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with the instrument calibration followed by sample extracts, and, every 10 injections a mid level calibration standard mix. The sequence ends when the set of samples has been injected or when qualitative and or quantitative QC criteria are exceeded.
- 7.5.3 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100 fold range, are acceptable if linearity is demonstrated.
- 7.5.4 Calibrate the system immediately prior to conducting any analyses. The



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calibration factor for each analyte to be quantitated must not exceed 10% difference. When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary before recalibrating and proceeding with sample analysis. All sample that were injected after the standard exceeding the criterion must be reinjected to avoid errors in quantitation, if the initial analysis indicated the presence of specific target analytes that exceeded the criterion.

- 7.5.5 Establish daily retention time windows for each analyte. Use the retention time for each analyte as the midpoint.
- 7.5.5.1 The daily retention time window equals the midpoint  $\pm$  three times the standard deviation determined from standards injected over a 72-hour period.
- 7.5.5.2 In those cases where the standard deviation for a particular standard is zero, substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.
- 7.5.5.3 A new retention time study is completed annually or whenever a new column is installed.
- 7.5.6 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Second column confirmation is performed on all extracts. The second column will meet all the calibration and second source requirements for analytes of interest as outlined in the calibration section of this SOP. If historical data is provided, the extracts may not be confirmed on the secondary column. When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results should be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula below.

$$RPD = (|R_1 - R_2|) / [(R_1 + R_2)/2] \times 100$$

Where:

R<sub>1</sub> = result on the primary column

R<sub>2</sub> = result on the secondary column

If one result is significantly higher (e.g., >30%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system during peak integration. If no anomalies are noted, review the chromatographic conditions. A dirty matrix may interfere with confirmation of a positive finding and the result is left to the analyst's best judgment. The confirmation between hits should be less than 30% RPD. For responses greater than 30% RPD between two columns the result should be reported as "not detected".

- 7.5.7 Validation of the GC system qualitative performance: Use the mid concentration standards every 10 injections throughout the analysis sequence to evaluate this criterion.
- 7.5.8 Refer to Section (8.0) Calculations (below) for guidance on calculating of concentration.
- 7.5.9 Using external calibration procedure, determine the identity and quantity of each component peak in the sample chromatogram, which corresponds to the compounds used for calibration purposes.



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- 7.5.10 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using EPA Method 3620B<sup>2</sup>. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove sulfur using EPA Method 3660B<sup>3</sup>. If EPA Method 3660B<sup>3</sup> is used for sulfur cleanup, only the tetra butyl ammonium (TBA)-sulfite option should be employed, since copper and mercury may destroy OP pesticides.
- 7.5.11 Manual integration: Make a hard copy of the original integration performed by the instrument. Perform the appropriate manual integration. Make a copy of the manual integration. Be sure that the scale of the copy is appropriate. Note on the manual integration copy the number of the reason (see list below) a new integration was performed, initial and date. Make a note to justify the new integration on the manual copy, date and initial. Save the manual integration electronically so that it can be retrieved at a later date if necessary. Place a copy of all integrations in the data folder to be reviewed by the section manager or his/her designee. After review by the section manager, the manager will date and initial. See SOP # ANA003 for further instructions.

- (1) Integration does not follow baseline
- (2) Non-target peak interference
- (3) To split a peak
- (4) To integrate a split peak
- (5) The peak was not integrated
- (6) Computer integrated wrong peak
- (7) Other - Explain

Upon client request the integrations will be reviewed by the QAU or his/her designee initialed and dated. The hard copies will be filed with the raw data.

### 8.0 Calculations

- 8.1 The sample/spike/surrogate is calculated against the initial calibration curve.
- 8.2 External standard calibration: The Enviroquant Data System performs the quantitation of each analyte. The algorithm is checked at least once per calibration curve and at least in every DVP package, by calculating the amount of analyte injected, from the peak response, using the calibration curve or the calibration factor. The following calculation is used to check the quantitation:

$$\text{Concentration (ppb)} = \frac{(A_s)(V_e)}{(RF_{avg})(V_o)} \times D$$

Where:

- $A_s$  = Response for the analyte to be measured, (area/height)  
 $RF_{avg}$  = Average response of analyte from calibration curve  
 $V_o$  = Volume of sample extracted (L or Kg)  
 $V_e$  = Final volume of extract (mL)  
 $D$  = Dilution factor if a dilution was made



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### 9.0 Quality Control

- 9.1 Method Proficiency: The procedures in place for demonstrating proficiency include: Precision and accuracy of the method using matrix spike/matrix spike duplicates and laboratory control spike/laboratory control spike duplicates and determining the method detection limit (MDL) as listed in point (9.4) below. Documented precision, bias, and MDL information is maintained.
- 9.2 Control Limits: Procedures are in place for establishing and updating control limits for analysis. Calculate the average percent recovery ( $p$ ) and standard deviation of the percent recovery ( $s$ ) for each of the spiking compounds when data from 30 QC samples is available. QC sample include, Matrix spikes, laboratory control spikes for spiking and surrogate compounds. Control limits are established for a given matrix by calculating the upper and lower control limit for percent recovery for each spiking analyte. This is the same procedure used for surrogate compounds also. (See SOP# QC016 for control chart generation.) This is done as follows:

$$\text{Upper Control Limit (UCL)} = p + 3s$$

$$\text{Lower Control Limit (LCL)} = p - 3s$$

At a minimum, the recovery limits are updated on a matrix-by-matrix basis, annually.

- 9.3 Typically, control limits for accuracy are based on the historical mean recovery plus or minus three standard deviation units, and control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units. The procedure in place for monitoring historical performance include graphical (control charts) and/or tabular presentations of the data.
- 9.4 Method Detection Limit: Seven aliquots of sample are spiked with a know concentration of all analytes of interest and taken through the entire analytical process. The replicated analyses answers are used in the following equation to determine the MDL:

$$\text{MDL} = (t)(S)$$

Where:

$t$  = the students' t value appropriate for 99% confidence level (7 replicates,  $t=3.143$ )

$S$  = Standard deviation of the replicate analyses

NOTE: This procedure is in place for determining the MDL for soil and water matrices.

- 9.5 Practical Quantitation Limit (PQL): The PQL is established by multiplying the MDL obtained above by 5 to 10 times. It is recognized that the experience of the analyst is important in this process.
- 9.6 Deviations: Any activity not performed in accordance with laboratory procedures or Quality Assurance Project Plan(s) is considered a deviation from plan. All deviations from plan will be documented as to the extent of, and reason for, the deviation.
- 9.7 Corrective Action: Errors, deficiencies, deviations, or laboratory events or data that fall outside of established acceptance criteria will be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the analytical system. The investigation of the problem and any subsequent corrective action taken is documented on a Quality Control Exception Report (QCER) and/or a Corrective Action Report (CAR).



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- 9.8 Method Blank: Before processing any samples, the analyst will demonstrate through the analysis of a method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank will be processed as a safeguard against chronic laboratory contamination. The blanks will be carried through all stages of the sample preparation and measurement. If there are detections above the quantitation limit, the entire batch associated with the blank will be re-extracted and reanalyzed. If not enough sample exists for a re-extraction the sample will be qualified with a "B" (compound found in the associated blank). The frequency of method blanks is 1 per batch (up to a maximum of 20 samples), unless the DQO or project specific QAPP specifies differently.
- 9.9 QC samples: Standard quality assurance practices will be used with this method. Field duplicates are collected by clients to validate the precision of the sampling technique. Laboratory spiked replicates will be analyzed to validate the precision and accuracy of the analysis. The spiked samples will be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. The frequency of QC samples are: 1 pair of Matrix Spike/Matrix Spike Duplicates MS/MSD per batch (up to a maximum of 20 samples), and 1 Laboratory Control Spike LCS per batch (up to a maximum of 20 sample), unless the DQO or project specific QAPP specifies differently. If the % recovery of a specific compound in the laboratory control spike is greater than the upper control limit and there are no positive findings for that compound, no further action is taken. If there are positive findings for that compound, reanalyze the spike and all effected samples or flag the results with a "J". If the % recovery of any compound fall below the lower control limit, reanalyze the spike and all effected samples. Client specific requirements for the exceptions are listed on the APPL Analysis Request Form (ARF).
- 9.10 Calibration Criteria: The relative percent difference (%RSD) for the initial calibration curve must be  $\leq 10\%$  to validate the sequence. The calibration factor of the continuing calibration check must be  $\leq 10\%$  from the average calibration factor in the initial calibration curve.
- 9.11 Surrogate Recovery: Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine recovery limits as discussed in point (2) above. Determine if recovery is within limits. Current recovery limit are found in APPL SOP #QC003. If recovery is not within limits, the following is required:
- Check to be sure that there are no errors in calculations or surrogate solutions. Also, check instrument performance.
  - Re-calculate the data and/or re-analyze the sample if any of the above checks reveal a problem.
  - Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration".
- 9.12 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits. This procedure is typically used with severe matrix interference. The extract and the associated blank will be analyzed.



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### 10.0 Data Validation

When QC parameters are exceeded, the following will take place: When the matrix spikes are outside of the limits they are re-digested and re-analyzed. When the LCS is outside of limits the entire batch is re-digested and re-analyzed. If there is not enough sample for re-digestion the Project Manager is notified whom in turn notifies the client by phone or fax. The case narrative or case letter explains the sequence of events and the data is qualified. If the calibration parameters are not met the standards are re-prepared and reanalyzed.

### 11.0 Pollution Prevention

All hazardous materials that are generated during the testing of samples must be properly collected and stored. Drums are available in the storage room for the following types of wastes-acidic, basic and solvents

### 12.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and lands disposal restrictions. The laboratory has the responsibility to protect the environment by minimizing and controlling all releases from fume hoods and bench operations.

### 13.0 Contingencies for Handling Out of Control or Unacceptable Data

In the event that an out of control situation occurs, the project manager will be notified immediately. The affect of the out of control situation will be assessed according to the project DQO. If sufficient sample remains, and the situation will significantly affect the quality of the results, the analysis will be repeated. If the situation does not significantly affect the quality of the data, the project manager will notify the client and instructions from the client will be followed. In the event no sample remains, the client will be notified immediately. All situations will be documented on the multi level sheet and initialed by the project manager. All out of control situations will be brought to the attention of the QAU in the form of a QCER. The QAU has the final authority to approve the actions taken

### 14.0 Deviations from the method

This standard operating procedure was compared to EPA Method 619. There are no deviations from the method.

### 15.0 Health and Safety

Lab coats and gloves are use at all times. All personnel handling raw samples must have been vaccinated or titered for infectious diseases. Follow all safety procedures as described in the SOP for samples suspected of containing biological hazards.



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### SALUTATION

This procedure applies to all personnel who analyze extracts for Triazine pesticides by EPA Method 619<sup>1</sup>.

APPL, Inc.  
Confidential

*Monica Aquilera*

Section Manager: \_\_\_\_\_

Date: 6/25/10

*Louanna Ledicia*

QAU Director: \_\_\_\_\_

Date: 6/25/10

#### References:

- <sup>1</sup>EPA Method 619, *Methods and Guidance For Analysis of Water*, Office of Water
- <sup>2</sup>EPA Method 3620B, SW846, *Third Edition Rev 1 July 1992*
- <sup>3</sup>EPA Method 3660B, SW846, *Third Edition Rev 1 July 1992*
- <sup>4</sup>CFR 40 Part 136, *Appendix B, Chapter 1 (7-1-95 Edition)*, Rev 1.11





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TABLE 1

619 <sup>1</sup> COMPOUNDS		
Compound	Water Limit (µg/L)	Soil Limit (µg/L)
Prometon	0.50	50
Atraton	0.50	50
Propazine	0.50	50
Atrazine	0.50	50
Simazine	0.50	50
Terbutylazine	0.50	50
Prometryn	0.50	50
Ametryn	0.50	50
Simetryn	0.50	50
Terbutryn	0.50	50
Cyanazine	0.50	50



## APPENDIX A

### Definitions

**INTERNAL STANDARD (IS)**- -A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution must be an analyte that is not a sample component.

**SURROGATE ANALYTE (SA)**- -A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount (s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

**LABORATORY DUPLICATES (LD1 and LD2)**- -Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analytes of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

**LABORATORY REAGENT BLANK (LRB)**- -An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

**FIELD REAGENT BLANK (FRB)** - -An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

**INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC)** - -A solution of one or more compounds (analytes, surrogate, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

**LABORATORY FORTIFIED BLANK (LFB)** - - An aliquot of reagent water or other matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

**LABORATORY FORTIFIED MATRIX (LFM)** - -An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.



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STOCK STANDARD SOLUTION (SSS) - - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials purchased from a reputable commercial source.

PRIMARY DILUTION STANDARD SOLUTION (PDS) - -A solution of several analytes prepared in the laboratory from stock solution and diluted as needed to prepare calibrations solutions and other needed analyte solutions.

CALIBRATION STANDARD (CAL)- - A solution prepared from the primary dilution standard solution or stock standard solution and the internal standards and surrogate analytes. The Cal solutions are used to calibrate the instrument response with respect to analyte concentration.

QUALITY CONTROL SAMPLE (QCS)- - A solutions of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

**APPENDIX XII. SOP ANA8081A. Organochlorine Pesticides By Gas Chromatography By EPA  
Method 8081A (Revision 22, 09/17/10)**



## Standard Operating Procedure

### ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY BY EPA METHOD 8081A<sup>1</sup>

#### STATEMENT OF PURPOSE

This procedure describes the extraction and analysis of organochloride pesticides compounds in water, groundwater, hazardous wastes, and solid samples.

#### INSTRUCTIONS

##### 1.0 Scope and Application

- 1.1 EPA Method 8081A<sup>1</sup> is used to determine the concentration of various organochlorine pesticides. See 8082 for PCB analysis
- 1.2 Table 1 lists the quantitation limits for each compound.
- 1.3 If an individual project has its own QAPP with client specific requirements that are different than the SOP, the QAPP overrides the SOP
- 1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

##### 2.0 Method Summary

- 2.1 EPA Method 8081A<sup>1</sup> provides gas chromatographic conditions for the detection of ppb concentrations of certain organochlorine pesticides. Prior to the use of this method, appropriate sample extraction techniques must be used. A 1 to 2  $\mu\text{L}$  sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD).
- 2.2 The sensitivity of this method usually depends on the concentration of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, EPA Method 8081A<sup>1</sup> may also be performed on samples that have undergone cleanup. APPL, Inc. SOP #CLN001 (EPA Method 3620B<sup>2</sup>, Florisil Column Cleanup), by itself or followed by APPL, Inc. SOP #CLN002 (EPA Method 3660B<sup>3</sup>, Sulfur Cleanup), may be used to eliminate interferences in the analysis.

##### 3.0 Sample Preservation, Containers, Handling and Storage

- 3.1 Containers used to collect samples for the determination of semivolatiles organic compounds are purchased precleaned. The sample containers for soils are brass or steel sleeves with Teflon caps or glass jars with Teflon lined screw caps. The sample containers for waters are 1 liter amber glass bottles with Teflon lined screw caps.
- 3.2 All samples will be taken and held at a temperature of  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  until delivery to the laboratory. When the samples are delivered to the laboratory they are placed into a refrigerator that is kept at  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  until extraction. No additional preservative is required. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

##### 4.0 Interferences and Potential Problems

- 4.1 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the



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chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially with solvent-wetted surfaces. Avoiding contact with any plastic materials can best minimize interferences from phthalates. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

- 4.2 Organic compounds inherent in all soils will interfere with the instrumentation and quantitation. A 1/20 dilution is performed prior to analysis of all soil samples. This dilution does not affect the current PQL.

### 5.0 Equipment/Apparatus

- 5.1 Gas chromatograph
  - 5.1.1 Gas chromatograph - Hewlett Packard 6890 gas chromatograph equipped with 7673A autosampler.
- 5.2 Columns
  - 5.2.1 Column 1 - DB35MS, length 30m, 0.32mm ID, 0.25µm df film thickness or equivalent
  - 5.2.2 Column 2 - DB-XLB, length 30m, 0.32mm ID, 0.5µm df film thickness or equivalent
- 5.3 Detectors
  - 5.3.1 Electron capture (ECD)
- 5.4 Hewlett Packard EnviroQuant Data System
- 5.5 Volumetric flasks, Class A: sizes as appropriate with ground-glass stoppers
- 5.6 Microsyringe
- 5.7 Syringes
- 5.8 Injection vials with crimp tops
- 5.9 Balances, Analytical, 0.0001 g

### 6.0 Reagents

- 6.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents used will be traceable at all steps of the procedure.
- 6.2 Solvents
  - 6.2.1 Hexane, C<sub>6</sub>H<sub>14</sub> - Pesticide quality
  - 6.2.2 Acetone, CH<sub>3</sub>COCH<sub>3</sub> - Pesticide quality
  - 6.2.3 Toluene, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> - Pesticide quality
- 6.3 Stock standard solutions
  - 6.3.1 Organochlorine stock standards (calibration and surrogate) are purchased in two mixes, Toxaphene and single component analytes in a separate mix. See SOP# ROU006.
  - 6.3.2 Secondary source stock standards are purchased from separate suppliers than calibration standards.
  - 6.3.3 The stock standard solutions are stored in the sealed ampules and are kept at 4°C ± 2°C and protected from light. Stock standards are to be checked for evaporation, especially just prior to preparing calibration standards from them.



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- 6.3.4 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.
- 6.3.5 The certified solutions must be accompanied by a certificate of analysis that states balances used in the manufacture of this standard are calibrated with weights traceable to NIST in compliance with ANSI/NCSL Z-540-1 and ISO 9001. Standards formulated in house are prepared with balances that are calibrated with weights traceable to NIST. (See SOP ROU003)
- 6.4 Calibration standards: Calibration standards at least five concentrations for each parameter of interest are prepared through dilution of the stock standards with hexane. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.
- 6.5 Surrogate standards: Three surrogate standards, Tetrachloro-m-xylene (TCMX), Decachlorobiphenyl (DECA) and Dibutylchloroendate are added to each sample, blank and QC sample. All three surrogate compounds are calculated for percent recovery. The majority of the reporting templates include only two of the surrogates (DECA and TCMX) as indicated in EPA 8081A. Procedures for establishing control limits are discussed in Section "9.2" below. Proceed with corrective action when all surrogates are out of limits for a sample.

### 7.0 Procedure

- 7.1 Extraction: Refer to APPL, Inc.'s SOPs for the following extraction procedures:
  - 7.1.1 Water:
    - 7.1.1.1 SOP# SEP001- Proper Use of Separatory Funnels
    - 7.1.1.2 SOP# SEP009 - OCL/OP/Triazines Separatory Funnel Extraction (EPA Method 3510C<sup>4</sup>)
    - 7.1.1.3 SOP# LIQ001 - Continuous Liquid-Liquid OCL/OP/Triazine/Carbamate Extraction (EPA Method 3520C<sup>5</sup>)
  - 7.1.2 Soil:
    - 7.1.2.1 SOP# SOX001- Set Up and Operation of Soxhlet Extraction Apparatus
    - 7.1.2.2 SOP# SON001- The Operation and Cleaning of Sonicators
    - 7.1.2.3 SOP# SON002 - OCL/OP/Triazines by Sonication Extraction (EPA Method 3550B<sup>7</sup>)
- 7.2 For Arizona projects: The approved methods are 3620B, and 3550B.
- 7.3 The extract will be transferred to a scintillation vial with a Teflon-lined screw cap. Proceed with gas chromatographic analysis if further cleanup is not required.
- 7.4 Gas chromatography column conditions: The following conditions are suggested starting points. Actual conditions may vary with optimization.
  - 7.4.1 Column 1: Carrier gas (5% methane/95% argon) flow rate: 5-8 mL/min
  - 7.4.2 Column 2: Carrier gas (5% methane/95% argon) flow rate: 5-8 mL/min
- 7.5 Operating Conditions:
  - 7.5.1 GC Conditions:
    - Oven Temperature: 150°C
    - Equib Time: 1.00 min
    - Oven Maximum: 325°C
    - Initial Temp: 150°C
    - Initial Time: 1.00min
  - 7.5.2 Temperature Program:
    - Rate: 8.0°C
    - Final Temp: 290°C



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Final Time: 11.50 min

Injection Temp: 200°C

Detector Temp: 325°C

- 7.6 Calibration: Prior to using this introduction technique for any GC method, the system is calibrated. One of the concentrations will be at the quantitation limit. Refer to Table 1 for list of quantitation limits. This list may be superseded by client specific requirements. The analyst must refer to the incoming sample notice for the Labworks code and look at the detection limits listed on the appropriate form 1 to determine the quantitation limit standard.
- 7.6.1 Calibration standards at a minimum of 5 concentrations for each parameter of interest are prepared through dilution of the stock standards with hexane. The concentrations of each compound in the mixes are 0.005, 0.055, 0.100, 0.150, 0.200, and 0.250 µg/mL for individual component pesticide mix. Toxaphene curve calibration levels are 0.10, 0.25, 0.50, 0.75, 1.0, and 1.5 µg/mL.
- 7.6.2 The initial calibration curve is a reflection of the performance of the instrument at any given time. Individual compounds react to the changing dynamic of the instrument. Therefore it is sometimes necessary to delete points for individual compounds in an initial calibration curve. When this occurs the following rules are used to ensure integrity of the data:
- 7.6.2.1 A standard must be included in the curve for each compound, which is less than or equal to the reporting limit.
- 7.6.2.2 The deletion of discrete points must never result in a calibration curve consisting of less than five points for each analyte of interest.
- 7.6.2.3 Points for an individual analyte in the middle of the curve may not be deleted, however unforeseen circumstances may occur such as a miss injection by the autosampler, a loose cap on an injection vial, etc. In this situation the entire level is deleted for all compounds and the reason for deletion is noted on the multilevel form. If this results in a calibration curve that consists of less than five points another level may be run before the analysis of samples begin.
- 7.6.2.4 Points at the low end and high end of the curve may be deleted if it is determined the compound ceases to be linear at either end. Any positive findings in the samples will be analyzed so as to fall within the linear range of that particular compound.
- 7.6.2.5 When the initial calibration curve has been established, no changes are made to it after the processing of samples has begun.
- 7.6.3 Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.
- 7.6.4 Analyze each calibration standard the same way actual samples are introduced into the gas chromatograph by using the HP 7276 autosamples for direct injection. The EnviroQuant data system tabulates peak height or area responses against the mass injected. The results are used to calculate a calibration factor (CF) for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is  $\leq 20\%$  over the working range, linearity through the origin can be assumed, and the mean calibration factor may be used to quantitate sample results.
- 7.6.5 A manual calculation must be performed once a day and documented on the quantitation sheet to verify the algorithm. A hardcopy printout of the initial calibration plot when linear (first order) or quadratic (second order) calibration is





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used should be included in the calibration folder. See SOP# DOC014 for calculations.

- 7.6.6 If the RSD of the calibration or response factors is >20% over the calibration range, then linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin.

7.6.6.1 The analyst should not force the line through the origin, but have the intercept calculated from the five data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0,0) as a sixth calibration point. The use of a linear regression may not be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99.

- 7.6.7 When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary before recalibrating and proceeding with analysis.

- 7.6.8 To manually check the data system, calculate calibration factors and percent RSD for each analyte of interest as follows:

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}}{\text{Mass injected (in nanograms)}}$$

Note: For multi-response pesticides and PCBs, the total area of 5 individual peaks used for quantitation of CF.

- 7.6.9 The percent RSD is calculated as follows:

$$\%RSD = (SD)(100\%)/(RF_{x1})$$

Where:

%RSD = Percent relative standard deviation.

$RF_{x1}$  = Mean of the initial RF for a compound.

SD = Standard deviation of the average RRF for a compound.

- 7.6.10 The working calibration factor must be verified on each working day by the injection of the 8081 standard analytes at a low and high concentration. The frequency of verification is every 10 samples. If the response for any analyte varies from the predicted response by more than ±15% calculate the average percent difference. If the average of the responses for all analytes is within ±15%, then the calibration has been verified. The data user must be provided with the calibration verification data or a list of those analytes that exceeded the ±15% limit.

7.6.10.1 If the calibration verification does not meet the ±15% limit, check the instrument operating conditions, and if necessary, restore them to the original settings and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±15%, then a new initial calibration must be prepared.



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7.6.10.2 If the calibration verification analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >15%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed.

$$\text{Percent Difference} = \frac{|R_1 - R_2|}{R_1} \times 100$$

Where:

R<sub>1</sub> = Average calibration factor from first analysis

R<sub>2</sub> = Calibration factor from continuing analysis

7.7 Second source calibration - The working calibration is verified once by the injection of a second source standard. This standard can be obtained from a vendor different from that of the initial calibration standard or the same vendor but a different lot. The client specific QAPP must be followed. If the second source calibration response varies from the predicted response by more than 15%D, inspect the GC system to determine the cause and perform the necessary maintenance before injecting a new calibration curve. If the laboratory control spike is prepared with a different lot or vendor and is less than ±15%D from the initial calibration, it may be used to satisfy this requirement.

7.8 Gas chromatographic analysis:

7.8.1 Organochlorinated pesticides are introduced by direct injection using a HP 7673 autosampler.

7.8.2 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with the instrument calibration followed by sample extracts and, every 10-20 injections a high and low level calibration standard mix. The sequence ends when the set of samples has been injected or when qualitative and or quantitative QC criteria are exceeded. NOTE: A 72-hour sequence is not required with this method.

7.8.3 As a standard operating procedure dilute all soil samples 1/20 before analysis to prevent instrumentation problems.

7.8.4 If the responses exceed the linear range of the system, dilute the extract and reanalyze. The extract is diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, is acceptable if linearity is demonstrated.

7.8.5 Verify calibration before any analysis is completed by using a low and/or high level calibration standard. The average calibration factor for the analytes to be quantitated must not exceed ±15% difference from the mean calibration factor calculated for the initial calibration. If the calibration factor for any analyte exceeds a ±15 percent difference calculate the average percent difference across all analytes in the calibration mix.

$$\% \text{ Difference} = \frac{CF - CF_v}{CF} \times 100$$

Where:

CF = Mean calibration factor from initial calibration

CF<sub>v</sub> = Calibration factor from the analysis of the CCV



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- 7.8.5.1 If a calibration approach other than the RSD method has been employed for the initial calibration (e.g. a linear model not through the origin, a non-linear calibration model, etc.) consult method 8000 for the specific details of calibration verification.
- 7.8.5.2 When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary before recalibrating and proceeding with sample analysis. All samples that were injected after the standard exceeding the criterion must be reinjected to avoid errors in quantitation, if the initial analysis indicated the presence of specific target analytes that exceeded the criterion. An initial calibration is completed only when the system falls outside continuing calibration criteria and can not be brought back into control.
- 7.8.6 Establish daily retention time windows for each analyte. Use the retention time for each analyte as the midpoint of the window for that day.
- 7.8.6.1 The daily retention time window equals the midpoint  $\pm$  three times the standard deviation determined from standards injected over a 72-hour period.
- 7.8.6.2 In those cases where the standard deviation for a particular standard is zero, substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.
- 7.8.6.3 A new retention time study is completed annually or whenever a new column is installed.
- 7.8.7 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Second column confirmation is performed on all extracts. The second column will meet all the calibration and second source requirements for analytes of interest as outlined in the calibration section of this SOP. If historical data is provided, the extracts may not be confirmed on the secondary column. When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results should be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula below.

$$RPD = (|R_1 - R_2|) / [(R_1 + R_2)/2] \times 100$$

Where:

$R_1$  = result on the primary column

$R_2$  = result on the secondary column

- 7.8.8 If one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system during peak integration. If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result if reporting with 8000B or report the lower result if reporting with 8000C. If the calculated RPD is > 40% and the results of both columns are above the reporting limit, the larger of the two results is reported and flagged with a "Y". A dirty matrix may interfere with confirmation of a positive finding and the result is left to the analyst's best judgment. If the calculated RPD is



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<40% and all the QC requirements are met for that analyte on both columns, the result reported is left to the analysts professional judgement.

- 7.8.9 Validation of the GC system qualitative performance: Use the high and low concentration standards every 10 injections throughout the analysis sequence to evaluate this criterion.
- 7.8.10 Refer to Section (8) Calculations (below) for guidance on calculating of concentration.
- 7.8.11 Check for degradation problems by injecting a degradation mix standard containing only 4,4'-DDT and endrin. This check is performed with the initial calibration analysis and then again every 12 hours). If degradation of either DDT or endrin exceeds 15% on both columns, the instrument is serviced and recalibrated. Calculate percent breakdown as follows:

$$\% \text{ Breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)} \times 100}{\text{DDT Total DDT peak area (DDT + DDE + DDD)}}$$

$$\% \text{ Breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)} \times 100}{\text{Total endrin peak area (endrin + endrin aldehyde + endrin ketone)}}$$

- 7.8.12 Using external calibration procedure, determine the identity and quantity of each component peak in the sample chromatogram, which corresponds to the compounds used for calibration purposes.
- 7.8.13 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using EPA Method 3620B<sup>2</sup>. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove sulfur using EPA Method 3660B<sup>3</sup>.
- 7.8.14 Manual integration: Make a hard copy of the original integration performed by the instrument. Perform the appropriate manual integration. Make a copy of the manual integration. Be sure that the scale of the copy is appropriate. Note on the manual integration copy the number of the reason (see list below) a new integration was performed, initial and date. Save the manual integration electronically so that it can be retrieved at a later date if necessary. Place a copy of all integrations in the data folder to be reviewed by the section manager or his/her designee.
- (1) Integration does not follow baseline
  - (2) Non-target peak interference
  - (3) To split a peak
  - (4) To integrate a split peak
  - (5) The peak was not integrated
  - (6) Computer integrated wrong peak
  - (7) Other - Explain
- 7.8.15 After review by the section manager, the manager will date and initial. Upon client request the integrations will be reviewed by the QAU or his/her designee initialed and dated. The hard copies will be filed with the raw data.



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### 7.9 Cleanup:

7.9.1 Proceed with APPL SOP #CLN001 (EPA Method 3620B<sup>2</sup>), followed by, if necessary, APPL SOP #CLN002 (EPA Method 3660B<sup>3</sup>), using the 10mL hexane extracts.

7.9.2 Following cleanup, GC, as described above should analyze the extracts.

7.9.3 If only PCBs are to be measured in a sample and clean up is needed, the Chromium trioxide method is used. See SOP# ANA8082.

### 8.0 Calculations

8.1 The sample/spike/surrogate is calculated against the initial calibration curve.

8.2 Formulas and calculations used to obtain and utilize the calibration curve can be found in SOP DOC014.

8.3 External standard calibration: the Enviroquant Data System performs the quantitation of each analyte. The algorithm is checked at least once per calibration curve and at least in every DVP package, by calculating the amount of analyte injected, from the peak response, using the calibration curve or the calibration factor. The following calculation is used to check the quantitation:

$$\text{Concentration (ppm)} = \frac{(A_s)(C_{st})(V_e) \times D}{(A_{st})(V_o)}$$

Where:

$A_s$  = Response for the analyte to be measured, (area/height)

$A_{st}$  = Response for the external standard

$C_{st}$  = Concentration of external standard ( $\mu\text{g/mL}$ )

$V_o$  = Volume of sample extracted (L or g)

$V_e$  = Final volume of extract (mL)

$D$  = Dilution factor if a dilution was made

### Average Response Factor

$$C_x (\mu\text{g/L}) = \frac{(A_x)}{(RF)}$$

Where:

$C_x$  = Concentration of the compound being measured

$A_x$  = Area response of the characteristic ion for the compound being measured

RF = Average response factor in the initial calibration for that analyte



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### Linear Regression

$$C_x (\mu\text{g/L}) = (A_x - b) / m$$

Where:

$C_x$  = Concentration of the compound being measured

$A_x$  = Area response of the characteristic ion for the compound being measured

$b$  = y intercept \*

$m$  = slope \*

\* = Obtained from the plot of the calibration curve in EnviroQuant

### Quadratic Regression

$$C_x (\mu\text{g/L}) = (+\text{SQRT}(b^2 - (4a(c-y)))) - b) / (2a)$$

Where:

$C_x$  = Concentration of the compound being measured

SQRT = Square root

$a^*$  =  $x^2$  slope

$b^*$  = s slope

$c^*$  = intercept

$y$  = Response (response of analyte)

\* = Obtained from the plot of the calibration curve in EnviroQuant

Use the following formula in Excel:

$$C_x (\mu\text{g/L}) = (+\text{SQRT}((A5^*A5) - ((4^*A4^*) * (A6 - A8)) - A5) / (2^*A4))$$

Where:

$C_x$  = Concentration of the compound being measured

SQRT = Square root

$A4^*$  =  $x^2$  slope (a)

$A5^*$  = s slope (b)

$A6^*$  = intercept (c)

$A8$  = Response ratio (analyte)

\* = Obtained from the plot of the calibration curve in EnviroQuant

8.4 A manual calculation must be performed once a day and documented on the quantitation sheet to verify the algorithm. A hardcopy printout of the initial calibration plot when linear (first order) or quadratic (second order) calibration is used should be included in the calibration folder. Also, see SOP# DOC014 for calculations.

8.5 Toxaphene quantitation:

8.5.1 Adjust sample size so that toxaphene major peaks are 10-70% full-scale deflection;

8.5.2 Construct the baseline of 5 major peaks in the standard



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- 8.5.3 Construct the baseline under the same 5 major peaks in the sample, using the distances of the peak troughs to baseline on the standard as a guide
- 8.5.4 Inject a 5-pt. curve and quantitate using the average R.F. having a %RSD<15%.
- 8.6 Chlordane is calculated as alpha and gamma chlordane. If Technical chlordane is requested follow the Toxaphene quantitation method.

### 9.0 Quality Control

- 9.1 The quality control set consists of a method blank, laboratory control spike (LCS), and a matrix spike/matrix spike duplicate for each batch of 20 samples or less. For USACE a LCS and LCSD must be performed. The surrogate compounds are added to all samples and QC prior to extraction.
- 9.2 Spike QC limits: The upper and lower control limits are established on 30 data points using control charts and are established on  $\pm 3$  standard deviations from the mean. The limits for the spike compound are listed in Appendix B. (See SOP# QC016 for control chart generation.)
- 9.2.1 Corrective Action: If the % recovery of a specific compound in the laboratory control spike is greater than the upper control limit and there are no positive findings for that compound, no further action is taken. If there are positive findings for that compound reanalyze the spike and all effected samples or flag the results with a 'J'. If the % recovery of any compound fall below the lower control limit, reanalyze the spike and all effected samples. Client specific requirements for the exceptions are listed on the APPL Analysis Request Form (ARF).
- 9.3 Surrogate limits: The upper and lower control limits are established on 30 data points using control charts and are established on  $\pm 3$  standard deviations from the mean. The limits for the surrogates are listed in Appendix B.
- 9.3.1 Corrective Action: If the % recovery falls outside of the control limits the project manager will contact the client to determine the course of action. If the client is unavailable, professional judgement should be used to determine if the sample would be reanalyzed or reported.
- 9.4 MS/MSD: The control limits established above in section 9.2 are also used the upper and lower control limits for the MS/MSD. The limits for the spike compound are listed in Appendix B. Acceptance limits between MS and MSD - Waters  $\leq 20\%$  RPD, Soils  $\leq 30\%$  RPD.
- 9.4.1 Corrective Action: Examine the project specific DQOs and contact the project manager who will in turn contract the client. Flag the parent sample with a "J" for failed analytes. Client specific requirements for the exceptions are listed on the APPL Analysis Request Form (ARF).
- 9.4.2 Corrective Action: If the MS/MSD does not meet acceptance criteria for RPD: Report with appropriate data qualifying codes. For DoD projects, J flag the parent sample result for the failing analytes.
- 9.5 Blanks: Acceptance criteria: All target analytes in the method blank must be  $< RL$ . Acceptance criteria for DoD clients: No analytes detected at  $\geq \frac{1}{2} RL$ . For common laboratory contaminants, no analytes detected  $\geq RL$ .
- 9.5.1 Corrective Action: If there is a detection above the quantitation limit (or  $> \frac{1}{2} RL$  for DoD) in the method blank the entire batch associated with the blank will be re-extracted and reanalyzed except when the sample analysis resulted in a non-detect. If not enough sample volume exists for a re-



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extraction the sample will be qualified with a 'B' with the flag 'compound found in the associated blank'.

9.6 Instrument calibration: Requirements for calibration are listed in the calibration section of this SOP.

9.6.1 Corrective action: If the initial calibration curve does not meet the requirements, the standards will be reformulated and reanalyzed. If the continuing calibration verification does not meet the requirements a new CCV is prepared and analyzed.

9.6.2 Method Detection Limits: Establish the LOD, LOQ and MDL according to SOP# QC018.

### 9.0 Data Validation

9.1 The analyst that completed the work first reviews data. The initial calibration curve is reviewed, the continuing calibration %D is reviewed and the spike recovery and precision is reviewed. If at any point the review shows an out of control situation the section manager is notified verbally and the problem is investigated. The correction may be one of several points considered; standard preparation, improper injection size, extraction technique, etc. The problem is potentially solved and reanalyses or re-extraction/reanalyses is completed. These points are documented on the Multilevel Quality Control Sign-Off worksheet.

9.2 The second level of review is either by a peer in the same section or the section manager. The review person signs off the Multilevel Quality Control Sign Off worksheet. The MQCS sheets are filed with the data package.

9.3 When QC parameters are exceeded, the following will take place: When the matrix spikes are outside of the limits they are re-extracted and reanalyzed. When the LCS is outside of limits the entire batch is re-extracted and reanalyzed. If there is not enough sample for re-extraction the Project Manager is notified whom in turn notifies the client by phone or fax. The case narrative or case letter explains the sequence of events and the data is qualified. If the calibration parameters are not met the standards are reprepared and reanalyzed.

### 10.0 Health and Safety

Lab coats and gloves are use at all times. All personnel handling raw samples must have been vaccinated or tittered for infectious disease. Follow all safety procedures as describes in the SOP for samples suspected of containing biological hazards.

### 11.0 Pollution Prevention

All hazardous materials that are generated during the testing of samples must be properly collected and stored. Drums are available in the storage room for the following types of wastes- acidic, basic and solvents.

### 12.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and lands disposal restrictions. The laboratory has the responsibility to protect the environment by minimizing and controlling all releases from fume hoods and bench operations.

### 13.0 Contingencies for Handling Out of Control or Unacceptable Data

In the event that an out of control situation occurs, the project manager will be notified immediately. The affect of the out of control situation will be assessed according to the





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project DQO. If sufficient sample remains, and the situation will significantly affect the quality of the results, the analysis will be repeated. If the situation does not significantly affect the quality of the data, the project manager will notify the client and instructions from the client will be followed. In the event no sample remains, the client will be notified immediately. All situations will be documented on the multi level sheet and initialed by the project manager. All out of control situations will be brought to the attention of the QAU in the form of a QCER. The QAU has the final authority to approve the actions taken.

### 14.0 Deviations from the Method

This standard operating procedure was compared to the EPA Method 8081A. There are no deviations from the method.

### SALUTATION

This procedure applies to all personnel who analyze extracts for organochlorine pesticides by EPA Method 8081A<sup>1</sup>.

Section Manager: \_\_\_\_\_ Date: \_\_\_\_\_

QAU Director: \_\_\_\_\_ Date: \_\_\_\_\_

### References:

- <sup>1</sup>EPA Method 8081B, Revision 2, November 2000
- <sup>2</sup>EPA Method 3620B, SW846, Third Edition Revision 2 December 1996
- <sup>3</sup>EPA Method 3660B, SW846, Third Edition Revision 3 December 1996
- <sup>4</sup>EPA Method 3510C, SW846, Third Edition Revision 3 December 1996
- <sup>5</sup>EPA Method 3520C, SW846, Third Edition Revision 3 December 1996
- <sup>6</sup>EPA Method 3550B, Revision 3, November 2000
- <sup>7</sup>EPA Method 8000C, Revision 3, March 2003
- <sup>8</sup>CFR 40 Part 136, Appendix B, Chapter 1 (7-1-95 Edition), Revision 1.11



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**TABLE 1**

Compound	8081A <sup>1</sup> COMPOUNDS	
	Water Quantitation Limit (µg/L)	Soil Quantitation Limit (µg/kg)
Aldrin	0.05	50
α-BHC	0.05	50
β-BHC	0.05	50
δ-BHC	0.05	50
Chlordane	0.05	50
Dieldrin	0.05	50
Endosulfan I	0.05	50
Endosulfan II	0.05	50
Endosulfan sulfate	0.05	50
Endrin	0.05	50
Endrin aldehyde	0.05	50
Endrin ketone	0.05	50
Heptachlor	0.05	50
Heptachlor epoxide	0.05	50
Lindane	0.05	50
4,4-DDE	0.05	50
4,4-DDT	0.05	50
4,4-TDE/DDD	0.05	50
Methoxychlor	0.05	50
Toxaphene	1.0	1000



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### Appendix A

#### Definitions

**Calibration standard** - A solution prepared from the primary dilution standard solution or stock standard solution and the internal standards and surrogate analytes. The calibration solutions are used to calibrate the instrument response with respect to analyte concentration.

**Field Reagent Blank** - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

**Instrument blank (Blk)** - An aliquot of reagent water or other blank matrix to demonstrate that the instrument is not contributing contaminants to the samples.

**Internal Standard (IS)** - A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

**Instrument Performance Check (IPC)** - A solution of one or more compounds (analytes, surrogate, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

**Laboratory control spike (LCS)** - An aliquot of reagent water or other matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

**Laboratory Reagent Blank** - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.



Appendix A con't

**Limit of Detection** - An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent. The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%)

**Limit of Quantitation** - The minimum levels, concentrations, or quantities of a target analyte that can be reported with a specified degree of confidence. The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. This also equates with the term Practical Quantitation Limit (PQL).

**Matrix** - A surrounding substance within which something originates, develops, or is contained, such as: drinking water, saline/estuarine water, aqueous substance other than drinking water or saline/estuarine water, non-aqueous liquid, biological tissue, solids, soils, chemical waste, and air.

**Matrix duplicate (MD)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of a matrix sample and matrix sample duplicate, indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

**Matrix spike (MS)** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the matrix spike corrected for background concentrations.

**Matrix spike duplicate (MSD)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of a matrix spike and matrix spike duplicate, indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.



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**Method blank** - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The method blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

**Method detection limit** - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, as determined from analysis of a sample containing the analyte in a given matrix, as described in 40 CFR Part 136, Appendix B, 1 July 1995 edition.

**Practical quantitation limit** - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The practical quantitation limit is generally three to ten times greater than the method detection limit.

**Primary Dilution Standard** - A solution of several analytes prepared in the laboratory from stock solution and diluted as needed to prepare calibration solutions and other needed analyte solutions.

**Quality Control Sample (QCS)** - A solution of method analytes of known concentrations which is used to fortify an aliquot of LCS or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

**Sample Duplicate (DUP1/DUP2)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analytes of DUP1/DUP2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures

**Stock Standard Solution** - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials purchased from a reputable commercial source.



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**Surrogate** - A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

**Extracted Ion Current Profile (EICP)**—The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number.

**STOCK STANDARD SOLUTION (SSS)** - - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials purchased from a reputable commercial source.

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**APPENDIX XIII. SOP ANA8141A. Organophosphorus Compounds: Capillary Column Technique By Gas Chromatography By EPA Method 8141A (Revision 14, 09/17/10)**



## Standard Operating Procedure

### ORGANOPHOSPHORUS COMPOUNDS: CAPILLARY COLUMN TECHNIQUE BY GAS CHROMATOGRAPHY BY EPA METHOD 8141A<sup>1</sup>

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#### STATEMENT OF PURPOSE

This procedure describes the extraction and analysis of Organophosphorus pesticides compounds in water, groundwater, hazardous wastes, and solid samples.

#### 1.0 Scope and Application

- 1.1 This method is a capillary gas chromatographic method used to determine the concentration of Organophosphorus compounds. The fused-silica, open-tubular columns specified in this method offer improved resolution, better selectivity, increased sensitivity, and faster analysis than packed columns.
- 1.2 A dual-column/dual-detector approach may be used for the analysis of relatively clean extracts. Two 15-m or 30-m x 0.53-mm ID fused silica, open-tubular columns of different polarities are connected to an injection tee and each is connected to a detector. Analysts are cautioned regarding the use of a dual column configuration when their instrument is subject to mechanical stress, when many samples are analyzed over a short time, or when extracts of contaminated samples are analyzed.
- 1.3 Table 1 lists reporting limits for the target analytes.
- 1.4 When EPA Method 8141A<sup>1</sup> is used to analyze unfamiliar samples, compound identifications is supported by confirmatory analysis (secondary column). Also, gas chromatograph/mass spectrometer (GC/MS) can be used for qualitative confirmation of compound identifications.
- 1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.
- 1.6 If an individual project has its own QAPP with client specific requirements that are different than the SOP, the QAPP overrides the SOP.

#### 2.0 Method Summary

- 2.1 EPA Method 8141A<sup>1</sup> provides gas chromatographic conditions for the detection of ppb concentrations of Organophosphorus compounds. Prior to the use of this method, appropriate sample preparation techniques must be used. See section (7.0).
- 2.2 Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. A gas chromatograph with a flame photometric or nitrogen-phosphorus detector is used for this multi-residue procedure.
- 2.3 Ultrasonic Extraction (EPA Method 3550B) is not an appropriate sample preparation method for EPA Method 8141A<sup>1</sup> and should not be used because of the potential for destruction of target analytes during the ultrasonic extraction process.

#### 3.0 Sample Preservation, Containers, Handling and Storage

- 3.1 Containers used to collect samples for the determination of Semivolatiles organic compounds are purchased pre-cleaned. The sample containers for soils are brass or steel sleeves with Teflon caps or glass jars with Teflon lined screw caps. The sample containers for waters are 1 liter amber glass bottles with Teflon lined screw caps.
- 3.2 All samples will be taken and held at a temperature of 4°C until delivery to the laboratory. When the samples are delivered to the laboratory they are placed into a refrigerator that





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is kept at 4°C until extraction. No additional preservative is required. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

### 4.0 Interferences and Potential Problems

- 4.1 The use of Florisil Cleanup for some of the compounds in this method has been demonstrated to yield recoveries less than 85 percent and is therefore not recommended for all compounds. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is not less than 85 percent.
- 4.2 Analytical difficulties encountered for target analytes include:
  - 4.2.1 Many analytes will degrade on reactive sites in the chromatographic system. Analysts must ensure that injectors and splitters are free from contamination and are silanized. Columns are installed and maintained properly.
  - 4.2.2 Performance of chromatographic systems will degrade with time. Column resolution, analyte breakdown and baselines may be improved by column washing. Oxidation of columns is not reversible.
  - 4.2.3 The following analytes indicate a strong affinity to water matrices: 1,2,4-Triazole, Methamidophos and Acephate. These analytes should be extracted by APPL SOP# MWE008 for water matrices and EPA Method 3550B for soil matrices.
  - 4.2.4 The target analyte Naled often has difficulty in maintaining calibration after the initial curve. If the CCV has increased in response, and the samples prior to the CCV are not detected, re-injection is not required. However, if the CCV has decreased in response, then previous and subsequent samples must be re-injected. For samples containing positive Naled responses, the opening and closing calibrations must meet the requirements of this SOP. Spikes may be quantitated using the CCV as a single point calibration.
- 4.3 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing reagent blanks.
- 4.4 Co-elution occurs on DB-5 column for the following:
  - Terbufos/tri-o-cresyl phosphate
  - Naled/Simazine/Atrazine
  - Dichlorofenthion/Demeton-O
  - Trichloronate/Aspon
  - Bolstar/Stirophos/Carbophenothion
  - Phosphamidon/Crotoxyphos
  - Fensulfothion/EPN
- 4.5 Analytical difficulties encountered for target analytes include:
  - 4.5.1 TEPP is an unstable diphosphate, which is readily hydrolyzed in water and is thermally labile. Care must be taken to minimize loss during analysis and preparation. Identification of bad standard lots is difficult since the electron impact mass spectrum of TEPP is nearly identical to its major breakdown product, triethyl phosphate.
  - 4.5.2 Dichlorvos recovery is poor from aqueous solutions due to its water solubility.
  - 4.5.3 Naled is converted to Dichlorvos on column by debromination. This reaction may also occur during sample prep. The extent of debromination will depend on the



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nature of the matrix being analyzed. The analyst must consider the potential for debromination when Naled is to be determined.

- 4.5.4 Trichlorfon rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form Dichlorvos and HCl. If this method is to be used for the determination of Organophosphate in the presence of Trichlorfon, the analyst should be aware of the possibility of rearrangement to Dichlorvos to prevent misidentification.
- 4.5.5 Demeton is a mixture of two compounds: Demeton-O and Demeton-S. Two peaks are observed in all the chromatograms corresponding to these two isomers. It is recommended that the early eluting compound (Demeton-S) be used for quantitation.
- 4.5.6 Dioxathion is a single-component pesticide. However, several extra peaks are observed in the chromatograms of standards. Because of this, Dioxathion is not included in composite standard mixtures.
- 4.5.7 Merphos is readily oxidized and will produce two peaks. Quantitation should be based on the sum of both peaks.
- 4.5.8 Retention time of Monocrotophos may increase with increasing concentrations in the injector. Analysts should check for retention time shifts in highly contaminated samples.

### 5.0 Equipment/Apparatus

- 5.1 Gas chromatograph
  - 5.1.1 Agilent Technologies 6890N gas chromatograph equipped with 7683 Autosamplers
  - 5.1.2 Hewlett Packard 6890 gas chromatograph equipped with 6890 Autosamplers
- 5.2 Columns
  - 5.2.1 Column 1 – DB-35MS - 30-m x 0.32-mm wide bore capillary column, 0.25 µm film thickness, chemically bonded with 35% phenyl methyl polysiloxane or equivalent
  - 5.2.2 Column 2 - DB-5MS - 30-m x 0.32-mm wide bore capillary column, 0.25 µm film thickness, chemically bonded with 5% phenyl polysiloxane, 95% methyl polysiloxane or equivalent.
- 5.3 Detectors
  - 5.3.1 Nitrogen-Phosphorus Detector (NPD) operated in the phosphorus specific mode
- 5.4 Hewlett Packard EnviroQuant Data System
- 5.5 Volumetric flasks, Class A: sizes as appropriate with ground-glass stoppers.
- 5.6 Syringes
- 5.7 Injection vials with crimp tops
- 5.8 Balances, Analytical, 0.0001g

### 6.0 Reagents

- 6.1 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents used will be traceable at all steps of the procedure.
- 6.2 Solvents
  - 6.2.1 Hexane - Pesticide quality
  - 6.2.2 Acetone - Pesticide quality
  - 6.2.3 Methylene chloride - Pesticide quality
  - 6.2.4 Methanol - Pesticide quality



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- 6.3 Stock standard solutions: The certified solutions must be accompanied by a certificate of analysis that states balances used in the manufacture of this standard are calibrated with weights traceable to NIST in compliance with ANSI/NCCL Z-540-1 and ISO 9001. Standards formulated in house are prepared with balances that are calibrated with weights traceable to NIST. (See SOP ROU006).
- 6.3.1 Organophosphate stock standards (calibration and surrogate) are prepared according to ROU006.
- 6.3.2 Secondary source stock standards are purchased from a separate source other than calibration stocks.
- 6.3.3 The stock standard solutions are stored in sealed ampules and are kept at 4°C and protected from light. Stock standards are to be checked for evaporation, especially just prior to preparing calibration standards from them.
- 6.3.4 Stock standard solutions must be replaced, once opened, after one year or sooner if comparison with check standards indicates a problem.
- 6.3.5 Standards for easily hydrolyzed chemicals including TEPP, Methyl Parathion, and Merphos should be checked every 30 days.
- 6.4 Calibration standards: Calibration standards at minimum of five concentrations for each parameter of interest are prepared through dilution of the stock standards with hexane.
- 6.5 Calibration solutions must be replaced after one year, or sooner, if comparison with check standards indicates a problem.
- 6.6 Surrogate standards: Tributylphosphate and triphenylphosphate are the surrogates added to each sample, blank, and all QC samples. Proceed with corrective action when surrogates are out of limits for a sample.

### 7.0 Procedure

7.1 Extraction: Refer to APPL, Inc.'s SOPs for the following extraction procedures:

7.1.1 Water:

7.1.1.1 SOP# SEP001- Proper Use of Separatory Funnels

7.1.1.2 SOP# SEP009- OCL/OP/Triazines Separatory Funnel Extraction (EPA Method 3510A)

7.1.1.3 SOP# LIQ001 - Continuous Liquid-Liquid OCL/OP/Triazine/Carbamate Extraction (EPA Method 3520B)

7.1.2 Soil:

7.1.2.1 SOP# SOX001- Set Up and Operation of Soxhlet Extraction Apparatus

7.1.2.2 SOP# SOX005- OCL/OP/Triazines by Soxhlet Extraction (EPA Method 3540C)

7.1.3 The extract will be transferred to a scintillation vial with a Teflon-lined screw cap. Proceed with gas chromatographic analysis if further cleanup is not required.

7.1.4 Cleanup procedures:

7.1.4.1 Florisil Column Cleanup (Method 3620B)

7.1.4.2 Sulfur Cleanup (Method 3660) (Do not use mercury or copper)

7.2 Gas chromatography column conditions. The following conditions are suggested starting points. Actual conditions may vary with optimization.

7.2.1 Column 1 NPD03: Carrier gas (Helium) flow rate: 2.9mL/min constant flow

7.2.2 Column 2 NPD03: Carrier gas (Helium) flow rate: 2.9mL/min constant flow

7.2.3 Column 1 NPD04: Carrier gas (Nitrogen) flow rate: 2.9mL/min constant flow

7.2.4 Column 2 NPD04: Carrier gas (Nitrogen) flow rate: 2.9mL/min constant flow



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### 7.3 Operating Conditions:

#### 7.3.1 GC Conditions:

- 7.3.1.1 Oven Temperature: 80°C
- 7.3.1.2 Equilibrium Time: 3.00 min
- 7.3.1.3 Oven Maximum: 280°C
- 7.3.1.4 Initial Temp: 80°C
- 7.3.1.5 Initial Time: 0.00 min

#### 7.3.2 Temperature Program:

- 7.3.2.1 Rate: 10.0°C
- 7.3.2.2 Final Temp: 280°C
- 7.3.2.3 Final Time: 14.0 min
- 7.3.2.4 Injection Temp: 225°C
- 7.3.2.5 Detector Temp: 290°C

### 7.4 Calibration: Prior to using this introduction technique for any GC method, the system is calibrated.

7.4.1 One of the concentrations will be at the quantitation limit. Refer to Table 1 for list of quantitation limits. This list may be superseded by client specific requirements. The analyst must refer to the incoming sample notice for the Labworks code and look at the detection limits listed on the appropriate form 1 to determine the quantitation limit standard.

7.4.2 The initial calibration curve is a reflection of the performance of the instrument at any given time. Individual compounds react to the changing dynamic of the instrument. Therefore it is sometimes necessary to delete points for individual compounds in an initial calibration curve. When this occurs the following rules are used to ensure integrity of the data:

7.4.2.1 A standard must be included in the curve for each compound, which is less than or equal to the reporting limit.

7.4.2.2 The deletion of discrete points must never result in a calibration curve consisting of less than five points for each analyte of interest.

7.4.2.3 Points for an individual analyte in the middle of the curve may not be deleted, however unforeseen circumstances may occur such as a misinjection by the autosampler, a loose cap on an injection vial, etc. In this situation the entire level is deleted for all compounds and the reason for deletion is noted on the initial calibration form. If these results in a calibration curve that consists of less than five points another level may be run before the analysis of samples begin.

7.4.2.4 Points at the low end and high end of the curve may be deleted if it is determined the compound ceases to be linear at either end. Any positive findings in the samples will be analyzed so as to fall within the linear range of that particular compound.

7.4.2.5 When the initial calibration curve has been established, no changes are made to it after the processing of samples has begun.

7.4.3 Calibration standards for each parameter of interest are prepared through dilution of the stock standards with hexane.

7.4.4 The curve is made daily from the calibration stock standard.

7.4.5 Analyze each calibration standard. Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph. Samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the



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calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used.

7.4.5.1 Calculate response factors or calibration factors and percent RSD for each analyte of interest as follows:

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}}{\text{Mass injected (in nanograms)}}$$

The percent RSD is calculated as follows:

$$\%RSD = (SD)(100\%)/(RF_{x1})$$

Where:

%RSD = Percent relative standard deviation.

RF<sub>x1</sub> = Mean of the initial RF for a compound.

SD = Standard deviation of the average RRF for a compound

7.4.6 A linear calibration based on least squares regression may be employed. This is most easily achieved by performing a linear least squares regression of the instrument response versus the mass of the analyte chromatographed. Make certain that the instrument response is treated as the dependent variable (y) and the amount as the independent variable (x).

$$X = C_s \quad \text{and} \quad y = A_s$$

Where:

x = the mass of the analyte in the sample aliquot introduced into the instrument

y = is the area (or height) of the response

7.4.6.1 In order for the linear regression model to be used for quantitative purposes, r, or r<sup>2</sup> must be greater than or equal to 0.99.

7.4.7 Formulas and calculations used to obtain and utilize the calibration curves are found in SOP DOC014.

7.4.8 Second source calibration – For DoD - The working calibration is verified once by the injection of a second source standard. This standard must be obtained from a vendor different from that of the initial calibration standard. If the second source calibration response varies from the predicted response by more than 15%D, inspect the GC system to determine the cause and perform the necessary maintenance before injecting a new calibration curve. If the laboratory control spike is obtained from a different vendor and is less than ±15%D from the initial calibration, it may be used to satisfy this requirement.

7.4.9 The working calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is every 10 samples or 12-hour time span. If the average response for the analytes varies from the predicted response by more than ± 15% on both columns, the subsequent samples must be re-injected. Previous samples may be used if the samples are “not detected”, provided the response is out with increasing



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sensitivity.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

Where:

$R_1$  = Average calibration factor from first analysis

$R_2$  = Calibration factor from continuing analysis

### 7.5 Gas chromatographic analysis:

- 7.5.1 Organophosphorus compounds are introduced by direct injection using HP autosamplers.
- 7.5.2 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with the instrument calibration followed by sample extracts, and, every 10 sample injections alternate between a low and high calibration standard mix. The sequence ends when the set of samples has been injected or when qualitative and or quantitative QC criteria are exceeded.
- 7.5.3 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100 fold range, are acceptable if linearity is demonstrated.
- 7.5.4 Calibrate the system immediately prior to conducting any analyses. The calibration factor for each analyte to be quantitated must not exceed 20% difference. When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary before recalibrating and proceeding with sample analysis. All samples that were injected after the standard exceeding the criterion must be re-injected to avoid errors in quantitation, if the initial analysis indicated the presence of specific target analytes that exceeded the criterion.
- 7.5.5 Establish daily retention time windows for each analyte. Use the retention time for each analyte as the midpoint of the window for that day.
  - 7.5.5.1 The daily retention time window equals the midpoint  $\pm$  three times the standard deviation determined from standards injected over a 72 hour period.
  - 7.5.5.2 In those cases where the standard deviation for a particular standard is zero, substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.
  - 7.5.5.3 A new retention time study is completed annually or whenever a new column is installed.
  - 7.5.5.4 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Second column confirmation is performed on all extracts. The second column will meet all the calibration and second source requirements for analytes of interest as outlined in the calibration section of this SOP. If historical data is provided, the extracts may not be confirmed on the secondary column. When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results should be evaluated after the identification has been confirmed.



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Calculate the relative percent difference (RPD) between the two results using the formula below.

$$RPD = (|R_1 - R_2|) / [(R_1 + R_2)/2] \times 100$$

Where:

R<sub>1</sub> = result on the primary column

R<sub>2</sub> = result on the secondary column

- 7.5.5.5 If one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system during peak integration. If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result. If the calculated RPD is > 40% and the results of both columns are above the reporting limit, the larger of the two results is reported and flagged with a "Y". A dirty matrix may interfere with confirmation of a positive finding and the result is left to the analyst's best judgment. If the calculated RPD is <40% and all the QC requirements are met for that analyte on both columns, the result reported is left to the analysts professional judgement.
- 7.5.6 Validation of the GC system qualitative performance: Use the mid concentration standards every 10 sample injections throughout the analysis sequence to evaluate this criterion.
- 7.5.7 Refer to Section (8.0) Calculations (below) for guidance on calculating of concentration.
- 7.5.8 Using external calibration procedure, determine the identity and quantity of each component peak in the sample chromatogram, which corresponds to the compounds used for calibration purposes.
- 7.5.9 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using EPA Method 3620A. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove sulfur using EPA Method 3660A. If EPA Method 3660A is used for sulfur cleanup, only the tetrabutylammonium (TBA)-sulfite option should be employed, since copper and mercury may destroy OP pesticides.
- 7.5.10 When analytes co-elute, the concentrations are added together in the calibration curve. If there is a hit for a co-eluting analytes, it is noted in the case narrative.
- 7.5.11 Manual integration: Make a hard copy of the original integration performed by the instrument. Perform the appropriate manual integration. Make a copy of the manual integration. Be sure that the scale of the copy is appropriate. Note on the manual integration copy the number of the reason (see list below) a new integration was performed, initial and date. Make a note to justify the new integration on the manual copy, date and initial. Save the manual integration electronically so that it can be retrieved at a later date if necessary. Place a copy of all integrations in the data folder to be reviewed by the section manager or his/her designee. After review by the section manager, the manager will date and initial. See SOP # ANA003 for further instructions.



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- (1) Integration does not follow baseline
- (2) Non-target peak interference
- (3) To split a peak
- (4) To integrate a split peak
- (5) The peak was not integrated
- (6) Computer integrated wrong peak
- (7) Other - Explain

The integrations will be reviewed by the QAU or his/her designee, initialed and dated. The hard copies will be filed with the raw data.

#### 8.0 Calculations

8.1 The sample/spike/surrogate is calculated against the initial calibration curve.

8.2 External standard calibration: The EnviroQuant Data System performs the quantitation of each analyte. The algorithm is checked at least once per calibration curve and at least in every DVP package, by calculating the amount of analyte injected, from the peak response, using the calibration curve or the calibration factor. The following calculation is used to check the quantitation:

$$\text{Concentration (ppb)} = \frac{(A_s)(V_e)}{(RF_{\text{avg}})(V_o)} \times D$$

Where:

- $A_s$  = Response for the analyte to be measured, (area/height)  
 $RF_{\text{avg}}$  = Average response of analyte from calibration curve  
 $V_o$  = Volume of sample extracted (L or Kg)  
 $V_e$  = Final volume of extract (mL)  
 $D$  = Dilution factor if a dilution was made

#### 9.0 Quality Control

9.1 The quality control set consists of a method blank, laboratory control spike (LCS), and a matrix spike/matrix spike duplicate for each batch of 20 samples or less. For USACE a LCS and LCSD must be performed. The surrogate compounds are added to all samples and QC prior to extraction.

9.2 Spike QC limits: The upper and lower control limits are established on 30 data points using control charts and are established on  $\pm 3$  standard deviations from the mean. The limits for the spike compound are listed in Appendix B. (See SOP# QC016 for control chart generation.)

- 9.2.1 Corrective Action: If the % recovery of a specific compound in the laboratory control spike is greater than the upper control limit and there are no positive findings for that compound, no further action is taken. If there are positive findings for that compound reanalyze the spike and all effected samples or flag the results with a 'J'. If the % recovery of any compound fall below the lower control limit, reanalyze the spike and all effected samples. Client specific requirements for the exceptions are listed on the APPL Analysis Request Form (ARF).





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- 9.3 **Surrogate limits:** The upper and lower control limits are established on 30 data points using control charts and are established on  $\pm 3$  standard deviations from the mean. The limits for the surrogates are listed in Appendix B.
- 9.3.1 **Corrective Action:** If the % recovery falls outside of the control limits the project manager will contact the client to determine the course of action. If the client is unavailable, professional judgement should be used to determine if the sample would be reanalyzed or reported.
- 9.4 **MS/MSD:** The control limits established above in section 9.2 are also used the upper and lower control limits for the MS/MSD. The limits for the spike compound are listed in Appendix B. Acceptance limits between MS and MSD - Waters  $\leq 20\%$  RPD, Soils  $\leq 30\%$  RPD.
- 9.4.1 **Corrective Action:** Examine the project specific DQOs and contact the project manager who will in turn contract the client. Flag the parent sample with a "J" for failed analytes. Client specific requirements for the exceptions are listed on the APPL Analysis Request Form (ARF).
- 9.4.2 **Corrective Action:** If the MS/MSD does not meet acceptance criteria for RPD: Report with appropriate data qualifying codes. For DoD projects, J flag the parent sample result for the failing analytes.
- 9.5 **Blanks:** Acceptance criteria: All target analytes in the method blank must be  $< RL$ . Acceptance criteria for DoD clients: No analytes detected at  $\geq \frac{1}{2} RL$ . For common laboratory contaminants, no analytes detected  $\geq RL$ .
- 9.5.1 **Corrective Action:** If there is a detection above the quantitation limit (or  $> \frac{1}{2} RL$  for DoD) in the method blank the entire batch associated with the blank will be re-extracted and reanalyzed except when the sample analysis resulted in a non-detect. If not enough sample volume exists for a re-extraction the sample will be qualified with a 'B' with the flag 'compound found in the associated blank'.
- 9.6 **Instrument calibration:** Requirements for calibration are listed in the calibration section of this SOP.
- 9.6.1 **Corrective action:** If the initial calibration curve does not meet the requirements, the standards will be reformulated and reanalyzed. If the continuing calibration verification does not meet the requirements a new CCV is prepared and analyzed.
- 9.6.2 **Method Detection Limits:** Establish the LOD, LOQ and MDL according to SOP# QC018
- 10.0 Data Validation**
- 10.1 The analyst completing the work first reviews data. The initial calibration curve is reviewed, the continuing calibration %D is reviewed and the spike recovery and precision is reviewed. If at any point the review shows an out of control situation the section manger is notified verbally and the problem is investigated. The correction may be one of several points considered; standard preparation, improper injection size, extraction technique, etc. The problem is potentially solved and re-analyses or re-digestion/re-analyses is completed. These points are documented on the Multilevel Quality Control Sign-Off worksheet.
- 10.2 The second level of review is either by a peer in the same section or the section manger. The review person signs off the Multilevel Quality Control Sign Off worksheet. The MQCS sheets are filed with the data package.



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10.3 When QC parameters are exceeded, the following will take place: When the matrix spikes are outside of the limits they are redigested and reanalyzed. When the LCS are outside of limits the entire batch is redigested and reanalyzed. If there is not enough sample for re-digestion the Project Manager is notified whom in turn notifies the client by phone or fax. The case narrative or case letter explains the sequence of events and the data is qualified. If the calibration parameters are not met the standards are re-prepared and reanalyzed.

### 11.0 Deviations to the method

This standard operating procedure was compared to the EPA Method 8141B. There are no deviations from the method.

### 12.0 Pollution Prevention

Hazardous materials that are generated during the testing of samples must be properly collected and stored. Drums are available in the storage room for the following types of wastes-acidic, basic and solvents.

### 13.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory has the responsibility to protect the environment by minimizing and controlling all releases from fume hoods and bench operations.

### 14.0 Contingencies for Handling Out of Control or Unacceptable Data

In the event that an out of control situation occurs, the project manager will be notified immediately. The affect of the out of control situation will be assessed according to the project DQO. If sufficient sample remains, and the situation will significantly affect the quality of the results, the analysis will be repeated. If the situation does not significantly affect the quality of the data, the project manager will notify the client and instructions from the client will be followed. In the event no sample remains, the client will be notified immediately. All situations will be documented on the multi level sheet and initialed by the project manager. All out of control situations will be brought to the attention of the QAU in the form of a QCER. The QAU has the final authority to approve the actions taken.

### 15.0 Health and Safety

Lab coats and gloves are use at all times. All personnel handling raw samples must have been vaccinated or tittered for infectious diseases. Follow all safety procedures as described in the SOP for samples suspected of containing biological hazards.



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### SALUTATION

This procedure applies to all personnel who analyze extracts for Organophosphorus pesticides by EPA Method 8141A<sup>1</sup>.

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*Monica Aguilera*

Section Manager: \_\_\_\_\_ Date: \_\_\_\_\_

*Francisco Leticia*

QAU Director: \_\_\_\_\_ Date: \_\_\_\_\_

### References:

<sup>1</sup>EPA Method 8141A, revision 1, September 1994

<sup>2</sup>CFR 40 Part 136, Appendix B, Chapter 1 (7-1-95 Edition), Rev 1.11



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TABLE 1

Compound	8141 <sup>1</sup> COMPOUNDS	
	Water Quantitation Limit (µg/L)	Soil Quantitation Limit (µg/kg)
Azinphosmethyl	5.0	100
Bolstar	0.5	50
Chlorpyrifos	0.5	50
Coumaphos	0.5	100
Def	0.5	50
Demeton	1.0	100
Diazinon	0.5	50
Dichlorvos	1.0	100
Dimethoate	0.5	100
Disulfoton	0.5	50
EPN	0.5	50
Ethion	0.5	50
Ethoprop	0.5	50
Fensulfothion	2.5	250
Fenthion	0.5	50
Malathion	0.5	50
Merphos	0.5	50
Mevinphos	3.5	350
Naled	2.5	250
Parathion, ethyl	0.5	50
Parathion, methyl	0.5	50
Phorate	0.5	50
Prowl	0.5	50
Ronnel	0.5	50
Sulfotep	0.5	50
Sulprofos	0.5	50
Tetrachlorvinphos	0.5	50
Tokuthion	0.5	50
Trichlorinate	0.5	50
Trifluralin	0.5	50



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### Appendix A

#### Definitions

**Calibration standard** - A solution prepared from the primary dilution standard solution or stock standard solution and the internal standards and surrogate analytes. The calibration solutions are used to calibrate the instrument response with respect to analyte concentration.

**Field Reagent Blank** - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

**Instrument blank (Blk)** - An aliquot of reagent water or other blank matrix to demonstrate that the instrument is not contributing contaminants to the samples.

**Internal Standard (IS)** - A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

**Instrument Performance Check (IPC)** - A solution of one or more compounds (analytes, surrogate, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

**Laboratory control spike (LCS)** - An aliquot of reagent water or other matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

**Laboratory Reagent Blank** - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.



Appendix A con't

**Limit of Detection** - An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent. The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%)

**Limit of Quantitation** - The minimum levels, concentrations, or quantities of a target analyte that can be reported with a specified degree of confidence. The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. This also equates with the term Practical Quantitation Limit (PQL).

**Matrix** - A surrounding substance within which something originates, develops, or is contained, such as: drinking water, saline/estuarine water, aqueous substance other than drinking water or saline/estuarine water, non-aqueous liquid, biological tissue, solids, soils, chemical waste, and air.

**Matrix duplicate (MD)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of a matrix sample and matrix sample duplicate, indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

**Matrix spike (MS)** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the matrix spike corrected for background concentrations.

**Matrix spike duplicate (MSD)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of a matrix spike and matrix spike duplicate, indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.



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**Method blank** - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The method blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

**Method detection limit** - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, as determined from analysis of a sample containing the analyte in a given matrix, as described in 40 CFR Part 136, Appendix B, 1 July 1995 edition.

**Practical quantitation limit** - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The practical quantitation limit is generally three to ten times greater than the method detection limit.

**Primary Dilution Standard** - A solution of several analytes prepared in the laboratory from stock solution and diluted as needed to prepare calibrations solutions and other needed analyte solutions.

**Quality Control Sample (QCS)** - A solution of method analytes of known concentrations which is used to fortify an aliquot of LCS or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

**Sample Duplicate (DUP1/DUP2)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analytes of DUP1/DUP2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures

**Stock Standard Solution** - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials purchased from a reputable commercial source.



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**Surrogate** - A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

**Extracted Ion Current Profile (EICP)**—The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number.

**STOCK STANDARD SOLUTION (SSS)** - - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials purchased from a reputable commercial source.

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**APPENDIX XIV. SOP HPL8321A. Method 8321A: LC-Mass Spec Instrument Analysis (Revision 19, 07/27/10)**



## Standard Operating Procedure

### METHOD 8321A LC-Mass Spec Instrument Analysis Of Carbamate / Urea / Methamidophos and Nitroaromatics / Nitrosamines Compounds in Water or Soil

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#### STATEMENT OF PURPOSE

This procedure covers the use of high performance liquid chromatography (LC), coupled with either the ESI (electrospray) or APCI (atmospheric pressure chemical ionization) LC/MS interfaces in the detection and quantitation of Carbamate and Urea compounds and Nitroaromatics and Nitrosamines in soil or water matrices. The method is not limited to but includes the analytes listed in Table 1.

#### INSTRUCTIONS

##### 1.0 SCOPE AND APPLICATION

- 1.1 This method is applicable to the determination of the target compounds and Practical Quantitation Limits (PQL) listed in Table 1.
- 1.2 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.
- 1.2. If an individual project has its own QAPP with client specific requirements that are different than the SOP, the QAPP overrides the SOP. This information will be specified in the comment section of the ARF.

##### 2.0 METHOD SUMMARY

- 2.1 This method provides reverse phase high performance liquid chromatographic and LC/MS interface conditions for the detection of the target analytes listed.
- 2.2 For Carbamates, the soil samples are extracted by Method 3550B, and the water samples are extracted by Method 3510C.
- 2.3 For Methamidophos, the water samples are extracted by SOP LIQ009.
- 2.4 For Nitroaromatics/Nitrosamines (including Picric Acid), the soil samples are extracted by Method 8330 and the water samples are extracted by Method 3535A.
- 2.5 The Nitroaromatics/Nitrosamines extracts are analyzed by HPLC-UV/VIS in series with a Mass Spectrometer, using APCI negative ion SIM mode. The three nitrotoluene isomers and the nitrobenzene do not ionize well on the LC/MS. They are calibrated and run on the UV/VIS in series with the LC/MS. Any detection of these compounds in any extract is confirmed on the HSGC/HSMS. The rest of the Nitroaromatics/Nitrosamines compounds are calibrated on both the UV/VIS and LC/MS.
- 2.6 The Picric Acid extracts are analyzed by HPLC-MS, using an ESI source run in full scan mode.

##### 3.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

- 3.1. Refer to introductory material to Chapter 4 (SW-846), Organic Analytes, section 4.1 Sampling Considerations. The analytes listed in this method do not require any special pH adjustments or preservation considerations.
- 3.2. All samples will be taken and held at a temperature of  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  until delivery to the laboratory. When the samples are delivered to the laboratory they are placed into a



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refrigerator that is kept at  $4^{\circ} \pm 2^{\circ}\text{C}$  until extraction. Soil samples must be extracted within 14 days. Extracts must be stored under refrigeration at  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and analyzed within 40 days from extraction.

#### 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- 4.1 Refer to methods 3500, 3600, 8000, 8330 and 8321A.
- 4.2 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines, or both, causing misinterpretation of chromatograms or spectra. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

#### 5.0 EQUIPMENT, APPARATUS AND MATERIALS

- 5.1 HPLC/MS - UV/VIS and HRGC/HRMS
  - 5.1.1 High performance Liquid Chromatograph (HPLC) - An analytical system with programmable solvent delivery system and all required accessories including injection loop, analytical columns, purging gases, etc. (HP 1090L or Agilent 1100 and 1200 LC). A UV/VIS detector is in series with the LC/MS for explosive analysis. The Nitrotoluene isomers and Nitrobenzene are confirmed separately by a Waters HRGC/HRMS AutoSpec with HP 6890 GC.
  - 5.1.2 HRGC Analytical Column:
    - 5.1.2.1 Nitrotoluene isomers and Nitrobenzene analysis: DB5-MS 60m x 0.25mm x 0.25um.
  - 5.1.3 HPLC Analytical columns.
    - 5.1.3.1 Carbamate and Methamidophos analysis C18 Column 25cm x 4.6mm
    - 5.1.3.2 Nitroaromatics/Nitrosamines analysis: Envirosep PP column 1.25cm x 4.6mm plus C18 Column 25cm x 4.6mm (connected in series)
    - 5.1.3.3 Picric Acid analysis: KP-RPPX250 4mm x 250mm
  - 5.1.4 APPL Inc maintains a Finnigan LCQ ion trap Mass Spectrometer and an Agilent Technologies 1100 G1946D SL Mass Spectrometer. The Finnigan system has ms/ms collision-associated dissociation (CAD) capabilities; the Agilent system is a single quad instrument. Both LC systems may be configured with either the APCI or ESI interfaces for either positive or negative ion modes of analysis. Certain carbamate compounds perform better in one or the other of these analysis modes. To help determine which mode is optimum look at the molecular structure of a particular analyte of interest. ESI is a more effective ionization technique for molecules that form ions in solution, and APCI is more effective for neutral molecules in solution. The mass spec may be set for negative ion polarity (for analytes with a high affinity for electrons after ionization has taken place) or positive ion polarity (for analytes with an affinity for protonation after ionization).
  - 5.1.5 Data System –
    - 5.1.5.1 The data acquisition software from each instrument supplier (Agilent, Finnigan and Waters), allows the continuous acquisition and storage of all masses obtained throughout the duration of the chromatographic program. The software allows any MS data file to be searched for ions of a specified mass, and such ion abundance's to be plotted versus time or scan number. This type of plot is defined as an Extracted ion Current



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Profile (EICP). The software also allows integration of the abundance's in any EICP between specified time or scan number limits.

5.1.5.2 APPL Inc. proprietary software uses the raw data (generated from the instrument supplier's acquisition software) to quantitate the data for the Finnigan LCQ-MS. See SOPs HPLFINQUANT for the procedures on using the proprietary software. EnviroQuant software is used to quantitate the data for the Agilent 1100 LC-MS. MassLynx software is used to quantitate the data for the Waters HRGC/HRMS.

5.1.5.3 Balance - Analytical, capable of accurately weighing to the nearest 0.0001g.

- 5.2 Centrifuge
- 5.3 Syringes
- 5.4 Volumetric flasks, Class A1, 10, 25, and 50mL.
- 5.5 Separatory funnel - 2 liter, with PTFE stopcock.
- 5.6 Rotary evaporator - equipped with 1000mL receiving flask.
- 5.7 Evaporation flasks: 500mL (Kontes K-570050-1025 or equivalent).
- 5.8 Boiling chips.
- 5.9 Concentrator adapter.
- 5.10 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 5^{\circ}\text{C}$ ).
- 5.11 Vials: 10 - 20mL scintillation vials.

### 6.0 REAGENTS

- 6.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 6.2 Organic free reagent water.
- 6.3 Sodium sulfate (granular, anhydrous),  $\text{Na}_2\text{SO}_4$ .
- 6.4 Ammonium acetate, solution (0.1M)
- 6.5 Acetic acid.
- 6.6 Solvents.
  - 6.6.1 Methylene chloride. Pesticide quality or equivalent.
  - 6.6.2 Methanol, HPLC quality or equivalent.
  - 6.6.3 Acetonitrile, HPLC Quality or Equivalent
- 6.7 Stock standard solutions: Refer to SOP HPL002 for calibration mix, spike and surrogate mix concentrations.
- 6.8 Stock standards may be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable.
  - 6.8.1 Prepare stock standard solutions by accurately weighing approximately 0.0100g of pure material and record the weight in the LC-STANDARDS PREPARATION BOOK (current documentation book). Dissolve the material in methanol or other suitable solvent, and dilute to a known final volume in a volumetric flask. Alternatively, stock standards may be purchased individually in solution or as



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- custom mixes from various chemical suppliers. The individual stock solutions should be kept under refrigeration (4°C) with a one-year expiration date from preparation.
- 6.8.2 Prepare a second source single-point standard at the mid-level of the calibration curve from a purchased mixture of approximately 1000ug/ml. The expiration date for the second source stock is one year from the date the ampule is opened. The second source should be purchased from a separate vendor from the primary calibration source. The working second source mid-point solution should be kept under refrigeration (4°C) with a two-month expiration date from preparation.
- 6.8.3 Prepare a spike mix using the individual stock solutions or a custom mix in solution. The spike mix should be stored under refrigeration (4°C) with a four-month expiration date.
- 6.9 Calibration standards - A minimum of five different concentrations for each parameter of interest should be prepared through dilution of the stock standards with methanol (or other suitable solvent). Routine carbamate calibration curves consist of seven levels – 0.1ppm, 0.2ppm, 0.4ppm, 0.8ppm, 1.6ppm, 3.2ppm, and 6.4ppm. Routine Nitroaromatics/Nitrosamines calibration curves consist of seven levels–0.12ppm, 0.24ppm, 0.48ppm, 1.0ppm, 2.0ppm, 4.0ppm and 8.0ppm. Picric Acid calibrations curves consist of six points: 0.10ppm, 0.25ppm, 0.50ppm, 1.0ppm, 2.5ppm and 5.0ppm. Working calibration standards should be kept under refrigeration (4°C) with a two-month expiration date from preparation. Practical quantitation limit must be supported with a calibration standard at or below the PQL.
- 6.10 Surrogate standards - The analyst should monitor the performance of the extraction, analytical system, and the performance of the method in dealing with each sample matrix, by spiking each sample blank and QA/QC sample with at least one surrogate. The surrogates currently employed are Tributyl phosphate and Isoxaben for carbamates and 1,2-Dinitrobenzene for Nitroaromatics and Nitrosamines. Purchased surrogate mixtures of 1000µg/mL are used to prepare the working surrogate mixture at 2.0µg/mL for carbamates and 5.0µg/mL for Nitroaromatics/Nitrosamines. The working surrogate mix should be kept under refrigeration (4°C) with a four-month expiration date. The 1000µg/mL surrogate stock will have a one-year expiration date from the date the ampule was opened.
- 6.11 Internal standards. The internal standards used for carbamate analysis in the positive ion mode are Azodrin (Monocrotophos), Ridomil (Metalaxyl), and Thiobencarb. Dioxacarb is the I.S. used for negative ion mode. The concentration in solution is at 1ppm, which is prepared from individual stock solutions (1000µg/mL). For Nitroaromatics/Nitrosamines analysis, the I.S. is Azodrin at 1ppm in solution. The working internal standards should be kept under refrigeration with an expiration date of four months.

## 7.0 PROCEDURE

### 7.1 Preparation of water samples:

- 7.1.1 For Carbamates, one liter quantities of sample for routine analysis, and 1.5 L quantities of sample for low-level analysis are extracted by Method 3510C (SOP# SEP009C). The extracts are concentrated down to dryness and brought up to volume with 1mL of LC/MS Internal standard @ 1ppm in methanol.
- 7.1.2 For Methamidophos, 800mL quantities of sample are extracted by continuous liquid-liquid (SOP LIQ009).



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- 7.1.3 For Nitroaromatics and Nitrosamines (including Picric Acid), Method 3535A extracts the water samples. 500mL of water sample is extracted by solid-phase chromatography for a final volume of 5mL (SOP# MWE3535).
- 7.2 Preparation of soil samples:
- 7.2.1 For Carbamates, thirty-gram quantities of soil are methylene chloride extracted by method 3550B. (SOP# SON002).
- 7.2.1.1 Concentration steps are achieved using a rotary evaporator.
- 7.2.1.2 The 5-10mL extracts are transferred to a 20mL scintillation vial. The extracts are then taken to dryness using an adapter on the rotary evaporator. One mL of LC/MS INTERNAL STANDARDS @ 1ppm is then added to the scintillation vial.
- 7.2.1.3 Samples are prepared for injection by transferring approximately 200µL of the final solution into a 300µL-injection vial and capped. The vial is spun in a centrifuge for approximately two minutes. The solution is then carefully transferred into another vial capped and is ready for injection.
- 7.2.1.4 For soils that are dark colored, a "water solubility test" must be performed prior to instrument analysis. Place one drop of sample extract into 0.5mL DI water in a 300uL-injection vial. Shake the solution, and if it is cloudy, then a 1:5 dilution should be performed on the original sample extract prior to being centrifuged. If the solution is clear, then no dilution is required. The solubility test is necessary for LC systems using methanol / water mobile phases. Extracts that are not soluble in water will cause the instrument to shut down upon sample introduction onto the guard column.
- 7.2.2 For Nitroaromatics and Nitrosamines (including Picric Acid), the soil samples are extracted by Method 8330. Ten gram quantities are sonicated with 20mL Acetonitrile. (SOP# MSE018).
- 7.3 HPLC and MS CONDITIONS:
- 7.3.1 For Carbamate analysis the mobile phase is Water / Methanol gradient
- 7.3.1.1 A minimum of two injections or analytical sequences (a positive and negative ion scheme) in order to be able to pick up all the compounds listed. Both the positive and negative ion sequences require water and methanol mobile phase. Acetic acid (1%) may be added to the mobile phase in order to achieve better chromatography for certain analytes.
- 7.3.1.2 Flow rate is 0.6mL/minute. Initial conditions are 5% methanol / 95% water. The ramp is to 100% methanol over 10 minutes. The 100% methanol is held for 5 minutes and then ramped back to 10% over 0.2 minutes. The 10% is held for 4.8 minutes before the next injection. The total run time is 30 minutes. Note that these are base parameters and are subject to analyst change and/or preference.
- 7.3.1.3 Total run time 20min
- 7.3.1.4 Injection volume 50uL:
- 7.3.1.5 Ionization Source = APCI in positive and negative ion Full Scan modes.
- 7.3.1.6 The Finnigan LCQ-MS instrument's ms/ms CAD mode may also be employed to help eliminate chromatographic background noise from samples exhibiting matrix effects or to help confirm the presence of potential hits from the full scan mode.
- 7.3.2 For Methamidophos analysis the mobile phase is 0.1% Acetic Acid Water / Methanol gradient.



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- 7.3.2.1 The flow rate and mobile phase gradient are the same as for carbamate analysis (see sect 7.3.1.2)  
Injection volume 50uL Ionization Source = APCI in positive MS-MS mode using the Finnigan LCQ instrument.
- 7.3.3 For Nitroaromatics/Nitrosamines LC-UV/MS analysis, the mobile phase is 50:50 Water/Methanol isocratic (flow rate 0.5mL/min).
- 7.3.3.1 Total run time 20min
- 7.3.3.2 Injection Volume 100uL
- 7.3.3.3 UV/MIS detector at 214nm.
- 7.3.3.4 Ionization Source = APCI in negative-ion Full Scan mode.
- 7.3.4 For Nitrotoluene isomers and nitrobenzene HRGC/HRMS analysis, the carrier gas is Helium, with a 1.0mL/min flow rate in constant pressure mode.
- 7.3.4.1 The initial oven temperature is 75°C, with a ramp of 15°C/min, held at 150°C for 1 min, then a ramp of 5°C/min for a final temp of 275°C.
- 7.3.4.2 The total run time is 26 min.
- 7.3.4.3 Injection volume 1µL
- 7.3.4.4 Ionization polarity is positive
- 7.3.5 For Picric Acid analysis, the mobile phase is 50:50 water/methanol, run isocratically, with a 0.6mL/min flow rate.
- 7.3.5.1 The total run time is 20 min.
- 7.3.5.2 Injection Volume 200uL
- 7.3.5.3 Ionization Source = ESI in full scan mode.
- 7.4 Agilent and Finnigan Mass Spectrometer Calibration
- 7.4.1 Tuning for mass axis calibration is performed annually by the instrument supplier's service engineer, as documented in the instrument maintenance log books. If the chromatography indicates that a tune is required more frequently than once per year, an auto-tune may be performed in accordance to the manufacturers instructions<sup>2,3</sup>. See SOP HPLMAIN for further information on instrument maintenance and troubleshooting.
- 7.4.2 Waters HRMS Mass Calibration
- 7.4.2.1 The mass axis is tuned before each calibration curve and at the beginning of each analytical sequence, using the Waters software.
- 7.4.3 Instruments are calibrated according to factory specifications.
- 7.5 Liquid chromatographic calibration and sample analysis:
- 7.5.1 Prepare calibration standards as outlined in Section 6.7 and 6.8.
- 7.5.2 The analysis scheme utilized consists of a calibration curve of a minimum of five data points, 2<sup>nd</sup> source single-point standard, a system blank, and then a series of QA/QC, blanks, and sample injections. Once a curve is generated twelve hours are allowed until a calibration check or recalibration is performed.
- 7.5.3 Calibration curves are generated by performing extracted ion profiles for the primary (most abundant) molecular ion for each compound of interest. Minimums of five points are to be used for quantitative analysis. It may be necessary to eliminate two higher points, or two lower data points, or a point off each end. No mid level points may be eliminated even if they are obvious outliers, unless the entire calibration point is eliminated due to mis-injection. Method 8000B protocols are adhered to. Response factors are used to quantitate the data, if the % RPD is > 20 %. Linear regression may also be used to quantitate the data if the correlation coefficient > 0.990. For DoD clients, the linear correlation coefficient should be > 0.995. The option of



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using relative response factors from internal standards is also available. Standard protocols are adhered to in relation to calibration criteria relating to the internal standard approach. If a calibration criterion is not met, then sample analysis may not proceed. Instrument maintenance or re-prep / re-analysis of the calibration curve may be required.

- 7.5.4 Calibration curves for the UV/VIS are generated using area response or peak heights. Minimums of five points are to be used for quantitative analysis. It may be necessary to eliminate two higher points, or two lower data points, or a point off each end. No mid level points may be eliminated even if they are obvious outliers, unless the entire calibration point is eliminated due to mis-injection. Method 8000B protocols are adhered to. Response factors are used to quantitate the data, if the % RPD is > 20 %. Linear regression may also be used to quantitate the data if the correlation coefficient > 0.990. For DoD clients, the linear correlation coefficient should be > 0.995. The option of using relative response factors from internal standards is also available. Standard protocols are adhered to in relation to calibration criteria relating to the internal standard approach. If a calibration criterion is not met, then sample analysis may not proceed. Instrument maintenance or re-prep / re-analysis of the calibration curve may be required.
- 7.5.5 Continuing calibrations and 2<sup>nd</sup> source calibration acceptance criteria is 20%D compared to the primary calibration curve. Samples following CCVs that fails to meet the 20%D criteria should be re-analyzed with acceptable CCVs. Instrument maintenance or re-prep / re-analysis of the CCV may be required.
- 7.5.6 LC-MS quantitation of target analytes in actual samples is performed using the appropriate calibration on the area counts generated from the extracted ion profiles generated from the samples' data file. A spectrum needs to contain the appropriate secondary ions for firm confirmation. If possible, the attempt will also be made to further confirm positive hits by MS/MS or an alternative ionization mode.
- 7.5.7 For Nitroaromatics/Nitrosamines analysis, the three nitrotoluene isomers and nitrobenzene do not ionize and have no response on the LC/MS. These compounds will only be quantitated and calibrated on the UV/VIS, using peak height or area response and retention times. The remaining Nitroaromatics/Nitrosamines will be quantitated using the area counts from the sample EIP data. If the nitrotoluene isomers and nitrobenzene compounds are present in the sample extracts, confirmation analysis will be performed using HRGC/HRMS, and calibration is performed using the area counts of the target ions.

### 8.0 Calculations

- 8.1 Example calculations for response (calibration) factor and linear regression calculations:

Response Factor Calculation:

$$\frac{\text{Sample response} - 0}{\text{Response factor}} \times \text{DF} = \text{concentration analyte } (\mu\text{g/kg})$$





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Linear Regression Calculation:

$$\frac{\text{Sample response} - \text{intercept}}{\text{Slope}} \times \text{DF} = \text{concentration analyte } \mu\text{g/kg}$$

DF = Final volume (1mL)/initial volume (0.030kg) for carbamate soil analysis

Final volume (1mL)/initial volume (1.0L or 1.5L) for carbamate water and LL water analysis respectively

Final volume (20mL)/initial volume (0.01kg) for explosives soil analysis

Final volume (5.0mL)/initial volume (0.5L) for explosives water analysis

### 9.0 QUALITY CONTROL

- 9.1 The quality control set consists of a method blank, laboratory control spike (LCS), and a matrix spike/matrix spike duplicate for each batch of 20 samples or less. For USACE a LCS and LCSD must be performed. The surrogate compounds are added to all samples and QC prior to extraction.
- 9.2 Spike QC limits: Assessing Laboratory Control Spike and Matrix spikes. With each group of samples (or analytical batch), analyze a Laboratory Control Spike and a minimum of one matrix spike / matrix spike duplicate. (Client must provide sufficient sample volume). Procedures are in place for establishing and updating control limits for each mode of analysis. See SOP QA036. The upper and lower control limits are established on 30 data points using control charts and are established on  $\pm 3$  standard deviations from the mean. The limits for the spike compound are listed in Appendix B. (See SOP# QC016 for control chart generation.)
  - 9.2.1 Corrective Action: If the % recovery of a specific compound in the laboratory control spike is greater than the upper control limit and there are no positive findings for that compound, no further action is taken. If there are positive findings for that compound reanalyze the spike and all effected samples or flag the results with a 'J'. If the % recovery of any compound fall below the lower control limit, reanalyze the spike and all effected samples. Client specific requirements for the exceptions are listed on the APPL Analysis Request Form (ARF).



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### 9.3 Control limits and Target Ions

COMPOUND (Carbamates)	SOIL CONTROL LIMITS	WATER CONTROL LIMITS	POSITIVE ION MODE (m/z) target	NEGATIVE ION MODE (m/z) target
Tributyl phosphate	60-114	36-140	267	NA
Isoxaben	60-114	47-134	333	331
Aldicarb	13-125	31-133	116	NA
Aminocarb	30-156	31-133	209	NA
Barban	58-140	40-136	222	184
Benomyl/Carbendazim	18-90	10-137	192	158
Bromacil	29-158	52-127	261	259
Carbaryl	31-191	44-133	145	143
Carbofuran	55-158	36-165	222	NA
Chloroxuron	30-156	31-133	NA	289
Chlorpropham	30-156	47-130	NA	212
Diuron	18-166	52-136	235	231
Fenuron	35-136	37-132	165	NA
Fluometuron	30-156	49-144	233	231
Linuron	16-167	49-144	249	247
Methiocarb	49-125	35-142	226	167
Methomyl	59-127	23-152	163	NA
Mexacarbate	51-121	55-126	223	NA
Monuron	20-166	53-130	199	197
Neburon	28-171	49-137	275	273
Oryzalin	30-156	31-133	347	345
Oxamyl	24-153	10-117	163	161
Propachlom	30-156	31-133	212	NA
Propham	54-115	54-123	138	178
Propoxur	67-122	56-121	210	NA
Siduron	30-156	31-133	233	NA
Tebuthiuron	36-133	49-136	229	NA
Methamidophos	NA	40-135	142 Full Scan	112 MS-MS

NA = Not applicable. See other ionization mode for target (m/z).





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COMPOUND (Nitroaromatics/Nitrosamines)	SOIL CONTROL LIMITS	WATER CONTROL LIMITS
1,3,5-TRINITROBENZENE	65-135	65-135
1,3-DINITROBENZENE	65-135	65-135
2,4,6-Trinitrotoluene (TNT)	65-135	65-135
2,4-DINITROTOLUENE	65-135	65-135
2,6-DINITROTOLUENE	65-135	65-135
2-Am-4,6- DINITROTOLUENE	65-135	65-135
2-NITROTOLUENE	65-135	65-135
3-NITROTOLUENE	65-135	65-135
4-Am-2,6-DINITROTOLUENE	65-135	65-135
4-NITROTOLUENE	65-135	65-135
RDX	65-135	65-135
Tetryl	65-135	65-135
NITROBENZENE	65-135	65-135
Nitroglycerin	65-135	65-135
HMX	65-135	65-135
PETN	65-135	65-135
1,2-DINITROBENZENE	65-135	65-135
Picric Acid	30-130	30-130

Note: for the Nitroaromatics / Nitrosamines compounds, the control limits are set at a default 65-135%, until sufficient data points (N = 30) are available to establish in-house control limits.

- 9.4 **Surrogate limits:** The upper and lower control limits are established on 20 to 30 data points using control charts and are established on  $\pm 3$  standard deviations from the mean. The limits for the surrogates are listed in Appendix B.
- 9.4.1 **Corrective Action:** If the % recovery falls outside of the control limits the project manager will contact the client to determine the course of action. If the client is unavailable, professional judgement should be used to determine if the sample would be reanalyzed or reported.
- 9.5 **MS/MSD:** Control limits for spiking analytes are the same as those for the Laboratory Control Spike. The control limits for the Relative Percent Difference (RPD) between the Matrix Spike and the Matrix Spike Duplicate is 25%. The control limits established above in section 9.2 are also used the upper and lower control limits for the MS/MSD. The limits for the spike compound are listed in Appendix B. Acceptance limits between MS and MSD - Waters  $\leq 20\%$  RPD, Soils  $\leq 30\%$  RPD.3
- 9.5.1 **Corrective Action:** Examine the project specific DQOs and contact the project manager who will in turn contract the client. Flag the parent sample with a "J" for failed analytes. Client specific requirements for the exceptions are listed on the APPL Analysis Request Form (ARF).
- 9.5.2 **Corrective Action:** If the MS/MSD does not meet acceptance criteria for RPD: Report with appropriate data qualifying codes. For DoD projects, J flag the parent sample result for the failing analytes.





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- 9.6 **Blanks:** Assessing Laboratory Reagent Blank. With each group or set of samples (20) processed, analyze a Laboratory Control Blank consisting of a background soil sample to determine background contamination. If there is insufficient sample volume remaining for re-extraction, then the sample data will be flagged for the analyte of contamination found in the blank. Acceptance criteria: All target analytes in the method blank must be < RL. Acceptance criteria for DoD clients: No analytes detected at  $\geq \frac{1}{2}$  RL. For common laboratory contaminants, no analytes detected  $\geq$  RL.
- 9.6.1 **Corrective Action:** If there is a detection above the quantitation limit (or  $> \frac{1}{2}$  RL for DoD) in the method blank the entire batch associated with the blank will be re-extracted and reanalyzed except when the sample analysis resulted in a non-detect. If not enough sample volume exists for a re-extraction the sample will be qualified with a 'B' with the flag 'compound found in the associated blank.
- 9.7 **Instrument calibration:** Requirements for calibration are listed in the calibration section of this SOP.
- 9.8 **Corrective action:** If the initial calibration curve does not meet the requirements, the standards will be reformulated and reanalyzed. If the continuing calibration verification does not meet the requirements a new CCV is prepared and analyzed.
- 9.9 **Method Detection Limits:** Establish the LOD, LOQ and MDL according to SOP# QC018.
- 9.10 **Corrective Action:** Errors, deficiencies, deviations, or laboratory events or data that fall outside of established acceptance criteria will be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the analytical system. The investigation of the problem and any subsequent corrective action taken is documented on a Quality Control Exception Report (QCER) and/or a Corrective Action Report (CAR)

### 10.0 Data Validation

- 10.1 The analyst completing the work first reviews data. The average calibration curve is reviewed, the spike recovery, and precision is reviewed. If at any point the review shows an out of control situation, the section manager is notified verbally and the problem is investigated. The correction may be one of several points considered; standard preparation, improper injection size, extraction technique, etc. The problem is potentially solved and re-analyzed or re-extraction/re-analysis is completed. These points are documented on the Multilevel Quality Control Sign-Off worksheet.
- 10.2 When QC parameters are exceeded, the sample is reanalyzed. If the sample is still outside QC parameters the following will take place: The case narrative or case letter explains the sequence of events and the data is qualified.

### 11.0 Health and Safety

Lab coats and gloves are used at all times. All personnel handling raw samples must have been vaccinated or titered for infectious disease. Follow all safety procedures as describes in the SOP for samples suspected of containing biological hazards

### 12.0 Pollution Prevention

All hazardous materials that are generated during the testing of samples must be properly collected and stored. Drums are available in the storage room for the following types of wastes- acidic, basic and solvents.



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### 13.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory has the responsibility to protect the environment by minimizing and controlling all releases from fume hoods and bench operations.

### 14.0 Contingencies for Handling Out of Control or Unacceptable Data

In the event that an out of control situation occurs, the project manager will be notified immediately. The affect of the out of control situation will be assessed according to the project DQO. If sufficient sample remains, and the situation will significantly affect the quality of the results, the analysis will be repeated. If the situation does not significantly affect the quality of the data, the project manager will notify the client and instructions from the client will be followed. In the event no sample remains, the client will be notified immediately. All situations will be documented on the multi level sheet and initialed by the project manager. All out of control situations will be brought to the attention of the QAU in the form of a QCER. The QAU has the final authority to approve the actions taken.

### 15.0 Deviation from the Method

EPA method 8321A<sup>1</sup> was written for the thermospray ionization technique, however APPL Inc. uses either Atmospheric Pressure Control Ionization or Electrospray Ionization since they are the most current technology in ionization techniques.

### SALUTATION

This procedure applies to all personnel who analyze extracts for the target compounds listed in Table 1 by EPA Method 8321A<sup>1</sup>

*Paula Young*

Section Manager: \_\_\_\_\_

Date: 7-27-10

*Thomas L. Lerner*

QAU Director: \_\_\_\_\_

Date: 7-27-10

### References:

<sup>1</sup>EPA Method 8321A, USEPA SW-846, REVISION 4 DECEMBER 1996

<sup>2</sup>Finnigan LCQ MS Detector Hardware Manual, Rev C April 1997

<sup>3</sup>Agilent 1100 Series LC/MSD Reference Collection on compact disc



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**TABLE 1**

(Recommended Practical Quantitation Limits in Water and Soil Matrices)

	WATER PQL- $\mu$ g/L	SOIL PQL- $\mu$ g/Kg	Low-Level WATER PQL- $\mu$ g/L
Aldicarb	1	20	0.4
Aminocarb	1	20	0.4
Barban	5	70	3.5
Benomyl/Carbendazim	1	20	0.4
Bromacil	1	20	0.4
Carbaryl	1	20	0.07
Carbofuran	1	20	0.07
Chloroxuron	1	20	0.4
Chlorpropham	5	70	3.5
Diuron	1	20	0.4
Fenuron	1	20	0.4
Fluometuron	1	20	0.4
Linuron	1	20	0.4
Methiocarb	1	20	0.4
Methomyl	1	20	0.07
Mexacarbate	5	70	0.8
Monuron	1	20	0.4
Neburon	1	20	0.4
Oryzalin	1	20	0.4
Oxamyl	1	20	0.4
Propachlor	5	70	3.5
Propham	5	70	3.5
Propoxur	1	20	0.4
Siduron	1	20	0.4
Tebuthiuron	1	20	0.4

	WATER PQL- $\mu$ g/L	SOIL PQL- $\mu$ g/Kg
Methamidophos	0.20	NA





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TABLE 1 (Cont.)

(Recommended Practical Quantitation Limits in Water and Soil Matrices)

	WATER PQL- $\mu\text{g/L}$	SOIL PQL- $\mu\text{g/Kg}$
2-Am-4,6-DNT	0.25	250
4-Am-2,6-DNT	0.25	250
1,3-DNB	0.25	250
2,4-DNT	0.25	250
2,6-DNT	0.25	250
HMX	0.25	250
Nitrobenzene	0.25	250
Nitroglycerine	1.25	1250
4-NT	0.25	250
3-NT	0.25	250
2-NT	0.25	250
PETN	1.25	1250
RDX	0.25	250
Tetryl	0.25	250
1,3,5-TNB	0.25	250
2,4,6-TNT	0.25	250
Picric Acid	0.12	240



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### Appendix A

#### Definitions

**Calibration standard** - A solution prepared from the primary dilution standard solution or stock standard solution and the internal standards and surrogate analytes. The calibration solutions are used to calibrate the instrument response with respect to analyte concentration.

**Extracted Ion Current Profile (EICP)**—The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number.

**Field Reagent Blank** - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

**Instrument blank (Blk)** - An aliquot of reagent water or other blank matrix to demonstrate that the instrument is not contributing contaminants to the samples.

**Internal Standard (IS)** - A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

**Instrument Performance Check (IPC)** - A solution of one or more compounds (analytes, surrogate, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

**Laboratory control spike (LCS)** - An aliquot of reagent water or other matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.



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**Laboratory Reagent Blank** - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

**Limit of Detection** - An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent. The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%)

**Limit of Quantitation** - The minimum levels, concentrations, or quantities of a target analyte that can be reported with a specified degree of confidence. The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. This also equates with the term Practical Quantitation Limit (PQL).

**Matrix** - A surrounding substance within which something originates, develops, or is contained, such as: drinking water, saline/estuarine water, aqueous substance other than drinking water or saline/estuarine water, non-aqueous liquid, biological tissue, solids, soils, chemical waste, and air.

**Matrix duplicate (MD)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of a matrix sample and matrix sample duplicate, indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

**Matrix spike (MS)** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the matrix spike corrected for background concentrations.





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**Matrix spike duplicate (MSD)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of a matrix spike and matrix spike duplicate, indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

**Method blank** - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The method blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

**Method detection limit** - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, as determined from analysis of a sample containing the analyte in a given matrix, as described in 40 CFR Part 136, Appendix B, 1 July 1995 edition.

**Practical quantitation limit** - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The practical quantitation limit is generally three to ten times greater than the method detection limit.

**Primary Dilution Standard** - A solution of several analytes prepared in the laboratory from stock solution and diluted as needed to prepare calibrations solutions and other needed analyte solutions.

**Quality Control Sample (QCS)** - A solution of method analytes of known concentrations which is used to fortify an aliquot of LCS or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

**Sample Duplicate (DUP1/DUP2)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analytes of DUP1/DUP2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures





## Standard Operating Procedure

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**Stock Standard Solution** - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials purchased from a reputable commercial source.

**Surrogate** - A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

APPL, Inc.  
Confidential

**APPENDIX XV. SOP 6.1A-5. Cladoceran, *Ceriodaphnia dubia*, Survival Test (Revision 2010-01, 06/15/10)**



**SOP Title: Cladoceran, *Ceriodaphnia dubia*, Survival Test  
(Renewal and Non-Renewal)**

**Copy No.: 2 of 2**

**SOP No.:** 6.1A-5 version 2010-01

**File:** SOP Section 6.1

**USEPA Protocol:** EPA 821-R-02-012 (5<sup>th</sup> Edition Acute)

**ELAP Code:** 113.023A (static)  
113.023B (renewal)

**Issue Date:** June 15, 2010

**Review Internal:** Annual

**Author:** J.L. Miller

**Authorized by:** original signed by Jeffrey L. Miller  
Jeffrey L. Miller, Ph.D., DABT, President

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## 1.0 Purpose of Test

This method measures the acute toxicity of effluents, receiving waters, or storm water to the cladoceran, *Ceriodaphnia dubia*, during a 24-, 48-, 72-, or 96-hour renewal or non-renewal exposure. The effects measured include the synergistic, antagonistic, and additive effects of all the chemical, physical, and biological components that adversely affect the physiological and biochemical functions of the test organisms. The protocol is summarized in Attachment 1. Apparatus, equipment, reagents and consumable materials needed for this test are listed in Attachment 2.

## 2.0 Test Organisms

*C. dubia* are obtained from in-house cultures maintained as described in SOP 1.1. Only test organisms that appear healthy, behave and feed normally, and have < 10% mortality in cultures are used. The *C. dubia* used at A-S are examined microscopically yearly to confirm genus and species. Representative test organisms are verified for genus and species annually by microscopic examination and confirmation in "Ecology and Classification of North American Freshwater Invertebrates" (Thorp & Couch, Editor, Year). Specimens are preserved and maintained for 2 years.

## 3.0 Test Organism Feeding

During culture, *C. dubia* are fed a mixture of YTA (yeast, trout chow and alfalfa) and algae (*S. capricornutum*) prepared as described in SOP 1.1). Food quality is considered adequate if *C. dubia* cultures survive, grow and reproduce normally. Test organisms are not fed in static studies. In renewal studies that continue beyond 48 hours, depending on the study design, food may be added to test solutions 2-4 hours prior to sample change-out.

## 4.0 Preparation, Storage, and Testing of Control Water

Well water is treated by reverse osmosis followed by carbon adsorption to produce reagent water that is equivalent to the Millipore Milli-Q® water. It is then amended with reagent grade chemicals and vigorously aerated overnight to achieve moderately hard specifications. Alternatively, Sierra Spring™ water is amended with reagent grade chemicals as described in the test protocol for moderately hard water (EPAMH), and aerated overnight. Depending on the study design, other control waters may be used. In such cases, these waters will be prepared as described in the test protocol, e.g., USEPA very hard, USEPA soft, USEPA very soft, etc. In cases where control waters other than EPAMH is used, the type of water will be noted on water quality data sheets. Each batch of reagent water is prepared and stored in a sanitized 5-gallon plastic container. Each container is issued a unique lot number at the time of reagent water preparation. Each batch of dilution water is bioassayed prior to use in testing. Two 20-mL aliquots of each lot containing 5 *C. dubia* are bioassayed for 96 hours. If mean survival in the two replicates is >90% and the organisms appear healthy, the lot of dilution water is considered adequate for use in culture and testing.

## **5.0 Test Samples**

Each test sample is logged in upon receipt. Information including client or source, date, time of log-in are recorded along with initial water quality parameters, including temperature, dissolved oxygen, conductivity, hardness, alkalinity, residual chlorine, and pH. Samples are stored in the dark at <4 °C until used. Prior to use, test samples are brought to test temperature and D.O. measured. If the sample D.O. is not acceptable (>100% or <40% saturation), the sample is adjusted to meet protocol specifications.

## **6.0 Test Facilities**

Tests are conducted in areas capable of maintaining test protocol temperatures (25 ±1°C), illumination levels (50-100 ft-c) and photoperiod (16 hr light:8 hr dark). Such areas may include water baths, temperature-controlled rooms, or environmental chambers. Temperatures are recorded continuously in a surrogate test container during the test period. The photoperiod in test areas is controlled by electronic timers.

## **7.0 Test Solution Preparation**

When indigenous organisms are suspected, the test samples are filtered through a Nitex 60 µm plankton net prior to testing. Test materials are either tested undiluted (100%) or in a dilution series containing five concentrations (e.g., 6.25, 12.5, 25, 50 and 100% sample). If the test sample is expected to exhibit high toxicity, or at the discretion of the Study Director, other dilution series may be used.

## **8.0 Water Quality Measurements**

In static tests, at a minimum, pH, conductivity, and residual chlorine are measured in the control and highest concentration of test sample at the beginning of the test, at test renewal and at test termination. If total residual chlorine is not detected at test initiation, it will not be measured at renewal or termination. If residual chlorine is detected, the client will be contacted and any action taken to dechlorinate the sample will be noted on the Dose Preparation sheets. D.O., pH and temperature are measured in the control and all test concentrations at the beginning of the test, daily thereafter, and at test termination. Total alkalinity and hardness will be measured in the control and highest test concentration at the beginning of the test and in each of the renewal solutions. Total ammonia will be measured in samples where toxicity may be contributed to by unionized ammonia, e.g., ≥5 mg/L total ammonia. D.O. will be monitored closely for the first 4-8 hours and measured daily thereafter in all test concentrations that have surviving organisms, and at test termination. At a minimum, temperature will be measured at test initiation and daily thereafter.

## **9.0 Test Initiation and Change-Out**

Tests are initiated by placing the test organisms into the test chambers in a manner consistent with the test protocol. Neonates (<24 hours old) in a 300 mL crystallizing dish are placed one or two at a time into the replicates using a random procedure. The time of test initiation is noted on the data sheet.

Tests conducted under static (non-renewal) conditions are not renewed during the test period. Tests conducted under renewal conditions are changed out at 24- or 48-hour intervals, depending on the test design. At renewal, neonates are pipetted into freshly prepared test

solutions in new scintillation vials, using particular caution to prevent injury to the organisms and minimize the volume of test solution transferred. The 24-hour old solutions are retained for water quality measurements (temperature, D.O. and pH).

The test boards are rotated daily. After each renewal, the boards are rotated 180 degrees to face the opposite direction and all boards are moved one position to the right, with the exception of the last column of chambers, which are moved to the positions vacated by the first board on the far left.

## **10.0 Daily Observations**

Mortality observations are made on a daily basis and recorded on the data sheets. Animals exhibiting abnormal behavior will remain in the test chambers but their behavior is noted on the data sheets.

## **11.0 Reference Toxicant Testing**

Sodium chloride is used as the reference toxicant for NPDES compliance tests. Data review of a given effluent or receiving water test will include review of the associated reference toxicant test and current control chart. A reference toxicant test is conducted on each batch of purchased test organisms or monthly on organisms cultured in-house. Verification for a valid test will include: frequency required by the permitting authority or recommended method, test acceptability criteria, test conditions, concentration-response relationship, and test sensitivity. The results of the reference toxicant test are plotted on a control chart and compared to the current control chart limits.

Reference toxicant tests that fall outside of recommended control chart limits are evaluated to determine the validity of associated effluent and ambient water tests. The degree to which the reference toxicant test results fell outside of control chart limits, the width of the limits, the direction of the deviation (increasing or decreasing sensitivity), the test conditions of both the effluent test and reference toxicant test, and the objective of the test will be considered.

## **12.0 Recording Data**

Computer-generated data sheets are prepared prior to test initiation. These include a dose preparation information sheet, water quality data sheets, and the cumulative mortality/behavioral observation record sheets. Copies of data sheets are found in Attachment 3.

Data is recorded neatly in black non-erasable ink. Entry errors are crossed-out with a single line that does not obscure the original entry. Pages with errors are corrected near where the error occurs, initialed, and dated by the person making the correction. Pages with multiple errors, or with major problems such as spills or illegible ink marking, are not discarded but remain with the rest of the data sheets. Annotations are sequentially numbered and made on a real-time basis to prevent loss of information. Prior to data analysis, all data sheets are checked for entry errors and missing information. Data are stored in a secure location after office copies are made.

## **13.0 Data Analysis**

The endpoints of toxicity tests using *Ceriodaphnia dubia* are based on the adverse effects on survival. Data analysis is performed using ToxCalc™ 5.23 (or greater) (Tidepool Software,

McKinleyville, CA), a statistical software package compatible with the US EPA electronic toxicity database requirements. IC<sub>p</sub> values (EC<sub>25</sub>, EC<sub>50</sub>, etc.) are calculated using EPA recommended point estimate techniques. LOEC and NOEC values, for survival, are obtained using a hypothesis test approach guided by the EPA statistical analysis flowchart. Formal tests for normality and homogeneity of variance are performed prior to selecting parametric or nonparametric methods of analyses.

#### **14.0 Test Termination**

The test is terminated and survival noted after 24, 48, 72, or 96 hours of exposure, depending on the study design. The time of test termination is noted on the data sheets immediately below the time of test initiation and initialed by the technician terminating the test.

#### **15.0 Acceptability of Test Results**

Minimum Survival: Minimum control survival is 90%. Tests exhibiting lower control survival will be repeated.

Test Variability: The within-test variability of individual tests will be reviewed according to EPA guidance on upper and lower percent minimum significant difference (PMSD) bounds (EPA 833-R-00-003).

Concentration-Response Relationships: All results for each multi-concentration test is reviewed and reported according to USEPA guidance on the evaluation of concentration-response relationships (EPA-821-B-00-004). This guidance provides review steps for 10 different concentration-response patterns that may be encountered in test data. Based on the review, the guidance provides one of three determinations: that calculated effect concentrations are reliable and should be reported, that calculated effect concentrations are anomalous and should be explained, or that the test was inconclusive and the test should be repeated with a newly collected sample. Tests that exhibit unexpected concentrations-response relationships also may indicate a need for further investigation and possible retesting.

## **16.0 Health and Safety**

AQUA-Science maintains a safety program that includes on-going safety instruction in proper handling of hazardous reagents, chemicals, and materials. The laboratory manager conducts regular safety inspections and discusses safety issues with personnel. The laboratory is equipped with proper safety equipment, including disposable gloves, safety glasses, laboratory coats, respirators and portable eye wash stations. All materials are clearly labeled. Solvents and volatile materials are stored in a flammable liquid cabinet.

Material Safety Data Sheets are maintained for chemicals and reagents purchased from suppliers. Acids, bases and solvents are stored in safety storage cabinets for hazardous and/or flammable materials.

Test samples are properly disposed of according to local, state, and federal rules. Effluent and ambient samples are disposed of in the sanitary sewer. Solvents are collected and either evaporated or taken to the Yolo County Landfill for recycling.

## Attachment 1

### Protocol Summary

**Test Type:** Cladoceran, *Ceriodaphnia dubia*, Survival Test  
(Static and Renewal)

**ELAP Code:** 113.023 005A (Static)  
113.023 005B (Renewal)

**USEPA Protocol:** EPA 821-R-02-012 (5<sup>th</sup> Edition Acute)

1. Test type: Static non-renewal or static-renewal
2. Test duration: 24, 48, 72, or 96 h
3. Temperature<sup>1</sup>: 20 °C ± 1 °C; or 25 °C ± 1 °C
4. Light quality: Ambient laboratory illumination
5. Light intensity: 10-20 µE/m<sup>2</sup>/s (50-100 ft-c)  
(ambient laboratory levels)
6. Photoperiod: 16 h light, 8 h darkness
7. Test chamber size: 30 mL (minimum)
8. Test solution volume: 15 mL (minimum)
9. Renewal of test solutions: Minimum, after 48 h
10. Age of test organisms: Less than 24-h old
11. No. organisms per test chamber: Minimum, 5 for effluent and receiving water tests
12. No. replicate chambers per concentration: Minimum, 4 for effluent and receiving water tests
13. No. organisms per concentration: Minimum, 20 for effluent and receiving water tests
14. Feeding regime: Feed YCT and *Selenastrum* while holding prior to the test; newly-released young should have food available a minimum of 2 h prior to use in a test; add 0.1 mL each of YCT and *Selenastrum* 2 h prior to test solution renewal.
15. Test chamber cleaning: Cleaning not required

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<sup>1</sup> Acute and chronic toxicity tests performed simultaneously to obtain acute/chronic ratios must use the same temperature and water hardness.

16. Test chamber aeration: None, unless specified by the study design
17. Dilution water: Moderately hard synthetic water prepared using MILLIPORE MILLI-Q® or equivalent deionized water and reagent grade chemicals or 20% DMW, receiving water, ground water, or synthetic water, modified to reflect receiving water hardness.
18. Test concentrations. Effluents: Minimum of five effluent concentrations and a control  
Receiving Waters: 100% receiving water and a control
19. Dilution series: Effluents:  $\geq 0.5$  dilution series  
Receiving Waters: None, or  $\geq 0.5$  dilution series
20. Endpoint: Effluent: Mortality (LC<sub>50</sub> or NOAEC)  
Receiving Waters: Mortality (Significant difference from control)
21. Sampling and sample holding requirements: Effluents and Receiving Waters: Grab or composite samples first used within 36 h of completion of the sampling period.
22. Sample volume required: 1 L
23. Test acceptability criterion: 90% or greater survival in controls



## ATTACHMENT 2

### Apparatus and Equipment

1. Laboratory *Ceriodaphnia dubia* culture unit providing sufficient numbers of organisms for toxicity test. (See A-S SOP Section 1.1 for culturing methods)
2. Environmental chamber, incubator, or equivalent facility with temperature control ( $20 \pm 1^\circ\text{C}$  or  $25 \pm 1^\circ\text{C}$ ).
3. Water purification system producing reagent water equivalent to the Millipore Milli-Q® water.
4. Analytical balance capable of accurately weighing 0.0001 g.
5. Class S reference weights for checking performance of balance.
6. Glass or electronic thermometers for measuring water temperature.
7. Disposable polyethylene pipets, droppers, and glass tubing with tire-polished edges, 2-mm ID for transferring organisms.
8. Test chambers: 10-20 mL borosilicate scintillation vials per concentration.
9. Racks for test chambers: scintillation vial racks capable of holding 24-50 vials.
10. Bulb-thermograph or electronic-chart type thermometers for measuring temperature.
11. National Bureau of Standards Certified thermometer.
12. Specific conductivity, dissolved oxygen and pH meters for routine physical and chemical measurements.
13. Light box for observation of test organisms
14. Mechanical shaker or magnetic stir plates for algal cultures.
15. Filtering apparatus for membrane and glass fiber filters. Positive pressure peristaltic pump for effluents and vacuum pump for dilution water.
16. Pipettors, adjustable volume repeating dispensers (Eppendorf and Oxford)
17. Volumetric pipets: Glass A, 1-100 mL.
18. Serological pipets: 1-10 mL, graduated.
19. Pipet bulbs and fillers: Propipet® or Repipet®
20. Wash bottles for rinsing small glassware, instrument electrodes and probes.

## Reagents and Consumable Materials

1. Test substance: final effluent, ambient water, or storm water
2. Control water: laboratory reagent/dilution water
3. Reference toxicant: NaCl
4. Standard pH buffers 7 and 10
5. Specific conductivity standards
6. Membranes and filling solutions for dissolved oxygen probe
7. Reagents for alkalinity and hardness calorimetric titration
8. Combined YCT food for *Ceriodaphnia* culture: yeast, alfalfa leaves, and digested trout chow (5.0 g of each in 3.0 L reagent water, mixed well in a blender)
9. Algal food for *Ceriodaphnia* culture: refrigerated algal concentrate (*Selenastrum capricornutum*), YTC concentrate
10. Pressure-sensitive labeling tape (colored)
11. Waterproof markers for labeling containers

**ATTACHMENT 3**

**Data Sheets**



**AQUA-Science**  
Environmental Toxicology Specialists

**MORTALITY AND BEHAVIOR OBSERVATIONS**

Test Number: _____	Study Director: _____ J.L. Miller
Protocol No.: _____ EPA 821/R-02/012	Technicians: _____ Walker/Concepcion/Sanford/Soyster/Martin
Test Material: _____	
Test Species: _____ <i>Ceriodaphnia dubia</i>	Animal Lot No.: _____ A/S RO: _____
Initiation Date: _____	Termination Date: _____ January 5, 1904

Samples @ 100%	Vessel No.	Cumulative Mortality				Comments
		Day 1	Day 2	Day 3	Day 4	
	A					n=5 animals/rep
	B					
	C					Test Initiation Info:
	D					Time:
	A					Tech:
	B					
	C					Test Termination Info:
	D					Time:
	A					Tech:
	B					
	C					
	D					
	A					
	B					
	C					
	D					
	A					
	B					
	C					
	D					

Technician Initials				
Observation Time				
Observation Date				



**APPENDIX XVI. SOP 6.2A-5. Fathead Minnow, *Pimephales promelas*, Survival Test (Revision 2010-01, 06/15/10)**

**SOP Title: Fathead Minnow, *Pimephales promelas*, Survival Test  
(Renewal and Non-Renewal)**

**Copy No.:** \_\_\_ of 2

**SOP No.:** 6.2A-5 version 2010-01

**File:** SOP Section 6.2

**EPA Protocol:** EPA 821-R-02-012 (5<sup>th</sup> Edition Acute)

**ELAP Code:** 113.021 001A (static)  
113.021 001B (renewal)

**Issue Date:** June 15, 2010

**Review Internal:** Annual

**Author:** J.L. Miller

**Authorized by:** original signed by Jeff Miller  
Jeffrey L. Miller, Ph.D., DABT, President

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## 1.0 Purpose of Test

This method measures the acute toxicity of effluents, receiving waters, or storm water to the fathead minnow, *Pimephales promelas*, during a 24-, 48-, 72-, or 96-hour renewal or non-renewal exposure. The effects measured include the synergistic, antagonistic, and additive effects of all the chemical, physical, and biological components that adversely affect the physiological and biochemical functions of the test organisms. The protocol is summarized in Attachment 1. Apparatus, equipment, reagents and consumable materials needed for this test are listed in Attachment 2.

## 2.0 Test Organisms

Test organisms (1-14 days old, <24 hours difference in age) are obtained from Aquatox, Inc. (Hot Springs, AK) or Thomas Fish Co. (Anderson, CA). Only test organisms that appear healthy, behave and feed normally, and have < 10% mortality upon receipt and in controls are used. The vendor provides documentation of hatch date/time, species identification and lot number, culture water quality characteristics, which are maintained in the laboratory. Upon arrival, small volumes of the shipping water are removed from the container and is slowly replaced with dilution water. When temperature acclimation is necessary, every effort is made to limit temperature changes to <3°C within any 12-hour period. Dissolved oxygen and temperature are measured daily on the "Test Organism Receipt and Acclimation Record".

## 3.0 Test Organism Feeding

Fish are fed *Artemia* nauplii concentrate while holding and 2 hours prior to test solution renewal at 48 hours. Fish are not fed during static tests.

## 4.0 Preparation, Storage, and Testing of Control Water

Well water is treated by reverse osmosis followed by carbon adsorption to produce reagent water that is equivalent to the Millipore Milli-Q® water. It is then amended with reagent grade chemicals and vigorously aerated overnight to achieve moderately hard specifications. Alternatively, Sierra Spring™ water is amended with reagent grade chemicals as described in the test protocol for moderately hard water (EPAMH), and aerated overnight. Depending on the study design, other control waters may be used. In such cases, these waters will be prepared as described in the test protocol, e.g., EPA very hard, EPA soft, EPA very soft, etc. In cases where control waters other than EPAMH is used, the type of water will be noted on water quality data sheets. Each batch of reagent water is prepared and stored in a sanitized 5-gallon plastic container. Each container is issued a unique lot number at the time of reagent water preparation. Each batch of dilution water is bioassayed prior to use in testing. Two 20-mL aliquots of each lot containing 5 *C. dubia* are bioassayed for 96 hours. If mean survival in the two replicates is >90% and the organisms appear healthy, the lot of dilution water is considered adequate for use in culture and testing.

## **5.0 Test Samples**

Each test sample is logged in upon receipt. If the sample temperature is  $\geq 7$  °C upon arrival, the client is notified. Information including client or source, date, time of log-in are recorded along with initial water quality parameters (temperature, dissolved oxygen, conductivity, hardness, alkalinity, residual chlorine, and pH measured). Samples are stored in the dark at  $< 4$  °C until used. Prior to use, test samples are brought to test temperature and D.O. measured. If the sample D.O. is not acceptable ( $> 105\%$  saturation or  $< 4.0$  mg/L D.O.), the sample is adjusted by gentle aeration to meet protocol specifications.

## **6.0 Test Facilities**

Tests are conducted in areas capable of maintaining test protocol temperatures ( $20$  or  $25 \pm 1$ °C), illumination levels (50-100 ft-c) and photoperiod (16 hr light:8 hr dark). Such areas may include water baths, temperature-controlled rooms, or environmental chambers. Temperatures are recorded continuously in a surrogate test container during the test period. The photoperiod in test areas is controlled by electronic timers.

## **7.0 Test Solution Preparation**

When indigenous organisms are suspected, the test samples are filtered through a Nitex 60  $\mu\text{m}$  plankton net prior to testing. Test materials are either tested undiluted (100%) or in a dilution series containing five concentrations (e.g., 6.25, 12.5, 25, 50 and 100% sample). If the test sample is expected to exhibit high toxicity, or at the discretion of the Study Director, other dilution series may be used.

## **8.0 Water Quality Measurements**

In static tests, at a minimum, pH, conductivity, and residual chlorine are measured in the control and highest concentration of test sample at the beginning of the test, at test renewal and at test termination. If total residual chlorine is not detected at test initiation, it will not be measured at renewal or termination. If residual chlorine is detected, the client will be contacted and any action taken to dechlorinate the sample will be noted on the Dose Preparation sheets. D.O., pH and temperature are measured in the control and all test concentrations at the beginning of the test, daily thereafter, and at test termination. Total alkalinity and hardness will be measured in the control and highest test concentration at the beginning of the test. Total ammonia will be measured in samples where toxicity may be contributed to by unionized ammonia, e.g.,  $\geq 5$  mg/L total ammonia. D.O. will be monitored closely for the first 4-8 hours and measured daily thereafter in all test concentrations that have surviving organisms, and at test termination. At a minimum, temperature will be measured at test initiation and daily thereafter. Temperature in a surrogate test container will be recorded continuously.

## **9.0 Test Initiation and Change-Out**

Tests are initiated by placing the test organisms into randomized test chambers (typically a 500 mL glass or plastic test chamber containing 250 mL of test solution). The loading rate of each test chamber will be determined by weighing 10 of the largest rainbow trout from each batch received and calculating loading densities. Loading densities will not exceed 0.4 g/L at 25 °C. At test initiation, the test organisms are placed one or two at a time into two or more test chambers per treatment until each replicate contains 10 fish. The time of test initiation is noted on the data sheet.

Tests conducted under static (non-renewal) conditions are not renewed during the test period. Tests conducted under renewal conditions are changed out at 24- or 48-hour intervals, depending on the test design. At renewal, approximately 80% of the test sample is removed using a pipette or baster. Debris, sediment and unconsumed nauplii are removed. Freshly prepared test solution is gently poured down the side of the test chamber to the initial level. The change-out solutions are retained for D.O. and pH measurements. At renewal, test chambers are rotated by moving the front chamber to the back of the row, and moving the rows one position to the right. The far right row is moved to the far left position.

## **10.0 Daily Observations**

Mortality observations are made on a daily basis and recorded on the data sheets. Animals exhibiting abnormal behavior will remain in the test chambers but their behavior is noted on the data sheets.

## **11.0 Reference Toxicant Testing**

Sodium chloride is used as the reference toxicant. Data review of a given effluent or receiving water test will include review of the associated reference toxicant test and current control chart. A reference toxicant test is conducted on each batch of purchased test organisms or monthly on organisms cultured in-house. Verification for a valid test will include: frequency required by the permitting authority or recommended method, test acceptability criteria, test conditions, concentration-response relationship, and test sensitivity. The results of the reference toxicant test are plotted on a control chart and compared to the current control chart limits.

Reference toxicant tests that fall outside of recommended control chart limits are evaluated to determine the validity of associated effluent and ambient water tests. The degree to which the reference toxicant test results fell outside of control chart limits, the width of the limits, the direction of the deviation (increasing or decreasing sensitivity), the test conditions of both the effluent test and reference toxicant test, and the objective of the test will be considered. Based on this information, the Study Director will determine the appropriate corrective action, including repeating the test.

## 12.0 Recording Data

Computer-generated data sheets are prepared prior to test initiation. These include a dose preparation information sheet, water quality data sheets, and the cumulative mortality/behavioral observation record sheets. Copies of data sheets are found in Attachment 3.

Data is recorded neatly in black non-erasable ink. Entry errors are crossed-out with a single line that does not obscure the original entry. Pages with errors are corrected near where the error occurs, initialed, and dated by the person making the correction. Pages with multiple errors, or with major problems such as spills or illegible ink marking, are not discarded but remain with the rest of the data sheets. Annotations are sequentially numbered and made on a real-time basis to prevent loss of information. Prior to data analysis, all data sheets are checked for entry errors and missing information. Data are stored in a secure location after office copies are made.

## 13.0 Data Analysis

The endpoints of toxicity tests using fathead minnows are based on the adverse effects on survival. Data analysis is performed using ToxCalc™ 5.23 (or greater) (Tidepool Software, McKinleyville, CA), a statistical software package compatible with the EPA electronic toxicity database requirements. IC<sub>p</sub> values (EC<sub>25</sub>, EC<sub>50</sub>, etc.) are calculated using EPA recommended point estimate techniques. LOEC and NOEC values, for survival, are obtained using a hypothesis test approach guided by the EPA statistical analysis flowchart. Formal tests for normality and homogeneity of variance are performed prior to selecting parametric or nonparametric methods of analyses.

## 14.0 Test Termination

The test is terminated after 24, 48, 72 or 96 hours of exposure, depending on the study design. Fish are placed in an MS-222 solution until dead. A randomly selected set of 10 control fish are weighed (to 0.001 g) and measured (fork length, to 1 cm). The time of test termination is noted on the data sheets immediately below the time of test initiation and initialed by the technician terminating the test.

## 15.0 Acceptability of Test Results

Minimum Requirements: Tests are acceptable if the mean survival in the control is 90%. Tests with less than 90% mean control survival are repeated.

Test Variability: The within-test variability of individual tests will be reviewed according to EPA guidance on upper and lower percent minimum significant difference (PMSD) bounds (EPA 833-R-00-003).

Concentration-Response Relationships: All results for each multi-concentration test is reviewed and reported according to EPA guidance on the evaluation of concentration-response relationships (EPA-821-B-00-004). This guidance provides review steps for 10 different concentration-response patterns that may be encountered in test data. Based on the review, the guidance provides one of three determinations: (1) that calculated effect concentrations are reliable and should be reported, (2) that calculated effect concentrations are anomalous and should be explained, or (3) that the test was inconclusive and the test should be repeated with a

newly collected sample. Tests that exhibit unexpected concentrations-response relationships also may indicate a need for further investigation and possible retesting.

## **16.0 Health and Safety**

AQUA-Science maintains a safety program that includes on-going safety instruction in proper handling of hazardous reagents, chemicals, and materials. The laboratory manager conducts regular safety inspections and discusses safety issues with personnel. The laboratory is equipped with proper safety equipment, including disposable gloves, safety glasses, laboratory coats, respirators and portable eye wash stations. All materials are clearly labeled. Solvents and volatile materials are stored in a flammable liquid cabinet.

Material Safety Data Sheets are maintained for chemicals and reagents purchased from suppliers. Acids, bases and solvents are stored in safety storage cabinets for hazardous and/or flammable materials.

Test samples are properly disposed of according to local, state, and federal rules. Effluent and ambient samples are disposed of in the sanitary sewer. Solvents are collected and either evaporated or taken to the Yolo County Landfill for recycling.

## Attachment 1

### Protocol Summary

**Test Type:** Fathead Minnow, *Pimephales promelas*, Survival Test  
(Static and Renewal)

**ELAP Code:** 113.021 001A (Static)  
113.021 001B (Renewal)

**EPA Protocol:** EPA 821-R-02-012 (5<sup>th</sup> Edition Acute)

24. Test type: Static non-renewal or static-renewal
25. Test duration: 24, 48, or 96 h
26. Temperature<sup>2</sup>: 20 °C ± 1 °C; or 25 °C ± 1 °C  
Test temperatures must not deviate (i.e., maximum minus minimum temperature) by more than 3 °C during the test.
27. Light quality: Ambient laboratory illumination
28. Light intensity: 10-20 µE/m<sup>2</sup>/s (50-100 ft-c)  
(ambient laboratory levels)
29. Photoperiod: 16 h light, 8 h darkness
30. Test chamber size: 250 mL
31. Test solution volume: 200 mL
32. Renewal of test solutions: Minimum, after 48 h
33. Age of test organisms: 1-14 days; less than or equal to 24-h range in age
34. No. organisms per test chamber: Minimum, 10 for effluent and receiving water tests
35. No. replicate chambers per concentration: Minimum, 2 for effluent tests, and 4 for receiving water tests
36. No. organisms per concentration: Minimum, 20 for effluent tests, and 40 for receiving water tests

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<sup>2</sup> Acute and chronic toxicity tests performed simultaneously to obtain acute/chronic ratios must use the same temperature and water hardness.

37. Feeding regime:	Artemia nauplii are made available while holding prior to the test; add 0.2 mL Artemia nauplii concentrate 2 h prior to test solution renewal at 48 h.
38. Test chamber cleaning:	Cleaning not required
39. Test chamber aeration:	None, unless D.O. concentration falls below 4.0 mg/L; rate should not exceed 100 bubbles/min
40. Dilution water:	Moderately hard synthetic water prepared using MILLIPORE MILLI-Q® or equivalent deionized water and reagent grade chemicals or 20% DMW, receiving water, ground water, or synthetic water, modified to reflect receiving water hardness.
41. Test concentrations.	Effluents: Minimum of five effluent concentrations and a control Receiving Waters: 100% receiving water and a control
42. Dilution series:	Effluents: $\geq 0.5$ dilution series Receiving Waters: None, or $\geq 0.5$ dilution series
43. Endpoint:	Effluent: Mortality Receiving Waters: Mortality
44. Sampling and sample holding requirements:	Effluents and Receiving Waters: Grab or composite samples first used within 36 h of completion of the sampling period.
45. Sample volume required:	20 L for effluents 40 L for receiving waters
46. Test acceptability criterion:	90% or greater survival in controls

## ATTACHMENT 2

### Apparatus and Equipment

21. Laboratory *Pimephales promelas* and *Artemia* culture units or reliable source of newly hatched larvae providing sufficient numbers of organisms for toxicity test and feeding.
22. Environmental chamber, incubator, or equivalent facility with temperature control ( $25 \pm 1$  °C).
23. Water purification system producing reagent water equivalent to the Millipore Milli-Q® water.
24. Analytical balance capable of accurately weighing 0.0001 g.
25. Class S reference weights for checking performance of balance.
26. Glass or electronic thermometers for measuring water temperature.
27. Glass tubing/baster with fire-polished edges, 4-mm ID for transferring organisms.
28. Test chambers: 2-4 400 mL plastic test chambers per concentration.
29. Non-toxic borosilicate glass or non-toxic disposable plastic beakers (1.5-2.5 L) are required for making test solutions.
30. Bulb-thermograph or electronic-chart type thermometers for measuring temperature.
31. National Bureau of Standards Certified thermometer.
32. Specific conductivity, dissolved oxygen and pH meters for routine physical and chemical measurements.
33. Volumetric pipets: Glass A, 1-100 mL.
34. Serological pipets: 1-10 mL, graduated.
35. Pipet bulbs and fillers: Propipet® or Repipet®
36. Wash bottles for rinsing small glassware, instrument electrodes and probes.
37. Separatory funnel (400-600 mL) for *Artemia* culture.
38. Aquarium pump (oil free air supply), for aeration of *Artemia* culture.
39. Air lines, plastic or Pasteur pipettes, for gently aerating water containing the fragile larvae and/or supplying air to test solution with low dissolved oxygen levels.
40. Volumetric flasks and graduated cylinders, 10-100 mL for making test solutions
41. Pipettors, adjustable volume repeating dispensers (Eppendorf and Oxford)



## Reagents and Consumable Materials

12. Test substance: final effluent, ambient water, or storm water
13. Control water: laboratory reagent/dilution water
14. Reference toxicant: NaCl
15. Standard pH buffers 7 and 10
16. Specific conductivity standards
17. Membranes and filling solutions for dissolved oxygen probe
18. Reagents for alkalinity and hardness calorimetric titration
19. Brine shrimp (*Artemia*) cysts
20. Ethanol (70%) for use as a preservative for the fish larvae.
21. Fresh solution of tricaine methanesulfonate (MS-222) for tranquilization of the fish larvae.  
(0.25 g MS-222 in 250 mL Type I ultrapure laboratory reagent water)
22. Seawater, filtered through 0.45 µm membrane for *Artemia* culture.
23. Pressure-sensitive labeling tape (colored)
24. Waterproof markers for labeling containers

**ATTACHMENT 3**

**Data Sheets**

**APPENDIX XVII. SOP 6.3C-4. Green Algae, *Selenastrum capricornutum*, Cell Growth Test  
(Revision 2010-01, 06/15/10)**

**SOP Title: Green Algae, *Selenastrum capricornutum*, Cell Growth Test  
Method 1003.0**

**Copy No.:** \_\_\_ of 2

**SOP Number:** 6.3C-4 version 2010-01

**File:** SOP Section 6.3

**EPA Protocol:** EPA 821-R-02-013 (4<sup>th</sup> Edition Chronic)

**ELAP Code:** 113.061 020

**Issue Date:** June 15, 2010

**Review:** As required

**Author:** J.L. Miller

**Authorized by:** *original signed by Jeff Miller*  
Jeffrey L. Miller, Ph.D., DABT, President

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## 1.0 Purpose and Description of Test

This method measures the chronic toxicity of effluents, ambient waters, or storm water to the freshwater green algae, *Selenastrum capricornutum*, during a 4-day static test. The effects measured include the synergistic, antagonistic, and additive effects of all the chemical, physical, and biological components that adversely affect the physiological and biochemical functions of the test organisms. The test organism population is exposed in a static system to a control and a series of concentrations of test material for 96 hours. The response of the population is measured in terms of changes in cell density (cell counts/mL or absorbance at 750 nm). The protocol is summarized in Attachment 1. Apparatus, equipment, reagents and consumable materials needed for this test are listed in Attachment 2. Data sheets are included in Attachment 3.

## 2.0 Test Organisms

*S. capricornutum* is obtained from University of Texas Type Culture Collection (Austin, TX). The inoculum is prepared no more than 2 to 3 hours prior to the beginning of the test, using *S. capricornutum* harvested from a stock culture in log phase growth. An electronic particle counter (Coulter Counter) is used to determine the amount of inoculum needed to provide an initial cell density of approximately 10,000 cells/mL ( $\pm 10\%$ ) in the test flasks.

## 3.0 Preparation, Storage, and Testing of Control Water

Well water is treated by reverse osmosis followed by carbon adsorption to produce reagent water that is equivalent to the Millipore Milli-Q® water. It is then amended with reagent grade chemicals and vigorously aerated overnight to achieve EPA moderately hard specifications (EPAMH). Alternatively, Sierra Spring™ water is amended with reagent grade chemicals as described in the test protocol for EPAMH, and aerated overnight. Depending on the study design, other control waters may be used. In such cases, these waters will be prepared as described in the test protocol, e.g., EPA very hard, EPA soft, EPA very soft, etc. In cases where control waters other than EPAMH is used, the type of water will be noted on water quality data sheets.

Each batch of reagent water is prepared and stored in a sanitized 5-gallon plastic container. Each container is issued a unique lot number at the time of reagent water preparation. Batches of dilution water are stored at 25 °C with gentle aeration until use. Each batch of dilution water is bioassayed prior to use in testing. Two 20-mL aliquots of each lot containing 5 *C. dubia* are bioassayed for 96 hours. If mean survival in the two replicates is >90% and the organisms appear healthy, the lot of dilution water is considered adequate for use in culture and testing.

## 4.0 Preparation of Algal Assay Media

Algal Assay Media (AAM) is prepared from micronutrient stock solutions shown in Table 1. One mL of each solution is added to 900 mL of laboratory dilution water, mixed and diluted to 1.0 L. The media is adjusted to pH  $7.5 \pm 0.1$  using 0.1N NaOH or 0.1 N HCl, as appropriate, and the media is filtered (0.22  $\mu\text{m}$ ). The EPA AAM contains EDTA, which may underestimate toxicity caused by cationic metals. Therefore, at the discretion of the Study Director and depending on the purpose of the study and the type of test sample, the test may be conducted without EDTA. All 4<sup>th</sup> edition NPDES-related algae tests will be conducted with EDTA. The test report will indicate if the test was conducted with or without EDTA.

<b>Stock Solution</b>	<b>Compound</b>	<b>Amount Dissolved in 500 mL MILLI-Q® Water</b>
Macronutrients	MgCl <sub>2</sub> •6H <sub>2</sub> O	6.08 g
	CaCl <sub>2</sub> •2H <sub>2</sub> O	2.20 g
	NaNO <sub>3</sub>	12.75 g
	MgSO <sub>4</sub> •7H <sub>2</sub> O	7.35 g
	K <sub>2</sub> HPO <sub>4</sub>	0.522 g
	NaHCO <sub>3</sub>	7.50 g
Micronutrients	H <sub>3</sub> BO <sub>3</sub>	92.8 mg
	MnCl <sub>2</sub> •4H <sub>2</sub> O	208.0 mg
	ZnCl <sub>2</sub>	1.64 mg <sup>1</sup>
	FeCl <sub>3</sub> •6H <sub>2</sub> O	79.9 mg
	CoCl <sub>2</sub> •6H <sub>2</sub> O	0.714 mg <sup>2</sup>
	Na <sub>2</sub> MoO <sub>4</sub> •2H <sub>2</sub> O	3.63 mg <sup>3</sup>
	CuCl <sub>2</sub> •2H <sub>2</sub> O	0.006 mg <sup>4</sup>
	Na <sub>2</sub> EDTA•2H <sub>2</sub> O	150.0 mg
	Na <sub>2</sub> SeO <sub>4</sub>	1.196 mg <sup>5</sup>

- 1 ZnCl<sub>2</sub> – Weigh out 164 mg and dilute to 100 mL. Add 1 mL of this solution to Stock 2, micronutrients.
- 2 CoCl<sub>2</sub>•6H<sub>2</sub>O – Weigh out 71.4 mg and dilute to 100 mL. Add 1 mL of this solution to Stock 2, micronutrients.
- 3 Na<sub>2</sub>MoO<sub>4</sub>•2H<sub>2</sub>O – Weigh out 36.6 mg and dilute to 10 mL. Add 1 mL of this solution to Stock 2, micronutrients.
- 4 CuCl<sub>2</sub>•2H<sub>2</sub>O – Weigh out 60.0 mg and dilute to 1000 mL. Take 1 mL of this solution and dilute to 10 mL. Take 1 mL of the second dilution and add to Stock 2, micronutrients.
- 5 Na<sub>2</sub>SeO<sub>4</sub> – Weigh out 119.6 mg and dilute to 100 mL. Add 1 mL of this solution to Stock 2, micronutrients

## 5.0 Test Samples

Each test sample is logged in upon receipt. Information including client or source, date, time of log-in are recorded along with initial water quality parameters, including temperature, dissolved oxygen, conductivity, hardness, alkalinity, residual chlorine, and pH. Samples are stored in the dark at <4 °C until used. Prior to testing, samples are filtered (0.45µm or 0.22 µm) to remove indigenous algae, are brought to test temperature, and D.O. measured.

## **6.0 Test Facilities**

Tests are conducted in areas capable of maintaining test protocol temperatures ( $25 \pm 1^\circ\text{C}$ ) and illumination levels. Such areas may include temperature-controlled rooms, or environmental chambers. Temperatures are recorded continuously in a surrogate test container during the test period. The photoperiod in test areas is continuous.

## **7.0 Test Solution Preparation**

All test samples are filtered through a  $0.45 \mu\text{m}$  and/or  $0.22 \mu\text{m}$  filter to remove indigenous algae prior to testing. Test materials are either tested undiluted (100%) or in a dilution series containing five or more concentrations (e.g., 6.25, 12.5, 25, 50 and 100% sample). If the test sample is expected to exhibit high toxicity, or at the discretion of the Study Director, other dilution series may be used. Immediately prior to test initiation, test solutions are aliquotted into the 10 replicate test containers. Care is taken to assure that the test concentrations remain at test temperature.

## **8.0 Test Initiation**

Flasks (250 mL) containing 100 mL of test solution, are inoculated with 10,000 cells ( $\pm 10\%$ ) using a precision pipette. The flasks are randomized and placed on a shaker table (100 revolutions/min) in an environmental chamber at  $25 \pm 1^\circ\text{C}$  with continuous "cool white" fluorescent lighting at  $400 \pm 40$  ft-c. Flasks are randomized twice daily. Temperature, D.O. and pH are measured at the end of each 24-hour exposure period in at least one flask in each test concentration and control.

## **9.0 Water Quality Measurements**

At a minimum, temperature, pH, dissolved oxygen (D.O.), and conductivity are measured in the control and all sample concentrations. Conductivity, alkalinity and hardness are measured in the control and in the high, medium and low sample concentrations. Residual chlorine is measured in the undiluted test sample only. If residual chlorine concentrations of concern are detected, the client is contacted for direction prior to test initiation. If the sample is dechlorinated, it will be noted on the dose preparation data sheet. At the discretion of the Study Director, total ammonia may also be measured. D.O. is checked before test initiation. If the D.O. level falls below 40% saturation, samples are gently aerated ( $<100$  bubbles/min using a 1-mL pipette and oil-free air). pH and temperature are measured at the end of each 24-hour exposure period in at least one surrogate test chamber of each test concentration. Temperature is also recorded continuously in a surrogate test container.

## **10.0 Reference Toxicant Testing**

Zinc chloride is used as the reference toxicant for NPDES compliance tests. Data review of a given effluent or receiving water test will include review of the associated reference toxicant test and current control chart. A reference toxicant test is conducted on each batch of purchased test organism or monthly on organisms cultured in-house. Other reference toxicants may be used for ambient samples at the discretion of the Study Director.

Verification for a valid test will include: frequency required by the permitting authority or recommended method, test acceptability criteria, test conditions, concentration-response

relationship, and test sensitivity. The results of the reference toxicant test are plotted on a control chart (ToxCalc™) and compared to the current control chart limits.

Reference toxicant tests that fall outside of recommended control chart limits are evaluated to determine the validity of associated effluent and ambient water tests. The degree to which the reference toxicant test results fell outside of control chart limits, the width of the limits, the direction of the deviation (increasing or decreasing sensitivity), the test conditions of both the effluent test and reference toxicant test, and the objective of the test will be considered.

### **11.0 Test Termination**

Algal cell growth is determined either by algal cell enumeration using an automated particle counter or absorbance at 750 nm using a spectrophotometer.

- a. Algal cells are enumerated using an automated particle counter (Coulter™ Counter). A 0.5-mL aliquot of each sample is diluted with ISOTON™, thoroughly mixed and counted using an aperture tube with a 100 µm aperture. Each replicate is counted three times and the cell count recorded on data sheets, OR
- b. Absorbance is measured using a HACH spectrophotometer (Model DR 2800) at 750 nm wavelength. A 10 mL aliquot of each sample is put into sample cell and measured at 750 nm. Each replicate is measured three times and the absorbance recorded on data sheets.

### **12.0 Recording Data**

Computer-generated data sheets are prepared prior to test initiation. These include a dose preparation information sheet, water quality data sheets, and the cumulative mortality/behavioral observation/neonate reproduction record sheets. Copies of data sheets are found in Attachment 3.

Data is recorded neatly in black non-erasable ink. Entry errors are crossed-out with a single line that does not obscure the original entry. Pages with errors are corrected near where the error occurs, initialed, and dated by the person making the correction. Pages with multiple errors, or with problems such as spills or illegible ink marking, are not discarded but remain with the rest of the data sheets. Annotations are sequentially numbered and made on a real-time basis to prevent loss of information. Prior to data analysis, all data sheets are checked for entry errors and missing information. Data are stored in a secure location after office copies are made.

### **13.0 Data Analysis**

Data analysis is performed using ToxCalc™ 5.23 (or greater) (Tidepool Software, McKinleyville, CA), a statistical software package compatible with the EPA electronic toxicity database requirements. ICp values (EC<sub>25</sub>, EC<sub>50</sub>, etc.) are calculated using EPA recommended point estimate techniques. LOEC and NOEC values, for survival, are obtained using a hypothesis test approach guided by the EPA statistical analysis flowchart. Formal tests for normality and homogeneity of variance are performed by ToxCalc™ prior to selecting parametric or nonparametric methods of analyses.



## 14.0 Acceptability of Test Results

Minimum Cell Growth: Tests must have a mean algal cell density of  $\geq 1 \times 10^6$  cells/mL.

Test Variability: The coefficient of variation (CV, calculated as the standard deviation x 100/mean) for algal cell density among the control replicates must not exceed 20%. The within-test variability of individual tests will be reviewed according to EPA guidance on upper and lower percent minimum significant difference (PMSD) bounds (EPA 833-R-00-003).

Note: If the test is conducted under non-NPDES applications and no EDTA is added to the nutrient stock solution, the test acceptability criteria is  $\geq 2 \times 10^5$  cells/mL in the controls and variability (CV%) among the control replicates of  $\leq 20\%$ .

Concentration-Response Relationships: All results for each multi-concentration test is reviewed and reported according to EPA guidance on the evaluation of concentration-response relationships (EPA-821-B-00-004). This guidance provides review steps for 10 different concentration-response patterns that may be encountered in test data. Based on the review, the guidance provides one of three determinations: that calculated effect concentrations are reliable and should be reported, that calculated effect concentrations are anomalous and should be explained, or that the test was inconclusive and the test should be repeated with a newly collected sample. Tests that exhibit unexpected concentrations-response relationships also may indicate a need for further investigation and possible retesting.

## 15.0 Health and Safety

AQUA-Science maintains a safety program that includes on-going safety instruction in proper handling of hazardous reagents, chemicals, and materials. The laboratory manager conducts regular safety inspections and discusses safety issues with personnel. The laboratory is equipped with proper safety equipment, including disposable gloves, safety glasses, laboratory coats, respirators and portable eye wash stations. All materials are clearly labeled. Solvents and volatile materials are stored in a flammable liquid cabinet and used in ventilated areas.

Material Safety Data Sheets are maintained for chemicals and reagents purchased from suppliers. Acids, bases and solvents are stored in safety storage cabinets for hazardous and/or flammable materials.

Test samples are properly disposed of according to local, state, and federal rules. Effluent and ambient samples are disposed of in the sanitary sewer. Solvents are collected and either evaporated or taken to the Yolo County Landfill for recycling.

## Attachment 1

### Protocol Summary

**Test Type:** Green Alga, *Selenastrum capricornutum*, Cell Growth Test Method 1003.0

**ELAP Code:** 113.061 020

**EPA Protocol:** EPA 821-R-02-013

47. Test type: Static non-renewal
48. Temperature:  $25 \pm 1$  °C  
Test temperatures must not deviate (i.e., maximum minus minimum temperature) by more than 3 °C during the test
49. Light quality: “Cool white” fluorescent lighting
50. Light intensity:  $86 \pm 8.6$   $\mu\text{E}/\text{m}^2/\text{s}$  ( $400 \pm 40$  ft-c or 4306 lux)
51. Photoperiod: Continuous illumination
52. Test chamber size: 125 mL or 250 mL
53. Test solution volume: 50 mL or 100 mL
54. Renewal of test solutions: None
55. Age of test organisms: 4 to 7 days
56. Initial cell density in test chambers: 10,000 cells/mL
57. No. replicate chambers per concentration: 4
58. Shaking rate: 100 cpm continuous
59. Aeration: None

60. Dilution water:	Algal stock culture medium, enriched uncontaminated source of receiving or other natural water, synthetic water prepared using MILLIPORE MILLI-Q® or equivalent deionized water and reagent grade chemicals or DMW
61. Test concentrations.	Effluents: Minimum of five concentrations and a control Receiving Waters: 100% receiving water (or minimum of 5) and a control
62. Test dilution factor:	Effluents: $\geq 0.5$ Receiving Waters: None, or $\geq 0.5$
63. Test duration:	96 hours
64. Endpoint:	Growth (cell counts, chlorophyll fluorescence, absorbance, or biomass)
65. Test acceptability criterion <sup>3</sup> :	Mean cell density of at least $1 \times 10^6$ cells/mL in the controls; and variability (CV%) among control replicates less than or equal to 20%
66. Sampling requirements:	For on-site tests, one sample collected at test initiation, and used within 24 h of the time it is removed from the sampling device. For off-site tests, holding time must not exceed 36h before first use.
67. Sample volume required:	1 L or 2L depending on test volume

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<sup>3</sup> If the test is conducted under non-NPDES applications (i.e., data are not submitted under NPDES permits) and used without EDTA in the nutrient stock solution, the test acceptability criteria are a mean cell density of at least  $2 \times 10^5$  cells/mL in the controls, and variability (CV%) among control replicates less than or equal to 20%.

## ATTACHMENT 2

### Apparatus and Equipment

42. Laboratory *Selenastrum capricornutum* culture unit providing sufficient numbers of log-phase-growth organisms for toxicity test. (See A-S SOP Section 1.2 for culturing methods)
43. Environmental chamber, incubator, or equivalent facility with “cool white” fluorescent illumination ( $86 \pm 8.6 \mu\text{E}/\text{m}^2/\text{s}$ , or  $400 \pm 40 \text{ ft-c}$ ) and temperature control ( $25 \pm 1 \text{ }^\circ\text{C}$ ).
44. Mechanical shaker capable of providing orbital motion at the rate of 100 cycles per minute (cpm).
45. Light meter with a range of 0-200  $\mu\text{E}/\text{m}^2/\text{s}$ .
46. Water purification system producing reagent water equivalent to the Millipore Milli-Q® water.
47. Analytical balance capable of accurately weighing 0.0001 g.
48. Class S reference weights for checking performance of balance.
49. Glass or electronic thermometers for measuring water temperature.
50. Bulb-thermograph or electronic-chart type thermometers for measuring temperature.
51. National Bureau of Standards Certified thermometer.
52. Specific conductivity, dissolved oxygen and pH meters for routine physical and chemical measurements.
53. Electronic particle counter (Coulter Counter, Model ZBI or equivalent) with mean cell (particle) volume determination, and/or spectrophotometer (Hach Model DR 2800 or equivalent).
54. Cuvettes for the Coulter Counter
55. Inverted or conventional microscope with 10X, 45X, and 100X objective lenses, 10X ocular lenses, mechanical stage, substage condenser, and light source.
56. Counting chamber: hemacytometer.
57. Filtering apparatus for membrane and glass fiber filters. Positive pressure peristaltic pump for effluents and vacuum pump for dilution water.
58. Volumetric flasks and graduated cylinders: Class A, 10-1000 mL borosilicate glass, for culture work and preparation of test solutions.
59. Volumetric pipets: Glass A, 1-100 mL.
60. Serological pipets: 1-10 mL, graduated.
61. Pipet bulbs and fillers: Propipet® or Repipet®

62. Wash bottles for rinsing small glassware, instrument electrodes and probes.
63. Culture chambers: 1-4 borosilicate, Erlenmeyer flasks.
64. Test chambers: 250 mL borosilicate, Erlenmeyer flasks.

#### **Reagents and Consumable Materials**

25. Test substance: final effluent, ambient water, or storm water
26. Control water: laboratory reagent/dilution water
27. Reference toxicant:  $\text{ZnCl}_2$
28. Standard pH buffers 7 and 10
29. Specific conductivity standards
30. Membranes and filling solutions for dissolved oxygen probe
31. Reagents for alkalinity and hardness calorimetric titration
32. Acetone: pesticide-grade or equivalent
33. Dilute (10%) hydrochloric acid
34. 1% sodium chloride electrolyte solution (Isoton®)
35. Nutrient stock for *Selenastrum capricornutum*, #1-5
36. Gilman™ Supor 0.22  $\mu\text{m}$  filter membrane

**ATTACHMENT 3**

**Data Sheets**

**APPENDIX XVIII. SOP 10-Day Static Freshwater Sediment Toxicity Tests With The Amphipod *Hyalella azteca* (Revision Unknown, 02/07/03)**

STANDARD OPERATING PROCEDURE

10-DAY STATIC FRESHWATER SEDIMENT TOXICITY TESTS WITH THE AMPHIPOD  
*HYALELLA AZTECA*

Revised: 7 February 2003

Page 1 of 4

I. PURPOSE

This method is designed to measure the toxicity of freshwater sediments to the amphipod *Hyalella azteca* using survival and growth as endpoints.

II. EQUIPMENT

- . Proven source of clean freshwater water (e.g., Culligan filtered water)
- . Environmental chamber maintained at  $20 \pm 1$  degrees Celsius ( $^{\circ}\text{C}$ ) or  $23 \pm 1^{\circ}\text{C}$
- . Cold room maintained at  $4^{\circ}\text{C}$  to hold sediment samples prior to test initiation
- . Thermometer, pH meter, dissolved oxygen (DO) meter, conductivity meter, dissecting light microscope, and analytical balance
- . 1-liter (L) glass jars with lids (or equivalent) to serve as exposure chambers (5 jars per test site, reference, and control); with holes in lids to permit aeration
- . 0.5-millimeter (mm) and 1.0-mm Nitex mesh screens, transfer pipets, and glass holding bowls
- . Aeration source, 1.0-milliliter (ml) pipets, and airline tubing
- . Test, control, and reference sediments
- . 30-ml disposable polystyrene cups for holding animals; freshwater squirt bottle
- . Safety equipment - lab coats, eye protection, gloves, and respirator as required

III. TEST PROCEDURE

A. Pre-test Set-up

1. *Hyalella*, 7 to 14 days in age, are purchased from a reliable, experienced dealer and shipped to the lab via next day delivery service. All animals in a single batch shall be within a two-day age range. Organisms are held in plastic bowls and allowed to acclimate to laboratory conditions for at least six hours prior to test initiation.
2. During the holding period, the bowls are aerated and animals are acclimated to lab conditions by slowly replacing culture water with laboratory water. Water is replaced by adding a slow drip using lab water. During acclimation temperature changes should not exceed  $2^{\circ}\text{C}$  per 24-hr period.

Approved By:

\_\_\_\_\_  
Laboratory Manager (Date)

\_\_\_\_\_  
QA Supervisor (Date)



**STANDARD OPERATING PROCEDURE**

**10-DAY STATIC FRESHWATER SEDIMENT TOXICITY TESTS WITH THE AMPHIPOD  
*HYALELLA AZTECA***

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4. Samples are logged in upon receipt. See procedural SOP for details on sediment sample check-in procedures.
5. Interstitial porewater is collected from each sample for the measurement of ammonia, pH, and conductivity. Interstitial water is collected by centrifuging a subsample of whole sediment at 3000 rpm for 15 min. Interstitial water may also be collected from overlying water in sediment collection containers. During shipment, sediments quickly settle, often leaving a layer of interstitial water on the sediment surface.
6. Sediment samples are sieved through a 0.5-mm screen to filter out any resident organisms and/or debris. The sieved sediment is placed in a clean, labeled, plastic bag, and stored at 4°C until tests are initiated.
6. A randomization key is made for all concurrently tested samples using Microsoft Excel

**24 Hrs Prior to Test Initiation**

7. Label test chambers according to the randomization key and add the appropriate site sediment to the labeled jars to a depth of 2-centimeters (cm).
8. Prepare an additional test chamber for each test site. This surrogate will be used for water quality measurements during the test period.
9. Fill jars with 900 ml laboratory test water.
10. Place jars in the 20 or 23°C environmental chamber to settle and equilibrate overnight.
11. Aerate test chambers using 1-ml glass pipettes placed through a hole in lid and at mid-depth in the water column with special care taken to prevent disturbing the sediment. Aeration should be performed at a rate of 2-3 bubbles per second.
12. Adjust light cycle in environmental chamber to a 16:8 hour light:dark cycle.

**B. Test Initiation - Day 0**

1. Measure and record water quality parameters (DO, conductivity, temperature, and pH) in each surrogate test chamber. Remove a subsample of overlying water for ammonia analysis from each site and preserve with 1 ml of 10% sulfuric acid.
2. Count 10 animals into a 30-ml polystyrene plastic cup containing clean laboratory water at the appropriate test temperature. All animals should be of similar size. Place 5 randomly chosen cups aside to obtain a mean time zero weight.

**STANDARD OPERATING PROCEDURE**

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*HYALELLA AZTECA*

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3. A second count is made by a different employee to verify that there are 10 animals in each cup and in healthy condition.
4. Randomly distribute 20 test animals (two cups) into each test chamber by gently rinsing the contents of each cup into a test chamber with a squirt bottle containing Culligan filtered water.
5. All test chambers are inspected within two hours of initiation to ensure that no amphipods are trapped in the surface tension of the water. Any floating animal observed is replaced with new animal.

**C. Daily Monitoring and Feeding Regime - Days 1 to 10**

1. Measure and record pH, DO, conductivity, and temperature daily in surrogate chambers.
2. Observe all chambers and correct obvious problems (e.g., aeration rate) as required.
3. Adjust aeration as needed to maintain the DO above 4.0 mg/L.
4. Feed test chambers every 48-hours with 1 ml of Tetramin® solution per test chamber. Food consists of 2g TetraMin® blended into 100 ml Culligan water. If there is an accumulation of excess food on the sediment surface, suspend feeding to avoid fungal growth and degraded water quality in the test chambers.

**D. Test Termination - Day 10**

1. Measure and record water quality (DO), pH, conductivity, and temperature) in surrogate test chambers. Remove a subsample for ammonia analysis from each site and preserve with 1 ml of 10% sulfuric acid.
2. Gently suspend sediment in the test chambers and pour onto 0.5-mm cylindrical screen. Rinse away remaining sediment using laboratory water within 2°C of the test temperature.
3. Count and record the number of surviving amphipods making note of any dead amphipods found.
4. Collect and rinse surviving amphipods with deionized water. Using forceps, gently place on an appropriately labeled and tared aluminum pan.
5. Dry in an oven at 60°C for 24 hours.
6. Remove animals from oven. Weigh to the nearest 0.0001g and record on the data sheet.

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**E. Reference Toxicant Testing**

1. A 96-hour reference toxicant is run with the same batch of animals with sediment tests as a quality assurance procedure to assess the health of the test organisms and soundness and consistency of procedures. Copper chloride is used as a reference toxicant. The testing concentrations for the reference toxicant are 0 (Control), 100, 200, 400, 800, and 1600 µg/L.
2. The LC<sub>50</sub> for survival is calculated and should be within two standard deviations of the historical control chart mean for AMEC.

**IV. TEST ACCEPTABILITY CRITERIA**

Mean control sediment survival at test termination must be 80 percent or greater. There is no acceptability criterion for the weight endpoint, as it is not specified in the protocol.

**V. HEALTH AND SAFETY**

Health and safety precautions and applicable regulations should be considered at all times. Gloves must always be worn when handling test sediments.

**VI. PERSONNEL**

Only qualified technicians who have been properly trained and can demonstrate competency with these techniques are permitted to conduct this test.

**VII. QUALITY ASSURANCE REQUIREMENTS**

Quality assurance practices encompass all aspects of testing including the collection, handling, and preparation of test organisms, samples, and dilution waters. Proper record keeping is required and concentrated efforts are made for complete documentation on a real-time basis.

**VIII. REFERENCES**

"Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S.- Testing Manual." Environmental Protection Agency Office of Water/Department of the Army, US Army Corps of Engineers. EPA-823-B-98-004, February 1998.

"Standard Test Methods for Measuring the Toxicity of Sediment-Associated Contaminants with Freshwater Invertebrates." ASTM E 1706-00, 2002.

"Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates (Second Edition)." EPA 600/R-99/064, 2000.

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**APPENDIX XIX. SOP ME075v07 Analytical Methodology for the Analysis of Glyphosate and/or AMPA (Aminomethyl phosphonic acid) in Drinking Water by EPA 547 (Revision 07, 10/17/03)**

	Name	Title	Date
REVISED BY:	_____	<u>CHEMIST</u>	____/____/____
APPROVED BY:	_____	<u>LAB SUPERVISOR</u>	____/____/____
APPROVED BY:	_____	<u>LAB MANAGER</u>	____/____/____
REVIEWED BY:	_____	<u>QA UNIT</u>	____/____/____

**1.0 TITLE**

Analytical Methodology for the Analysis of Glyphosate and/or AMPA (Aminomethyl phosphonic acid) in Drinking Water by EPA 547.

**2.0 SCOPE**

To provide detailed documentation for analytical methodology to analyze for glyphosate and/or AMPA in drinking water by EPA 547.

**3.0 DEFINITIONS**

Not Applicable

**4.0 REFERENCE(S)**

Determination of Glyphosate in Drinking Water by Direct-Aqueous-Injection HPLC, Post-Column Derivatization, and Fluorescence Detection. EPA Method 547. July 1990. T.W. Winfield, W.J. Bashe, T.V. Baker. Environmental Monitoring System Laboratory Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

**5.0 SUMMARY**

An aliquot of drinking water (~1 mL) is filtered and analyzed on an HPLC post-column system using a fluorescence detector.

**6.0 REPORTING LIMITS**

The reporting limit is 10.0 µg/L (PPB)

**7.0 STORAGE OF SAMPLES AND HOLDING TIMES**

The holding time for glyphosate in water is 14 days at 4°C or 18 months if frozen. In general, glyphosate samples are frozen upon arrival at NCL and they are thawed on the day of the analysis.

**8.0 STANDARD PREPARATION FOR GLYPHOSATE BY EPA 547**

**8.1 Equipment**

- analytical balance capable of weighing 0.0001 g

**8.2 Glassware and Supplies**

- 25 mL polyethylene vials
- 8 mL polyethylene vials
- various syringes
- volumetric flasks and volumetric pipettes

**8.3 Reagents**

- HPLC water
- 0.005 M K<sup>+</sup>, pH 2.0 phosphate buffer or 20mm H<sub>3</sub>PO<sub>4</sub>.

**8.4 Preparation of Glyphosate and/or AMPA Standard**

Order neat glyphosate and/or AMPA from ChemService (or equivalent).

To prepare a 1000 PPM standard weigh ~0.010 g of neat standard into a 25 mL polyethylene vial and record the weight to 0.0001 g. Add the appropriate amount of HPLC water so that the concentration of the standard is 1000 PPM. To calculate the amount of water use the following equation:

$$\text{amount of water (mL)} = \frac{\text{weight (g)} \times \text{concentration of neat } (\mu\text{g/g})}{\text{final concentration (PPM} = \mu\text{g/mL)}}$$

A 10 PPM standard is prepared by adding 100  $\mu\text{L}$  of the 1000 PPM standard to a 10 mL volumetric flask that is brought to mark with HPLC water, or 9.9 mL of HPLC water in a 25 mL polyethylene vial. Store the 10 PPM standard in a polyethylene vial.

8.4.1 The stock standard expiration date is one year from the preparation date or the expiration date of the neat standard, whichever comes first.

#### 8.5 Preparation of Internal Standard

NA

#### 8.6 Preparation of Surrogate Standard

NA

#### 8.7 Preparation of Working Standards

Five levels of working standards are prepared in 5 mL volumetric flasks as follows:

Amount of 10 PPM Standard (Glyphosate and/or AMPA)	Amount of 0.005 M K <sup>+</sup> , pH 2.0 Phosphate Buffer	Final Working Standard Concentration
2.5 $\mu\text{L}$	to 5 mL mark	5.0 PPB
5 $\mu\text{L}$	to 5 mL mark	10 PPB
12.5 $\mu\text{L}$	to 5 mL mark	25 PPB
25 $\mu\text{L}$	to 5 mL mark	50 PPB
50 $\mu\text{L}$	to 5 mL mark	100 PPB

## 9.0 **SAMPLE PREPARATION FOR GLYPHOSATE BY EPA 547**

### 9.1 Equipment

- ultrasonic waterbath
- vortex mixer

### 9.2 Glassware and Supplies

- 5 mL volumetric flasks with polyethylene stoppers
- Pasteur pipettes with bulbs
- 3 cc syringes
- 0.2 μ syringe filters
- 1.5 mL snap cap vials with snap lined screw cap lids
- 8 mL scintillation vials

### 9.3 Reagents

- HPLC grade water
- 1M H<sub>3</sub>PO<sub>4</sub>

### 9.4 Preparation Procedure (For Flowchart - See Exhibit A)

9.4.1 Retrieve sample from storage (see SOP LA 003)

9.4.2 Place the frozen polyethylene sample storage vials in an ultrasonic waterbath at 50°C with the sonicator on until the samples are thawed.

9.4.3 Prepare all samples by adding 50 μL of 1M H<sub>3</sub>PO<sub>4</sub> to a 5 mL volumetric flask

and bringing the final volume to 5 mL with sample.

9.4.4 Prepare the laboratory control samples and matrix spikes by adding 50 μL of 1M H<sub>3</sub>PO<sub>4</sub> to ~2 mL HPLC water/sample in a 5 mL volumetric flask. Spike with 25 μL of 10 PPM glyphosate standard and/or 25 μL of 10 PPM AMPA standard and bring the final volume to 5 mL with HPLC water/sample. The matrix spike and matrix spike duplicate must be spiked with a lot other than the lot used for calibration standards. The QC samples will have a concentration of 50 PPB with respect to a 5 mL sample.

$$25 \mu\text{L} \times \frac{10 \text{ ng}}{\mu\text{L}} = \frac{250 \text{ ng}}{5 \text{ mL}} = 50 \text{ ng/mL (PPB)}$$

After bringing up all volumetric flasks to 5 mL marks with respective contents, cap and invert 10 times or vortex before filtering.

9.4.5 Filter each blank, lab control sample, sample spike, and sample through 0.2 μ syringe filters into 8 mL plastic scintillation vials.

9.4.6 Put 1 mL of each standard, QC, and sample into a 1.5 mL snap cap vial for analysis.

### 9.5 Special Precautions - Sample Preparation and Extraction

NA

## 10.0 **ANALYSIS - GLYPHOSATE IN DRINKING WATER BY EPA 547**

### 10.1 Equipment

- HPLC with post-column derivatization and fluorescence detector
- TotalChrom Data System

## 10.2 Glassware and Supplies

- Assorted syringes
- 1.5 mL storage vials with Teflon® lined lids

## 10.3 Reagents

- All reagents need to be degassed (See SOP LA 018)
- mobile phase (Pickering # K200): 0.005 M K<sup>+</sup>, pH 2.0 phosphate buffer or for confirmation: 20 mM H<sub>3</sub>PO<sub>4</sub> – 1.35 mL conc. H<sub>3</sub>PO<sub>4</sub> to 1 L HPLC H<sub>2</sub>O.
- oxidizing reagent: add 200 µL of 5% sodium hypochlorite to 1000 mL of degassed hypochlorite diluent (Pickering # GA116). Swirl gently to mix. – If using for AMPA analysis, use only 100 µL 5% sodium hypochlorite to 1L hypochlorite diluent.
- OPA reagent: weigh 2.0 g of thiofluor (Pickering # 3700-2000) and add to 1 L OPA diluent (Pickering # GA104). Weigh 0.25 g OPA (Pickering # 0120) into an 8 mL plastic scintillation vial. Dissolve in 3 mL methanol (Fisher # A452-4) and add to OPA with thiofluor. Shake to mix and degas prior to use.

## 10.4 Procedure for Calibration

A five-point curve will be run and the instrument will be calibrated using a best-fit line or six-point for a quadratic. The type of curve will be at the analysts' discretion. The correlation coefficient for the curve should be  $\geq 0.995$ . A mid-level continuing calibration verification (CCV) will be analyzed every 8 hours and at the end of the analysis.

## 10.5 Procedure for Analysis

NOTE: The parameters listed are suggested as guidelines and may be altered to reflect changes in the column, injector, and detector conditions as long as proper sensitivity is maintained.

### 10.5.1 HPLC Conditions:

Method Name: 547W  
Raw Data File: 547W

(Place sequential alphabetical letters in the blank space to distinguish the various runs.)

Channel: A: fluorescence detector plugged into ChannelA  
Run Time: 12 min, 30 min (confirmation)  
Flow Rate: 0.8 mL/min  
Column Temp: 55°C  
Gradient: isocratic  
Column Type: Hamilton PRP-X400, Adsorbosphere SAX for Glyphosate only confirmation or Hamilton PRP-X400, Adsorbosphere SAX in series for AMPA confirmation  
Reactor Temp: 36°C  
Injection Volume: 250 µL  
Mobile Phase: 0.005 M K<sup>+</sup>, pH 2.0 phosphate buffer (Pickering #K200), or 20 mM H<sub>3</sub>PO<sub>4</sub> (confirmation)

For PE LC240 Detector:

- Excitation: 350 nm factor: 64
- Emission: 440 nm response: 3



- 10.5.2 PC Pump Conditions
  - Pump # 1 flow rate: 0.3 mL/min
  - Pump # 2 flow rate: 0.3 mL/min

#### 10.6 Confirmation of Positive Samples

Standards, blanks, quality control, and positive samples are rerun on the column not used in the initial run, and with appropriate mobile phase to go with the column. All other conditions the same – see analysis section for further detail.

#### 10.7 Special Precautions - Analysis

Degassing all solvents is extremely important before every analysis. It is important that the post column pump is flushed with HPLC water for a half-hour after the analysis. While the post column system is flushing with water, run ~5 injections of 0.1N potassium EDTA. Store the column in the run buffer. If there is a loss of either peak shape or retention time, the column can be regenerated by running methanol through it for at least fifteen minutes. If there is no peak detected when shooting a working standard remake the reagents.

#### 11.0 **CALCULATIONS**

None

#### 12.0 **ACCEPTANCE RANGES**

See the most current limits in Omega.

#### 13.0 **REPORTING AND DOCUMENTATION**

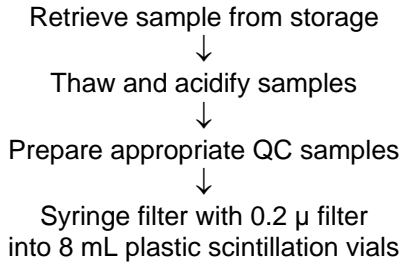
Extraction data will be documented as per SOP LA-003. Analytical data will be reported using Omega, which is the Laboratory Information Management System (LIMS).

#### 14.0 **WASTE DISPOSAL**

Once the analysis is complete, all samples are deposited in the general pesticide satellite accumulation storage container. All expired neat, stock, and working standards are also deposited in the general pesticide satellite accumulation storage container.

## EXHIBIT A

### Flowchart for EPA 547 Sample Preparation



#### Matrix Spikes/Laboratory Control Samples:

Add 25 μL of 10 PPM glyphosate and/or 25 μL of 10 PPM AMPA standard to sample or HPLC water respectively. The matrix spikes/laboratory control samples will have a final concentration of 50 PPB with respect to a 5.0 mL water sample. The matrix spike and matrix spike duplicate must be spiked with a lot other than the lot used for calibration standards.

$$25 \mu\text{L} \times \frac{10 \text{ ng}}{\mu\text{L}} = \frac{250 \text{ ng}}{5 \text{ mL}} = 50 \text{ ng/mL (PPB)}$$

**APPENDIX XX. SOP HPL549. EPA Method 549.2 Diquat and Paraquat Aqueous Sample Solid Phase Extraction and Analysis by LC-UV Diode Array (Revision 5, 04/20/10).**



## Standard Operating Procedure

### EPA METHOD 549.2<sup>1</sup> Diquat and Paraquat Aqueous Sample Solid Phase Extraction and Analysis by LC-UV Diode Array

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#### **STATEMENT OF PURPOSE**

The purpose of this SOP is to describe the procedure for extracting and analyzing aqueous samples for Diquat and Paraquat using solid phase extraction (SPE) media and subsequent instrumental analysis by LC-UV Diode Array.

#### **INSTRUCTIONS**

##### **1.0 Scope and Application**

This SOP applies to all personnel involved in the solid phase extraction and LC-UV analysis for Diquat and Paraquat in aqueous samples.

##### **2.0 Method Summary**

- 2.1 A measured volume of sample (usually 250mL) is extracted by passing it through an SPE (C8) cartridge, which is held in an extraction device using vacuum filtration.
- 2.2 The target analytes are eluted from the SPE cartridge using 5mL solvent.
- 2.3 The sample is then analyzed by LC-UV Diode Array detection at the following wavelengths: Diquat 308nm and Paraquat 257nm.

##### **3.0 Sample Preservation, Containers, Handling and Storage**

- 3.1 Non-preserved samples are collected in amber 1liter amber PVC high-density plastic containers and stored @ 4°C ± 2°C.
- 3.2 Samples expected to contain chlorine must be preserved with Sodium Thiosulfate.
- 3.3 Samples expected to be biologically active must be preserved with Sulfuric Acid (pH<2).
- 3.4 Samples must be extracted within 7 days of collection and analyzed within 21 days of extraction.

##### **4.0 Interference's and Potential Problems**

- 4.1 Paraquat and Diquat cations adsorb to glass surfaces; therefore it is recommended to use plastic supplies rather than glassware for all steps of this procedure.
- 4.2 If glassware is used, then silanization is required for containers coming into contact with the samples.

##### **5.0 Equipment and Apparatus**

- 5.1 SPE Vacuum extraction assembly
- 5.2 SPE (C8) cartridges
- 5.3 Glass Volumetric flasks, 5mL
- 5.4 Plastic 250mL bottles
- 5.5 Plastic 20mL scintillation vials
- 5.6 Plastic injection vials with septum cap (2mL)
- 5.7 Syringe, 1000µL
- 5.8 pH strips



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- 5.9 Nylon Membrane Filter 0.45µm
- 5.10 Phenomenex Kinetix C18, 2.6u x 4.6mm x 150mm
- 5.11 HPLC-Isocratic pumping system
- 5.12 UV-Diode Array Detector

#### 6.0 Reagents

- 6.1 HPLC-grade Methanol
- 6.2 Phosphoric Acid (85% w/v)
- 6.3 Diethylamine
- 6.4 Concentrated Sulfuric Acid
- 6.5 Concentrated Hydrochloric Acid 12N
- 6.6 Sodium Thiosulfate
- 6.7 Cetyl-Trimethyl Ammonium Bromide
- 6.8 Sodium 1-Hexanesulfonate
- 6.9 Sodium 1-Heptanesulfonate
- 6.10 Ammonium Hydroxide
- 6.11 Sylon CT
- 6.12 Mobile Phase
  - 6.12.1 Add 13.5mL phosphoric acid, 10.2mL diethylamine, 3.0g sodium 1-hexanesulfonate to deionized water in a 1000mL volumetric flask.
- 6.13 Conditioning Solution A
  - 6.13.1 Add 0.50g cetyl-trimethyl ammonium bromide and 5mL ammonium hydroxide to deionized water in a 1000mL volumetric flask.
- 6.14 Conditioning Solution B
  - 6.14.1 Add 10.0g of sodium 1-hexanesulfonate and 10mL ammonium hydroxide to deionized water in a 500mL volumetric flask.
- 6.15 Sodium Hydroxide Solution
  - 6.15.1 Add 50g sodium hydroxide to deionized water in a 500mL volumetric flask
- 6.16 Hydrochloric Acid Solution
  - 6.16.1 Add 50mL concentrated HCL to deionized water in a 500mL volumetric flask.
- 6.17 SPE Eluting Solution
  - 6.17.1 Add 13.5mL phosphoric acid and 10.3mL diethylamine to deionized water in a 1000mL volumetric flask. Prior to cartridge elution, the SPE eluting solution is heated to 60°C.
- 6.18 Ion Pair Concentrate
  - 6.18.1 Add 3.75g sodium 1-hexanesulfonate to a 25mL volumetric flask.
  - 6.18.2 Bring up to volume with the SPE Eluting Solution
- 6.19 Stock Standards
- 6.20 Certified stock solutions of Diquat and Paraquat may be purchased from a chemical supplier at 1000ug/ml concentrations, , and stored under refrigeration for up to one year, or until comparison with a second source indicates a problem. Intermediate stocks (10ug/ml to 100ug/mL) may be stored under refrigeration for up to 6 months.
  - 6.20.1 The calibration stock and second source stock are prepared in the same manner as a sample, and should be extracted with every analytical batch, as follows:
    - 6.20.1.1 Add 500uL of a 1000ug/ml Paraquat/Diquat stock standard mix (primary or second source) to 250mL DI water. Process the



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250mL of spiked DI water according to steps 7.6 through 7.15 of this SOP. The resulting calibration stock will be 10ug/mL in solution (store under refrigeration for up to 6 months). This calibration stock is then used to serially prepare the working calibration standards in the following manner:

- 6.20.1.2 The working calibration curve is prepared from the 10ug/ml calibration stock from 6.20.1.1. Dilute the calibration stock into SPE eluent and follow 7.13 through 7.16 to achieve the following concentrations in solution: 0.02ug/ml, 0.10ug/ml, 0.50ug/ml, 1.0ug/ml and 1.5ug/ml. See Table 6 for the proper aliquots of calibration stock to add to 1.0mL eluent for each calibration level.
- 6.20.1.3 Continuing calibrations will be prepared from the same stock as the calibration curve, at two varying concentrations into SPE eluent (0.10 and 1.0)µg/mL. The CCVs are injected before sample analysis and will bracket every ten samples injections.
- 6.20.1.4 The working second source is prepared from the 10ug/ml second source stock from 6.20.1.1. Dilute the SS stock SPE eluent to achieve a concentration of 0.5ug/ml. The SS is injected once after each ICAL.
- 6.20.3 The working ICAL, CCV and SS may be stored under refrigeration for up to six months.
- 6.20.4 The certified solutions must be accompanied by a certificate of analysis that states balances used in the manufacture of this standard are calibrated with weights traceable to NIST in compliance with ANSI/NCCL Z-540-1 and ISO 9001. Standards formulated in house are prepared with balances that are calibrated with weights traceable to NIST. (See SOP HPL002).
- 6.20.5 One of the concentrations will be at the quantitation limit. Refer to Table 1 for list of quantitation limits. This list may be superseded by client specific requirements. The analyst must refer to the incoming sample notice for the lab works code and look at the detection limits listed on the appropriate form 1 to determine the quantitation limit standard.

The Spike Mix is prepared from a second source supplier in deionized water, at the concentrations listed in Table 4. The spike mix can be stored under refrigeration for up to 3 months.

#### 7.0 Solid Phase Extraction Procedure

- 7.1 For samples containing particulate matter, filter the water using a 0.45µm nylon membrane prior to extraction.
- 7.2 Measure 250mL of sample water into a marked - calibrated 250mL plastic container.
- 7.3 For the blank and LCS, measure 250mL deionized water. For the MS/MSD, measure 250mL sample water. The frequency of the blank and lab control spikes is every 20 field samples (20%) or once per 24 hour period, whichever is greater. The frequency of the MS/MSD is every 10 field samples, as long as the client provides enough sample matrix.
- 7.4 For the spikes, add 0.250mL Diquat/Paraquat spike solution (See Table 4 for concentrations) and mix well.
- 7.5 Measure the pH of each sample, and adjust to pH between 7 and 9. Use 10% sodium hydroxide to increase the pH or 10% hydrochloric acid to decrease the pH.



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7.6 Assemble the SPE C8 cartridges in the vacuum apparatus according to manufacturer's instructions. Pre-condition the cartridges by eluting the following solutions in the order listed:

- 7.6.1 Deionized water-5mL
- 7.6.2 Methanol-5mL
- 7.6.3 Deionized water-5mL
- 7.6.4 Conditioning Solution A-5mL
- 7.6.5 Deionized water-5mL
- 7.6.6 Methanol-10mL
- 7.6.7 Deionized water-5mL
- 7.6.8 Conditioning Solution B-20mL

**Discard the solutions as waste, except for the Conditioning Solution B. Retain this final solution in the cartridge to keep it activated.**

7.7 Silanize the 5mL volumetric flasks by rinsing each flask with 1-2mL Omni-Pur EnviroCoat Silanizing solution.

- 7.7.1 Ensure that the interior surface of the flask is thoroughly coated. Discard the solution and rinse 3-4 times with HPLC grade methanol.
- 7.7.2 Discard the methanol and rinse 3-4 times with Millipore water.
- 7.7.3 Allow to drain dry completely before final sample elution.

7.8 Attach the sample reservoirs to the top of each C8 cartridge, and start pouring some of the 250mL sample volume into the reservoir.

7.9 Turn the vacuum on, release the stopcock and draw the sample through the cartridge at a rate of approximately 3-6mL/min until the entire sample has passed through the cartridge. Use the stopcocks to adjust the flow. If particulate matter plugs the cartridge and slows the flow, increase the vacuum to maintain a reasonable flow rate.

7.10 Once the entire sample has passed through the cartridge, add 5mL methanol. Continue to draw air through the cartridge for one minute after the methanol has passed through.

7.11 Turn the vacuum off and open the bleed valve. Dispose of the water / methanol waste collected in the vacuum trap.

7.12 Place a 5mL silanized glass volumetric flask inside the manifold, making sure the correct sample tube is inside the correct flask.

7.13 Immediately before the final elution step, heat the SPE Eluting Solution to 60°C by placing some of the eluting solution into a VOA vial, and then placing the VOA vial into a 60°C water bath. The temperature is verified with a calibrated thermometer.

7.14 Target compounds are then eluted from the cartridge by adding approximately 4.5mL of heated SPE Eluting Solution to the top of the sample cartridge and allowing the solvent to pass through the cartridge under gravity flow. The sample extract is then collected in the volumetric flask.

7.15 Remove the volumetric flasks and fortify each extract with 100µL of the Ion Pair Concentrate.



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- 7.16 Bring up to a final volume of 5mL with SPE Eluting Solution and transfer the extract to a 20mL plastic scintillation vial.
- 7.17 Store extracts in a refrigerator between 2°C and 4°C in LCMS department.

#### 8.0 Instrument Analysis by LC-UV Diode Array Detector

8.1 The samples are analyzed by LC-UV using the following instrument parameters:

**Column:** Hamilton PRB-1 Column (5.0u x 150mm x 4.1mm) or equivalent

**Mobile Phase:** Diethylamine fortified with phosphoric acid and sodium 1-hexanesulfonate

**Flow Rate:** 1.0mL/min Isocratic

**Injection volume:** 100uL

**Photodiode array wavelength:** 210nm-370nm (The quant wavelength for Diquat is 308nm and the quant wavelength for Paraquat is 257nm)

**Sample rate:** 1 scan/sec

**Wavelength step:** 1nm

**Integration time:** 1 sec

**Run time:** 10 minutes

#### 8.2 Retention Time Study

8.2.1 Analyze a series of Diquat and Paraquat standards throughout a 24 hour period.

8.2.2 Calculate the retention time window as 3 times the standard deviation of the mean retention time.

8.3 Compounds are identified based on the retention time of the peaks in the samples that fall within the retention time window established by the standards.

8.4 Confirmation of the analyte is obtained by using the diode array full spectra of each analyte in the standard and comparing it to the sample spectra.

8.5 Additional confirmation may be obtained by replacing the sodium 1-hexanesulfonate with sodium 1-heptanesulfonate in the mobile phase and re-analyzing the samples. Comparison of the ratio of the retention times in the samples by the two mobile phases with that of the standards will provide additional confirmation. The RT ratios of the samples must be within 20% of the RT ratios of the standards.

#### 9.0 Calculations

9.1 To manually check the data system, use the External Standard quantitation technique to calculate the response factors and percent RSD as follows:

$$\text{Response Factor} = \frac{A_s}{C_s}$$

Where:

$A_s$  = Peak area (or height) of the target analyte in the standard

$C_s$  = Concentration of the standard





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9.2 The percent RSD is calculated as follows:

$$\%RSD = (SD)(100\%)/(RF_{x1})$$

Where:

%RSD = Percent relative standard deviation.

RF<sub>x1</sub> = Mean of the initial RF for a compound.

The acceptance criterion for the initial calibration curve is 20%RSD, or 0.99 linear regression coefficient. If this criterion is not met, then re-analyze the curve before sample analysis may proceed.

9.3 The working calibration factor must be verified on each working day by the injection of the CCV standard. The frequency of verification is every 10 sample injections. If the response for the target analytes varies from the predicted response by more than +/- 20%, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{|R_1 - R_2|}{R_1} \times 100$$

Where:

R<sub>1</sub> = Average response factor from first analysis

R<sub>2</sub> = Response factor from continuing analysis

9.4 Sample and spike quantitation may be calculated as follows:

$$\frac{A_s \times DF}{RF}$$

Where:

A<sub>s</sub> = Peak area (or height) of the target analyte in the sample extract

RF = Response Factor

DF = Extraction Ratio times dilution factor (if the sample was diluted)

9.5 Spike recovery may be calculated as follows:

$$\%R = \frac{(MSSR - SR)}{SA} \times 100$$

Where:

MSSR = Matrix Sample Results

SR = Sample Result

SA = Spike Added

Laboratory control spikes are calculated using the same equation, with the removal of the MSSR.



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9.6 The Relative % Difference between the Matrix Spike and Matrix Spike Duplicate is as follows:

$$\%RPD = \frac{(S - D) \times 100}{(S + D)/2}$$

Where:

S = Matrix Spike result

D = Matrix Spike Duplicate result

#### 10.0 Quality Control

10.1 One method blank, one lab control and a set of matrix spikes must accompany each set of ten samples (or fewer).

10.2 If there is insufficient volume to perform MS/MSD analysis, then extract an LCS/LCSD.

10.3 Spikes LCS, MS, MSD

10.3.1 Calculate spike recovery on all lab control and matrix spikes. Determine if the recovery is within method control limits (See Table 2). If recovery is not within limits, the following procedures are required:

10.3.1.1 Check to be sure there are no errors in calculations, spike solutions and internal standard solutions. Also, check instrument performance.

10.3.1.2 Recalculate the data and/or reanalyze the extract if any of the above check reveal a problem.

10.3.1.3 Re-extract and reanalyze the samples associated with the failed LCS if none of the above are a problem or flag the data as "estimated concentration".

9.1.1.1 The LCS may also meet the method requirement for a quarterly Quality Control Sample (QCS), which has been prepared with a standard from a second source. The QCS acceptance criteria will be 80-120% recovery. If this criterion is not met, a fresh QCS will be prepared.

10.4 Method Blank

10.4.1 The PQL (Practical Quantitation Limit) corresponds to the second lowest calibration point in the ICAL (0.02µg/mL). See Table 1 for PQL. All method blanks will be screened to the PQL for Paraquat and Diquat responses. If Paraquat and Diquat responses are detected above the PQL in the blank, then the blank should be re-prepared and re-analyzed.

10.5 Calibration

10.5.1 The Initial Calibration Curve will be evaluated using the External Standard quantitation technique. A minimum of three concentration levels is required for this method. The ICAL will consist of at least three points from the following levels: 0.02µg/mL, 0.10µg/mL, 0.50µg/mL, 1.0µg/mL and 1.5µg/mL. The (0.02µg/mL) standard must be included with each curve, in order to support the PQL. The relative standard deviation from the response factors in the curve should be 20% RSD or less. The average response factor is then used to quantitate the sample results. If the ICAL does not meet acceptance criteria, it should be re-prepared and re-analyzed. Sample analysis should not proceed until the problem has been corrected.



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- 10.5.2 The Continuing Calibrations will be analyzed at a frequency of every 10 sample injections and at the beginning and end of each analytical run sequence. The CCV is to consist of two injections at varying concentrations in the calibration curve. The low CCV is 0.10µg/mL, and the high CCV is 1.0µg/mL. The CCVs are evaluated by comparing the average response factor of the curve to the response factor of the CCV. The % Difference acceptance criteria is 20%D for the low and high CCV. If the CCV fails to meet acceptance criteria, then samples associated with this CCV should be re-analyzed after the problem is corrected.
- 10.5.3 The second source will be analyzed immediately following the calibration curve. The acceptance criteria for the second source is 20%D. If this criterion is not met, the second source will be re-prepared and re-analyzed before proceeding with sample analysis.
- 10.5.4 Corrective action will be taken if the calibration criteria listed above are not met, and samples will be re-analyzed where bracketing calibration criteria is exceeded. Corrective measures include re-preparing the standards, re-injecting the standards or instrument maintenance.
- 10.6 Manual integration:
- 10.6.1 Make a hard copy of the original integration performed by the instrument. Perform the appropriate manual integration. Make a copy of the manual integration. Be sure that the scale of the copy is appropriate. Note on the manual integration copy the number of the reason (see list below) a new integration was performed, initial and date. Make a note to justify the new integration on the manual copy, date and initial. Save the manual integration electronically so that it can be retrieved at a later date if necessary. Place a copy of all integrations in the data folder to be reviewed by the section manager or his/her designee. After review by the section manager, the manager will date and initial. See SOP # ANA003 for further instructions.
- (1) Integration does not follow baseline
  - (2) Non-target peak interference
  - (3) To split a peak
  - (4) To integrate a split peak
  - (5) The peak was not integrated
  - (6) Computer integrated wrong peak
  - (7) Other – Explain

The section manager or designee will review the manual integrations, then initial and date. The hard copies will be filed with the raw data.

#### 11.0 Data Reduction

When QC parameters are exceeded, the following will take place: When the matrix spikes are outside of the limits they are re-prepared and re-analyzed. When the LCS is outside of limits the entire batch is re-prepared and re-analyzed. If there is not enough samples to re-prepare the Project Manager is notified who in turn notifies the client by phone or fax. The case narrative or case letter explains the sequence of events and the data is qualified. If the calibration parameters are not met the standards are re-prepared and reanalyzed.



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### 12.0 Deviations from the method

This SOP was compared to EPA method 549.2<sup>1</sup>, and the following variances were made: The EPA method sect 10.2 says to prepare a calibration stock standard (similar to a sample) by spiking the eluent with target analytes. In order to closely match the sample preparation, APPL Inc. will spike the DI water with target analytes for the calibration stock. The working calibration curve will then be prepared according to the method by spiking the eluent with the calibration stock.

### 13.0 Health and Safety

Lab coats and gloves are used at all times. All personnel handling raw samples must have been vaccinated or titered for infectious disease. Follow all safety procedures as describes in the SOP for samples suspected of containing biological hazards.

### 14.0 Pollution Prevention

All hazardous materials that are generated during the testing of samples must be properly collected and stored. Drums are available in the storage room for the following types of wastes- acidic, basic and solvents.

### 15.0 Waste Management

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory has the responsibility to protect the environment by minimizing and controlling all releases from fume hoods and bench operations.

### 16.0 Contingencies for Handling Out of Control or Unacceptable Data

In the event that an out of control situation occurs, the project manager will be notified immediately. The affect of the out of control situation will be assessed according to the project DQO. If sufficient sample remains, and the situation will significantly affect the quality of the results, the analysis will be repeated. If the situation does not significantly affect the quality of the data, the project manager will notify the client and instructions from the client will be followed. In the event no sample remains, the client will be notified immediately. All situations will be documented on the multi level sheet and initialed by the project manager. All out of control situations will be brought to the attention of the QAU in the form of a QCER. The QAU has the final authority to approve the actions taken.

### SALUTATION

This procedure is applicable to all personnel who extract and analyze Diquat and Paraquat from aqueous samples using Solid Phase Extraction.

*Sharon Schmalow*

Section Manager: \_\_\_\_\_

Date: 4-20-10

*Thomas L. Linton*

QAU Director: \_\_\_\_\_

Date: 4-20-10

<sup>1</sup> EPA Method 549.2, Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and HPLC Chromatography with UV Detection



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**TABLE 1**  
**PQL Diquat and Paraquat IN WATER**

Diquat	0.40µg/L
Paraquat	0.40µg/L

**TABLE 2**  
**LCS/MS/MSD CONTROL LIMITS Diquat and Paraquat in WATER**

Diquat	70 – 130%
Paraquat	70 – 130%

**TABLE 3**  
**Quarterly QCS CONTROL LIMITS Diquat and Paraquat in WATER**

Diquat	80 – 120%
Paraquat	80 – 120%

**TABLE 4**  
**Spike Mix Concentrations in 250mL water**

Diquat	2.0ug/L
Paraquat	2.0ug/L

**TABLE 5**  
**Extracted Calibration Stock (primary and second Sources)**

Diquat	10µg/mL
Paraquat	10µg/mL

**TABLE 6**  
**Calibration Curve (prepared in 1.0mL final volume of SPE eluent)**

Level 1	0.02 µg/mL	(20µL Cal Level 4-1.0ppm)
Level 2	0.10 µg/mL	(10µL Cal Stock-10ppm)
Level 3	0.50 µg/mL	(50µL Cal Stock-10ppm)
Level 4	1.0 µg/mL	(100µL Cal Stock-10ppm)
Level 5	1.50µg/mL	(150µL Cal Stock-10ppm)



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#### APPENDIX I

##### DEFINITIONS

**EXTRACTION RATIO** The ratio of the final extract volume to the initial volume of water. For the EPA 549.2 method, the extraction ratio is 5mL / 250mL.

**LABORATORY DUPLICATE (LD1 AND LD2)** Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures.

**FIELD DUPLICATE (FD1 AND FD2)** Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures.

**LABORATORY REAGENT BLANK (LRB or method blank)** An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples.

**FIELD REAGENT BLANK (FRB or field blank supplied by client)** An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation and all analytical procedures.

**LABORATORY FORTIFIED BLANK (LFB or LCS)** An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory.

**LABORATORY FORTIFIED SAMPLE MATRIX (LFM or MS/MSD)** An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory.

**QUALITY CONTROL SAMPLE (QCS)** A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB (LCS) or sample matrix (MS/MSD). The QCS is obtained from a source external to the laboratory and different from the source of calibration standards.

**APPENDIX XXI, Caltest SOP B-MMOMUG-REV11. The Detection of Total Coliforms and *E. coli* Using Colilert Media Standard Method 9223 B (Revision 11, 07/16/09)**

**CALTEST STANDARD OPERATING PROCEDURE  
 THE DETECTION OF ENTEROCOCCI USING ENTEROLERT and TOTAL  
 COLIFORMS AND E. COLI USING COLILERT MEDIA  
 Standard Methods 9223B**

Reviewed by: Michael Soon                      Title: Wet Chemistry Coordinator    Date: 7-15-09  
 Reviewed by : Carmelita Oliveros            Title: Quality Assurance Officer    Date: 7-15-09  
 Approved by : Christine Horn                Title: Laboratory Director            Date: 7-16-09

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require a revision to this SOP. Any deviations from this SOP require prior authorization from the departmental Coordinator/Manager and the QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

Amendment Pages	Summary of Changes	Date	Initials Coord, L D, QAO
#1 _____	_____	____/____/____	_____
#2 _____	_____	____/____/____	_____
#3 _____	_____	____/____/____	_____
#4 _____	_____	____/____/____	_____
#5 _____	_____	____/____/____	_____

A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision.



CALTEST ANALYTICAL LABORATORY  
**THE DETECTION OF TOTAL COLIFORMS AND E. COLI  
AND ENTEROCOCCI**  
Standard Methods 9223B and Enterolert

1. SCOPE AND APPLICATION

- 1.1 Enterolert media is applicable to detect enterococci such as *E. faecium* and *E. faecalis* in fresh, marine, and wastewater.

2. SUMMARY OF METHOD.

- 2.1 To determine enterococci in fresh, marine, or wastewater, the sample plus the Enterolert media package is poured into the quantiTray. The samples are incubated for a minimum of 24 hours, not to exceed 28 hours.

3. DEFINITIONS

- 3.1 P/A : Presence/Absence.. Describes whether the sample changed color confirming the presence of enterococci or not.
- 3.2 Enterolert : The simultaneous detection of and confirmation Enterococci in water by defined substrate technology.
- 3.3 MPN : Most Probable Number.

4. INTERFERENCE

- 4.1 The work area should be disinfected to prevent contamination from the laboratory. Instructions on sampling need to be followed explicitly to prevent contamination at the source.

## 5. SAFETY

- 5.1 Prior to performing this analysis, review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing, including gloves and safety glasses, should be worn when handling samples or reagents.
- 5.2 Maintain a clean and uncluttered workspace. Return all chemicals, reagents, and resultant wastes to their designated storage area at the completion of the test.
- 5.3 Disinfect working area before and after test setup. Avoid breathing dust from the test substrate. Masks are available for use on a voluntary basis.

## 6. EQUIPMENT AND SUPPLIES:

- 6.1 Incubator at  $35.0 \pm 0.5^{\circ}\text{C}$
- 6.2 Sterile pipets
- 6.3 Sealer.

## 7. REAGENTS AND STANDARDS

- 7.1 Enterolert Reagent Snap Pack
- 7.2 Quanti Tray 2000 reaction trays.

## 8. SAMPLE COLLECTION AND STORAGE

- 8.1 Samples should be collected using aseptic technique as described in the 20th ed. of Standard Methods for the Examination of Water and Wastewater.
- 8.2 Samples not analyzed immediately must be stored in a refrigerator and analyzed within 30 hours for drinking water and 6 hours for waste water.
- 8.3 250mL bottles are used for Enterococci. Enough headspace should remain in the bottle so that the sample can be adequately shaken.
- 8.4 Samples need to be resampled if the volume for Total Coliforms and E.Coli is < 100mL or the container is cracked. If samples for enterococci do not have 1 inch headspace, they need to be resampled.

## 9. QUALITY CONTROL

- 9.1 Positive enterococci, as well as two negative controls, and a blank must be performed on each lot of media. *Enterococcus faecium* is used as the positive control (fluorescence). *Serratia marcescens*, (gram -), and *Aerococcus viridans*, (gram +), are used as the negative controls (no fluorescence). These cultures are purchased and may be placed into a sterile sample bottle filled to 100ml with sterile water or buffered phosphate water. They are treated as samples and read between 24 and 28 hours. Record results in the Colilert QC logbook. See Colilert QC Worksheet and Procedure in the microbiology laboratory.
- 9.2 Sample Bottle Sterility Checks for Colilert Worksheet and Procedure and Sample Bottle Volume Calibration Verification Worksheet and Procedure are situated in Microbiology.
- 9.3 All samples must be logged into the Microbiology logbook with sample number, date, time set, time read, final results and analyst initials.

## 10. CALIBRATION AND STANDARDS

- 10.1 Not applicable

## 11. PROCEDURE

### 11.1 Enterococci MPN using Quanti Tray 2000.

- 11.2.1 Samples must be set within 6 hours of sampling. All samples must be logged into the quanti tray log book prior to setting the samples. All samples must be shaken before analyses.
- 11.2.2 Use one hand to hold the Quanti Tray upright with the well side facing the palm. Squeeze the upper part of the tray so that it bends towards the palm. Pull the foil tab to separate the foil from the tray. Avoid touching the inside. Pour 100 mL of the reagent sample mixture directly into the tray. Tap to allow the release of air bubbles. Place the tray on the rubber insert of the sealer with the well side down and seal according to instructions.
- 11.2.3 Incubate at 35°C for 24-28 hours.

11.2.4 Count large and small positive wells and refer to the Quanti Tray MPN table to find the most probable number.

11.3 Maintenance of the Quanti Tray Sealer.

11.3.1 Unplug the unit and let it cool down for 90 minutes.

11.3.2 Loosen hold-down screws, which secure the lower roller assembly to the bottom of the sealer.

11.3.3 Remove lower roller by lifting straight up and then out, to ensure roller clearance of the locating pins on the bottom of the sealer.

11.3.4 Clean all accessible surfaces inside the sealer, and lower roller assembly with mild detergent. Dry all areas with paper towel.

11.3.5 Reinstall bottom roller assembly on the locating pins and tighten down the screws.

11.3.6 Fasten the access panel and reattach the tray shelf.

12. CALCULATIONS

12.1 Not applicable.

13. POLLUTION PREVENTION

13.1 The use of the Enterolert reduces the amount of sample and media that is necessary to identify enterococci traditionally.

14. DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

14.1 Not applicable

15. CORRECTIVE ACTION FOR OUT OF CONTROL DATA

Not applicable

16. CONTINGENCIES for HANDLING OUT of CONTROL or UNACCEPTABLE DATA

NA

17. WASTE MANAGEMENT

17.1 All samples are autoclaved and sewerred.

18. REFERENCES

18.1 Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition (1998)

18.2 40 CFR 141, 136

**APPENDIX XXII. Caltest SOP W-HARD-rev8. Total Hardness EPA 130.2/SM2340C (Revision 8, 10/29/08)**

Caltest Standard Operating Procedure

**TOTAL HARDNESS**  
**SM2340C**

Reviewed by: Nancy Pacheco	Title: Wet Chemistry Analyst	Date: 10-29-08
Reviewed by: Michael Soon	Title: Wet Chemistry Coordinator	Date: 10-29-08
Reviewed by: Carmelita Oliveros	Title: Quality Assurance Officer	Date: 10-29-08
Approved by: Christine Horn	Title: Laboratory Director	Date: 10-29-08

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require a revision to this SOP. Any deviations from this SOP require prior authorization from the departmental Coordinator/Manager and the QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

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#1	_____	_____	___/___/___	_____
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#4	_____	_____	___/___/___	_____
#5	_____	_____	___/___/___	_____

**A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision.**

<b>Total Hardness SM 2340</b>
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1. Scope and Application
  - 1.1 This procedure describes the method used to determine hardness in drinking, surface, and saline waters, as well as domestic industrial waste.
  - 1.2 The method is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25 mg CaCO<sub>3</sub>.
2. Summary of Method
  - 2.1 Calcium and magnesium ions in the sample are sequestered upon the titrated addition of disodium ethylenediamine tetraacetate (Na<sub>2</sub>EDTA), a sequestering agent. The endpoint of the reaction is detected by means of Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium cations, and a blue color when the cations are sequestered.
3. Definitions
  - 3.1 Hardness – the amount of calcium carbonate and magnesium carbonate dissolved in water, usually expressed as parts per million calcium carbonate.
  - 3.2 Titration – a method of analyzing the composition of a solution by adding known amounts of a standardized solution until a given reaction (i.e., color change) is produced.
  - 3.3 Sequestering agent – a substance that removes a metal ion from a solution system by forming a complex ion that does not have the chemical reactions of the ion that is removed; can be a chelating or a complexing agent.
4. Interferences
  - 4.1 Excessive amounts of heavy metals can interfere. These interferences can be overcome by complexing the metals with cyanide, sulfide, or hydroxylamine hydrochloride. Refer to EPA and/or Standard Methods for procedures to remove specific metal interferences.
5. Safety and Precautions



- 5.1 Prior to performing this analysis, review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing and safety glasses should be worn when handling samples or reagents.
- 5.2 Maintain a clean and uncluttered workspace. Return all chemicals, reagents, and resultant wastes to their designated storage area at the completion of the test.

## 6. Equipment and Supplies

- 6.1 Class A Glass burette equipped with stopcock.
- 6.2 125 mL Erlenmeyer flasks.
- 6.3 Graduated Cylinders, 50 mL.
- 6.4 Plastic bulb pipette, 5 mL.
- 6.5 Volumetric pipettor, 5 mL, with disposable tips.

## 7. Reagents

- 7.1 EDTA solution: dissolve 3.723 g disodium ethylenediamine tetraacetate dehydrate ( $\text{Na}_2\text{EDTA}$ ) in 1000 mL DI  $\text{H}_2\text{O}$ . Store in a labeled plastic container for no more than one month.
  - 7.1.1 Standardize as follows: Titrate 10 mL of 0.02 N  $\text{CaCO}_3$  (section 7.4) with EDTA solution. The titration should take about 1 mL EDTA to complex with each mL of  $\text{CaCO}_3$  added to the solution. EDTA is also commercially available.

$$7.1.2 \quad N \text{ of EDTA} = \frac{N_{\text{CaCO}_3} \text{ Vol}_{\text{CaCO}_3}}{\text{Vol}_{\text{EDTA}}} \quad 0.2^*$$

where:  $N_{\text{CaCO}_3}$  = normality of  $\text{CaCO}_3$  solution  
 $\text{Vol}_{\text{CaCO}_3}$  = Volume of  $\text{CaCO}_3$  titrated in mL.  
 $\text{Vol}_{\text{EDTA}}$  = Volume of EDTA required in mL.

\* factor used if 10 mL of 0.02 N  $\text{CaCO}_3$  solution is used for the standardization of the EDTA.

- 7.2 Hardness Buffer: dissolve 16.9 g ammonium chloride ( $\text{NH}_4\text{Cl}$ ), in 143mL concentrated Ammonium Hydroxide ( $\text{NH}_4\text{OH}$ ) Add 1.25g Magnesium salt of EDTA (available commercially) and dilute to 250mL with DI water. Store in labeled plastic or borosilicate glass container for no more than one month. Commercial buffers are also available.

- 7.3 Eriochrome Black T indicator: mix 0.5 g Eriochrome Black T with 4.5 g hydroxylamine hydrochloride. Dissolve in 100 mL of 95% ethanol or isopropanol. Commercial indicators are also available
- 7.4 Calmagite indicator: Dissolve 0.10g Calmagite in 100 mL DI H<sub>2</sub>O. Use 1 mL per 50 mL solution to be titrated. Store in borosilicate glass or polyethylene bottles.
- 7.5 Calcium Carbonate standard (CaCO<sub>3</sub>). 0.02 N: dissolve 0.500 g anhydrous CaCO<sub>3</sub> into a 250 mL Erlenmeyer flask. Place a funnel in the flask neck and slowly add 1 + 1 hydrochloric acid (HCl) until all CaCO<sub>3</sub> has dissolved. Add 100 mL DI H<sub>2</sub>O and boil for a few minutes to expel CO<sub>2</sub>. Cool, add a few drops of methyl red indicator, and adjust to an intermediate orange color by adding 1+1 hydrochloric acid (HCl), as required. Transfer to a 500 mL volumetric flask and dilute to mark with DI H<sub>2</sub>O (1 mL of this solution = 1 mg CaCO<sub>3</sub>). Commercial standards are also commercially available.
- 7.6 Calcium Carbonate Lab Control Standard: Prepare a 10x dilution of ERA Hardness WasteWtr solutions as follows:
- 7.6.1 Pipette 5 mL of LCS solution into a 50 mL volumetric flask and dilute with DI H<sub>2</sub>O up to mark.
- 7.6.2 Any equivalent source of Calcium Carbonate solution may be used in place of ERA Hardness WasteWtr as long as it is a secondary source standard different than the solution used to EDTA Standardization.
8. Sample Collection, Preservation, Shipment and Storage
- 8.1 Cool to 4°C, HNO<sub>3</sub> to pH <2.
- 8.2 Samples must be analyzed within 6 months in order to yield valid results.
- 8.3 Sample should be at or near room temperature for analysis.
9. Quality Control Requirements
- For each sample batch of 20 samples or less, analyzed within a given day, the following QC analyses to be performed:
- 9.1 One Method Blank - An aliquot of DI water to determine the hardness of water used for dilution of sample.
- 9.2 A Laboratory Control Sample (or Blank Spike) - A standard made from a source independent of the calibration standard that is treated as a sample. The LCS recovery demonstrates the accuracy of the method; the results of the % recovery of the LCS should not exceed 120% nor be less than 80%.

- 9.3 Matrix Spike/Matrix Spike duplicate - For each analytical batch, a sample aliquot must be spiked with a portion of the LCS solution to confirm accurate quantitation. The results of the % recovery should not exceed 120%, nor be less than 80%.
10. Calibration and Standardization
- 10.1 See Sections 9.1, 9.2, 9.3, and 11.7
11. Procedure
- 11.1 Sample should require less than 15 mL EDTA titrant and titration should be completed within 5 minutes of the addition of buffer.
- 11.2 Place 50 mL of sample or diluted sample in a 125 mL Erlenmeyer flask and dilute with DI H<sub>2</sub>O up to 50.0 mL. If the hardness result is less than 5ppm, a larger sample could be used.
- 11.3 Add 2 mL buffer solution.
- 11.4 Add 1 to 2 drops Eriochrome Black T indicator solution, or 1 mL of calmagite indicator.
- 11.5 Titrate slowly with EDTA titrant until the red color turns purple, then blue. Swirl flask continuously and allow solution to react for 3-5 seconds between each addition of EDTA.
- 11.6 If the endpoint is not sharp or if the color fades, an inhibitor must be added prior to titration. Refer to EPA and/or Standard Methods for procedure to remove specific interferences.
- 11.7 For hardness values <5 mg/L, titrate a 200 mL aliquot with appropriate amounts with reagents. Also retitrate a blank using an increase volume of DI H<sub>2</sub>O.
12. Calculation
- 12.1 Hardness (EDTA) as mg CaCO<sub>3</sub>/L =  $\frac{A \times B \times 1000}{\text{mL of sample}}$
- Where:
- A = mL of EDTA used for titration.
- B = mg CaCO<sub>3</sub> equivalent to 1.00 mL EDTA titrant.
13. Pollution Prevention
- 13.1 The samples analyzed in this method may pose a threat to the environment. All samples, as well as old standards, from this analysis must be disposed of as heavy metals. When done with the analysis, decant any remaining samples, standards, etc, into the >STLC waste drum in the waste storage area.

- 13.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.
  
14. Data Assessment and Acceptance Criteria for QC Measures
  - 14.1 See Internal QC Summary
  
15. Corrective Actions for Out-of-Control Data
  - 15.1 See Internal Quality Control Summary
  
16. Contingencies for Handling Out-of-Control or Unacceptable Data
  - 16.1 See SOP # Q-CORRECT
  
17. Waste Management
  - 17.1 The waste from this analysis can be poured into the greater than STLC metals containers. This drum is designated by a label stating nitric acid/heavy metals.
  - 17.2 All waste is segregated according to type, and tested before disposal. The results are reviewed by the waste disposal coordinator. If they are greater than is allowed for general disposal, the waste is removed by a licensed hauler. If the results of testing are less than allowable limits for general disposal, the waste is poured into the sewer after neutralization.
  - 17.3 For further information, see the Caltest Waste Management Coordinator.
  
18. Method Performance
  - 18.1 See Reference 19.3, Section 9.
  
19. Reference
  - 19.1 Methods for Chemical Analysis of Water and Wastewater, EPA 600/4-79-020, March 1983.
  - 19.2 Standard Methods for Examination of Water and Wastewater, 20th Edition, 1998.
  - 19.3 EPA Methods and Guidance for Analysis of Water, June 1999.

**APPENDIX XXIII, Caltest SOP M-200.8-3MODE rev2. EPA 200.8 Inductively Coupled Argon Plasma-Mass Spectrometry Analyses Three Modes (Revision 2, 03/19/09)**



<p><b>CALTEST STANDARD OPERATING PROCEDURE</b></p> <p><b>EPA 200.8</b></p> <p><b>INDUCTIVELY COUPLED ARGON PLASMA-MASS</b></p> <p><b>SPECTROMETRY ANALYSES THREE MODES</b></p>
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Approved by :	Christine Horn	Title: Laboratory Director	Date: 3-19-09

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require a revision to this SOP. Any deviations from this SOP require prior authorization from the departmental Coordinator/Manager and the QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

Amendment	Pages	Summary of Changes	Date	Initials Coord, L D, QAO
#1	_____	_____	____/____/____	____/____
#2	_____	_____	____/____/____	____/____
#3	_____	_____	____/____/____	____/____
#4	_____	_____	____/____/____	____/____
#5	_____	_____	____/____/____	____/____

**EPA 200.8**  
**DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES**  
**BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY**

**1.0 Scope and Application**

- 1.1 This method provides procedures for determination of acid-soluble aluminum and dissolved elements in ground waters, surface waters and drinking water. It may also be used for determination of total recoverable element concentrations in these waters as well as wastewaters, sludges and soils samples. This method is applicable to the following elements:

Analyte:

Aluminum	Lithium	Calcium
Antimony	Manganese	Magnesium
Arsenic	Molybdenum	Sodium
Barium	Nickel	Potassium
Cadmium	Selenium	Iron
Chromium	Silver	SiO <sub>2</sub>
Cobalt	Thallium	Vanadium
Copper	Tin	Beryllium
Lead	Titanium	
Boron	Zinc	
Gallium	Zirconium	
Tungsten	Strontium	

- 1.2 Dissolved elements are determined after suitable filtration and acid preservation. In order to reduce potential interferences, dissolved solids should not exceed 0.2% (w/v).
- 1.3 Acid-soluble aluminum is determined after preservation by acidification to a pH between 1.5 and 2.0 and filtration after 10 minutes to 24 hours.
- 1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the samples have been properly preserved with acid and have turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis".
- 1.5 For the determination of total recoverable analytes in aqueous samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material >1% (w/v) should be extracted as a solid type sample.
- 1.6 The total recoverable sample digestion procedure given in this method is not suitable for the determination of volatile organo-mercury compounds. However, for "direct analysis" of drinking water

(turbidity <1 NTU), the combined concentrations of inorganic and organo-mercury in solution can be determined by "direct analysis" pneumatic nebulization provided gold is added to both samples and standards alike to eliminate memory interference effects.

## 2.0 SUMMARY OF METHOD

- 2.1 An aliquot of a well mixed, homogeneous aqueous sample is accurately measured for sample processing. For total recoverable analysis of an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of acid-soluble aluminum, dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is <1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid and HCl, and then diluted to a predetermined volume and mixed before analysis.
- 2.2 The method describes the multi-element determination of trace elements by ICP-MS. Sample material in solution is introduced by pneumatic nebulization into 1-3 a radiofrequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are detected by an electron multiplier or Faraday detector and the ion information processed by the data handling system. Interferences relating to the technique must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. The use of the alternate gas modes, the helium collision cell mode and the hydrogen reaction cell mode can compensate for these. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standards.

## 3.0 DEFINITIONS

- 3.1 Calibration Blank - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.
- 3.2 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.3 Dissolved Analyte - The concentration of analyte in an aqueous sample that will pass through a 0.45  $\mu\text{m}$  membrane filter assembly prior to sample acidification.
- 3.4 Field Reagent Blank (FRB) - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all



analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

- 3.5 Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 9 replicate measurements of the calibration blank signal at the selected analytical mass(es).
- 3.6 Internal Standard - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component (Sections 7.5 and 9.4.5).
- 3.7 Laboratory Duplicates (LD1 and LD2) - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.8 Laboratory Control Sample (LCS) - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 3.9 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations. This is also known as the Matrix Spike (MS).
- 3.10 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.
- 3.11 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.
- 3.12 Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.
- 3.13 Initial Calibration Verification (ICV) - A solution of method analytes of known concentrations used to verify the accuracy of the calibration curve. It is obtained from a reputable commercial source different than that of the calibration standards.
- 3.14 Stock Standard Solution - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

- 3.15 Total Recoverable Analyte - The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of <1 NTU, or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s).
- 3.16 Tuning Solution - A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses.
- 3.17 Water Sample - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.
- 3.18 Acid-soluble aluminum - the aluminum that passes through a 0.45  $\mu\text{m}$  membrane filter after the sample has been acidified to a pH between 1.5 and 2.0 with nitric acid.

#### 4.0 INTERFERENCES

- 4.1 Several interference sources may cause inaccuracies in the determination of trace elements by ICP-MS. These are:
- 4.1.1 Isobaric elemental interferences - Are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method (Table 4), only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.
- 4.1.2 Abundance sensitivity - Is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.
- 4.1.3 Isobaric polyatomic ion interferences - Are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified<sup>3</sup>, and these are listed in Table 2 together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion

interferences will be highly dependent on the sample matrix and chosen instrument conditions. In particular, the common  $^{82}\text{Kr}$  interference that affects the determination of both arsenic and selenium, can be greatly reduced with the use of high purity krypton free argon.

- 4.1.4 Physical interferences - Are associated with the physical processes which govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction and/or skimmer cones reducing the effective diameter of the orifices and therefore ion transmission. Dissolved solids levels not exceeding 0.2% (w/v) have been recommended<sup>3</sup> to reduce such effects<sup>4</sup>. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards ideally should have similar analytical behavior to the elements being determined.
- 4.1.5 Memory interferences - Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples.
- 4.1.6 Interferences found in 4.1.1, 4.1.3 and 4.1.4 in many cases can be eliminated by the use of the collision or reaction cell modes.

## 5.0 SAFETY

- 5.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Specifically, concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.
- 5.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples must be done in a fume hood.

## 6.0 EQUIPMENT AND SUPPLIES

- 6.1 Inductively coupled plasma mass spectrometer: Agilent 7500 ICP-MS ChemStation (G1834B)
  - 6.1.1 Argon gas supply - High purity grade (99.99)
  - 6.1.2 Helium gas supply -High purity grade
  - 6.1.3 Hydrogen gas supply- High purity grade
  - 6.1.4 A variable-speed peristaltic pump is required for solution delivery to the nebulizer.
- 6.2 Analytical balance with capability to measure to 0.1 mg for use in weighing solids, preparing standards, and for determining dissolved solids in digests or extracts.
- 6.3 A temperature adjustable hot block capable of maintaining a temperature of 95°C.
- 6.4 An air displacement pipetter capable of delivering volumes ranging from 0.1-2500 µL with an assortment of high quality disposable pipet tips.
- 6.5 Mortar and pestle, ceramic or nonmetallic material.
- 6.6 Labware - For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include soaking overnight and thoroughly washing with laboratory-grade detergent and water, rinsing with tap water, and soaking for four hours or more in 20% (V/V) nitric acid or a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with reagent grade water and storing clean. Note: Chromic acid must not be used for cleaning glassware.
  - 6.6.1 Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes.
- 6.7 Assorted calibrated pipettes.
- 6.8 50ml centrifuge tubes and 15ml centrifuge tube or 10ml plastic tubes. Metals free.

## 7.0 REAGENTS AND STANDARDS

Reagents may contain elemental impurities that might affect the integrity of analytical data. Owing to the high sensitivity of ICP-MS, high-purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade. Nitric acid is preferred for ICP-MS in order to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid is used however, it should be noted that hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for the chloride polyatomic ion interferences must be applied to all data.

- 7.1 Nitric acid, concentrated (sp.gr. 1.41).
- 7.2 Hydrochloric acid, concentrated (sp.gr. 1.19).
- 7.3 Reagent water - All references to reagent grade water refer to ASTM Type I water.
- 7.4 Commercial Standard Stock Solutions – 10,000ppm Na, K, Ca, Mg, Fe, Si  
 \_1000ppm As, Cd, Mo, Sb, Se, Tl, Be, Ba, Cu, Cr, Co B, Pb, Ni, Mn, V,  
 Zn, Li, Sn, Ti, Sr, Al
- 7.5 Working Standard Stock Standard Solutions Prep: –
  - 7.5.1 Soln. A: 10ppm As, Cd, Mo, Sb, Se, Tl, Be.
  - 7.5.2 Soln. B: 10ppm, Ba,Cu, Cr, Co, B, Pb, Ni, Mn, V, Zn, Li, Sn, Ti, Sr, Al
  - 7.5.3 Soln. C: 1000 ppm Na, K, Mg, Fe, Ca. These are made from 10,000ppm solutions.
  - 7.5.4 Soln D: 4ppm Ag

Preparation of “Working Standard Stock” - fresh multielement working stock standard should be prepared every 6 months or as needed. Dilute each of the commercial stock multi-element standard solutions to levels appropriate to the operating range of the instrument using reagent water containing 1% (v/v) nitric acid and 0.5 % HCl. The element concentrations in the standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. The concentrations ranges are from 0.1-200 µg/L and 0.05 to 50 mg/L. Please note, this “Working Stock Standards” will be used to make the daily calibration standard. The “Working Stock Standards are prep in a larger batch and can be stored over time. Total volume for each solution is 100 ml except for the 4ppm Ag that is 200ml and Commercial Standard Stocks are used to make the solutions below:

*****Soln A*****		*****Soln B *****		*****Soln C*****		***Soln D***	
10ppm Vol. from		10 ppm Vol. from		1000pp m Vol. from		4ppm vol. from stock(ml)	
Analytes Stock (ml)		Analytes Stock (ml)		Analytes Stock (ml)		Analytes )	
Tl	1	Cu	1	Ca	10	Ag	0.2
Be	1	Cr	1	Mg	10		
Sb	1	Co	1	Na	10		
Se	1	Ba	1	K	10		
As	1	B	1	Fe	10		
Mo	1	Pb	1				
Cd	1	Ni	1				
		Mn	1				
		V	1				
		Zn	1				
		Li	1				

Sn	1
Ti	1
Sr	1
Al	1

7.6 Internal Standards Stock Solution – 10ppm Sc, In,Y, Tb, Bi (commercial) and 1000 ppm Ge(commercial) are used to prep the internal standard. Make a 500 ppb internal standard using both standards. Use this solution concentrate for the online addition to blanks, calibration standards and samples.

7.7 Blanks - Three types of blanks are required for this method. A **calibration blank** is used to establish the analytical calibration curve, the **laboratory reagent blank** is used to assess possible contamination from the sample preparation procedure and to assess spectral background, and the **rinse blank** is used to flush the instrument between samples in order to reduce memory interferences.

7.7.1 Calibration blank - Consists of 1% (v/v) nitric acid and 0.5 % HCl in reagent grade water.

7.7.2 Laboratory reagent blank (LRB) - Must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the same entire preparation scheme as the samples including digestion, when applicable.

7.7.3 Rinse blank - Consists of 2% (v/v) nitric acid and 2% (v/v) hydrochloric acid in reagent grade water.

Note: If mercury is to be determined by the "direct analysis" procedure, add gold to the rinse blank to a concentration of 100 µg/L.

7.8 Tuning Solution - This solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by diluting a 1000ppm solution to 10ppb of Li, Y, Tl, Mg, Be, In, Ce, Co and Pb.

7.9 Initial Calibration Verification (ICV) – Standards made from a source other than the calibration standards.

7.10 Laboratory Control Sample (LCS) - To an aliquot of LRB, add aliquots from multielement stock standards to prepare the LCS. The fortified concentration used is 20 µg/L except for Aluminum, which is 40 ug/L and 2 mg/L for the cations. The LCS must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable. .

7.11 P/A Tune solution: this is solution is part of a tuning process that needs to be conducted every morning before running the samples. Add .5 ml of the two commercial P/A solutions to 50ml of water with 1% Nitric acid and 0.5%HCl. Also add 0.5ml of 15ppm B standard

7.12 The EPA published methods require no expiration period for metals' standards. In pursuit of good laboratory practice, it is Caltest's standard to adopt the following:

*All standards will be replaced by their expiration date. Reorder new standard/s two months before it expires. When standards are reordered, the shelf containing the standards must be reviewed to determine if other standards are close to expiration and should be reordered. Analysts must check the expiration dates before using standards.*

## 8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to aliquoting for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months before analysis.
- 8.2 For the determination of dissolved elements, the sample must be filtered through a 0.45  $\mu\text{m}$  pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.
- 8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples).
- 8.4 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.
- 8.5 For the determination of acid-soluble Aluminum, the sample must be acidified with nitric acid to pH between 1.5 and 2.0 and must be filtered after 10 minutes to 24 hours.

## 9.0 Sample Extraction Procedure

### 9.1 Aqueous Sample Preparation - Dissolved Analytes

- 9.1.1 For the determination of dissolved analytes in ground and surface waters, pour an aliquot of the filtered, acid preserved sample into a 50 mL polypropylene centrifuge tube. Add 0.5 mL concentrated  $\text{HNO}_3$  and 0.25 mL  $\text{HCl}$ , cap the tube and mix. The sample is now ready for analysis. Note: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure in Section 9.2 prior to analysis.

### 9.2 Aqueous Sample Preparation - Total Recoverable Analytes

- 9.2.1 For the analysis of total recoverable analytes in drinking water samples containing turbidity <1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure described in Section 9.1.1

9.3 For the determination of total recoverable analytes in aqueous samples (other than drinking water with <1 NTU turbidity), transfer a 50 mL aliquot from a well mixed, acid preserved sample to a centrifuge tube.

- 9.3.1 Add 0.5 mL concentrated  $\text{HNO}_3$  and 0.25 mL concentrated  $\text{HCl}$ . Spike LCS and MS / MSD with 20  $\mu\text{g/L}$  of all analytes with the exception of aluminum, which is spiked with 40  $\mu\text{g/L}$ .

9.3.2 Reduce the volume of the sample aliquot to about 10 mL by gentle heating at 85°C. **DO NOT BOIL**. This step takes about one hour for a 50 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL.

9.3.3 Gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H<sub>2</sub>O azeotrope.)

9.3.4 Allow the sample to cool. Make the volume up to 50 ml and mix.

9.3.5 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.

Prior to analysis, pipet 5 or 10 mL sample into a 15 mL centrifuge tube. (If the dissolved solids in this solution are >0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones. The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

## 10.0 QUALITY CONTROL

10.1 Linear calibration ranges - Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined sample analyte concentrations that are greater than the highest standard must be diluted and reanalyzed. The LDRs should be verified whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be re-determined.

10.1.1 Method detection limits (MDL) should be established for all analytes, using reagent water fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven (7) replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$\text{MDL} = (t) \times (S)$$

where:

t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates] and

S = standard deviation of the replicate analyses



The MDLs must be sufficient to detect analytes at the required levels according to compliance monitoring regulation. MDLs should be determined annually, or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be re-determined.

## 10.2 Assessing Laboratory Performance.

10.2.1 Laboratory reagent blank (LRB) - Analyze at least one LRB with each batch of 20 or fewer of samples of the same matrix. LRB data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing.

10.2.2 Laboratory Control Standard (LCS) - The laboratory must analyze at least one LCS with each batch of samples. Calculate the accuracy as percent recovery using the following equation:

$$R = \frac{LCS - LRB}{s} \times 100$$

where:

R = percent recovery

LCS = laboratory control standard

LRB = laboratory reagent blank

s = concentration equivalent of analyte added to fortify the LBR solution

If the recovery of any analyte falls outside the required control limits of 85 – 115 %, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses. See the Caltest Internal QC summary for the Metals Department.

10.3. Instrument performance - For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration, run the ICV (Initial Calibration Verification) as a surrogate sample immediately following each calibration routine, then run the CCV after every ten analyses and at the end of the sample run. The results of the analyses of the standards will indicate whether the calibration remains valid. The analysis of the ICV must be within 10% of calibration. If the calibration cannot be verified within the specified limits, the instrument must be recalibrated. If the continuing calibration verification is not confirmed within 15%, the previous 10 samples must be reanalyzed after recalibration. If the sample matrix is responsible for the calibration drift, it is recommended that the previous 10 samples are reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

## 10.4 Assessing Analyte Recovery and Data Quality.

10.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect.

- 10.4.2 The laboratory must add a known amount of analyte to 10% of the routine samples. In each case the MS / MSD aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the laboratory control standard.
- 10.4.3 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated MS / MSD recovery range of 85 - 115%. Recovery calculations are not required if the concentration of the analyte added is less than 30% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where:

R = percent recovery     $C_s$  = fortified sample concentration

C = sample background concentration

s = concentration equivalent of analyte added to fortify the sample

- 10.4.4 If recovery of any analyte falls outside the designated range, and laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related.
- 10.4.5 Internal standards responses - Monitor the internal standards and the ratios of the internal standards responses against each other. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60-125% of the original response in the calibration blank. If deviations greater than these are observed, flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are not within the limit, take a fresh aliquot of the sample, dilute by a further factor of two and reanalyze. If after flushing the response of the internal standards in the calibration blank are out of limits, terminate the analysis and determine the cause of the drift. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

## 11.0 CALIBRATION AND STANDARDIZATION

11.1 Operating conditions - The instrument conditions are set up as follows (but are subject to change in order to get optimal performance and sensitivity out of the instrument).

RF Power	1500watts
Plasma Gas Flow	15L/min
Auxiliary Gas Flow	1L/min
Nebulizer Gas Flow	0.95L/min
Solution Pump Rate	0.1 rps

Rinse Time	35 seconds
Sample Uptake Time	25 seconds
Equilibration Time	10 seconds
Analysis Time	2.06 mins
Detector	Dual Mode
Scanning Mode	Peak Hopping
Number of Points/Peak	1
Dwell Time	100ms per point
Number of Replicates	3

- 11.2 Precalibration routine - The following precalibration routine must be completed prior to calibrating the instrument until such time it can be documented with periodic performance data that the instrument meets the criteria listed below without daily tuning.
- 11.2.1 Initiate proper operating configuration of instrument and data system.  
Allow a period of not less than 30 minutes for the instrument to warm up.  
After warmup conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by Lithium 7, midrange Yttrium 89, and high range by Thallium 205.
- For good performance adjust spectrometer resolution to produce a peak width of less than 0.75 amu at 5% peak height or 0.60-0.85 at 10% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.
- 11.2.2 Instrument stability must be demonstrated by running the tuning solution a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.
- 11.3 Internal Standardization - Internal standardization must be used in all analyses to correct for instrument drift and physical interferences.  
For full mass range scans, a minimum of three internal standards must be used. Procedures described in this method for general application, detail the use of four internal standards; scandium, germanium, indium, and terbium. Internal standards must be present in all samples, standards and blanks at identical levels. This is achieved by having the internal standard mixed with the samples and standards at the pump.
- 11.4 Calibration - Prior to initial calibration, set up proper instrument software routines for quantitative analysis. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.
- 11.5 The rinse blank should be used to flush the system between solution changes for blanks, standards and samples. Allow sufficient rinse time to remove traces of the previous sample. Solutions should be aspirated for 30 seconds prior to the acquisition of data to allow equilibrium to be established.

## 12.0 Analyzing Samples

### 12.1 Instrument set up

Clean the sampler skimmer cones when the sensitivity drops, by sonicating them in E-pure H<sub>2</sub>O for 15-20 minutes. Do not touch the cones. This can decrease the sensitivity. Check the tubing on the autosampler pumps and place the internal standard line in E-pure water. Check that the water recirculator is on. Using the Instrument window icon, light the plasma, allow 30 minutes for the instrument to warm up.

12.2 Tune the instrument according to manufacturers instructions. Open the tune window and select the "nogas" tune file. With the sample uptake in the tuning solution, click on the start button. Check the parameters then click stop. Switch to the "He" tune file and repeat. Lastly switch to the "H<sub>2</sub>" tune. If for any reason the parameters are off than what are stated below. Adjust each running condition on the left hand side and see if it makes any difference to the parameters. If it does not, click on "restore" at the bottom and it will go back to the original setting. Only when the condition change, you want to save the setting. For the "Nogas" tune, we found that the carrier gas is what makes a big difference in the result. However the manufacture have provided a list of things to attempt changing during each tune. All the parameters must pass for the 3 tunes.

#### Parameters for tuning (use 10 ppb tune solution)

Nogas	He	H <sub>2</sub>
Li(7) >10000 counts	Co(59) ~10000 counts	Co(59) ~10000 counts
Y(89) >20000	V(51) <100 counts	Se(78) <10 counts
Tl(205) >10000 counts	As75 <10	56 Fe <3000
Oxides(156/140) ~1.5%	51/59 <= 2%	
Double charged (70/140) <~3%		
RSD <5%		

If the RSD is high in (7) and (89), this may be due to the tubing. This might be a good time to change the tubing. Tubing actually have two different section in one straight line separated by two separators. It is ok, if the section along the tubing has not been used before to use that section. However, if both sections on tubing have been used, then change out the whole tubing. When adjusting the tubing, make sure that it is not too tight or loose. This may cause the water movement to either pulse or air bubble. You want the solution in the tubing to be very smooth and consistent going into the machine.

Mass calibration must be less than 0.1 amu from the true value and the peak with at 10% of the peak height should be 0.60-0.85 amu or less than 0.75 amu at 5%.

- 12.3 Go back to "nogas" and perform an autotune under the tune section. Using the same tune solution, start the auto tune run. When complete, check parameters. Result will be printed.
- 12.4 If autotune passed, tune P/A factor and tell the probe to go to the P/A factor solution and click start. Result will be printed. Rinse the probe before starting the 10ppb tuning
- 12.5 If all the tunings have passed, exit the tuning page and go to sequence. First load the sequence, change the data file to the date of the run and then run sequence. Run Tune sequence with 10 ppb tune solution that is normally use for the Elan machine. If all parameters pass, continue with calibration. If the tune doesn't

pass, go back to the tuning menu and repeat tuning. When everything pass, it is time to run the Calibration curve and follow by the samples. However, analyst must enter the calibration and sample run first.

### 13.0 Entering daily run (Setting up a Calibration and Sequence)

13.1 In the software, click on "sequence" icon, and go to "edit sample log". In the block, go to Calibration. The calibration has been set up and is used for the daily run. Save it under the right date (running date).

13.2 Next click on sample box and enter all the samples which will be run. Note that for ever 10 sample, there has be to a CCB, CCV1, CCV2, CCB. At the end of the sample log enter "Keyword" under the type column and "Stand by" under the data line. Save and print sequence.

13.3 Placing each tube into the rack for analysis can be tricky. There are 4 racks, each rack has 5 rows and in each rack there are 12 spot. (X) will be rack 1, row 2, spot 02. So the vial location will be 1202. (Y) is at 1411.

Rack 1

	X			
			Y	

### 14.0 Loading calibration curve and samples

14.1 Calibration curve will get loaded first. Sample starts at spot #1401. Earlier we have prepped the "Working Stock Standard". We will be using this standard to make our daily running calibration. There are 6 calibration points. Each working calibration will be made up in a 50ml centrifuge tube with 0.5ml Nitric acid and 0.25ml HCl.

STD	*****Working Standard Stock*****			Ag	commerical SiO2
	1	2	3		
1					10x dil of Std 2
2					10x dil of Std 3
3	0.05	0.05	0.25	0.125	0.025
4	0.5	0.5	0.5	1.25	0.05
5	X	1	1	X	0.1
6	X	2	2.5	X	0.2

Table below lists all concentration of each Daily calibration and analytes.

	<u>Std 1</u>	<u>Std 2</u>	<u>Std 3</u>	<u>Std 4</u>	<u>Std 5</u>	<u>Std 6</u>
<b>Elements</b>	Be, Tl, Ba Ni, V, Mn Co, Cu, As, Mo, Ag, Cd, Sb, Pb, Cr	Be, Tl, Ba Ni, V, Mn, Co, Cr Se, Zn, Al As, Mo, Ag, Cd, Sb, Pb, Cu, B, Ti, Li, Sn, Sr	Be, Tl, Ba Ni, V, Mn, Co, Cr Se, Zn, Al As, Mo, Ag, Cd, Sb, Pb, Cu, B, Ti, Li, Sn, Sr	Ni, V, Mn Co, Cu, As, Mo, Ag, Cd, Sb, Pb, Se, Zn, Al Cr, Ba, B, Ti, Li, Sn, Sr	Ni, V, Mn, Co, Cu, Pb, Zn, Al, Cr, Ba, B, Ti, Li, Sn, Sr	
<b>Concentration</b>	0.1 ppb	1 ppb	10ppb	100ppb	200 ppb	
<b>Elements</b>	<u>Na, K, Ca,</u> <u>Mg, Fe</u>	<u>Na, K,</u> <u>Ca, Mg,</u> <u>Fe</u>	<u>Na, K,</u> <u>Ca, Mg,</u> <u>Fe</u>	<u>Na, K,</u> <u>Ca, Mg,</u> <u>Fe</u>	<u>Na, K,</u> <u>Ca, Mg,</u> <u>Fe</u>	<u>Na, K,</u> <u>Ca, Mg,</u> <u>Fe</u>
<b>Concentration</b>	0.05 ppm	0.5 ppm	<u>5 ppm</u>	10 ppm	20 ppm	50 ppm
<b>Elements</b>	<u>SiO2</u>	<u>SiO2</u>	<u>SiO2</u>	<u>SiO2</u>	<u>SiO2</u>	<u>SiO2</u>
<b>Concentration</b>	0.107 ppm	1.07 ppm	10.7 ppm	21.4 ppm	42.8 ppm	85.6 ppm

14.2 The ICV and CCV concentrations are as follows

	33 ug/L	50 ug/L	67 ug/L	67 ug/L	100 ug/L	133 ug/L
		Be, Ti, As, Se, Mo, Cd			Ni, V, Mn, Co, Cu, Pb,	

ICV		Sb, Ag			Cr, Zn, Ba B, Ti, Sr, Sn
Low CCV	Be, Ti, As, Se, Mo, Cd Sb, Ag			Ni, V, Mn, Co, Cu, Pb Cr, Zn, Al, Ba B, Ti, Sr, Sn	
Mid CCV		Be, Ti, As, Se, Mo, Cd, Sb, Ag			Sn Ni, V, Mn, Co, Cu, Pb, Ba, Zn, Al Cr, B, Ti, Sr
High CCV			Be, Ti, As, Se, Mo, Cd Sb, Ag		Ti, Sr, Sn Ni, V, Mn, Co, Cu, Pb, Cr, Zn, Al, Ba, B

	Ca Mg Na K Fe	SiO <sub>2</sub>
ICV	25 mg/L	42.8 mg/L
Low CCV	17 mg/L	28.5 mg/L
Mid CCV	25 mg/L	42.8 mg/L
High CCV	33 mg/L	57.1 mg/L

\*The CCV concentrations are rotated every 4 months from low to mid to high, then back to low, etc.

- 14.3 To start the analysis. . . Click on sequence, then run. Change data path to MS3date and click run.
- 14.4 For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for data reporting.
- 14.5 The rinse blank is used to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of one minute. Samples should be aspirated for 30 seconds prior to the collection of data.
- 14.6 Samples having concentrations higher than the highest standard should be diluted into range and re-analyzed. The sample should first be analyzed for the trace elements in the sample, protecting the detector from the high concentration elements, if necessary, by the selection of appropriate scanning windows. The sample should then be diluted for the determination of the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided quality control data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.



## 15.0 DATA ANALYSIS AND CALCULATIONS

All results including sample concentrations, internal standard recoveries, sample and QC standard results are calculated using Agilent software.

## 16.0 Pollution Prevention

16.1 In order to reduce the volume of acid waste generated, we have reduced the initial amount of sample used from 100 mL to 50 mL.

16.1.1 The sample duplicate has been eliminated, and the matrix spike, matrix spike duplicate are being used to evaluate rpd's.

16.2 All digestion tubes and final volume tubes are rinsed with DI water before being disposed of into the general trash. The rinsate is put into the acid waste 50-gallon drum.

## 17.0 Data Assessment and Acceptance Criteria for Quality Control Measures

17.1 See Internal Quality Control Summary

### 17.2 Corrective Actions for Out-of-Control Data

17.3 See Internal Quality Control Summary

### 17.4 Contingencies for Handling Out-of-Control or Unacceptable Data

17.5 See SOP # Q-CORRECT-003

## 18.0 Waste Management

18.1 All waste coming off of the instruments goes into a 5-gallon acid waste bottle which contains a neutralizing agent (solid  $\text{CaCO}_3$  chunks). These acid waste bottles are emptied into the acid waste 50-gallon drum located in metals prep area.

- 18.2 After the aqueous samples and digestates have been stored at ambient temperature for 6 months, they are considered waste. Solid wastes are segregated into a covered solid wastes bin.
- 18.3 All waste is tested prior to disposal, and the results are reviewed by the waste management coordinator. If the results are found to be greater than is allowed for general disposal, the waste is removed by a licensed hauler. The metals waste is disposed of as corrosive liquid waste. If the results of testing are found to be less than allowable limits for general disposal, the waste is poured into the sewer *after* neutralization.
- 18.4 For further information see the Caltest Waste Management Coordinator.

#### 19.0 Method Performance

- 19.1 For a complete review of the Method Performance study see reference 11, Section 16.0 of EPA Method 200.8, revision 5.4.

#### 20.0 References

EPA 200.8 Revision 7

**TABLE 1. ELEMENTS For ICP-MS DETERMINATION**

Analyte	Internal Standard	Mass
Li		7
Be		9
B		11
Na		23
Mg		24
Al		27
K		39
Ca		44
	Ge	74
Ti		47
Fe		54
<hr/>		
V		51
Cr		52
Mn		55
Co		59
Ni		60
Cu		65
Zn		66
Ga		69
	Ge	74
As		75
<hr/>		
Se		78
Rb		85
Sr		88
Zr		90
<hr/>		
Mo		95
Ag		107
Cd		111
	In	115
Sn		120
Sb		121
<hr/>		
Ba		138
	Tb	159
Tl		205
Pb		208
<hr/>		

**APPENDIX XXIV, Caltest SOP W-NNO3-rev2. Nitrate + Nitrite As N EPA 353.2/SM 4500-NO3-F  
(Revision 2, 05/29/08)**

CALTEST STANDARD OPERATING PROCEDURE

**NITRATE+NITRITE AS N**  
**EPA Method 353.2 / SM 4500NO3-F**  
**SKALAR**

Reviewed by: \_\_\_Michael Soon                      Title: Wet Chemistry Coordinator                      Date: 5-28-08

Reviewed by: \_\_\_Carmelita Oliveros                      Title: Quality Assurance Officer                      Date: 5-28-08

Approved by: \_\_\_Christine Horn                      Title: Laboratory Director                      Date: 5-29-08

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require a revision to this SOP. Any deviations from this SOP require prior authorization from the department Coordinator/Manager and the QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

Amendment	Pages	Summary of Changes	Date	Initials Coordinator, L D, QAO
#1	_____	_____	___/___/___	_____
#2	_____	_____	___/___/___	_____
#3	_____	_____	___/___/___	_____
#4	_____	_____	___/___/___	_____
#5	_____	_____	___/___/___	_____

**Nitrate + Nitrite**  
**EPA Method 353.2 / SM 4500NO3-F**

**1. Scope and Application**

- 1.1 This method pertains to the determination of nitrite singly, or nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes. The applicable range of this method is 0.05 to 10.0 mg/L nitrate-nitrite nitrogen. The range may be extended with sample dilution.

**2. Summary of Method**

- 2.1 Nitrate ( $\text{NO}_3^-$ ) is reduced quantitatively to nitrite ( $\text{NO}_2^-$ ) in the presence of cadmium (Cd). The nitrate in the sample is reduced to nitrite by passing through a glass column filled with cadmium granules. The nitrite produced is mixed with a sulfanilamide solution and an N-(1-naphthyl)-ethylenediamine dihydrochloride (NED) solution to form a highly colored azo dye which may be measured colorimetrically at 540nm and quantitated against a standard curve. The method is applicable between 0.05-2.00 mg/L.

**3. Definitions**

- 3.1 Azo Dye – any of a broad series of synthetic dyes that have  $-\text{N}=\text{N}-$  as a chromophore group. They are produced from amino compounds by diazotization and coupling.
- 3.2 Chromophore group – a chemical grouping that when present in an aromatic compound (the chromogen), gives color to the compound by causing a displacement of, or appearance of, absorbent bands in the visible spectrum.
- 3.3 Diazotization - the reaction of a primary aromatic amine with nitrous acid in the presence of excess mineral acid to produce a diazo ( $-\text{N}=\text{N}-$ ) compound.
- 3.4 Colorimetrically – a method of analytically determining minute quantities of substances in solution based on color intensity.

**4. Interferences**

- 4.1 Suspended matter will restrict flow and should be filtered out prior to analysis.
- 4.2 High levels of metals reduce column efficiency. They should be removed by adding EDTA to the sample.

- 4.3 Oil and Grease will coat the cadmium and should be removed using an organic solvent.
- 4.4 Residual chlorine should be removed by using sodium thiosulfate.

## 5. Safety and Precautions

- 5.1 Prior to performing this analysis, review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing and safety glasses should be worn when handling samples or reagents.
- 5.2 Maintain a clean and uncluttered workspace. Return all chemicals, reagents, and resultant waste to their designated storage area and at the completion of the test.
- 5.3 Due to the cadmium, the waste is considered to be hazardous and should be disposed of appropriately.

## 6. Equipment and Supplies

- 6.1 Automated Cd reduction analyzer.
- 6.2 pH meter
- 6.3 Beakers and funnels
- 6.4 Whatman No. 40 filter paper or equivalent.

## 7. Reagents and Standards

- 7.1 Cadmium filled glass column. Cadmium granules, 40-60 mesh washed in 6N HCl, rinsed with DI, and stirred in a 2% copper sulfate solution. Drain and repeat copper sulfate treatment until a brown precipitate forms and the solution remains blue. Rinse with copious amounts of water until all precipitate is gone. Immediately fill glass column and fill with buffer solution. Store column filled with buffer until use.
- 7.2 Stock nitrate solutions (100mg/L) purchased from supplier.
- 7.3 Ammonium chloride, EDTA buffer solution - Dissolve 25 g ammonium chloride in + 800mL DI water. Adjust the pH to 8.2 with the ammonia solution (10% NH<sub>4</sub>OH). Fill up to 1 Liter, add the Brij 35 and mix well.

- 7.4 NED color reagent - Dilute 150 mL (85% H<sub>3</sub>PO<sub>4</sub>) o-phosphoric acid carefully in approx. 800 mL DI water. Hereafter 10 g sulphanilamide and 0.5g alpha-naphthylethylenediamine dihydrochloride are added and dissolved. Fill up to 1 Liter and mix well.
  - 7.5 10N NaOH
  - 7.6 1:10 bleach solution
- 8. Sample preservation and Storage**
- 8.1 Cool to 4°C, pH < 2.
  - 8.2 Analyze samples within 28 days.
- 9. QC Requirements**
- 9.1 The following QC samples are prepared and analyzed with each batch of 20 samples or less.
    - 9.1.1 One Method Blank must be  $\leq$  RL.
    - 9.1.2 One LCS must be within control limits (90-110% recovery)
    - 9.1.3 One MS must be within control limits (80-120% recovery)
    - 9.1.4 One MSD (same as MS)
  - 9.2 Calibration Verification Standard (ICV), from a source different than that of the calibration standards must be acceptable before starting the sample analysis. A continuing calibration verification (CCV) at a mid-curve concentration and a continuing blank (CCB), must be analyzed after every 10 samples and end of run. The acceptance limits of the ICV and CCV are  $\pm$  10% of the true value.
  - 9.3 All data must be maintained and available for easy reference or inspection.
  - 9.4 If any QC fails outside of the acceptance limits, complete an Out of Control form and report to the departmental coordinator and consult with that individual and the QAO or Lab Director as to the appropriate corrective action.



## 10. Calibration and Standardization

- 10.1 A calibration curve must consist of at least five standards and a reagent blank.
- 10.2 The curve must exhibit correlation coefficient of no less than 0.995 assuring the linearity of the calibration curve.
  - 10.2.1 If this requirements is not met, the analyst must recalibrate the spectrophotometer.
  - 10.2.2 If recalibration does not yield a linear calibration curve, the analyst must remake the calibration standards.

## 11. Procedure

- 11.1 Turn on the chemistry unit and autosampler. Lock pump housing in place, push down reagent lines, put sample line and reagent lines into bleach solution and run system for 15-30 minutes. Remove lines and rinse with DI for 10 minutes. Note: Do not attach Cd column during clean-up.
- 11.2 Place lines into appropriate containers, attach Cd column and allow system to equilibrate.
- 11.3 Turn on computer and select SKALAR and then CH16SPPL to control the system. Turn on the chart recorder and attach appropriate wires to the recorder. Turn on the signal detector and when the signal is stable, adjust channel B so the reading on LCD is 150-250. Select ADC READINGS on the menu and adjust channel A so that channel 4 on screen reads 150-250.
- 11.4 Make nitrate standards with the following concentrations: 0.1, 0.5, 1.0, 1.5, and 2.0 mg/L and an LCS concentration of 1.0mg/L. Also make a 1.0mg/L Nitrite Standard.
- 11.5 Place two vials filled with the 2.0 mg/L standard into the autosampler and set the sample number at 2. Start the sample and wait until a signal is seen. Remove the cover from the signal recorder and adjust the signal to approximately 3800 when the sample reaches its peak. To adjust the signal, turn the #4 potentiostat; the signal increases by turning counterclockwise.
- 11.6 Go to TABLE SETUP and select edit table. Select 4NO3 and type in new table.
- 11.7 Load a few samples into the autosampler and begin run by selecting LOAD TABLE, (select NO3), LOAD PARAMETERS, (select 4 NO3), SAVE DATA (save corrected results), and finally under ANALYSIS, (select yes under start run, save by entering a file name and analyst initials). Note: make sure printer is on-line or the program will not function.
- 11.8 Dial in the number of samples into the autosampler and hit the start switch to begin run.
- 11.9 Go to DISPLAY ANALOG SIGNAL to see the signal on screen.

11.10 Additions to the schedule are allowed by editing the sample table and increasing the number of samples on the autosampler.

**12. Calculations**

12.1 Prepare appropriate standard curve or curves derived from processing NO<sub>2</sub> and/or NO<sub>3</sub> standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

**13. Pollution Prevention**

13.1 The samples analyzed in this method pose little threat to the environment when recycled and managed properly.

13.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

**14. Data Assessment and Acceptance Criteria for QC Measures**

14.1 See Internal QC Summary

**15. Corrective Actions for Out-of-Control Data**

15.1 See Internal Quality Control Summary

**16. Contingencies for Handling Out-of-Control or Unacceptable Data**

16.1 See SOP # Q-CORRECT-003

**17. Waste Management**

17.1 The waste from this analysis can be poured into general lab waste containers. \

17.2 The instrument waste contains Cadmium and must be separated into the appropriate wastes stream.

17.3 All waste is segregated according to type, and tested before disposal. The results are reviewed by the waste disposal coordinator. If they are greater than is allowed for general disposal, the waste is removed by a licensed hauler. If the results of testing are less than allowable limits for general disposal, the waste is poured into the sewer after neutralization.

17.4 For further information, see the Caltest Waste Management Coordinator.



18. **Method Performance**



18.1 None available at this time.

19. **References**

19.1 *Methods for Chemical Analysis of Water and Wastewater*, EPA 600/4-79-020. March 1983

19.2 *Standard Methods for Examination of Water and Wastewater*, 18th Edition, 1992.

**APPENDIX XXV, Caltest SOP W-PHOS-rev8. Ortho and Total Phosphate EPA 365.2/SM 4500P E  
(Revision 8, 10/04/09)**

CALTEST STANDARD OPERATING PROCEDURE

**ORTHO AND TOTAL PHOSPHATE**

**SM 4500P E**

Reviewed by: Arthur Lewis	Title: Wet Chemisrty Analyst	Date: 9/22/2009
Reviewed by: Michael Soon	Title: Wet Chemisrty Coordinator	Date: 10/1/2009
Reviewed by: Sonya Babcock	Title: Quality Assurance Officer	Date: 10/2/2009
Approved by: Patrick Ingram	Title: Laboratory Director	Date: 10/4/2009

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#2	_____	_____	____/____/____	_____
#3	_____	_____	____/____/____	_____
#4	_____	_____	____/____/____	_____
#5	_____	_____	____/____/____	_____

**A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision.**

**ORTHO AND TOTAL PHOSPHATE**  
SM4500P E

**1. SCOPE AND APPLICATION**

- 1.1 This method is applicable to the determination of phosphorus in drinking water, surface and saline water, and domestic and industrial wastes.
- 1.2 This method is applicable in the range of 0.05 to 1.0 mg/L P.

**2. METHOD SUMMARY**

- 2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorous to form an antimony-phospho-molybdate complex. The complex is reduced to an intensely blue colored complex by ascorbic acid. The color is proportional to the phosphorous concentration.

**3. DEFINITIONS**

- 3.1 Colorimetric Analysis – Analysis based on the law that intensity of color of certain solutions is proportional to the amount of substance in solution.
- 3.2 Total Phosphorus (P)--all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure. (Storet #00665)
- 3.3 Total Orthophosphate (P, ortho)--inorganic phosphorus  $[(PO_4)^{-3}]$  in the sample as measured by the direct colorimetric analysis procedure. (Storet #70507)

**4. INTERFERENCES**

- 4.1 Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate. Concentrations as low as 0.1 mg As/L interfere with phosphate determination. Hexavalent chromium and  $NO_2^-$  interfere to give results about 3% low at concentrations of 1 mg/L and 10 to 15% low at 10 mg/L. Sulfide and Silicate do not interfere at concentrations of 1.0 and 10 mg/L.

- 4.2 *Note: Correction for Turbidity or interfering color: Natural color of water generally does not interfere at a high wavelength used. For highly colored or turbid waters, prepare a blank by adding all reagents except ascorbic acid and antimony potassium tartrate to the sample. Subtract blank absorbance from absorbance of each sample.*

## 5. SAFETY AND PRECAUTIONS

- 5.1 Prior to performing this analysis review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing and safety glasses should be worn when handling samples or reagents.
- 5.2 Maintain a clean and uncluttered workspace. Return all chemicals and reagents to the designated storage area at the completion of the test.

## 6. APPARATUS:

- 6.1 Autoclave - capable of operating at 98 to 137 kPa.
- 6.2 Scoop, to hold the required amount of persulfate crystals.
- 6.3 Spectrophotometer, with photo tube for use at 880 nm, providing a light path of 1.0 cm or longer.
- 6.4 Acid-washed glassware

## 7. REAGENTS:

- 7.1 Persulfate Digestion:
- 7.1.1 Phenolphthalein indicator aqueous solution
- 7.1.2 11N Sulfuric acid solution: Slowly add 300 mL conc.  $H_2SO_4$  to 600 mL DI water and dilute to 1 L.
- 7.1.3 Sodium Hydroxide, NaOH, 10N.
- 7.1.4 Potassium persulfate,  $K_2S_2O_8$ , solid



7.2 Colorimetric: Ascorbic Acid Method

- 7.2.1 Sulfuric Acid,  $H_2SO_4$ , 5N: Dilute 70 mL conc  $H_2SO_4$  to 500mL DI water.
- 7.2.2 Antimony potassium tartrate solution: Dissolve 1.3715 g  $K(SbO)C_4H_4O_6 \cdot 1/2 H_2O$  in 400 mL DI water in a 500-mL volumetric flask and dilute to volume. Store in a glass stoppered bottle.
- 7.2.3 Ammonium molybdate solution: Dissolve 20 g  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  in 500 mL DI water. Store in glass stoppered bottle.
- 7.2.4 Ascorbic Acid, 0.1M: Dissolve 1.76 g ascorbic acid in 100 mL DI water. The solution is stable for about 1 week at 4 ° C.
- 7.2.5 Combined Reagent: Mix the above reagent in the following proportions for 100 mL of combined reagent: 50 mL 5N  $H_2SO_4$ , 5mL antimony potassium tartrate solution, 15 mL ammonium molybdate solution, and 30 mL ascorbic acid solution. Mix after addition of each reagent. Let all reagents reach room temperature before they are mixed and mix in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until turbidity disappears before proceeding. The reagent is stable for 4 hrs.
- 7.2.6 50 mg/L stock phosphate solution: Dissolve in DI water 219.7mg anhydrous  $KH_2PO_4$  and dilute to 1000mL; 1.00 mL = 50  $\mu$ g P; add 7 drops of toluene to preserve.

8. SAMPLE HANDLING AND PRESERVATION

- 8.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.
- 8.2 If analysis (total phosphate) cannot be performed the day of collection, the sample should be preserved by addition of 2 mL  $H_2SO_4$  per liter. Hold time is 28 days.
- 8.3 The holdtime for O- $PO_4$  analysis is 48 hours. Samples which are not analyzed immediately should be stored at just above freezing to 6°C.

## 9. QC REQUIREMENTS

- 9.1 The following QC samples are prepared and analyzed with each batch of 20 samples or less.
- One Method Blank must be  $\leq$  RL.
  - One LCS must be within control limits (90-110% recovery)
  - One LCSD (performed when insufficient sample for MS/MSD)
  - One MS must be within control limits (90-110% recovery)
  - One MSD (same as MS)
- 9.2 A calibration curve must consist of at least five standards and a reagent blank. The curve must exhibit correlation coefficient of no less than 0.995 assuring the linearity of the calibration curve. If these requirements are not met, the analyst must recalibrate the spectrophotometer. If recalibration does not yield a linear calibration curve, the analyst must remake the calibration standards.
- 9.3 Calibration Verification Standard (ICV), from a source different than that of the calibration standards must be acceptable before starting the sample analysis. A continuing calibration verification (CCV) at a mid-curve concentration and a continuing blank (CCB), must be analyzed after every 10 samples and end of run. The acceptance limits of the ICV and CCV are + 10% of the true value.
- 9.4 All data must be maintained and available for easy reference or inspection.
- 9.5 If any QC fails outside of the acceptance limits, complete an Out of Control form and report to the departmental coordinator and consult with that individual and the QAO or Lab Director as to the appropriate corrective action.
- 9.6 An MDL study needs to be performed every six months..

## 10. DIGESTION (for total phosphate analysis)

- 10.1 Persulfate Digestion Method: EPA 365.2
- To 50 mL Blank, LCS, MS, MSD, and samples:

- 10.1.1 Add 0.05 mL (1 drop) phenolphthalein indicator solution. If a red color develops, add 5N H<sub>2</sub>SO<sub>4</sub> solution dropwise to just discharge the color.
- 10.1.2 Add 1 mL 11N H<sub>2</sub>SO<sub>4</sub>
- 10.1.3 Add 0.5g (one scoop) solid K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.
- 10.1.4 Digest in autolave for 30 minutes.
- 10.1.5 Cool to room temperature.
- 10.1.6 Add 3 drops phenolphthalein solution.
- 10.1.7 Neutralize to a faint pink color with 10N NaOH.
- 10.1.8 Rinse digested sample into a 100 mL graduated cylinder (do not exceed 80-85mL while rinsing)
- 10.1.9 Bring up to 100 mL with DI water. Pour back into milk bottle. Mix well.

*Note: In some samples a precipitate may form. Do not filter! The precipitate redissolves under the acidic conditions of the colorimetric analysis.*

- 10.1.10 Go to colorimetric analysis.
- 10.2 Alternate digestion:
  - 10.2.1 Digest samples using hot plate in metals department. Use boiling chips to prevent bumping of sample.
  - 10.2.2 Bring volume down to 10 - 20 mL.
- 10.3 Prepare standard concentrations: 0.0, 0.01, 0.05, 0.1, 0.25, 0.5, 1.0 mg/L PO<sub>4</sub>-P.

## 11. COLORIMETRIC: Ascorbic Acid Method (for Ortho and Total Phosphate)

- 11.1 Into a 125 mL Erlenmeyer flask, measure 50 mL of sample or diluted sample. For O-PO<sub>4</sub> add phenolphthalein indicator to ensure neutrality of sample.

- 11.2 Leave remaining sample in milk bottle for further analysis (for Total Phosphate), if necessary.
- 11.3 Prepare combined reagent.
- 11.4 Add 2 drop 5N H<sub>2</sub>SO<sub>4</sub> solution to each 50 mL sample. Mix. If pink color is not discharged, add more drops (one at a time) until pink color is just discharged.
- 11.5 Add 8 mL combined reagent by Oxford macro-pipetter to each sample.
- 11.6 Between 10-30 minutes, measure the absorbance of samples and standards against a DI blank at 880 nm. For analyses requiring a standard reporting limit of 0.1 mg/L for Total Phosphate use a 1 cm disposable cuvet. For analyses requiring a low level reporting limit of 0.01 mg/L use a 2.5 cm glass cuvet.

## 12. CALCULATIONS

- 12.1 Calculate PO<sub>4</sub>-P concentration of samples against standard curve.
- 12.2 Multiply all (T - PO<sub>4</sub>) results by 2 to compensate for 2x dilution factor.

## 13.0 POLLUTION PREVENTION

- 13.1 The samples analyzed in this method pose little threat to the environment when recycled and managed properly.
- 13.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

## 14. DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

- 14.2 See Internal Quality Control Summary

## 15. CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

- 15.2 See Internal Quality Control Summary

**16. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA**

16.1 See SOP # Q-CORRECT

**17. WASTE MANAGEMENT**

17.1 The waste from this analysis can be poured into general lab waste containers.

17.2 All waste is segregated according to type, and tested before disposal. The results are reviewed by the waste disposal coordinator. If they are greater than is allowed for general disposal, the waste is removed by a licensed hauler (SOP Doc. #: X-HAZWASTE). If the results of testing are less than allowable limits for general disposal, the waste is poured into the sewer after neutralization (SOP Doc. #: X-WASTENeut).

17.3 For further information see the Caltest Waste Management Coordinator.

**18. Method Performance**

18.1 See method performance Section 13 365.2 rev2 1993.

18.2 See Standard Methods 4500P.E.

**19. REFERENCES**

19.1 *Methods for Chemical Analysis of Water and Wastewater*, EPA 600/4-79-020. March 1983

19.2 *Standard Methods for Examination of Water and Wastewater*, 18th Edition, 1992.

19.3 *EPA Methods and Guidance for Analysis of Water*, June 1999

**APPENDIX XXVI, Caltest SOP W-TDS-rev8. Total Dissolved Solids (TDS) SM 2540C/EPA 160.1  
(Revision 8, 05/13/09)**

CALTEST STANDARD OPERATING PROCEDURE

**TOTAL DISSOLVED SOLIDS (TDS)**

**SM 2540C**

**EPA 160.1 Drinking water**

Reviewed by: Josephine Cayanan	Title: Wet Chemisrty Analyst	Date: 5/12/09
Reviewed by: Michael Soon	Title: Wet Chemisrty Coordinator	Date: 5/12/09
Reviewed by: Carmelita Oliveros	Title: Quality Assurance Officer	Date: 5/21/09
Approved by: Christine Horn	Title: Laboratory Director	Date: 5/13/09

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require a revision to this SOP. Any deviations from this SOP require prior authorization from the departmental Coordinator/Manager and the QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

Amendment	Pages	Summary of Changes	Date	Initials
				Coordinator, L D, QAO
#1	_____	_____	____/____/____	_____
#2	_____	_____	____/____/____	_____
#3	_____	_____	____/____/____	_____
#4	_____	_____	____/____/____	_____
#5	_____	_____	____/____/____	_____

A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision.

**Total Dissolved Solids (TDS)**  
**SM 2540C /EPA 160.1 Drinking Water**

**1. Scope and Application**

- 1.1 This method is applicable to drinking, surface, and saline waters, in addition to industrial wastes. The practical range of application for this method is 10 mg/L to 20,000 mg/L.

**2. Method Summary**

- 2.1 A well mixed sample is filtered through a standard glass fiber filter. In order to quantify the total dissolved solids in the sample, the filtrate is evaporated and dried to a constant weight at  $180^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . The increase in weight corresponds to the dissolved solids in the sample. Values are reported in mg/L.

**3. Definitions**

- 3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at  $180^{\circ}\text{C} \pm 2^{\circ}\text{C}$ .

**4. Interferences**

- 4.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
- 4.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at  $180^{\circ}\text{C} \pm 2^{\circ}\text{C}$  to insure that all the bicarbonate is converted to carbonate.
- 4.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.



**5. Safety & Precautions**

- 5.1 Prior to performing this analysis, review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing and safety glasses should be worn when handling samples or reagents.
- 5.2 Maintain a clean and uncluttered workspace. Return all chemicals, reagents, and resultant wastes to their designated storage area at the completion of the test.

**6. Equipment and Supplies**

- 6.1 125 mL glass or porcelain evaporating dishes or beakers.
- 6.2 Buchner funnel with adapter.
- 6.3 Whatman 934 AH glass fiber filter paper, 4.7 cm, without organic binder.
- 6.4 250 mL vacuum flask.
- 6.5 Oven, for operation at  $180^{\circ} \pm 2^{\circ}\text{C}$ .
- 6.6 Desiccator, with a desiccant containing a color indicator of moisture concentration. Desiccant chips must be blue. If the chips are pink, replace with new desiccant.
- 6.7 Analytical balance, capable of weighing 0.1 mg.

**7. Reagents and Standards**

- 7.1 NaCl, granular
- 7.2 Deionized reagent water.

**8. Sample Collection, Preservation, Shipment and Storage**

- 8.1 The holdtime for these samples is seven days.
- 8.2 Analyze as soon as possible. Preservation is not practical. Store at temperature not frozen to  $6^{\circ}\text{C}$ .

**9. Quality Control**

- 9.1 A deionized H<sub>2</sub>O blank must be run along with all TDS analysis. The weight of the blank may be either a positive or a negative number, however the value should not exceed 1.0 mg (0.0010 g).
- 9.2 Duplicate determinations should be analyzed and must have a relative percent difference of less than 20%.
- 9.3 External Standard (ERA Minerals Standards or equivalent) should be within acceptance limits. Generally, 500 mg/L (0.5 gm NaCl/1000 ml) is used as standard LCS.
- 9.4 All Quality control must be performed on each batch of 20 samples.

**10. Standardization and Calibration**

- 10.1 Preparation of the evaporating dish / beakers:
  - 10.1.1 Label clean evaporating dishes (include dishes for QC) / beakers.
  - 10.1.2 Bake for one hour at  $180^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . Reduce temp. of the oven to  $80^{\circ}\text{C}$  after removing the dried evaporating dishes/ beakers.
  - 10.1.3 Transfer dishes immediately into a desiccator and cool to room temperature before weighing, approximately for 90 minutes.
  - 10.1.4 Check balance calibration and document.
  - 10.1.5 Weigh the dishes/ beakers to a minimum reading of 0.1 mg and record the weight in grams.
  - 10.1.6 Using a vacuum flask, magnetic funnels and 934-AH Whatman filter paper, rinse filter paper with 3 successive 20 mL volumes of D.I. water. Continue suction to remove all traces of water. Discard the washings.

## 11. Procedure

### 11.1 Selection of sample size:

Choose sample volume to yield between 2.5 and 200 mg of dried residue. For samples with low TDS, use additional sample ( up to 1 liter is available), so that the 2.5mg minimum can be reached. If more than 10 minutes are required to complete the filtration, increase the filter size or decrease sample volume. When very low suspended solids are encountered (less than 10 mg/L), less dried residue may be collected; compensate by a high-sensitivity balance (0.002 mg).

### 11.2 Sample Analysis:

11.2.1 Shake sample container to mix well, or stir sample with a magnetic stirrer.

11.2.2 Measure sample in a 100 mL graduated cylinder on to a glass fiber filter with applied vacuum.

11.2.3 Wash with three successive 10 mL volumes of D.I. water. Allow complete drainage between washings and continue suction for about 3 minutes after filtration is complete.

11.2.4 Transfer total filtrate (with washings) to a weighed evaporating dish and dry overnight at 80°C. DO NOT allow the temperature of the oven to go above 80°C. The objective is to evaporate the water off, boiling of the water might lead to erroneously low results. Document the time in and the temperature in the oven logbook.

11.2.5 Once evaporation appears to be complete (i.e. no visible liquid), heat the dishes at 180°C for one hour. Document the time and the temperature in the oven logbook.

11.2.6 Place baked dishes in a desiccator to cool (approx. 90 min.), to room temperature. Document the time out the final temperature in the oven logbook

11.2.7 Weigh dishes and record the weight in the log book. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight loss is less than 4% of previous weight or 0.5 mg, whichever is less. Some samples will continue to lose weight. After five weighings, accept weight and footnote report.

11.2.8 Place dishes in the glassware area (*in TDS dirty container*) to be cleaned.

## 12. Calculations

$$\text{TDS (mg/L)} = \frac{(\text{WEIGHT}_{\text{final}} - \text{WEIGHT}_{\text{initial}}) * 1,000,000}{\text{Sample Volume}}$$

where: WEIGHT = mass of evaporating dish & sample/residue in grams  
Sample Volume = volume of original sample in mL

## 13.0 Pollution Prevention

13.1 The samples analyzed in this method pose little threat to the environment when recycled and managed properly.

13.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

## 14.0 Data Assessment and Acceptance Criteria for Quality Control Measures

14.1 See Internal Quality Control Summary

## 15.0 Corrective Actions for Out-of-Control Data

15.1 See Internal Quality Control Summary

## 16.0 Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 See SOP # Q-CORRECT

## 17.0 Waste Management

- 17.1 The waste from this analysis can be poured into general lab waste containers.
- 17.2 All waste is segregated according to type, and tested before disposal. The results are reviewed by the waste disposal coordinator. If they are greater than is allowed for general disposal, the waste is removed by a licensed hauler. If the results of testing are less than allowable limits for general disposal, the waste is poured into the sewer after neutralization.
- 17.3 For further information see the Caltest Waste Management Coordinator.

## 18. Method Performance

- 18.1 Not available at this time.

## 19. References

- 19.1 Methods for Chemical Analysis of Water and Wastes, EPA 160.1, March 1983.
- 19.2 Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition, method 2540C

**APPENDIX XXVII, Caltest SOP W-NH3-TKN-rev10. Analysis of Ammonia as N, Method 350.2 and Total Kjeldahl Nitrogen, Method 351.3 SM 4500C (Revision 10, 03/06/09)**

**CALTEST STANDARD OPERATING PROCEDURE**

**ANALYSIS OF AMMONIA AS N  
 AND TOTAL KJELDAHL NITROGEN  
 SM 4500C**

Reviewed by: Nancy Pacheco	Title: Analyst	Date: 2-23-09
Reviewed by: Michael Soon	Title: Wet Chemistry Coordinator	Date: 2-23-09
Reviewed by: Carmelita Oliveros	Title: Quality Assurance officer	Date: 3-6-09
Approved by: Christine Horn	Title: Laboratory Director	Date: 3-6-09

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require a revision to this SOP. Any deviations from this SOP require prior authorization from the departmental Coordinator/Manager and the QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

Amendment Pages	Summary of Changes	Date	Initials Coordinator, Lab Dir, QAO
#1 _____	_____	____/____/____	_____
#2 _____	_____	____/____/____	_____
#3 _____	_____	____/____/____	_____
#4 _____	_____	____/____/____	_____
#5 _____	_____	____/____/____	_____

**A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision.**

**Analysis of Ammonia as N  
and Total Kjeldahl Nitrogen  
SM 4500C**

**1. Scope and Application**

- 1.1 These two methods are applicable to drinking water, wastewater, surface water, fuels, and soils.

**2. Method Summary**

- 2.1 The two methods are similar in that the final analysis is done by automatic titration using the Tecator analyzer. Total Kjeldahl nitrogen, TKN, is first digested before analyzing for ammonia.

**3. Definitions**

- 3.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$ , under the conditions of digestion described below.
- 3.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion, as outlined below.

**4. Interferences**

- 4.1 Very oily samples may be hard to distill or may coat titration cell, use a lower volume.

**5. Safety and Precautions**

- 5.1 Prior to performing this analysis review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions.
- 5.2 Gloves, glasses, and lab coat must be worn during the analysis. For the digestion, make sure you work in a fume hood.
- 5.3 Maintain a clean and uncluttered workspace. Return all chemicals and reagents to the designated storage area at the completion of the test.



**6. Equipment and Supplies**

- 6.1 Tecator auto analyzer, Model 2400
- 6.2 FOSS 20 place Digester Block with Aspirated Fume Manifold
- 6.3 Tecator digestion tubes (250 mL)
- 6.4 Foss 2460 kjeltec Auto Sampler
- 6.5 Foss Scrubber

**7. Reagents and Standards**

- 7.1 Tecator water: 3.0 g anhydrous sodium sulfate diluted to 6 liters of reagent water.
- 7.2 11N Sodium Hydroxide
- 7.3 1:1 H<sub>2</sub>SO<sub>4</sub>
- 7.4 Receiving solution
  - 7.4.1 60 g Boric Acid
  - 7.4.2 60 mL Bromocresol Green (100mg/100mL) in methanol
  - 7.4.3 40 mL Methyl Red (100mL diluted to 100mL) in methanol
  - 7.4.4 Adjust the pH to light green color with 1N NaOH.
  - 7.4.5 Dilute to 6 liter with DI water.
- 7.6.2 7.5 Kjeldahl digestion pellets

**8. Sample Collection, Preservation, Shipment and Storage**

- 8.1 Sampling should be done as per Standard Methods. The samples should be analyzed within 48 hours of sampling or preserved with 10 mL of 1:1 H<sub>2</sub>SO<sub>4</sub>, which must be analyzed within 28 days.

**9. Quality Control**

- 9.1 The following QC samples are prepared and analyzed with each batch of 20 samples or less.

- 9.2 One Method Blank must be  $\leq$  RL
- 9.3 One LCS must be within control limits (90 - 110 % recovery)
- 9.4 One LCSD (performed when insufficient sample for MS/MSD)
- 9.5 One MS and one MSD must be within control limits (90 - 110% recovery)
- 9.6 All data must be maintained and available for easy reference or inspection.
- 9.7 If any QC fails outside of the acceptance limits, complete an Out of Control form and report to the departmental coordinator and consult with that individual and the QAO or Lab Director as to the appropriate corrective action.
- 9.8 An MDL study must be performed every six months.

## 10. Standardization and Calibration

- 10.1 This applies to TKN only. A 100 mL sample, or dilution thereof, is placed in the digestion tube. To this sample, add 10 mL of 1 + 1 H<sub>2</sub>SO<sub>4</sub> and one Kjeldahl digestion tablet. Add a few boiling chips and carefully place tubes into the preheated digestion block, using the tray as support and a guide. Allow the samples to boil until the steam turns to white smoke. At this point, place the fume manifold over the tubes and start the aspirator\*. Or use the automated digester and aspirator. Wait until all of the samples are clear. The black residue is carbon and must be completely digested to get true TKN.

*\*The aspirator unit should stay in the hood and the hose should not be disconnected (except for cleaning). The tubing should be situated such that fluid will not accumulate in the aspirator tubing.*

## 11. Procedure

- 11.1 Turn the power Tecator and Autosampler power on. Allow approximately 5 minutes to warmup.
- 11.2 After warmup, place a 250 mL tube filled with 100 mL of DI water in an autosampler rack. Load two additional tubes with 100 mL of DI water in the rack for ammonia and four additional tubes for TKN. Load the rack into the autosampler by pressing A, B, or C on the panel for the corresponding wing and hooking the rack on the screws. These tubes will be used for Tecator manual set-up and initial water blanks.
- 11.3 Press the "hand" key to enter manual options.
- 11.4 Press "Move" to wing A, B, or C, whichever wing the loaded rack is on.

- 11.5 Press "Move" tube 1, or whichever tube position the first loaded tube is in.
- 11.6 Press "Tube Up" to place the tube into the chamber.
- 11.7 Press "Add Receiver" to make sure receiver solution is pumped into the titration cell.
- 11.8 Press "Add Alkali" to make sure alkali solution is pumped into the tube.
- 11.9 Press "Empty Burette" to drain the acid burette, then press "Fill Burette" to refill the burette. This is done to purge the lines of air.
- 11.10 Press "Steam On" and allow the system to warm up for 3-4 minutes. Press the "Steam On" again to stop the steaming process.
- 11.11 Press "Tube Down" to place the tube back in the rack. The instrument is ready to use.
- 11.12 It is necessary to run DI blanks before starting an analytical batch. This is done by analyzing the tubes loaded in the rack with the manual set up tube. Press [←] and enter "yes" to delete the previous schedule. Press [→] and enter to register the new schedule. First, select the program: Kjeldahl 1 for ammonia and Kjeldahl 2 for TKN, which adds more alkali. Then select type of samples. Scroll to "Result" and select "Blank". For ammonia, register two blanks and for TKN register four blanks. To begin analysis on these registered tubes, press the analysis key and scroll to the wing in which the rack is loaded in and select the correct batch that was just registered for the warm-up tubes. Next to "Start", scroll to the correct batch and the correct tube position you wish to use. Then scroll down to "Start Analyse" and press [↵] to start. The result for the fourth tube for TKN set up should be recorded as DI blank.
- 11.13 Place 100mL of blank, standard, sample, or diluted sample into a tube or make sure to add 100mL of DI water to the digested TKN tubes. Place tubes into autosampler racks. Remove rack with the manual set up and initial warm up tubes from the autosampler when they are finished analyzing. Load the racks with the samples into the autosampler. For ammonia, the first tube in the first rack should be 100 mL of DI water; for TKN, the first tube should be the first digested blank. The second tube on ammonia and TKN should be ICV.
- 11.14 Register the samples. The first registration slot should be scheduled as "Blank". This will be recorded as the Instrument Blank and is used as a correction for the calculation of ammonia and TKN. Then enter the samples by selecting "Result" as mgN/l and change the volume to 100mL. Register the correct amount of samples since this programs the autosampler.
- 11.15 Press the analysis key and set up the registered batches on the corresponding wings. Select which batch and tube the autosampler should start with.

11.16 **BEFORE STARTING** the run, it is necessary to set up the computer to capture the data. Upload LIMS batch into the LimsLink Program. Set up the batch for either TKN or ammonia and change sample volume if any dilutions were made. Now start the run on the Tecator. The results should transfer over to the LimsLink program. Once the run is finished, the data can be uploaded to LIMS.

11.17 After the run is complete, empty the tubes into the appropriate waste containers. Empty the instrument waste and clean up the instrument. Always wipe down the sample push rod.

11.18 Record the results into the logbook and factor in dilutions.

11.19 After the run is complete, shut off the instrument, dump your waste into the appropriate containers, and the titration cell with DI water.

## 12. Calculations

12.1 The calculations are done by the instrument except for dilutions, which are done in LimsLink.

## 13. Pollution Prevention

13.1 The samples analyzed in this method pose little threat to the environment when recycled and managed properly.

13.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

## 14. Data Assessment and Acceptance Criteria for Quality Control Measures

14.1 See Internal Quality Control Summary

## 15. Corrective Actions for Out-of-Control Data

15.2 See Internal Quality Control Summary

## 16. Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 See SOP # Q-CORRECT

## 17. Waste Management

17.1 All waste is general waste except for TKN sample in the tubes. These contain high Selenium and must be disposed of as heavy metals.

17.2 All waste is segregated according to type, and tested before disposal. The results are reviewed by the waste disposal coordinator. If they are greater than is allowed for general disposal, the waste is removed by a licensed hauler. If the results of testing are less than allowable limits for general disposal, the waste is poured into the sewer after neutralization.

17.2 For further information see the Caltest Waste Management Coordinator.

**18. Method Performance**

18.1 See *Standard Methods for Examination of Water and Wastewater*, 20th Edition, 1998, method 2540C, section 5.

**19. References**

19.1 *Methods for Chemical Analysis of Water and Wastewater*, EPA 600/4-79-020. March 1983

19.2 *Standard Methods for Examination of Water and Wastewater*, 20th Edition, 1998.

19.3 *EPA Methods and Guidance for Analysis of Water*, June 1999, Method 351.3

19.4 Tecator Operating Manual

**APPENDIX XXVIII, Caltest SOP W-TOC/DOC-rev10. Total and Dissolved Organic Carbon (TOC and DOC) EPA Method 415.1/SM5310B/9060 (Revision 10, 04/29/09)**

CALTEST STANDARD OPERATING PROCEDURE <b>TOTAL and DISSOLVED ORGANIC CARBON</b> <b>(TOC and DOC)</b> <b>SM5310B/9060</b>
--

Reviewed by: Arthur Lewis	Title: Wet Chemistry Analyst	Date: 4-29-09
Reviewed by: Michael Soon	Title: Wet Chemistry Coordinator	Date: 4-29-09
Reviewed by: Carmelita Oliveros	Title: Quality Assurance Officer	Date: 4-29-09
Approved by: Christine Horn	Title: Laboratory Director	Date: 4-29-09

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require a revision to this SOP. Any deviations from this SOP require prior authorization from the departmental Coordinator/Manager and the QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

Amendment Pages	Summary of Changes	Date	Initials Coord., L D, QAO
#1 _____	_____	____/____/____	_____
#2 _____	_____	____/____/____	_____
#3 _____	_____	____/____/____	_____
#4 _____	_____	____/____/____	_____
#5 _____	_____	____/____/____	_____

A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision.

## TOTAL and DISSOLVED ORGANIC CARBON (TOC and DOC)

### 1.0 Scope and Application

- 1.1 This method covers the determination of total organic carbon (TOC) and dissolved organic carbon (DOC) in drinking water and other waters which contain carbonaceous matter that is soluble, or matter which has a particle size of 0.2mm or less. The applicable range for the instrument is 0.5 mg/L to 200 mg/L. For higher concentrations, analyze a diluted sample.
- 1.2 A preserved sample contained in a 40 mL VOA vial is placed into an autosampler, Shimadzu TOC CSH. The TOC analyzer is a Shimadzu TOC CSH. The sample is sparged in acid and injected onto a furnace containing a platinum catalyst. The sample is combusted in an oxygen rich environment to form carbon dioxide which is carried to the non-dispersive infra-red, (NDIR), detector. This produces an electrical output (or peak) that is integrated and scaled by the numeric processor and displayed.
- 1.3 Dissolved Organic Carbon

An unpreserved sample is filtered through a 0.45  $\mu\text{m}$  filter at the time of collection and the filtrate acidified with sulfuric or hydrochloric acid to a pH of  $<2$ . If it is not possible to filter the sample in the field, then it must be filtered as soon as possible after arrival at the laboratory. Then follow the order in section 1.2.

### 2.0 Summary of Method

- 2.1 Inorganic and organic carbon in a sample is converted to carbon dioxide ( $\text{CO}_2$ ) by catalytic combustion at  $680^\circ\text{C}$  in an oxygen rich environment. The  $\text{CO}_2$  formed can be measured directly by an infrared detector. The amount of  $\text{CO}_2$  or  $\text{CH}_4$  is directly proportional to the concentration of carbonaceous material in the sample.

### 3.0 Definitions

- 3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
  - A) soluble, nonvolatile organic carbon; for instance, natural sugars.
  - B) soluble, volatile organic carbon; for instance, mercaptans.
  - C) insoluble, partially volatile carbon; for instance, oils.
  - D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.



E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.

- 3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

#### 4. Interferences

- 4.1 Make sure all glassware, reagents, and water are clean and of the highest purity.
- 4.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.
- 4.2.1 A low result will occur if large carbon-containing particles fail to enter the needle.
- 4.3 Samples with halogenated functionality, ozone, or other species may interfere with the infrared detector.
- 4.4 Make sure the NDIR detector is free of water by periodically replacing the permeation drying tube.

#### 5. Safety and Precautions

- 5.1 Prior to performing this analysis, review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing and safety glasses should be worn when handling samples or reagents.
- 5.2 Maintain a clean and uncluttered workspace. Return all chemicals, reagents, and resultant wastes to their designated storage area at the completion of the test.

#### 6. Equipment and Supplies

- 6.1 Shimadzu TOC-Vcsh Analyzer
- 6.2 Shimadzu 68 place autosampler model ASI-V
- 6.3 40 mL VOA vials

- 6.4 45 µm filter syringe with filter attachment.
- 6.5 Various volumetric flasks, class A, for dilutions
- 7. Reagents and Standards**
  - 7.1 Carbon-free DI water
  - 7.2 TOC standards diluted from 1000 mg/L standard of potassium hydrogen phthalate (this solution is usually purchased).
  - 7.3 25% Phosphoric Acid.
  - 7.4 Hydrocarbon free air
  - 7.5 2N Hydrochloric Acid
- 8. Sample Collection, Preservation, Shipment and Storage**
  - 8.1 Samples should be sampled in duplicate and stored in Teflon sealed 40 mL VOA vials with no headspace. Alternatively, larger sealed glass containers may be used.
  - 8.2 If samples cannot be analyzed within 2 hours from the time of sampling, the sample should be acidified ( $\text{pH} \leq 2$ ) with  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  and stored at  $4^\circ\text{C}$ . The preserved sample must be analyzed within 28 days.  $\text{HCl}$  is the preferred acid for this instrument.
- 9. Quality Control**
  - 9.1 A blank, LCS, will be run in each batch of 20 samples or less. If analyzing DOC's, a filter blank must also be analyzed.
  - 9.2 The blank consists of carbon free DI water.
  - 9.3 The LCS is prepared from the same solution in which the calibration curve is made.
  - 9.4 QC Samples.
    - 9.4.1 Run one blank per batch.
    - 9.4.2 Run CCV every 10 samples.
    - 9.4.3 Run one spike and spike duplicate sample for every 10 samples.
  - 9.5 A 10 mg/L spike solution and sample value is prepared in the following manner: 1 mL of a 1000 mg/L TOC standard is diluted to 100 mL with sample or diluted sample in a volumetric flask. A CCV is run every ten samples and an ICV every 20 samples.

## 10. System Startup

- 10.1 Turn on hydrocarbon free air tank, set to 60 psi.
- 10.2 Turn on the analyzer and autosampler. Allow the system to startup for 2 minutes.
- 10.3 Turn on the computer. Click on TOC software, connect to instrument.
- 10.4 Wait for the system to reach 680°C. Open the "background monitor" to check the system status.
- 10.5 Wait for the baseline to stabilize, at least 1 hour. The "background monitor" should show all green checks. If any of the indicators are red, address the problem, and wait for the system to stabilize.

## 11. Procedure

- 11.1 Remove samples from the refrigerator. Choose a sample with extra volume to perform QC. Run an MS/MSD for every 10 samples.
- 11.2 Creating a curve:
  - 11.2.1 Open the "Sample Table", select 'Calibration Curve'.
  - 11.2.2 Make the following selections:
    - Page 1: <enter>
    - Page 2: 'Edit calibration curves manually
    - Page 3: Select NPOC, clear default lines, select linear regression, assign a file name. Leave checked boxes unchecked.
    - Note: you need to create two curves monthly, (a low and a high range), or when conditions change. Use the following format DDMMYYcurve10 and DDMMYYcurve200 as names.
    - Page 4: Units – mg/L, injections 2of3, washes 2, SD and CV max 5%
    - Page 5: Create curve, curve 10 – 0.0, 0.5, 1.0, 2.0, 5.0, and 10.0. Curve 200 – 10.01, 20.0, 50.0, 100.0, and 200.0. **SELECT 100uL** as an injection volume.
    - Page 6: Select 'Correlation Coefficient Check' – 1<sup>st</sup> time – Repeat, 2<sup>nd</sup> time – Stop, Lower limit – 0.995.
    - Page 7: <enter>
    - Page 8: Do not enable history log, just <enter>.
- 11.3 Creating a Method:
  - 11.3.1 Page 1: <enter>
  - 11.3.2 Page 2: Select NPOC, clear default lines, assign a file name. Use format DDMMYYmethod

- 11.3.3 Page 3: Select Curve 10 in box 1 created above, Curve 200 in box 2 created above.
- 11.3.4 Page 4: <enter>
- 11.3.5 Page 5: <enter>
- 11.3.6 Page 6: Leave box unchecked, <enter>.
- 11.3.7 Page 7: <enter>
- 11.4 Creating a Schedule:
  - 11.4.1 Click 'Sample Run'
  - 11.4.2 Save schedule: use format DDMMYY, a blank table will appear.
  - 11.4.3 Select Autogenerate under the Insert toolbar.
  - 11.4.4 Select method you just created
  - 11.4.5 Select 2 vials starting on vial 1, <enter> -these are the initial blanks
  - 11.4.6 For vial 3, select calibration curve, (curve10), vials 1 starting with vial 3.
  - 11.4.7 For vial 4, select calibration curve, (curve 200), vials 1 starting with vial 4.
  - 11.4.8 For vial 5 on select method and vials needed for the batch starting with vial 5.  
Make sure to account for all QC when planning the number of vials.
  - 11.4.9 For the rest of the pages, just <enter>. At the end another window will come up showing the autosampler tray. All vials should be blue. If not, fix the position number at this time in the vial field.
  - 11.4.10 Omit the calibration curve for subsequent runs until another curve is required.
  - 11.4.11 Once the table is created, save it, and now you can edit the sample information in the table. Save and print the table after editing.
  - 11.4.12 Remove the autosampler tray, verify that the samples are preserved, and load the tray according to the schedule.
  - 11.4.13 Replace the tray and check the 'Background monitor' to verify that the system is ready to run. Check that all liquid levels are sufficient for the run, the gas is at least 500 psi, and check the waste drum.
- 11.5 For Method 9060
  - 11.5.1 Homogenize the sample in a blender.
  - 11.5.2 Lower the pH of the sample to 2.
  - 11.5.3 Run quadruplicate analysis.
  - 11.5.4 Report both average and the range.
- 11.6 Starting The Run
  - 11.6.1 Click the lightening bolt on the top toolbar to connect to the system.
  - 11.6.2 The stoplight should be activated – click this to start the run.
  - 11.6.3 The standby window will come up. Select 'shutdown instrument'
  - 11.6.4 The run will start.

## 12. Calculations

- 12.1 Area counts are plotted against concentration to produce a linear curve. Sample, standards area counts are then compared to the curve to produce concentrations. The curve coefficient must be 0.995 or greater.
  - 12.2 If dilutions are needed, then the analyst will need to apply the correct dilution factor to the concentration read-out. Any results above 200 mg/L need dilution and rerun. Any dilution factors need to be manually calculated.
  - 12.3 When the run is finished, click on the run title and then right click print tables and print sample report. Combine data in a folder and submit for approval.
- 13. Pollution Prevention**
- 13.1 The samples analyzed in this method pose little threat to the environment when recycled and managed properly.
  - 13.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.
- 14.0 Data Assessment and Acceptance Criteria for QC Measures**
- 14.1 See Internal QC Summary
- 15.0 Corrective Actions for Out-of-Control Data**
- 15.1 See Internal Quality Control Summary
- 16.0 Contingencies for Handling Out-of-Control or Unacceptable Data**
- 16.1 See SOP # Q-CORRECT
- 17.0 Waste Management**
- 17.1 All waste is segregated as to type, and put into the appropriate waste container.
  - 17.2 All waste is tested prior to disposal, and the results are reviewed by the waste disposal coordinator. If the results are found to be greater than is allowed for general disposal, the waste is removed by a licensed hauler. This metals waste is disposed of as corrosive liquid waste by an approved hazardous waste vendor. If the results of testing are found to be less than allowable limits for general disposal, the waste is poured into the sewer after neutralization.
  - 17.3 For further information see the Caltest Waste Management Coordinator.

**18. Method Performance**

18.1 See EPA Methods and Guidance for Analysis of Water, June 1999.  
Method 415.1, Section 9.

18.2 Standard Methods for the Examination of Water and Wastewater. 18<sup>th</sup> Edition Section 6.

**19. References**

19.1 Methods for Chemical Analysis of Water and Wastes, EPA 415.1, 1983.

19.2 O/I Analytical instrument manuals.

19.3 EPA Methods and Guidance for Analysis of Water, June 1999.  
Method 415.1.

19.4 Standard Methods for the Examination of Water and Wastewater. 18<sup>th</sup> Edition

19.5 SW-846 Method 9060 Revision 0, September 1996

**APPENDIX XXIX, Caltest SOP W-TURB-rev7. Turbidity EPA 180.1/SM 2130B (Revision 7, 03/18/09)**

CALTEST STANDARD OPERATING PROCEDURE

**TURBIDITY**

**EPA 180.1 / SM 2130B**

Reviewed by	Nancy Pacheco	Title:Wet Chemisrty Analyst	Date:	3-18-09
Reviewed by:	Michael Soon	Title:Wet Chemisrty Coordinator	Date:	3-18-09
Reviewed by:	Carmelita Oliveros	Title: Quality Assurance Officer	Date:	3-18-09
Approved by:	Christine Horn	Title: Laboratory Director	Date:	3-18-09

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require an amendment to this SOP with the approval of the department Coordinator, Laboratory Director(LD) and QAO. All amendments must be identified below, and attached to this document to be considered valid changes. Any deviations from this SOP require prior authorization from the department Coordinator, Lab. Director and QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

Amendment	Pages	Summary of Changes	Date	Initials Coordinator, L D, QAO
#1	_____	_____	___/___/___	_____
#2	_____	_____	___/___/___	_____
#3	_____	_____	___/___/___	_____
#4	_____	_____	___/___/___	_____
#5	_____	_____	___/___/___	_____

A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision.



**TURBIDITY**  
**EPA 180.1 / SM2130B**

**1. Scope and Application:**

- 1.1 This method is applicable to drinking, surface, and saline waters in the range of turbidity from 0 to 40 nephelometric turbidity units (NTU). Turbidity in water is caused by suspended matter, such as clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, plankton and other microscopic organisms. Higher values may be obtained with dilution to the sample.

**2. Method Summary**

- 2.1 The Nephelometric method for turbidity is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity.

**3. Definitions**

- 3.1 **Calibration Blank (CB)** -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.
- 3.2 **Instrument Performance Check Solution (IPC)** -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.
- 3.3 **Method Blank (MB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 3.4 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

- 3.5 **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.
  - 3.6 **Primary Calibration Standard (PCAL)** -- A suspension prepared from the primary dilution stock standard suspension. The PCAL suspensions are used to calibrate the instrument response with respect to analyte concentration.
  - 3.7 **Laboratory Control Sample (LCS)** -- A solution of the method analyte of known concentrations that is used to fortify an aliquot of LRB matrix. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance.
  - 3.8 **Secondary Calibration Standards (SCAL)** -- Commercially prepared, stabilized sealed liquid or gel turbidity standards calibrated against properly prepared and diluted formazin or styrene divinylbenzene polymers.
  - 3.9 **Stock Standard Suspension (SSS)** -- A concentrated suspension containing the analyte prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source. Stock standard suspension is used to prepare calibration suspensions and other needed suspensions.
4. **Interferences**
- 4.1 The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles will affect results in a positive manner.
  - 4.2 The presence of true color, that is the color of water that is due to dissolved substances which absorb light, will cause turbidities to be low.
5. **Safety and Precautions:**
- 5.1 Prior to performing this analysis, review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing and safety glasses should be worn when handling samples or reagents.
  - 5.2 Maintain a clean and uncluttered work space. Return all chemicals, reagents and resultant wastes to their designated storage area at the completion of the test.
6. **Apparatus**
- 6.1 Turbidimeter, VWR Scientific
  - 6.2 Sample tube
  - 6.3 Graduated cylinders (needed for dilutions).

**7. Reagents:**

7.1 Turbidity free water (D.I.)

7.2 Stock Formazin turbidity suspensions: (prepare monthly)

7.2.1 Solution 1:

Dissolve 1.00g hydrazine sulfate  $(\text{NH}_2)_2\text{H}_2\text{SO}_4$  in D.I. water and dilute to 100mLs.

7.2.2 Solution 2:

Dissolve 10.00g hexamethylenetetramine in D.I. and dilute to 100mLs.

7.2.3 In a 100 mL volumetric flask, mix 5.0 mL of solution 1 with 5.0 mL of solution 2.

Allow to stand 24 hours at  $25 \pm 0.5^\circ\text{C}$ , then dilute to 100 mL (400NTU)

7.3 Standard Formazin Suspension: (prepare weekly)

7.3.1 Dilute 2.5, 1.0, 0.1mls stock suspension to 100 mLs. The turbidity of this suspension is defined as 10, 4.0, 0.4 NTU.

7.4 Purchased Standards are also available-we mainly use 0.4, 4.0, 10 NTU Standards. Other concentrations are used depending on availability.

**8. Sample Handling and Preservation**

8.1 Preservation of sample is not practical; analysis should begin as soon as possible. Refrigeration of the sample at  $4^\circ\text{C}$  minimizes bacterial decomposition. Samples must be analyzed within 48 hours.

**9. Quality Control**

9.1 Run a set of duplicates every batch, not to exceed 20 samples. No spike is required.

9.2 Run one LCS per batch of 20 samples or less. LCS recovery should be 90-110%. If LCS recovery is outside control limits, check reagents and calculations.

**10. Calibration and Standardization**

10.1 Allow all samples and standards to come to room temperature.

10.2 Adjust meter to zero with DI water using the instrument offset adjust screw, on the side panel. Calibrate the 20 scale with 10NTU, adjust with a screw driver on the side panel.

10.3 For 20 scale, measure 4.0 NTU. A secondary source of 0.4 NTU is also measured. The recovery should be 90-110% and every 10 samples.

10.4 Fill sample to the line when measuring samples and standards.

## 11. Procedure

11.1 Following the calibration, read 4.0 and 0.4 NTU on 20 scale.

11.2 Run the LCS prior to analysis (Standard Formazin suspension). Use one concentration for each range available on the instrument.

11.3 Run the sample:

11.3.1 For samples with turbidity less than the dynamic range of the instrument, thoroughly invert the sample. Wait until air bubbles disappear, then pour the sample into the sample tube. Wipe the tube and read turbidity on appropriate pre-calibrated scale.

11.3.2 For samples with turbidity greater than the dynamic range of the instrument, invert the sample thoroughly. Pipet a Known volume into a graduated cylinder and dilute to volume with turbidity-free water. Mix well and pour into the sample tube. Wipe the tube and read the turbidity. Record the turbidity and dilution in the logbook.

## 12. Calculations

12.1 Not applicable

## 13. Pollution Prevention

13.1 The samples analyzed in this method pose little threat to the environment when recycled and managed properly.

13.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

## 14. Data Assessment and Acceptance Criteria for QC Measures

14.1 See Internal QC Summary

## 15. Corrective Actions for Out-of-Control Data

15.1 See Internal Quality Control Summary

**16. Contingencies for Handling Out-of-Control or Unacceptable Data**

16.1 See SOP # Q-CORRECT

**17. Waste Management**

17.1 The waste from this analysis can be poured into general lab waste containers.

17.2 All waste is segregated according to type, and tested before disposal. The results are reviewed by the waste disposal coordinator. If they are greater than is allowed for general disposal, the waste is removed by a licensed hauler. If the results of testing are less than allowable limits for general disposal, the waste is poured into the sewer after neutralization.

17.3 For further information, see the Caltest Waste Management Coordinator.

**18. Method Performance**

18.1 Not available at this time.

**19. References:**

19.1 Methods for Chemical Analysis of Water and Wastewater, EPA 180.1, EPS 600/4-79-020, March 1983

19.2 Standard Methods for Examination of Water and Wastewater, 18th Edition, 1992

**APPENDIX XXX. Caltest SOP B-TSS-rev7. Caltest SOP Residue, Non-Filterable EPA  
160.2/SM2540D (Gravimetric, Dried at 103-105°C) (Revision 7, 05/05/09)**

CALTEST STANDARD OPERATING PROCEDURE

**RESIDUE, NON-FILTERABLE**  
**SM 2540D (Gravimetric, Dried at 103-105°C)**

Reviewed by: Andra Stoddard	Title: Analyst	Date: 5-4-09
Reviewed by: Michael Soon	Title: WetChem/Bio Coordinator	Date: 5-5-09
Reviewed by: Carmelita Oliveros	Title: Quality Assurance Officer	Date: 5-5-09
Approved by: Christine Horn	Title: Laboratory Director	Date: 5-5-09

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Amendment	Summary of Changes	Date	Initials
Pages			Coord., Lab Dir, QAO
#1 _____	_____	____/____/____	_____
#2 _____	_____	____/____/____	_____
#3 _____	_____	____/____/____	_____
#4 _____	_____	____/____/____	_____
#5 _____	_____	____/____/____	_____

A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision

**CALTEST ANALYTICAL LABORATORY**

**Residue, Non-Filterable**  
**SM 2540D (Gravimetric, Dried at 103-105°C)**

1. Scope and Application
  - 1.1 This method is applicable to industrial and domestic wastes, drinking, surface and saline waters.
  - 1.2 The practical range of the determination is 3 mg/L to 20,000 mg/L.
  - 1.3 A well mixed sample is filtered through a weighed glass fiber filter and the residue retained on the filter is dried to a constant weight at 103-105°C.
  - 1.4 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to a constant weight at 103-105°C.
2. Summary
  - 2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105°C.
  - 2.2 The filtrate from this method may be used for Residue, Filterable.
3. Definitions
  - 3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103-105°C.
4. Interferences
  - 4.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
  - 4.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter minimizes the potential interference



5. Safety

5.1 Prior to performing this analysis, review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing and safety glasses should be worn when handling samples or reagents.

5.2 Maintain a clean and uncluttered workspace. Return all chemicals, reagents, and resultant wastes to their designated storage area at the completion of the test.

6. Equipment and Supplies

6.1 Glass Microfiber Filters Whatman 934-AH 90 mm and 125mm (required for Anheuser-Busch only); or equivalent.

6.2 Buchner funnels, 70 mm, 100mm.

6.3 Filter Flasks, 1000 mL.

6.4 Drying oven, 103-105°C.

6.5 Desiccator.

6.6 Analytical balance, capable of weighing to 0.1 mg.

6.7 Aluminum pans, 70 mm., 100 mm

6.8 Wide bore pipets.

6.9 Graduated cylinders.

6.10 Forceps.

7. Reagents and Standards

Celite, Johns-Manville

8. Sample Handling and Preservation

8.1 Non-representative particulates such as leaves, sticks, insects, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is

not desired in the final result. Any alteration of sample due to nonrepresentative particulates should be appropriately documented in the Analytical Logbook.

- 8.2 Analysis should begin as soon as possible. Refrigeration or icing to just above freezing to 6°C, to minimize microbiological decomposition of solids, is required. Hold time is 7 days. Sample cannot be chemically preserved (i.e. with H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub>).

## 9. Quality Control

- 9.1 A blank must be done with each batch of 20 samples analyzed. Follow the same procedure in Section 11.3.

- 9.2 A standard must be done with each batch of 20 samples analyzed. Follow the same procedure as in Section 11.3. Use a 50mL volume of the 500 mg/L Celite Standard.

### 9.2.1 Preparation of Laboratory Control Standard 500mg/L:

Dry Celite for at least two hours at 120C. Place dried Celite in Desiccator and let cool for 15 to 20 minutes. Weigh 0.5g of dried Celite and transfer to 1000mL Volumetric flask. Bring the flask up to volume with 20°C DI water. Transfer to an amber liter for use and store at 4°C. The standard is good for one month.

- 9.3 A set of duplicates must be done daily or with each batch of 20 samples analyzed, whichever is more frequent. To analyze duplicates, choose a sample (Anheuser-Busch, if available) and follow the procedure in Section 11.3.

## 10. Calibration and Standardization

Not applicable

## 11. Procedure

- 11.1 Get samples out of the refrigerator. Set up analytical batch on the computer. Preparations of glass fiber filter:

Insert glass fiber filter into bottom of Buchner funnel with wrinkled surface up. While vacuum is applied, wash the filter with three successive 20mL volumes of reagent-grade water, allowing each washing to filter completely. Remove all traces of water from filter by continuing to apply vacuum after water has passed

**CALTEST ANALYTICAL LABORATORY**

through filter (3-4 minutes). Remove filter from Buchner funnel and place in marked aluminum pan. Handle filter and pan with forceps only from this point on. Dry in an oven at 103-105C for one hour. Place dried filters and pans in a desiccator for at least 15 minutes to balance temperature. Weigh filter and pan, and record weight. Repeat cycle of drying, desiccating, and weighing until a constant weight is obtained (or until weight change is less than 0.5mg) from previous weighing. Store in a desiccator until needed.

#### 11.2 Selection of sample volume:

Choose sample volume to yield between 5 and 200mg dried residue (i.e. AB 50mL, most clear effluent or pond water 5-200mL, most influents and cloudy industrial effluents 50 mL, and sludges 5-25mL). If more than 5 minutes are required to complete filtration, decrease sample volume by approximately half.

#### 11.3 Sample analysis:

Remove filter and pan from desiccator and insert filter into bottom of Buchner funnel. Seat filter in funnel with a small amount of reagent grade water. Mix sample thoroughly by inverting sample container vigorously 20 times. Immediately transfer predetermined sample volume selected in Section 11.2 to the filter using a graduated cylinder or wide bore pipet. After completing filtration, wash the graduated cylinder or wide bore pipet and filter three successive 20mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for 3-4 minutes. Carefully remove filter from Buchner funnel (using forceps), and place in aluminum pan. Dry for one hour at 103-105°C in oven. Cool in desiccator for at least 15 minutes to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight loss is less than 4% of previous weight or 0.5 mg, whichever is less. Some samples will continue to lose weight. After five weighings, accept weight and footnote report.

#### 11.4 Record date, analyst initials, time in & time out, lab number, client, pan I.D., all weight values, and any observations in the TSS logbook.

### 12. Calculations

#### 12.1 Calculate non-filterable residue as follows:

$$\text{Non-filterable residue, mg/L} = \frac{(A-B) \times 1000\text{mg/g} \times 1000 \text{ mL/L}}{\text{Sample Volume, mL}}$$

where:

A = weight of filter + dried sample residue + weigh dish, g

B = weight of filter + weigh dish, g

Detection limit: 3mg/L

13. Pollution Prevention
  - 13.1 There are no particular pollution prevention steps taken by the laboratory for this test. The pans that are weighed gravimetrically are re-used.
14. Data assessment and acceptance criteria for quality control measures
  - 14.1 The criteria is referenced in Caltest Internal QC Summary Manual.
15. Corrective actions for out of control data
  - 15.1 The criteria is referenced in Caltest Internal QC Summary Manual
16. Contingencies for handling out of control or unacceptable data
  - 16.1 The contingencies for handling out of control or unacceptable data is addressed in the Caltest SOP: Q-CORRECT.
17. Waste Management
  - 17.1 The filtrate is stored in non-hazardous waste jugs and is not disposed off until it has been analyzed and cleared by the waste coordinator. The pans are cleaned and re-used, and the filters are discarded to municipal disposal.
18. References
  - 18.1 Methods for Chemical Analysis of Water and Wastewater, EPA 600/4-79-020, March 1983.

**APPENDIX XXXI. Caltest SOP W-RESIDUE-rev7. TOTAL RESIDUE, SM 2540B / EPA METHOD 160.3, TOTAL VOLATILE RESIDUE, SM 2540 G / EPA METHOD 160.4 (Revision 7, 03/18/09)**

CALTEST STANDARD OPERATING PROCEDURE

**TOTAL RESIDUE, SM 2540B**

**TOTAL VOLATILE RESIDUE, SM 2540 G / EPA METHOD 160.4**

Reviewed by:	Nancy Pacheco	Title: Wet Chemisrty Anlyst	Date: 3-18-09
Reviewed by:	Michael Soon	Title: Wet Chemisrty Coordinator	Date: 3-18-09
Reviewed by:	Carmelita Oliveros	Title: Quality Assurance Officer	Date: 3-18-09
Approved by:	Christine Horn	Title: Laboratory Director	Date: 3-18-09

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require a revision to this SOP. Any deviations from this SOP require prior authorization from the department Coordinator/Manager and the QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

Amendment	Pages	Summary of Changes	Date	Initials Coordinator, LD, QAO
#1	_____	_____	___/___/___	_____
#2	_____	_____	___/___/___	_____
#3	_____	_____	___/___/___	_____
#4	_____	_____	___/___/___	_____
#5	_____	_____	___/___/___	_____

**A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision.**

**TOTAL RESIDUE, SM 2540 B (Gravimetric)**

**TOTAL VOLATILE RESIDUE, SM2540 B / EPA METHOD 160.4**

**1.0 Scope and Application**

- 1.1 This method is applicable to drinking surface waters, saline waters, domestic wastes, industrial wastes, solids and semisolid samples as river and lake sediments or other sludge cakes from vacuum filtration, centrifugation or other sludge dewatering processes.
- 1.2 The practical range of the determination is from 10 mg/L to 20,000 mg/L for aqueous waste and percentage levels for semisolid and solid type matrices.

**2.0 Method Summary**

- 2.1 A well mixed aliquot of the sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105°C.

**3.0 Definitions**

- 3.1 Gravimetric Analysis – a type of quantitative analysis involving precipitation of a compound that can be weighed and analyzed after drying.
- 3.2 Residue – the solid matter left after all liquid has been removed from a solution or sludge sample.
- 3.3 Volatility – the tendency of a solid or liquid material to pass into the vapor state at a given temperature.

**4.0 Interferences**

- 4.1 Non-representative particulars such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
- 4.2 Floating oil and grease, if present, should be included and dispersed by a blender device before aliquoting.

## 5.0 Safety and Precautions

- 5.1 Prior to performing this analysis, review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing and safety glasses should be worn when handling samples or reagents.
- 5.2 Maintain a clean and uncluttered workspace. Return all chemicals, reagents, and resultant wastes to their designated storage area at the completion of the test.
- 5.3 This method is used to analyze potentially hazardous samples. Care should be taken when handling all samples, standards and reagents.

## 6.0 Equipment and Supplies

- 6.1 Evaporating dishes or aluminum pans.
- 6.2 Drying oven capable of 103-105 °C
- 6.3 Calibrated analytical balance.
- 6.4 Desiccator with dry desiccant. Desiccant chips must be blue. If chips are pink replace with new desiccant.
- 6.5 Muffle furnace (550±50°C).

## 7.0 Reagents and Standards

- 7.1 NaCl – granular
- 7.2 Deionized reagent water



## 8.0 Sample Handling and Preservation

- 8.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigerate or ice from just above freezing to 6°C to minimize microbiological decomposition of solids and analyze within 7 days of sampling.

## 9.0 QC Requirements – Quality Control

For each sample batch of 20 or less, the following QC samples must be prepared and analyzed:

- 9.1 One method blank - an aliquot of uncontaminated matrix (using DI water) used to demonstrate that there is no source of contamination and that constant weight has been achieved.
- 9.2 One sample duplicate - A replicate aliquot of a sample used to demonstrate the precision of a method. The RPD should be  $\leq 20\%$ .

## 10.0 Calibration and Standardization

- 10.1 None other than the QC requirements.

## 11.0 Procedure

- 11.1 Get samples out of the refrigerator. Set up analytical batch on the computer (see Appendix 1).
- 11.2 For aqueous sample, heat the clean beaker or disposable aluminum dishes (*dish is mainly used, but if sample is low, use beaker*) to 103-105°C for one hour. If volatile residue is to be measured, heat vycor dishes or heat resistant equivalent dishes at 550 +/- 50° for one hour in a muffle furnace. Cool, desiccate, weigh and store in dessicator until ready for use.
- 11.3 Measure 100 mL sample (*for samples with low % solids*) or an aliquot of sample sufficient to contain a residue of at least 2.5mg for aqueous and 10 grams for solids.

- 11.4 Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness in a drying oven at least 98°C but no less than 80 °C for 12-18 hours to prevent boiling and splattering of sample.
- 11.5 Dry the evaporated sample for at least 1 hour at 103-105°C. Cool in a desiccator and weigh. Record results.
- 11.6 Reheat the sample for an additional hour at 103-105°C. Cool in a desiccator, weigh and record results. Weigh dishes and record the weight in the log book. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight loss is less than 4% of previous weight or 0.5 mg, whichever is less. If this criteria cannot be met by two successive measurements, additional drying must be performed. Some samples will continually lose weights. After five weighings, accept weight and footnote report.
- 11.7 If volatile solids analysis is requested, place sample in a muffle furnace for one hour at 250°C and one hour at 550°C. Cool in desiccator and weigh.

## 12.0 Calculation

- 12.1 Calculate total residue as follows:

$$\text{Total Residue mg/L or mg/kg} = \frac{(A - B) * 1000}{C}$$

Where A = mass of dried sample and dish in mg  
 B = mass of empty dish in mg  
 C = volume of sample in mL or mass in grams

$$\text{Total Residue(\%)} = \frac{(A - B) * 100}{(C - B)}$$

Where A = mass of dried sample and dish in grams, B = mass of empty dish in grams, and C = mass of sample in grams

- 12.2 Calculate volatile residue as follows:

- 12.2.1 Aqueous Samples:

$$\text{Volatile Residue (mg/L)} = \frac{(A - B) * 1000}{C}$$

Where A = mass of sample and dish dried at 550 °C  
 B = mass of sample and dish ignited at 550 °C  
 C = volume of sample initially used in mL

- 12.2.2 Solid or Semisolid Samples: (This result is expressed in terms of % relative to the total residue as determined in 12.1)

$$\text{Volatile Residue (\%)} = \frac{(A - B) * 100}{A}$$

Where A = mass of sample and dish dried at 550 °C\*  
B = mass of sample and dish ignited at 550 °C\*

\* the units for the mass measurements must be the same for both A and B

### 13.0 Pollution Prevention

- 13.1 The samples analyzed in this method pose little threat to the environment when recycled and managed properly.
- 13.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

### 14.0 Data Assessment and Acceptance Criteria for Quality Control Measures

- 14.1 See Internal Quality Control Summary

### 15.0 Corrective Actions for Out-of-Control Data

- 15.1 See Internal Quality Control Summary

### 16.0 Contingencies for Handling Out-of-Control or Unacceptable Data

- 16.1 See SOP # Q-CORRECT

### 17.0 Waste Management

- 17.1 The waste from this analysis can be poured into general lab waste containers.

- 17.2 All waste is segregated according to type, and tested before disposal. The results are reviewed by the waste disposal coordinator. If they are greater than is allowed for general disposal, the waste is removed by a licensed hauler. If the results of testing are less than allowable limits for general disposal, the waste is poured into the sewer after neutralization.

17.3 For further information see the Caltest Waste Management Coordinator.

## 18.0 Method Performance

- 18.1 None available at this time.

## 19.0 References

- 19.1 Standard Methods for Examination of Water and wastewater, 18th Edition, 1992.
- 19.2 Test Methods for Chemical Analysis of Water and Wastewater, EPA 600/4-79-020, March 1983.
- 19.3 EPA Methods and Guidance for Analysis of Water, June 1999.

## APPENDIX 1

### GRAVIMETRIC LOGBOOK PROCEDURE

1. Create a batch in the Horizon system.
  - 1.1 Batch may be created by choosing a Blank and an LCS. Note the Batch and Queue.
2. Open Microsoft Excel.
3. Open a new file using the top toolbar under the file tab.
4. Choose appropriate logbook under templates
  - 4.1 Moisture for % M, % S (Results in %)
  - 4.2 Solids for TSS, TDS, TS ( Results in mg/L)
  - 4.3 OG for Oil and Grease.
  - 4.4 Vol Solids for VSS and VS
5. Enter LOGIN data
  - 5.1 Initials
  - 5.2 Password
  - 5.3 Queue
  - 5.4 Batch
6. Fill out sample ID#, Pan/Dish ID #, Tare wt. (printed from balance), sample volum if applicable.
7. Perform analysis, print weights from balance.
8. Once the entire sheet is finished, go back to Horizon batch and enter samples in the order they appear on the excel logbook. The Blank, LCS, LCSD, and Duplicate (R1, R2) will be assigned Horizon QC numbers.
9. Enter the numbers into the EXCEL Logbook.
10. Refresh Batch. This will prompt you for your password again. Every thing should turn blue. If not, check that you have all of the sample ID's are correct. Fix and refresh again.
11. Once the batch is complete, post batch.

**APPENDIX XXXII. Caltest SOP O-Pyrethroidsncirev1. Caltest SOP Pyrethroids By GCMS Selective Ion Monitoring (Revision 1, 07/2009)**

## CALTEST STANDARD OPERATING PROCEDURE

### PYRETHROIDS BY NCI-GCMS- SIM/MICRO ECD

Reviewed by: Rick Heines	Title: Organics Coordinator	Date: 7/2009
Reviewed by: Sonya Babcock	Title: Quality Assurance Officer	Date: 7/2009
Approved by: Patrick Ingram	Title: Laboratory Director	Date: 7/2009

This SOP outlines the exact procedure to be followed by all staff of Caltest Laboratory who are performing the indicated method. It is the responsibility of any individual performing the procedure to follow these instructions outlined in this document. Any significant modifications to this method require an amendment to this SOP with the approval of the department Coordinator, Laboratory Director (LD) and QAO. All amendments must be identified below, and attached to this document to be considered valid changes. Any deviations from this SOP require prior authorization from the department Coordinator, Lab. Director and QAO. In addition, all deviations from the written procedure require complete documentation in the appropriate logbook.

Amendment	Pages	Summary of Change	Date	Initials
#1	_____	_____	_____	____/____/____
#2	_____	_____	_____	____/____/____
#3	_____	_____	_____	____/____/____
#4	_____	_____	_____	____/____/____
#5	_____	_____	_____	____/____/____

A maximum of 5 amendments can be added to each SOP, at which point the entire SOP warrants revision.

## PYRETHROIDS BY NCI-GCMS- SIM/MICRO ECD

### 1. *Scope and Application*

- 1.1 This document details the procedures necessary for the analysis of extracts by NCI-GCMS SIM. This method is appropriate for extracts of all matrices prepared by EPA Method 3510A, EPA Method 3520C, EPA Method 3535, EPA Method 3540C, EPA Method 3541, EPA Method 3550, EPA Method 3580A.
- 1.2 All soils and sludges are either air dried or freeze dried before extraction. Any residual water in the extracts adversely affects the response.

### 2. *Summary of Method*

- 2.1 The samples are prepared for analysis by gas chromatography/NCI-mass spectrometry-SIM using the appropriate sample preparation.
- 2.2 The compounds are introduced into the GC/MS through the injection of the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with mass spectrometer (MS) connected to the gas chromatograph. If needed to minimize matrix enhancements the analytes can be split onto two detectors, a MSD and micro ECD in a 5:1 split ratio. The micro ECD may not be as affected by matrix enhancements as much as the MSD, when operated in the negative chemical ionization mode. In the dual detector mode, results could be reported from either the micro ECD, which is confirmed by the MSD as long as all data meets method criteria or NCI on its own. Both detectors require sample clean up before analysis. All soils/sludges and waters require extensive clean up before being analyzed (refer to clean up SOP DOC#: O-3-phase clean up-rev.1).
- 2.3 Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a calibration curve of five points or more. On the MSD, the target analytes are identified by comparing their selective mass ion ratios to the mass ion ratios of an authentic standard.

### 3. *Definitions*

The following terms are defined for use in this document:

- 3.1 ACCURACY: The closeness of agreement between an observed value and



an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

- 3.2 **BATCH:** A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.
- 3.3 **CONTROL SAMPLE:** A QC sample introduced into a process to monitor the performance of the system.
- 3.4 **FIELD DUPLICATES:** Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.
- 3.5 **LABORATORY CONTROL:** A known matrix spiked with compound(s) representative of sample target analytes. This is used to document laboratory performance.
- 3.6 **MATRIX:** The component or substrate (e.g., surface water, drinking water), which contains the analyte of interest.
- 3.7 **MATRIX DUPLICATE:** An intralaboratory-split sample, which is used to document the precision of a method in a given sample matrix.
- 3.8 **MATRIX SPIKE:** An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.
- 3.9 **MATRIX SPIKE DUPLICATES:** Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.
- 3.10 **METHOD BLANK:** An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank should be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.
- 3.11 **PRECISION:** The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the

relative standard deviation (RSD) or the coefficient of variation (CV),  $RSD = CV = 100 \frac{S}{x}$ ,

where:

$x$  = the arithmetic mean of the measurements, and  $S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n}}$  variance; and the relative percent difference (RPD) when only two samples are available.

$RPD = 100 \left[ \frac{|x_1 - x_2|}{(x_1 + x_2)/2} \right]$ .

- 3.12 REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.
- 3.13 REAGENT WATER: Water that has been generated by any method, which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.
- 3.14 STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards, which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.
- 3.15 SURROGATE: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.
- 3.16 SIM: Selective ion monitoring
- 3.17 PCI: Positive Chemical Ionization
- 3.18 NCI: Negative Chemical Ionization
- 3.19 MSD: Mass selective detector.
- 3.20 GCMS: Gas Chromatography Mass Spectrometry
- 3.21 ECD: Electron Capture Detector
- 3.22 SOURCE: Component of MSD where ionization and ion focusing take place

#### 4. Interferences

- 4.1 Solvents, reagents, glassware and other hardware used during extract and standards preparation can yield interferences. The lot numbers, the Caltest reagent ID number or Caltest source number of all reagents and solvents used for standards preparation should be recorded in the Standards Log Book to trace any sources of contamination that may occur.
- 4.2 Plastics should be avoided during the extract preparation procedure to eliminate sources of phthalate esters. Care should also be taken to limit contact of latex gloves with the sample or reagents. Only Teflon, glass or metal equipment should be used, such as Teflon squirt bottles, and all surfaces that come in contact with the sample should be solvent rinsed with methylene chloride.
- 4.3 Avoid cross-contamination between samples by rinsing any materials used for multiple samples between samples. Do not touch pipettes, graduated cylinders or squirt bottles to any of the glassware.
- 4.4 Matrix interference.
  - 4.4.1 IS Interference - Low or high internal standard areas may be corrected by diluting the sample or by using the external standard calibration technique if target compounds are not affected by the interference.
  - 4.4.2 Carryover - Contamination may occur from a previous injection. If this is suspected, re-analyze the sample with instrument blanks before and after the sample. Dirty extracts may require dilution and/or additional clean up to prevent interference, carryover, or overloading the column and detectors. Document any dilution or cleanup procedure in the Instrument Log Book. Footnote the report as appropriate.
  - 4.4.3 Dirty Injection Port - Maintenance such as replacing the injection port liner, seal, and clipping the front of the column should be done routinely.
  - 4.4.4 Column bleed - Rising baselines late in the chromatogram indicate column bleed. Utilize the column conditioning techniques outlined by the column manufacturer; trim both ends of the column, or solvent rinse the column.
  - 4.4.5 Chemical Ionization source requires more cleaning than the electron impact source, and cannot tolerate any residual water in the extracts or any air leaks. If either air or water is introduced into the chemical ionization source, response and mass signal to noise are severely degraded.

## 5. *Safety and Precautions*

- 5.1 This method is used to analyze potentially hazardous samples. Use of a hood is required.
- 5.2 Prior to performing this analysis, review the MSDS for all standards and reagents to be used. Observe the recommended safety precautions. Protective clothing and safety glasses should be worn when handling samples or reagents, and all manipulations are to be conducted in a hood.
- 5.3 Maintain a clean and uncluttered workspace. Return all chemicals, reagents and resultant wastes to their designated storage area at the completion of the test.

## 6. *Equipment and Supplies*

- 6.1 2 mL ALS vials, inserts, and crimp top seals.
- 6.2 Crimper, 12mm
- 6.3 Analytical column: 30 meter x 0.25 mm I.D., 0.25  $\mu$ m df, capillary fused silica.
- 6.4 Vials - 8 mL, 4 mL and 2 mL screw-cap vials with Teflon faced septum, clear and amber.
- 6.5 Syringes: 10  $\mu$ l, 25  $\mu$ l, 100  $\mu$ l, 500  $\mu$ l, 1000  $\mu$ l (Hamilton). Autosampler syringes: 10  $\mu$ l (Hamilton).
- 6.6 Volumetric flasks (Class A): 5.0 mL, 10.0 mL, 100.0 mL.
- 6.7 Data System: Agilent MS ChemStation (E.02.00.493) with ThruPut Target Data Analysis Software, Revision 4.12.
- 6.8 GC/MS system: Agilent 7890A-GC with Agilent 5975 inert XL/EI/CI-MSD equipped with Agilent 7683B autosampler.
- 6.9 Misc. Chromatography supplies: ferrules- 0.4mm (85% vespel-15% graphite, and 100% graphite) Restek 4.0mm double gooseneck deactivated injection port liners with glass wool, 1.2 mm inlet seals, 10 mm diameter septa.
- 6.10 Balance -Mettler analytical balance capable of reading to 0.01g.

## 7. *Reagents and Standards*

- 7.1 Methylene chloride, Burdick & Jackson, High purity solvent.
- 7.2 Acetone, Mallinkrodt, Nanograde.
- 7.3 Hexane, Omnisolve, high purity solvent.
- 7.4 Internal Standard Solution, 2000 ug/mL, 4,4'-Dibromooctafluorobiphenyl; Accustandard M-625-06-10x  
Six-month expiration date upon opening ampule.
  - 7.4.1 Working Internal Standard Solution, 0.04 ug/mL.  
Six month expiration date.
- 7.5 Calibration Standards: custom Pyrethroid standard, 1000ug/mL, Accustandard S-12458-R4  
Six month expiration date upon opening ampules.
- 7.6 Surrogate mix: Decachlorobiphenyl, Accustandard, neat, C-209N One year expiration date upon opening ampule.
- 7.7 Working Standards with Surrogate-0.25 ppm, Six month expiration date.
- 7.8 Second source Standards: Custom Pyrethroid standard, 1000ug/ml. Accustandard, S- 12458-R4 (different lot and gravimetric weighing than the calibration standard)  
Six month expiration date upon opening ampule.

## 8. *Sample Preservation and Storage*

- 8.1 The containers used for sampling and storage should be glass or Teflon and have screw caps with Teflon. All samples and extracts should be stored at not frozen to 6°C.
- 8.2 Aqueous Samples should be extracted within 14days of sampling, with the exception of Cyhalothrin and Permethrin which shows lack of stability after 3days (per USGS and CA Department of Food and Ag).
- 8.3 Soils can be frozen to extend the stability time to 6 months per USGS.

## 9. *Quality Control Procedures*

- 9.1 A method blank (MB) is included for every 24-hour extraction batch, or every 20 samples, and should be subjected to the same procedures as the samples. The blank is spiked with the same surrogate used in the samples. The blank should be free of contamination. If there are any target hits found in the analysis of the blank, a fresh extract aliquot should be prepped and run to determine if the contamination is a result of extraction or instrument contamination. If instrument contamination is suspected, run a solvent blank to confirm the problem.
- 9.2 Acceptance Criteria for Spiking Compounds in LCS and MS/MSD can be found in Caltest internal QC. Recovery outside of these limits must be checked and noted. The batch may need re-extraction.
- 9.3 Internal Standard QC-An area range of plus 100% and minus 50% is calculated from the average ISTD area from the calibration curve or from the continuing calibration standard. An ISTD area outside of the acceptance range necessitates prepping and analyzing a fresh extract to verify the results. If the problem is due to matrix interference, dilute the sample, inject ISTD and analyze. Repeated ISTD failures within the sequence indicate a problem with the system or ISTD solution. Correct any problems and rerun with a fresh ISTD solution. Re-prepare fresh sample extracts if new ISTD solution has been prepared.

9.4 Surrogate QC-The surrogates, spike level, and the acceptance criteria are listed in Caltest internal QC.

### 9.5 Qualitative Data Analysis

- 9.5.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample quantitation of secondary and tertiary ion ratio. The reference selective mass ion ratios must be generated by the laboratory using the conditions of this method. Compounds should be identified as present when the criteria below are met
- 9.5.2 The intensities of the characteristic ions of a compound maximize at the same scan or within one scan of each other. Selection of a peak by a data system where identification is based on the presence of chromatographic peaks containing ions specific for the target compound at a known retention time will be accepted as meeting this criterion
- 9.5.3 The Relative Retention Time of the sample component is within  $\pm 0.06$  RRT units of the RRT of the standard component 
$$RRT = \frac{RT \text{ sample}}{RT \text{ Istd}}$$

RT sample = Retention Time of sample component

RT Istd = Retention Time of internal standard.

- 9.5.4 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference selective mass ion ratios.
- 9.5.5 The GC oven program has been developed so that structural isomers either have partial resolution or elute close together so they can be integrated as one peak and the isomers are reported as a total pesticide residue.
- 9.5.6 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When a peak obviously represents more than one sample component, appropriate selection of analyte spectra and any necessary background spectra subtraction is important. Examination of extracted ion current profiles of target ions can aid in the selection of spectra and in the qualitative identification of compounds. When analytes co elute, the identification criteria can be met, but each analyte spectrum will contain a portion of the individual compounds co eluting.

## 10. Calibration and Standardization

- 10.1 Calibration Criteria-The GC/MS system must pass the following criteria prior to the analysis of any samples. Should any criterion not be met, the problem must be corrected before proceeding. (i.e.: instrument maintenance performed and/or standards and samples rerun.)
- 10.1.1 The GC/MS system must be tuned prior to sample analysis.
- 10.1.1.1 Adjust methane reagent gas flow in PCI mode before doing an auto tune. Then do the auto tune in the PCI mode first. Review the PCI auto tune report for air leaks and proper methane flow. Then load the NCI tune method and do a second auto tune in the NCI mode. If the auto tune completes, it passes. There is no tune check standard.
- 10.2 Initial Calibration -An initial calibration is performed prior to the analysis of any samples using a minimum of five points containing all the compounds of interest. The laboratory analyses standards that range from 0.0005ppm to 0.05pp
- 10.3 Using 4µl injections for the split mode or 3µl injections if only the MSD is being used. Each standard is acquired on the appropriate detector. Tabulate area responses against

concentration for each compound of interest including the Internal Standard, and calculate the Response Factor (RF) for each compound using the following equation:

$$RF = (AsCis)/(AisCs) \text{ where:}$$

As = Response for the parameter to be measured.

Ais = Response for the Internal Standard.

Cis = Concentration of the Internal Standard (ug/L).

Cs = Concentration of the parameter to be measured (ug/L).

The results are used to plot a calibration curve of Response Ratios, vs. RF. The linearity of the curve for each compound is checked and adjustments are made as necessary. A calibration curve is considered linear (acceptable) if the average RF is  $\leq 15\%$  and/or the grand mean average RF of all the target analytes is  $\leq 15\%$ . If a quadratic curve is used you must use no less than 6 calibration points and achieve a correlation coefficient of 0.995 or higher (approaching 1.0).

- 10.4 A mid-level secondary standard is injected following the calibration curve to verify the validity of the primary standards. This standard is from a different Lot # and gravimetric weighing than those purchased for the initial calibration. All compounds should meet 30% acceptance criteria. Should any compound not meet the criteria, the samples will be additionally reviewed for that compound. Should the sample prove positive for that compound, the discrepancy between the calibration and the secondary standard will be resolved and the sample re run.

## 11. Procedure

- 11.1 Proper documentation is essential at all points of sample preparation.

- 11.1.1 Before preparing any sample extract for analysis, check the extraction sheet for any comments concerning extraction and multiplier; check the Semi-volatiles Worklist for any work notes, test requested, age, client ID, matrix, and sample description.

Confirm any anomalies against the Lab Confirmation or the Chain of Custody. Notify the department manager or project manager if there are any discrepancies.

- 11.1.2 The GC/MS Instrument Run Log must be created during the course of the analysis. See Doc. #: Q-LGBK for the correct procedure for logbook entries. The following information is needed to complete the GC/MS Instrument Logbook (See Appendix 1 for a sample of the logbook page).

- 11.1.2.1 Operator - Enter the Initials of the analyst(s) responsible for loading the samples and standards.



- 11.1.2.2 Method - Enter acquisition and data analysis method if separate.
- 11.1.2.3 Column - Analytical column
- 11.1.2.4 Comments-Lot #s for Standards, detailed information about sample dilutions (i.e.: 100µl-500µl=5x), and any other comments.
- 11.1.3 All containers or glassware used to hold the samples or QC should be clearly marked to prevent confusions or switching of samples.
- 11.1.4 ALS vials-Label with sample number, date extract was prepared for analysis, Analytical code, and any dilution made to the sample.
- 11.1.5 The Semi volatiles Standards Log Book must be completed whenever standards or reagents are prepared. See Doc. #: Q-LGBK for the correct procedure for logbook entries.
- 11.1.6 MSDF Maintenance Log Book: Any maintenance; routine or special, column changes, additions or changes performed on the system must be recorded in the MSDF Maintenance Log Book. The result of any maintenance procedures must also be recorded.

## 11.2 Acquisition

- 11.2.1 Refer to instrument maintenance logbook for run instrument parameters. Update run instrument parameters every time they are changed.

## 11.3 Analysis

- 11.3.1 The samples are extracted according to Caltest SOP's O-3510PREP, O-3550PREP and O- GCMSPREP. ALS vials are labeled appropriately (See 6.1.3.1). Samples may be diluted with hexane. **The ISTD must have equilibrated at room temperature before use.** A dilution on the sample, or a new curve must be prepared that will properly bracket the concentration of that compound. All dilutions are recorded on the extract vial, in the Instrument Log Book, within the analytical sequence and on the final LIMS fast track worksheet.

- 11.3.2 Sequence - A typical sequence is:

- 11.3.2.1 Mid level Standard Mix.(CCV): Pass = ±15% drift from ICAL RF for each individual analyte and /or grand mean average RF drift of all target analytes is  $\leq$ 15%. If it does not pass recalibrate.

- 11.3.2.2 Secondary source standard, mid level.  
(Only if a new calibration curve is run)
  - 11.3.2.3 QC samples-MB, LCS, LCSD, MS, MSD.
  - 11.3.2.4 Samples
  - 11.3.2.5 Closing response check (0.0005ppm) to check source inertness.
- 11.4 Sample extracts in the refrigerator at not frozen to 6°C until prepped and analyzed. Analyzed extracts should be archived until the data is reviewed for completeness. Neat extracts will be kept for 60 days past the extraction date. All extracts must be disposed in the proper manner.
- 11.5 Data Reporting, and Archival
- 11.5.1 Generate Quant Reports using Target software for samples and QC. IS and surrogate recoveries must pass QC criteria outlined in section 7 of this document. Corrective steps may be taken when necessary to achieve QC requirements ( i.e.: manual integration of a peak, dilution of the sample, or other measures
  - 11.5.2 Using the Review feature of the Target software, check any hits that are suspect. Manual integration of a peak may be necessary to accurately quantitate the sample. Regenerate the report after any changes are made.
  - 11.5.3 Taking into account the multiplier for the sample, report concentrations of compounds that meet all of the following criteria:
    - 11.5.3.1 The mass spectral data meets the criteria set forth in section 10.
    - 11.5.3.2 The peak has a retention time that falls within the retention time window. See section 10.
    - 11.5.3.3 The concentration calculated is above the reporting limit taking into account the sample extraction and dilution factors.
    - 11.5.3.4 The experience of the analyst must weigh heavily in the interpretation of chromatograms.
- 11.6 Sample Data Entry - When reporting sample results on the LIMS system, enter the following data as appropriate:
- 11.6.1 DILUTION FACTOR: The detection limits in LIMS assume a dilution factor of 1 reflecting a 1L -> 1mL prep for aqueous samples and a 30g -> 2mL for

soils/sludges. All dilutions entered in LIMS should be rounded to one significant figure. ). To calculate dilution factor multipliers, if two or more dilutions were made on a sample, enter the product dilution factor.

- 11.6.2 RESULTS - Report all hits with two significant figures. For non-detected target compounds, enter "0" for Non-Detect.
- 11.7 To report QC results on LIMS, first generate a TARGET QC report. Report all QC data results with three significant figures.
- 11.8 Completed data results are to be given to the coordinator/manager for data approval and filing.
- 11.9 Trouble shooting
- 11.9.1 Low response-Check the autosampler syringe for breakage or partial blockage. If press-tights connectors are being used, check them for leaks first. Check ferrule nuts at injector and detector and tighten if necessary. Check gas supplies and check for leaks. Replace septum. Check for septum particles in the injector liner. Cut several inches of column from the injector end and/or detector end. Low responses may also be caused by a dirty source, poorly performing filaments, or an old multiplier (voltage >2400mV)
- 11.9.2 No peaks-Check the autosampler syringe for breakage and replace if necessary. Check vu-unions or press-tights for leakage. Check the gas supplies and replace tanks as necessary. Verify flow through the column. Check injector liner for septum debris.
- 11.9.3 Large, misshapen peaks-Compounds in the sample may be overloading the detector. Dilute the sample and rerun.
- 11.9.4 Noisy baseline- remove column nuts and check for crushed ferrule and/or column. Remove a few inches of column, replace with a new ferrule and bake out system at 325° C for 30 minutes and check for baseline stability. Further problems may indicate a contaminated column requiring solvent rinsing or replacement.

## 12. Calculations

- 12.1 The internal standard technique -The Enviroquant GC software automatically calculates the concentrations of analytes using the following equation:

$$\begin{aligned} \text{Concentration, ug/L} &= \frac{(A_s) (I_s)}{(A_{is}) (RF)} \\ &= \end{aligned}$$

As = Quant ion response for the compound to be measured.  
Is = Amount of internal standard.  
Ais= Quant ion response for the internal standard.  
RF = Response factor as determined in section 6.3.3

- 12.2 If the external standard technique is to be employed in cases where there is interference with the IS, calculate the amount of material injected from the peak response using the calibration curve. The concentration can be determined by using the following equation:

$$\text{Concentration } \mu\text{g/L} = \frac{A_{uk} \times C_s}{A_s}$$

Auk = Quant ion response of the compound being measured.  
As = Quant ion response of the compound in the standard.  
Cs = Concentration of the standard.

This technique should only be used when the target analytes are unaffected by matrix interferences. When used, any such calculations should be clearly annotated and footnoted on the LIMS report.

- 12.3 Multipliers are used to relate the results calculated in the final analysis to the reported units.

12.3.1 Liquid matrices

Analysis units = ug/mL      Reporting units = ug/L

Result: on column amount x  $\frac{\text{Final Volume}}{\text{Initial Volume}}$  x Dilution Factor

12.3.2 Solid matrices

Analysis units = ug/mL      Reporting units = mg/Kg

Result: on column amount x  $\frac{\text{Final Volume}}{\text{Initial Volume}}$  x Dilution Factor

13. *Pollution Prevention*

- 13.1 There are no particular pollution prevention steps taken by the laboratory for this test.

14. **Data Assessment and Acceptance Criteria for Quality Control Measures.**

14.1 The data is referenced in Caltest's internal QC summary manual.

**15. *Corrective Actions for Out of Control Data.***

15.1 The data is referenced in Caltest's internal QC summary manual.

**16. Contingencies for Handling Out-Of-Control or Unacceptable Data.**

16.1 The contingencies for handling out-of-control or unacceptable data are addressed in the Caltest SOP: Q-CORRECT.

**17. *Waste Management***

17.1 All solvent saturated aqueous waste is collected in a drum. The waste is shipped out for disposal using a hazard waste disposal company. It is profiled as waste corrosive liquid.

17.2 All dichloromethane is collected in a solvent drum. The waste is shipped out for disposal using a hazard waste disposal company. It is profiled as waste Dichloromethane.

17.3 All Acetone waste is collected in a drum. The waste is shipped out for disposal using a hazard waste disposal company. It is profiled as waste flammable liquid.

**18. Method Performance**

18.1 This is not currently available.

**19. *References***

19.1 Analytical Method for the Determination of Synthetic Pyrethroids in Sediment by Gas Chromatography-Negative Chemical Ionization Mass Spectrometry. Neil J. Robinson, Syngenta Ltd.

Appendix 1

*Pyrethroid List of Analytes*

Pyrethroid Analyte	CAS Number	Ret Time	1°	2°	3°
Bifenthrin (Biphenthrin)	82657-04-3	19.7	386	387	241
Cyfluthrin (Baythroid)	68359-37-5	24.4	207	209	171
Lambda-Cyhalothrin	91465-08-6	21.5	241	205	243
Cypermethrin	52315-07-8	24.9	207	209	171
Fenvalerate / Esfenvalerate (Pydrin)	51630-58-1	26.7	211	213	212
Tau-Fluvalinate	102851-06-9	26.7	294	296	295
Fenpropathrin *(Danitol)	39515-41-8	20.0	141		
Permethrin	52645-53-1	23.3	207	209	
Tralomethrin/ Deltamethrin	66841-25-6	27.8	81	295	297
Allethrin	584-79-2	13.6	167	168	
Tetramethrin	7696-12-0	19.8	331	332	
Phenothrin	26002-80-2	19.8	167	168	

Additional Analyte per request:

Analyte	CAS Number		1°	2°	3°
Chlorpyrifos	2921-88-2	12.3	315	214	313
*Diazinon	333-41-5	9.6	169		

Ret Time = retention time.

1° = Quantitation Ion

2° = Qualifying Ion

3° = Monitoring Ion

\* = NCI only produces one ion; the compound qualifies using 1° and retention time.

**APPENDIX XXXIII. PTS SOP #3. PARTICLE SIZE BY DRY SIEVE PROCEDURE (Method: ASTM D422-63 Reapproved 1998) (Revision number unknown, 1998)**

## PARTICLE SIZE BY DRY SIEVE PROCEDURE

(Method: ASTM D422-63 Reapproved 1998)

### Scope

Particle size distribution of sediments is determined by sieving which consists of using a set of standard square-mesh, woven-wire cloth sieves that conform to ASTM E-11 in conjunction with a Ro-Tap mechanical shaker unit.

Weighed particles can range from 0.25 to 0.0012 inches and are determined as the fraction of each sample is collected and weighed in each standard sieve. The complete set of sieves is:

<u>U.S. Sieve Number</u>	<u>Opening, Inches</u>	<u>Opening, mm</u>	<u>Phi of Screen</u>
1	0.9844	25.002	-4.64
1/2	0.4922	12.501	-3.64
3/8	0.3740	9.500	-3.25
1/4	0.2500	6.351	-2.67
4	0.1875	4.757	-2.25
6	0.1324	3.364	-1.75
10	0.0787	2.000	-1.00
14	0.0557	1.414	-0.50
18	0.0394	1.000	0.00
25	0.0278	0.707	0.50
35	0.0197	0.500	1.00
40	0.0166	0.420	1.25
45	0.0139	0.354	1.50
60	0.0098	0.250	2.00
80	0.0070	0.177	2.50
120	0.0049	0.125	3.00
200	0.0029	0.074	3.75
270	0.0021	0.053	4.25
400	0.0015	0.037	4.75

### Method Summary

The soil sample is dried and gently disaggregated using a wooden mortar and pestle. Samples that contain heavy concentrations of hydrocarbons are extracted by Dean-Stark distillation (API RP40) using either toluene or a chloroform-methanol azeotrope as the solvent prior to disaggregation. A representative portion of the sample, 50-1000 grams, is introduced into a stack of sieves beginning with U.S. Standard Sieve number 1/4 and is continuously shaken on the Ro-Tap shaker unit for a period of no less than 20 minutes and no greater than 30 minutes. Weights of the sample retained on each standard sieve number are recorded.

### Quality Control

Calibration is determined by standards created by PTS Laboratories, Inc. by multiple size separation runs. Each screen is inspected prior to use for signs of excessive wear, distortion of the wire cloth or other aberrations. Sieves suspected of having a flaw are replaced and given to the laboratory supervisor for microscopic inspection, after which they are tested with standards, repaired or discarded. Duplicate samples are run for each batch of twenty samples and blind mixes of standards are run weekly. Duplicate sample acceptance ranges are 80-120 %, blind sample acceptance ranges are 90-110%.





## PARTICLE SIZE BY DRY SIEVE PROCEDURE

(Method: ASTM D422-63 Reapproved 1998)

### Reporting

Data is reported in tabular and graphical formats corresponding to the ASTM/USCS Classification system and can be presented in an EDD format. Statistical data of mean, median, standard deviation, sorting, skewness and kurtosis are included.

## SAMPLE PREPARATION FOR PARTICLE SIZE ANALYSIS PROCEDURE

(ASTM D421/422M Method)

### Sampling

1. Sub-sample approximately 20-30 grams of representative material at the requested interval.
2. Break up aggregations using a wood or rubber-covered pestle.
3. Dry sample at room temperature until weight is stable.
  - a. If RUSH turnaround time is required, dry sample at 150°F until weight is stable.
  - b. If sample is contaminated with petroleum hydrocarbons, sample must be cleaned.
    - i. Package sample in thimble or cellulose envelope for Dean-Stark or Soxhlet extraction.
    - ii. Extract for 4-8 hours or until sample is clean.
    - iii. Dry sample at 150°F in vacuum oven until weight is stable.
4. For LPSA analysis, material passing a No. 10 (2.00-mm) sieve is required.
5. **Note:** For non-sediment (soil) samples, contact client to develop procedure.

### ATTACHMENTS

ASTM D422 Method

## PARTICLE SIZE BY LASER LIGHT SCATTERING PROCEDURE

(Method: ASTM D4464M-85)

### **Scope**

Particle size distribution of sediments is determined by using laser light diffraction to measure the amount and patterns of light scattered by a particle's surface. This is done using laser light with a 750 nm wavelength, a Fourier lens focusing system and an array of 126 detectors. Light is diffracted around a particle at angles inversely proportional to the size of the particle; the smaller the particle the larger the angle of diffraction.

Measured particles can range from 0.4-2000  $\mu\text{m}$  and are determined as the sample, dispersed in a transport fluid, is circulated through the analyzer. Extended range analyses, 0.4 - >2000  $\mu\text{m}$  is accomplished by combining the >2000  $\mu\text{m}$  fraction from screen sieving with the <2000  $\mu\text{m}$  fraction from light scattering.

The procedure is a modification of ASTM D4464-85 (reapproved in 2000) to measure the particle size of catalytic material. The modification is that the procedure has been extended to include the measurement of unconsolidated soils and sediments. The procedure is in current use by the USGS, City of Los Angeles, University of Florida and major petroleum companies. Local, state and federal regulatory agencies have recognized the method as an alternative to ASTM D422 (hydrometer) and the pipette method.

### **Method Summary**

For soils the sample is dried and gently disaggregated using a wooden mortar and pestle. Samples that contain heavy hydrocarbons are extracted by Dean-Stark distillation (API RP40) using either toluene or a chloroform-methanol azeotrope as the solvent prior to disaggregation. A representative portion of the sample, 5-10 grams, is introduced into the fluid module of the analyzer and is continuously circulated through the laser beam. Water samples are introduced directly into the fluid module. The circulation fluid is filtered to 0.2  $\mu\text{m}$  and contains a dispersant to prevent coagulation along with an internal sonification unit to further separate the particles.

The laser beam passes through the sample cell where the suspended particles scatter the incident light. Fourier optics collect the diffracted light and focus it on to three sets of detectors, one for low-angle scattering, the second for mid-angle scattering and the third for high-angle scattering. The composite, time-averaged diffraction pattern is measured by 126 detectors placed at angles to  $\sim 35^\circ$  from the optical axis. Sizes are computed by the Fraunhofer Model for Light Scattering and summed into normal ASTM, USCS or Wentworth distribution classifications for 0.4-2000  $\mu\text{m}$ .

### **Quality Control**

Calibration is determined by the optical design. Therefore, no calibration is required. All necessary adjustments are made by measuring electrical offsets and aligning the laser beam. Quality control samples of traceable diameter are run at regular intervals or as required on a project basis. Repeatability is <1% about the mean size (repeat runs of the same sample).

### **Reporting**

Data is reported in tabular and graphical formats corresponding to the ASTM/USCS Classification system and can be presented in an EDD format. Statistical data of mean, median, standard deviation, sorting, skewness and kurtosis are included.

## SAMPLE PREPARATION FOR PARTICLE SIZE ANALYSIS PROCEDURE (ASTM D421/422M Method)

### Sampling

1. Sub-sample approximately 20-30 grams of representative material at the requested interval.
2. Break up aggregations using a wood or rubber-covered pestle.
3. Dry sample at room temperature until weight is stable.
  - a. If RUSH turnaround time is required, dry sample at 150°F until weight is stable.
  - b. If sample is contaminated with petroleum hydrocarbons, sample must be cleaned.
    - i. Package sample in thimble or cellulose envelope for Dean-Stark or Soxhlet extraction.
    - ii. Extract for 4-8 hours or until sample is clean.
    - iii. Dry sample at 150°F in vacuum oven until weight is stable.
4. For LPSA analysis, material passing a No. 10 (2.00-mm) sieve is required.
5. **Note:** For non-sediment (soil) samples, contact client to develop procedure.

### LPSA Sample Preparation

1. Disaggregate sample material to grain size using wood or rubber-covered pestle being careful not to break individual grains.
2. Separate test sample by sieving with a No. 10 (2-mm) sieve.
  - a. Record weight of any retained material and passing material weight.
3. By use of a micro sample splitter, select a portion of sample suitable for occlusion (8-12 percent occlusion) of the Laser Particle Size Analyzer (LPSA).
4. Place the sample in a 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution.
  - a. A solution of sodium hexametaphosphate is prepared at a rate of 40 grams of sodium hexametaphosphate per liter of distilled or demineralized water.
  - b. Stir or agitate until the soil is thoroughly wetted.
  - c. Allow to soak for at least 16 hours.
5. Following soaking period, disperse sample prior to introduction into Laser Particle Size Analyzer.
6. Stir with stainless steel or glass stirrer or use sonicator.
7. **Note:** For non-sediment (soil) samples, contact client to develop procedure.

### LPSA Analysis

1. Wash sample into LPSA fluid module using distilled or demineralized water making sure all sample is washed from beaker.
2. Allow to circulate for at least 20 seconds or until the sample is completely dispersed before measuring.
3. Measure sample particle size distribution per Method ASTM D4464M.

Test results are presented in tabular and graphical formats.

**PARTICLE SIZE ANALYSIS PROCEDURE**  
(ASTM D421/422M Method, ASTM D4464M)

**Additional**

Dry Sieve data may be mathematically combined with Laser Diffraction data to create a combination report presenting grain size distribution from 1" to 0.375um.

**ATTACHMENTS**

ASTM D4464M Method



## Standard Test Method for Particle-Size Analysis of Soils<sup>1</sup>

This standard is issued under the fixed designation D 422; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75  $\mu\text{m}$  (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75  $\mu\text{m}$  is determined by a sedimentation process, using a hydrometer to secure the necessary data (Note 1 and Note 2).

NOTE 1—Separation may be made on the No. 4 (4.75-mm), No. 40 (425- $\mu\text{m}$ ), or No. 200 (75- $\mu\text{m}$ ) sieve instead of the No. 10. For whatever sieve used, the size shall be indicated in the report.

NOTE 2—Two types of dispersion devices are provided: (1) a high-speed mechanical stirrer, and (2) air dispersion. Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20- $\mu\text{m}$  size and appreciably less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20  $\mu\text{m}$ .

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants<sup>2</sup>

E 11 Specification for Wire-Cloth Sieves for Testing Purposes<sup>3</sup>

E 100 Specification for ASTM Hydrometers<sup>4</sup>

### 3. Apparatus

3.1 *Balances*—A balance sensitive to 0.01 g for weighing the material passing a No. 10 (2.00-mm) sieve, and a balance sensitive to 0.1 % of the mass of the sample to be weighed for weighing the material retained on a No. 10 sieve.

3.2 *Stirring Apparatus*—Either apparatus A or B may be used.

3.2.1 Apparatus A shall consist of a mechanically operated

stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10 000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Fig. 1. The shaft shall be of such length that the stirring paddle will operate not less than  $\frac{3}{4}$  in. (19.0 mm) nor more than  $1\frac{1}{2}$  in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Fig. 2 shall be provided to hold the sample while it is being dispersed.

3.2.2 Apparatus B shall consist of an air-jet dispersion cup<sup>5</sup> (Note 3) conforming to the general details shown in Fig. 3 (Note 4 and Note 5).

NOTE 3—The amount of air required by an air-jet dispersion cup is of the order of 2 ft<sup>3</sup>/min; some small air compressors are not capable of supplying sufficient air to operate a cup.

NOTE 4—Another air-type dispersion device, known as a dispersion tube, developed by Chut and Davidson at Iowa State College, has been shown to give results equivalent to those secured by the air-jet dispersion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When the air-dispersion tube is used, it shall be so indicated in the report.

NOTE 5—Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the air line, or by blowing the water out of the line before using any of the air for dispersion purposes.

3.3 *Hydrometer*—An ASTM hydrometer, graduated to read in either specific gravity of the suspension or grams per litre of suspension, and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference.

3.4 *Sedimentation Cylinder*—A glass cylinder essentially 18 in. (457 mm) in height and  $2\frac{1}{2}$  in. (63.5 mm) in diameter, and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000-mL mark is  $36 \pm 2$  cm from the bottom on the inside.

3.5 *Thermometer*—A thermometer accurate to 1°F (0.5°C).

3.6 *Sieves*—A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of Specification E 11. A full set of sieves includes the following (Note 6):

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved Nov. 21, 1963. Originally published 1935. Replaces D 422 – 62.

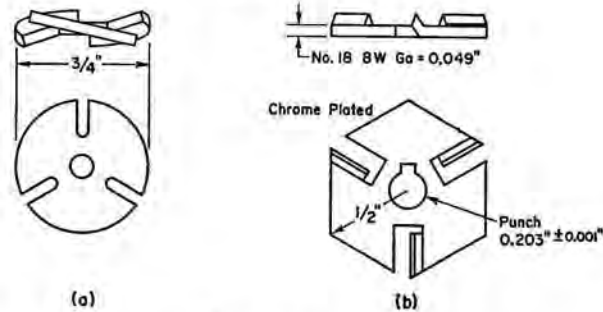
<sup>2</sup> Annual Book of ASTM Standards, Vol 04.08.

<sup>3</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>4</sup> Annual Book of ASTM Standards, Vol 14.03.

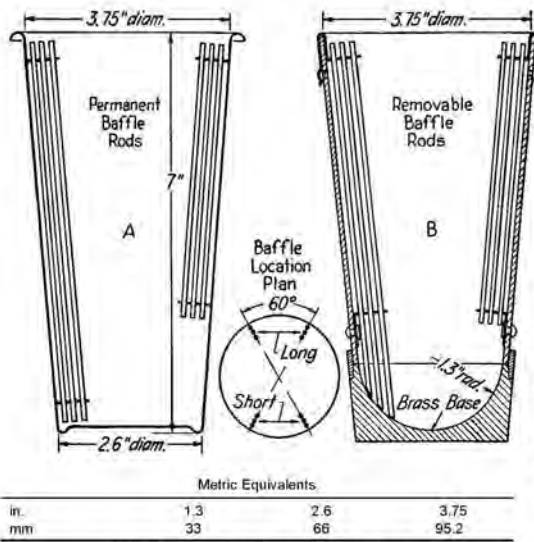
<sup>5</sup> Detailed working drawings for this cup are available at a nominal cost from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19105. Order Adjunct No. 12-404220-00.

D 422



Metric Equivalents					
in.	0.001	0.049	0.203	1/2	3/4
mm	0.03	1.24	5.16	12.7	19.0

FIG. 1 Detail of Stirring Paddles



Metric Equivalents			
in.	1.3	2.6	3.75
mm	33	66	95.2

FIG. 2 Dispersion Cups of Apparatus

3-in. (75-mm)	No. 10 (2.00- $\mu$ m)
2-in. (50-mm)	No. 20 (850- $\mu$ m)
1 1/2-in. (37.5-mm)	No. 40 (425- $\mu$ m)
1-in. (25.0-mm)	No. 60 (250- $\mu$ m)
3/4-in. (19.0-mm)	No. 140 (106- $\mu$ m)
3/8-in. (9.5-mm)	No. 200 (75- $\mu$ m)
No. 4 (4.75-mm)	

NOTE 6—A set of sieves giving uniform spacing of points for the graph, as required in Section 17, may be used if desired. This set consists of the following sieves:

3-in. (75-mm)	No. 16 (1.18-mm)
1 1/2-in. (37.5-mm)	No. 30 (600- $\mu$ m)
3/4-in. (19.0-mm)	No. 50 (300- $\mu$ m)
3/8-in. (9.5-mm)	No. 100 (150- $\mu$ m)
No. 4 (4.75-mm)	No. 200 (75- $\mu$ m)
No. 8 (2.36-mm)	

3.7 *Water Bath or Constant-Temperature Room*—A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 68°F (20°C). Such a device is illustrated in Fig. 4. In cases where the work is performed in a room at an automatically controlled constant temperature, the water bath is not necessary.

3.8 *Beaker*—A beaker of 250-ml. capacity.

3.9 *Timing Device*—A watch or clock with a second hand.

#### 4. Dispersing Agent

4.1 A solution of sodium hexametaphosphate (sometimes called sodium metaphosphate) shall be used in distilled or demineralized water, at the rate of 40 g of sodium hexametaphosphate/litre of solution (Note 7).

NOTE 7—Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions should be prepared frequently (at least once a month) or adjusted to pH of 8 or 9 by means of sodium carbonate. Bottles containing solutions should have the date of preparation marked on them.

4.2 All water used shall be either distilled or demineralized water. The water for a hydrometer test shall be brought to the temperature that is expected to prevail during the hydrometer test. For example, if the sedimentation cylinder is to be placed in the water bath, the distilled or demineralized water to be used shall be brought to the temperature of the controlled water bath; or, if the sedimentation cylinder is used in a room with controlled temperature, the water for the test shall be at the temperature of the room. The basic temperature for the hydrometer test is 68°F (20°C). Small variations of temperature do not introduce differences that are of practical significance and do not prevent the use of corrections derived as prescribed.

#### 5. Test Sample

5.1 Prepare the test sample for mechanical analysis as outlined in Practice D 421. During the preparation procedure

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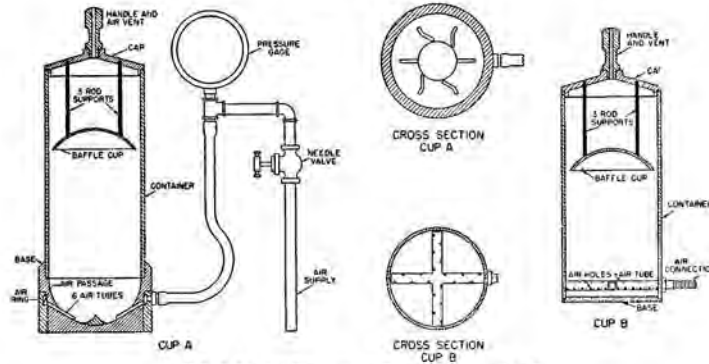
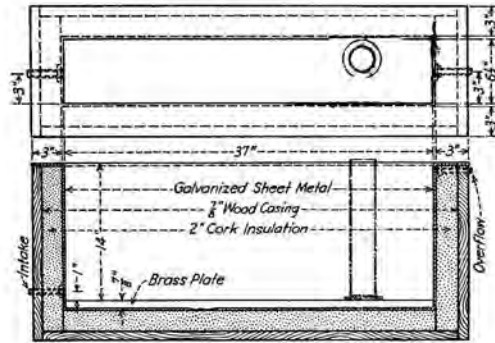


FIG. 3 Air-Jet Dispersion Cups of Apparatus B



Metric Equivalents						
in.	3/8	1	3	6 1/4	14	37
mm	22.2	25.4	76.2	158.2	356	940

FIG. 4 Insulated Water Bath

the sample is divided into two portions. One portion contains only particles retained on the No. 10 (2.00-mm) sieve while the other portion contains only particles passing the No. 10 sieve. The mass of air-dried soil selected for purpose of tests, as prescribed in Practice D 421, shall be sufficient to yield quantities for mechanical analysis as follows:

5.1.1 The size of the portion retained on the No. 10 sieve shall depend on the maximum size of particle, according to the following schedule:

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
3/8 (9.5)	500
1/4 (19.0)	1000
1 (25.4)	2000
1 1/2 (38.1)	3000
2 (50.8)	4000
3 (76.2)	5000

5.1.2 The size of the portion passing the No. 10 sieve shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.

5.2 Provision is made in Section 5 of Practice D 421 for weighing of the air-dry soil selected for purpose of tests, the separation of the soil on the No. 10 sieve by dry-sieving and washing, and the weighing of the washed and dried fraction retained on the No. 10 sieve. From these two masses the percentages retained and passing the No. 10 sieve can be calculated in accordance with 12.1.

NOTE 8—A check on the mass values and the thoroughness of pulverization of the clods may be secured by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve.

**SIEVE ANALYSIS OF PORTION RETAINED ON NO. 10 (2.00-mm) SIEVE**

**6. Procedure**

6.1 Separate the portion retained on the No. 10 (2.00-mm) sieve into a series of fractions using the 3-in. (75-mm), 2-in.

(50-mm), 1½-in. (37.5-mm), 1-in. (25.0-mm), ¾-in. (19.0-mm), ⅝-in. (9.5-mm), No. 4 (4.75-mm), and No. 10 sieves, or as many as may be needed depending on the sample, or upon the specifications for the material under test.

6.2 Conduct the sieving operation by means of a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 min of sieving. When mechanical sieving is used, test the thoroughness of sieving by using the hand method of sieving as described above.

6.3 Determine the mass of each fraction on a balance conforming to the requirements of 3.1. At the end of weighing, the sum of the masses retained on all the sieves used should equal closely the original mass of the quantity sieved.

**HYDROMETER AND SIEVE ANALYSIS OF PORTION PASSING THE NO. 10 (2.00-MM) SIEVE**

**7. Determination of Composite Correction for Hydrometer Reading**

7.1 Equations for percentages of soil remaining in suspension, as given in 14.3, are based on the use of distilled or demineralized water. A dispersing agent is used in the water, however, and the specific gravity of the resulting liquid is appreciably greater than that of distilled or demineralized water.

7.1.1 Both soil hydrometers are calibrated at 68°F (20°C), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.

7.1.2 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.

7.1.3 The net amount of the corrections for the three items enumerated is designated as the composite correction, and may be determined experimentally.

7.2 For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed. Measurement of the composite corrections may be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values.

7.3 Prepare 1000 mL of liquid composed of distilled or demineralized water and dispersing agent in the same proportion as will prevail in the sedimentation (hydrometer) test. Place the liquid in a sedimentation cylinder and the cylinder in the constant-temperature water bath, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus

formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hydrometer 152H it is the difference between the reading and zero. Bring the liquid and the hydrometer to the other temperature to be used, and secure the composite correction as before.

**8. Hygroscopic Moisture**

8.1 When the sample is weighed for the hydrometer test, weigh out an auxiliary portion of from 10 to 15 g in a small metal or glass container, dry the sample to a constant mass in an oven at 230 ± 9°F (110 ± 5°C), and weigh again. Record the masses.

**9. Dispersion of Soil Sample**

9.1 When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.

9.2 Place the sample in the 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/L). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 h.

9.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus A or B. If stirring apparatus A is used, transfer the soil-water slurry from the beaker into the special dispersion cup shown in Fig. 2, washing any residue from the beaker into the cup with distilled or demineralized water (Note 9). Add distilled or demineralized water, if necessary, so that the cup is more than half full. Stir for a period of 1 min.

NOTE 9—A large size syringe is a convenient device for handling the water in the washing operation. Other devices include the wash-water bottle and a hose with nozzle connected to a pressurized distilled water tank.

9.4 If stirring apparatus B (Fig. 3) is used, remove the cover cap and connect the cup to a compressed air supply by means of a rubber hose. A air gage must be on the line between the cup and the control valve. Open the control valve so that the gage indicates 1 psi (7 kPa) pressure (Note 10). Transfer the soil-water slurry from the beaker to the air-jet dispersion cup by washing with distilled or demineralized water. Add distilled or demineralized water, if necessary, so that the total volume in the cup is 250 mL, but no more.

NOTE 10—The initial air pressure of 1 psi is required to prevent the soil-water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.

9.5 Place the cover cap on the cup and open the air control valve until the gage pressure is 20 psi (140 kPa). Disperse the soil according to the following schedule:

Plasticity Index	Dispersion Period, min
Under 5	5
6 to 20	10
Over 20	15

Soils containing large percentages of mica need be dispersed for only 1 min. After the dispersion period, reduce the gage pressure to 1 psi preparatory to transfer of soil-water slurry to the sedimentation cylinder.



**10. Hydrometer Test**

10.1 Immediately after dispersion, transfer the soil-water slurry to the glass sedimentation cylinder, and add distilled or demineralized water until the total volume is 1000 mL.

10.2 Using the palm of the hand over the open end of the cylinder (or a rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 min to complete the agitation of the slurry (Note 11). At the end of 1 min set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation), or as many as may be needed, depending on the sample or the specification for the material under test: 2, 5, 15, 30, 60, 250, and 1440 min. If the controlled water bath is used, the sedimentation cylinder should be placed in the bath between the 2- and 5-min readings.

NOTE 11—The number of turns during this minute should be approximately 60, counting the turn upside down and back as two turns. Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.

10.3 When it is desired to take a hydrometer reading, carefully insert the hydrometer about 20 to 25 s before the reading is due to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduate of clean distilled or demineralized water.

NOTE 12—It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.

10.4 After each reading, take the temperature of the suspension by inserting the thermometer into the suspension.

**11. Sieve Analysis**

11.1 After taking the final hydrometer reading, transfer the suspension to a No. 200 (75- $\mu$ m) sieve and wash with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container, dry in an oven at  $230 \pm 9^\circ\text{F}$  ( $110 \pm 5^\circ\text{C}$ ) and make a sieve analysis of the portion retained, using as many sieves as desired, or required for the material, or upon the specification of the material under test.

**CALCULATIONS AND REPORT**

**12. Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00-mm) Sieve**

12.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 sieve by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.

12.2 To secure the total mass of soil passing the No. 4 (4.75-mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To secure the total mass of soil passing the  $\frac{3}{8}$ -in. (9.5-mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the  $\frac{3}{8}$ -in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.

12.3 To determine the total percentage passing for each sieve, divide the total mass passing (see 12.2) by the total mass of sample and multiply the result by 100.

**13. Hygroscopic Moisture Correction Factor**

13.1 The hygroscopic moisture correction factor is the ratio between the mass of the oven-dried sample and the air-dry mass before drying. It is a number less than one, except when there is no hygroscopic moisture.

**14. Percentages of Soil in Suspension**

14.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass by the hygroscopic moisture correction factor.

14.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used by the percentage passing the No. 10 (2.00-mm) sieve, and multiplying the result by 100. This value is the weight  $W$  in the equation for percentage remaining in suspension.

14.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows (Note 13): For hydrometer 151H:

$$P = [(100 000/W) \times G(G - G_s)](R - G_s) \quad (1)$$

NOTE 13—The bracketed portion of the equation for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

For hydrometer 152H:

$$P = (Ra/W) \times 100 \quad (2)$$

where:

- $a$  = correction fraction to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1).
- $P$  = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,
- $R$  = hydrometer reading with composite correction applied (Section 7),
- $W$  = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 14.2), g,
- $G$  = specific gravity of the soil particles, and
- $G_s$  = specific gravity of the liquid in which soil particles are suspended. Use numerical value of one in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for  $R$  is based on a value of one for  $G_s$ .

**15. Diameter of Soil Particles**

15.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' law (Note 14), on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is measuring the density of the suspension. According to Stokes' law: see Table 2

**TABLE 1** Values of Correction Factor,  $\alpha$ , for Different Specific Gravities of Soil Particles<sup>a</sup>

Specific Gravity	Correction Factor <sup>a</sup>
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

<sup>a</sup>For use in equation for percentage of soil remaining in suspension when using Hydrometer 152H.

$$D = \sqrt{[30m/980(G - G_j)] \times L/T} \quad (3)$$

where:

- $D$  = diameter of particle, mm,
- $n$  = coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),
- $L$  = distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (see Table 2)),
- $T$  = interval of time from beginning of sedimentation to the taking of the reading, min.
- $G$  = specific gravity of soil particles, and
- $G_j$  = specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

NOTE 14—Since Stokes' law considers the terminal velocity of a single sphere falling in an infinity of liquid, the sizes calculated represent the diameter of spheres that would fall at the same rate as the soil particles.

15.2 For convenience in calculations the above equation may be written as follows: see Table 3

$$D = K\sqrt{L/T} \quad (4)$$

where:

- $K$  = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of  $K$  for a range of temperatures and specific gravities are given in Table 3. The value of  $K$  does not change for a series of readings constituting a test, while values of  $L$  and  $T$  do vary.

15.3 Values of  $D$  may be computed with sufficient accuracy, using an ordinary 10-in. slide rule.

NOTE 15—The value of  $L$  is divided by  $T$  using the  $A$ - and  $B$ -scales, the square root being indicated on the  $D$ -scale. Without ascertaining the value of the square root it may be multiplied by  $K$ , using either the  $C$ - or  $CT$ -scale.

## 16. Sieve Analysis Values for Portion Finer than No. 10 (2.00-mm) Sieve

16.1 Calculation of percentages passing the various sieves used in sieving the portion of the sample from the hydrometer

**TABLE 2** Values of Effective Depth Based on Hydrometer and Sedimentation Cylinder of Specified Sizes<sup>a</sup>

Hydrometer 151H		Hydrometer 152H	
Actual Hydrometer Reading	Effective Depth, $L$ , cm	Actual Hydrometer Reading	Effective Depth, $L$ , cm
1.000	16.3	0	16.3
1.001	16.0	1	16.1
1.002	15.8	2	16.0
1.003	15.5	3	15.8
1.004	15.2	4	15.6
1.005	15.0	5	15.5
1.006	14.7	6	15.3
1.007	14.4	7	15.2
1.008	14.2	8	15.0
1.009	13.9	9	14.8
1.010	13.7	10	14.7
1.011	13.4	11	14.5
1.012	13.1	12	14.3
1.013	12.9	13	14.2
1.014	12.6	14	14.0
1.015	12.3	15	13.8
1.016	12.1	16	13.7
1.017	11.8	17	13.5
1.018	11.5	18	13.3
1.019	11.3	19	13.2
1.020	11.0	20	13.0
1.021	10.7	21	12.9
1.022	10.5	22	12.7
1.023	10.2	23	12.5
1.024	10.0	24	12.4
1.025	9.7	25	12.2
1.026	9.4	26	12.0
1.027	9.2	27	11.9
1.028	8.9	28	11.7
1.029	8.8	29	11.5
1.030	8.4	30	11.4
1.031	8.1		
1.032	7.8		
1.033	7.6		
1.034	7.3		
1.035	7.0		
1.036	6.8		
1.037	6.5		
1.038	6.2		

<sup>a</sup>Values of effective depth are calculated from the equation:  
 $L = L_1 + 1/2 [L_2 - (V_h/A)]$  (5)

where:

- $L$  = effective depth, cm,
- $L_1$  = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,
- $L_2$  = overall length of the hydrometer bulb, cm,
- $V_h$  = volume of hydrometer bulb, cm<sup>3</sup>, and
- $A$  = cross-sectional area of sedimentation cylinder, cm<sup>2</sup>

Values used in calculating the values in Table 2 are as follows:

- For both hydrometers, 151H and 152H:
  - $L_2$  = 14.0 cm
  - $V_h$  = 67.0 cm<sup>3</sup>
  - $A$  = 27.8 cm<sup>2</sup>

- For hydrometer 151H:
  - $L_1$  = 10.5 cm for a reading of 1.000
  - = 2.3 cm for a reading of 1.031

- For hydrometer 152H:
  - $L_1$  = 10.5 cm for a reading of 0 g/litre
  - = 2.3 cm for a reading of 50 g/litre

test involves several steps. The first step is to calculate the mass of the fraction that would have been retained on the No. 10 sieve had it not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total

TABLE 3 Values of K for Use in Equation for Computing Diameter of Particle in Hydrometer Analysis

Temperature, <sup>a</sup> C	Specific Gravity of Soil Particles								
	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85
16	0.01510	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01496	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.1323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01225	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149

percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 14.2), and the result divided by 100.

16.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve, and subtract this sum from the mass of the total sample (as calculated in 14.2).

16.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 12.2.

16.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 16.3) by the total mass of sample (as calculated in 14.2), and multiply the result by 100.

17. Graph

17.1 When the hydrometer analysis is performed, a graph of the test results shall be made, plotting the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an arithmetic scale as the ordinate. When the hydrometer analysis is not made on a portion of the soil, the preparation of the graph is optional, since values may be secured directly from tabulated data.

18. Report

- 18.1 The report shall include the following:
  - 18.1.1 Maximum size of particles,
  - 18.1.2 Percentage passing (or retained on) each sieve, which may be tabulated or presented by plotting on a graph (Note 16),
  - 18.1.3 Description of sand and gravel particles:
    - 18.1.3.1 Shape—rounded or angular,
    - 18.1.3.2 Hardness—hard and durable, soft, or weathered and friable,
    - 18.1.4 Specific gravity, if unusually high or low,
    - 18.1.5 Any difficulty in dispersing the fraction passing the No. 10 (2.00-mm) sieve, indicating any change in type and amount of dispersing agent, and
    - 18.1.6 The dispersion device used and the length of the dispersion period.

NOTE 16—This tabulation of graph represents the gradation of the sample tested. If particles larger than those contained in the sample were removed before testing, the report shall so state giving the amount and maximum size.

18.2 For materials tested for compliance with definite specifications, the fractions called for in such specifications shall be reported. The fractions smaller than the No. 10 sieve shall be read from the graph.

18.3 For materials for which compliance with definite specifications is not indicated and when the soil is composed almost entirely of particles passing the No. 4 (4.75-mm) sieve, the results read from the graph may be reported as follows:

- (1) Gravel, passing 3-in. and retained on No. 4 sieve ..... %
- (2) Sand, passing No. 4 sieve and retained on No. 200 sieve ..... %
  - (a) Coarse sand, passing No. 4 sieve and retained on No. 10 sieve ..... %
  - (b) Medium sand, passing No. 10 sieve and retained on No. 40 sieve ..... %
  - (c) Fine sand, passing No. 40 sieve and retained on No. 200 sieve ..... %
- (3) Silt size, 0.074 to 0.005 mm ..... %
- (4) Clay size, smaller than 0.005 mm ..... %
  - Colloids, smaller than 0.001 mm ..... %


18.4 For materials for which compliance with definite specifications is not indicated and when the soil contains material retained on the No. 4 sieve sufficient to require a sieve analysis on that portion, the results may be reported as follows (Note 17):

SIEVE ANALYSIS	
Sieve Size	Percentage Passing
3-in.	..... %
2-in.	..... %
1½-in.	..... %
1-in.	..... %
¾-in.	..... %
½-in.	..... %
No. 4 (4.75-mm)	..... %
No. 10 (2.00-mm)	..... %
No. 40 (425-µm)	..... %
No. 200 (75-µm)	..... %
HYDROMETER ANALYSIS	
0.074 mm	..... %
0.005 mm	..... %
0.001 mm	..... %

NOTE 17—No. 8 (2.36-mm) and No. 50 (300-µm) sieves may be substituted for No. 10 and No. 40 sieves.

19. Keywords

19.1 grain-size; hydrometer analysis; hygroscopic moisture; particle-size; sieve analysis

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## Standard Test Method for Particle Size Distribution of Catalytic Material by Laser Light Scattering<sup>1</sup>

This standard is issued under the fixed designation D 4464; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method covers the determination of the particle size distribution of catalyst and catalyst carrier particles and is one of several found valuable for the measurement of particle size. The range of particle sizes investigated was 30 to 300  $\mu\text{m}$  equivalent spherical diameter. The technique is capable of measuring particles above and below this range. The angle and intensity of laser light scattered by the particles are selectively measured to permit calculation of a volume distribution using light-scattering techniques.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 3766 Terminology Relating to Catalysts and Catalysis<sup>2</sup>
- E 105 Practice for Probability Sampling of Materials<sup>3</sup>
- E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods<sup>3</sup>
- E 456 Terminology Relating to Quality and Statistics<sup>3</sup>
- E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>3</sup>
- E 1617 Practice for Reporting Particle Size Characterization Data<sup>3</sup>

### 3. Terminology

3.1 Definitions and recommended nomenclature pertaining to catalysts and to materials used in their manufacture can be found in Terminology D 3766.

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *background*—extraneous scattering of light by material present in the dispersion fluid other than the particles to be measured. It includes scattering by contamination in the measurement path.

3.2.2 *Fraunhofer Diffraction*—the optical theory that de-

scribes the low-angle scattering of light by particles that are large compared to the wavelength of the incident light.

3.2.3 *Mie Scattering*—the complex electromagnetic theory that describes the scattering of light by spherical particles. It is usually applied to particles with diameters that are close to the wavelength of the incident light. The real and imaginary indices of light refraction of the particles are needed.

3.2.4 *multiple scattering*—the re-scattering of light by a particle in the path of light scattered by another particle. This usually occurs in heavy concentrations of a particle dispersion.

### 4. Summary of Test Method

4.1 A prepared sample of particulate material is dispersed in water or a compatible organic liquid and is circulated through the path of a laser light beam or some other suitable source of light. The particles pass through the light beam and scatter it. Photodetector arrays collect the scattered light which is converted to electrical signals to be analyzed using Fraunhofer Diffraction, or Mie Scattering, or both. Scattering information, typically, is analyzed assuming a spherical geometry for the particles. Calculated particle sizes are, therefore, presented as equivalent spherical diameters.

### 5. Significance and Use

5.1 It is important to recognize that the results obtained by this test method or any other method for particle size determination utilizing different physical principles may disagree. The results are strongly influenced by physical principles employed by each method of particle size analysis. The results of any particle sizing method should be used only in a relative sense and should not be regarded as absolute when comparing results obtained by other methods.

5.2 Light scattering theories (Fraunhofer Diffraction<sup>4</sup> and Mie Scattering<sup>5</sup>) that are used for determination of particle size has been available for many years. Several manufacturers of testing equipment now have units based on these principles. Although each type of testing equipment utilizes the same basic principles for light scattering as a function of particle size, different assumptions pertinent to application of the theory and different models for converting light measurements

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.02 on Physical-Mechanical Properties.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 05.05.

<sup>3</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>4</sup> Born, M., and Wolf, E., *Principles of Optics*, Chptr 8, Pergamon Press, Oxford, 1957.

<sup>5</sup> van Hulst, H.C., *Light Scattering by Small Particles*, Chptr 9, John Wiley & Sons, New York, 1908.

to particle size, may lead to different results for each instrument. Furthermore, any particles which are outside the size measurement range of the instrument will be ignored, causing an increase in the reported percentages within the detectable range. A particle size distribution which ends abruptly at the detection limit of the instrument may indicate that particles outside the range are present. Therefore, use of this test method cannot guarantee directly comparable results from different types of instruments.

5.3 This test method can be used to determine particle size distributions of catalysts and supports for materials specifications, manufacturing control, and research and development work.

## 6. Interferences

6.1 Air bubbles entrained in the circulating fluid will scatter light and then be reported as particles. Circulating fluids, typically, do not require degassing, but should be bubble-free on visual inspections.

6.2 Contaminants, such as non-aqueous solvents, oil or other organic coatings on the sample may emulsify in an aqueous carrier, scatter light, and be reported as part of the particle size distribution. Samples containing such contaminants may be analyzed in a non-aqueous carrier solvent to dissolve the contaminants or washed free of the contaminant with a compatible aqueous solvent.

6.3 Reagglomeration or settling of particles during analysis will cause erroneous results. Dispersions shall be prepared so a stable dispersion is maintained throughout the analysis.

6.4 Insufficient sample loading may cause electrical noise interference and poor data reproducibility. High sample loading may cause excessive light attenuation and multiple scattering, resulting in erroneous particle size distributions.

## 7. Apparatus

7.1 *Particle Size Analyzer*, based on Fraunhofer Diffraction or Mie Scattering, or both, light scattering analysis techniques. Ensure that the analyzer system or subsystem is optimum for the range of the powder being tested.

7.2 *Micro Sample Splitter*, used in accordance with MNL 32,<sup>6</sup> to obtain the test portion of sample.

7.3 *Ultrasonic Probe or Bath*, if needed, to ensure dispersion of agglomerates prior to analysis.

## 8. Reagents and Materials

8.1 The selected liquid carrier shall:

8.1.1 Be compatible with the construction materials of the sample delivery system.

8.1.2 Not cause dissolution or clumping of the particles.

8.1.3 Be sufficiently clean to achieve acceptable background levels.

8.2 The use of surfactant(s) is often recommended by equipment manufacturers. However, agents such as surfactants, antifoams, and viscosity modifiers should be used with caution. An interlaboratory study of this test method showed that the

use of different types and concentrations of surfactant can significantly affect the results. In calculating the precision of this test method, results obtained using surfactants were excluded because they contributed disproportionately to the scatter in results. Comparisons between laboratories should be performed with liquid carriers which are identical in all respects.

## 9. Sampling and Sample Size

9.1 A representative test sample shall be obtained according to Practice E 105. The test portion shall be extracted from the test sample using a micro sample splitter according to Manual 32. Quartering shall not be used.

9.2 Refer to the equipment manufacturer's recommendation to ensure that the amount of the test portion is acceptable to achieve optimum light scattering conditions. A wide range of sample portions is acceptable depending upon median particle size, particle density, and the sample delivery system.

9.3 For liquid dispersed materials, redisperse as necessary to ensure representative samples.

## 10. Preparation of Apparatus

10.1 Allow the instrument to warm up according to the manufacturer's recommendations.

10.2 Install and fill the desired sample delivery system and select applicable instrument range as indicated by the instrument manufacturer's instructions.

10.3 Establish correct optical alignment and calibration at a frequency in accordance with the manufacturer's requirements.

## 11. Calibration and Standardization

11.1 Performance of the instrument is defined by the geometry of the optical components. (Refer to the manufacturer's instruction manual.)

11.2 Spherical particle standards are available. Diagnostic powders are available from some equipment manufacturers to ensure consistent instrument function. (Some instruments may permit the use of reticles for calibration.)

NOTE 1—A partial list of standards, powders, and reticles can be found in the D32 research report for this test method.

## 12. Procedure

12.1 Measure the background in the mode in which the analysis will be carried out. Be sure that the carrier is flowing through the light path while measuring the background. Background values shall not exceed the manufacturer's specifications. If background values exceed manufacturer's recommendations, perform the necessary procedures as specified by the manufacturer to bring the background values within acceptable limits.

12.2 Obtain representative sample according to Section 9.

12.3 Select appropriate run time for the sample. This procedure is very specific to the application and is generally gauged by the run-to-run repeatability.

12.4 Select the desired output parameters according to the requirements set forth by the instrument manufacturer.

12.5 Transfer a representative aliquot to the sample delivery system and allow it to circulate for at least 20 s or until the solid is uniformly dispersed before measuring. (Determine that

<sup>6</sup> *ASTM Manual Series: MNL 32, "Manual on Test Sieving Methods,"* Pope, L.R. and Ward, C.W., eds., 4th ed, 1998.

the sample is not settling out in the circulation system. This can be checked by repeated runs at higher circulation rates.)

12.6 Perform the sample analysis according to the manufacturer's instructions.

12.7 Drain and fill the sample dispersion system in preparation for the next sample analysis. Drain and clean, as necessary, to avoid contamination of the subsequent sample.

**13. Report**

13.1 Information shall be reported as agreed between supplier and user, in accordance with Practice E 1617. The basis of the reported results is percent volume distribution calculated as equivalent spherical diameter. If all particles have the same density, this is the same as percent weight distribution.

**14. Precision and Bias <sup>7</sup>**

14.1 *Test Program*—An interlaboratory study was conducted in which particle size was measured as three points in seven separate laboratories on three materials. Each laboratory conducted a single determination on each of three subsamples of each material. Practice E 691, modified for nonuniform data sets, was followed for the data reduction.

14.2 *Precision*—Pairs of test results obtained by a procedure similar to that described in the study are expected to differ in absolute value by less than the 95 % probability interval, which is equal to 2.772\*S, where S is the estimate of standard deviation.

<sup>7</sup> Use of the terms repeatability, reproducibility, precision and bias is in accordance with Terminology E 456 and Practice E 177. Supporting data are available from ASTM Headquarters. Request RR: D32-1013.

14.3 *Summary of Precision Results*—The test results are shown in micrometres as Fraction Smaller Than (FST) at the indicated diameter at three selected points on the cumulative particle size distribution. Repeatability is the within laboratory agreement and reproducibility is the agreement between laboratories, expressed both in micrometres and as percent of consensus mean. See Table 1.

14.4 *Bias*—The test method is without known bias.

**15. Keywords**

15.1 catalyst; Fraunhofer Diffraction; light scattering; Mie Scattering

**TABLE 1 Precision**

Fraction Smaller Than (FST)	Consensus Median Diameter, µm	Repeatability	Reproducibility
<i>D3295001</i>			
10 volume %	37.11	0.81 (1.65 %)	4.68 (12.5 %)
50 volume %	68.04	1.18 (1.74 %)	2.85 (4.19 %)
90 volume %	120.8	3.69 (2.98 %)	9.66 (9.01 %)
<i>D3291003</i>			
10 volume %	39.71	1.91 (4.81 %)	8.59 (21.6 %)
50 volume %	83.28	3.13 (3.76 %)	7.49 (8.99 %)
90 volume %	153.2	6.82 (4.45 %)	16.31 (10.7 %)
<i>D3295003</i>			
10 volume %	57.79	5.53 (9.57 %)	12.30 (21.3 %)
50 volume %	140.4	9.70 (6.91 %)	16.38 (11.7 %)
90 volume %	254.6	17.53 (6.88 %)	53.82 (21.1 %)

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**APPENDIX XXXIV. PTS SOP #4. TOTAL ORGANIC CARBON PROCEDURE (Method: Walkley-Black) (Revision number unknown, date unknown)**



## TOTAL ORGANIC CARBON PROCEDURE

(Method: Walkley-Black)

### Scope

The Walkley-Black method is a common acid digestion method for the analysis of organic matter in soils. The method in use since the 1930's uses chromic acid to measure the oxidizable organic carbon in the soil. The Walkley-Black method is very accurate and precise on soils with less than 2% organic matter. The Walkley-Black method may result in low-test results for soils with excessively high concentrations of organic matter due to the incomplete oxidation of organic carbon in the sample. The upper limit for the method is approximately 6% organic matter. The loss on ignition method should be used for soils containing >6% organic matter.

### Method Summary

The Walkley-Black method involves a known volume of acidic dichromate solution reacting with an aliquot of soil in order to oxidize the organic carbon. The oxidation step is then followed by titration of the excess dichromate solution with ferrous sulfate. The organic carbon is calculated using the difference between the total volume of dichromate added and the volume titrated after reaction.

### Laboratory Procedure

1. Obtain 15 grams of representative soil.
2. Extract samples by Dean-Stark method (if there is evidence of hydrocarbon) and dry for 16 hours in a vacuum drying oven at 150°F.
3. Grind soil using a mortar and pestle (no steel or iron) until it can pass through a #40 sieve (< 0.5 mm) making sure to clean the mortar and pestle between samples with methanol.
4. Weigh out 0.5-2 grams of soil. 0.5-1.5 grams for samples that appear to have organic material, 1-2 grams for clean samples. Record sample weight in TOC logbook along with ID, client, file number, date and flask number.
5. Transfer weighed material to a 500 ml Erlenmeyer flask.
6. Add 10 ml EXACTLY of fluid #1 (0.5N  $K_2Cr_2O_7$ ) to each flask and agitate for 30 seconds making sure of complete mixing.
7. Add 20 ml EXACTLY of sulfuric acid,  $H_2SO_4$ , and increase the speed on the shaker to 2 on the speed setting. Agitate for one minute.
8. Set lab timer for 30 minutes and allow flasks to cool.
9. Add EXACTLY 200 ml of deionized water to each flask.
10. Remove flask from the shaker unit and add 3-4 drops of fluid #2 (Ferrouin,  $\alpha$ -Phenanthroline-ferrous complex 0.025M).
11. Drop a small clean stir bar into the flask. Place flask on stir plate and spin at low speed.
12. Record the starting volumetric reading for fluid #3 (0.5N Ferrous sulfate heptahydrate solution) burette in the TOC logbook. Always start the burette at the 25 ml mark or lower.
13. Slowly add fluid #3 until the mixture turns dark green, and then titrate drop by drop until the color changes sharply from blue to red.
14. Record the final burette reading in the TOC logbook.
15. Using the excel file TOC.xls, calculate the TOC value for each sample according to the following formula:

Organic Carbon, % =  $[(\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4) \times 0.003 \times 100] / \text{soil weight, g} \times \text{response factor, rf}$ .

## TOTAL ORGANIC CARBON PROCEDURE

(Method: Walkley-Black)

### **Reporting**

Data is reported in tabular format and can be presented in an EDD form at.

### **Quality Control**

Blank Acceptance Range (RF): 97-103%, 1.261-133.9

Standard Acceptance Range: 70-130%

Method Detection Limit: 100 mg/kg (ppm)

- (1) As listed in **METHODS OF SOIL ANALYSIS, Part 2, Chemical and Microbiological Properties, Second Edition:**  
American Society of Agronomy, Inc.; Soil Science Society of America, Inc. 1982

### **ATTACHMENTS**

Walkley-Black procedure.

TOTAL ORGANIC CARBON  
WALKLEY-BLACK METHOD

GENERAL INFORMATION							0.5N FeSO <sub>4</sub> Titration			CALCULATED DATA					
Run Date	PTS File Number	Client	Project Number	Sample ID	Depth, ft	Flask Number	Soil Weight, g	Start Burette	End Burette	Total	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> meq	FeSO <sub>4</sub> meq	Response factor	TOC, %	TOC, mg/kg
20-Jan	33999	Client		MW-1		26	0.471	0.000	18.750	18.75	10.002	9.442	1.30	0.46	4636
20-Jan				SQC Blank		21	0.000	0.000	19.750	19.75	10.002	9.946	1.30	0.00	0
20-Jan				SQC Standard		22	0.460	0.000	17.850	17.85	10.002	8.989	1.30	0.86	8590

Blank Acceptance Range (RF): 97-103%  
Standard Acceptance Range: 70-130%  
Method Detection Limit: 100 mg/kg (ppm)

Rounding:  
100-999: Nearest 10  
1000-9999: Nearest 50  
>10000: Nearest 100

All values between -999 and 99 are listed as <100 mg/kg

obtained if dichromate methods are applied to soils containing significant amounts of carbonized materials. Dry combustion methods are most appropriate for soils containing large amounts of elemental C.

### 29-3.5.2 WALKLEY-BLACK PROCEDURE (Walkley, 1946; Peck et al., 1947; Greveling & Peck, 1960)

#### 29-3.5.2.1 Reagents

1. Potassium dichromate ( $K_2Cr_2O_7$ ), 1*N*: Dissolve 49.04 g of reagent-grade  $K_2Cr_2O_7$  (dried at 105°C) in water, and dilute the solution to a volume of 1,000 ml.
2. Sulfuric acid ( $H_2SO_4$ ), concentrated (not less than 96%): If  $Cl^-$  is present in soil, add  $Ag_2SO_4$  to the acid at the rate of 15 g/liter.
3. Phosphoric acid ( $H_3PO_4$ ), concentrated.
4. *o*-Phenanthroline-ferrous complex, 0.025*M*: Dissolve 14.85 g of *o*-phenanthroline monohydrate and 6.95 g of ferrous sulfate heptahydrate ( $FeSO_4 \cdot 7H_2O$ ) in water. Dilute the solution to a volume of 1,000 ml. The *o*-phenanthroline-ferrous complex is available under the name of Fer-rolin from the G. Frederick Smith Chemical Co. (Columbus, Ohio).
5. Barium diphenylamine sulfonate: Prepare a 0.16% aqueous solution. This reagent is an optional substitute for no. 4.
6. Ferrous sulfate heptahydrate ( $FeSO_4 \cdot 7H_2O$ ) solution, 0.5*N*: Dissolve 140 g of reagent-grade  $FeSO_4 \cdot 7H_2O$  in water, add 15 ml of some sulfuric acid ( $H_2SO_4$ ), cool the solution, and dilute it to a volume of 1,000 ml. Standardize this reagent daily by titrating it against 10 ml of 1*N* potassium dichromate ( $K_2Cr_2O_7$ ), as described below.

**29-3.5.2.2 Procedure.** Grind the soil to pass through a 0.5-mm sieve, avoiding Fe or steel mortars. Transfer a weighed sample, containing 10 to 25 mg of organic C, but not in excess of 10 g of soil, into a 500-ml wide-mouth Erlenmeyer flask. Add 10 ml of 1*N*  $K_2Cr_2O_7$ , and swirl the flask gently to disperse the soil in the solution. Then rapidly add 20 ml of conc  $H_2SO_4$ , directing the stream into the suspension. Immediately swirl the flask gently until soil and reagents are mixed; then more vigorously for a total of 1 min. Allow the flask to stand on a sheet of asbestos for about 30 min. Then add 200 ml of water to the flask, and filter the suspension if experience shows that the endpoint of the titration cannot otherwise be clearly discerned. Add 3 to 4 drops of *o*-phenanthroline indicator, and titrate the solution with 0.5*N*  $FeSO_4$ . As the endpoint is approached, the solution takes on a greenish cast and then changes to a dark green. At this point, add the ferrous sulfate heptahydrate drop by drop until the color changes sharply from blue to red (maroon color in reflected light against a white background). Make a blank determination in the same manner, but without soil, to standardize the  $Cr_2O_7^{2-}$ . Repeat the determination with less soil if >75% of the dichromate is reduced.

Calculate the results according to the following formula, using a correction factor  $f = 1.30$  or a more suitable value found experimentally:

$$\text{Organic C, \%} = \frac{(\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4)(0.003)(100)}{\text{g water-free soil}} \times f \quad [13]$$

**29-3.5.2.3 Comments.** Ferrous ammonium sulfate is also a suitable titrant for excess  $Cr_2O_7^{2-}$  in conjunction with the Walkley-Black method. The Smith and Weldon (1941) modification involving complete reduction of  $Cr_2O_7^{2-}$  with  $Fe^{2+}$ , and subsequent back-titration of excess  $Fe^{2+}$  with  $MnO_2$ , solution may also be used to estimate unreacted  $Cr_2O_7^{2-}$ . Other oxidation-reduction indicators that have provided satisfactory results include barium diphenylamine sulfonate and *N*-phenylanthranilic acid. The amounts of  $Cr_2O_7^{2-}$  reduced to  $Cr^{3+}$  by reaction with soil organic matter may also be estimated colorimetrically.

### 29-3.5.3 MODIFIED MIERHUS PROCEDURE

#### 29-3.5.3.1 Special Apparatus

1. Erlenmeyer flasks (125 ml) fitted with female standard-taper 24/40 ground-glass joints (Coring 5000 or Kimble 26510).
2. West condensers (30 cm) fitted with male standard-taper 24/40 ground-glass joints at the lower end (Coring 2800 or Kimble 18190).
3. Electric hot plate extraction unit (six plates per unit) fitted with individual rheostat controls (Labconco 60300, Precision 65500, Lab-Linc Multi-Unit Extraction Heater, or equivalent).

#### 29-3.5.3.2 Reagents

1. Potassium dichromate solution ( $K_2Cr_2O_7$ ), 0.5*N*: Dissolve 24.5125 g of  $K_2Cr_2O_7$  (oven-dry) in 200 ml of deionized water, and dilute to 1 liter.
2. Sulfuric acid ( $H_2SO_4$ ), concentrated, not less than 96%.
3. Ferrous ammonium sulfate hexahydrate solution [ $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ ], 0.2*N*: Dissolve 78.390 g of  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$  in 50 ml of conc  $H_2SO_4$ , and dilute to 1 liter with deionized water (must be standardized daily because of slow oxidation).
4. Indicator solution: Dissolve 0.100 g of *N*-phenylanthranilic acid and 0.107 g of sodium carbonate ( $Na_2CO_3$ ) in 100 ml of water.

**29-3.5.3.3 Procedure.** Weigh an amount of <100-mesh soil ( $\leq 0.5$  g) containing not greater than 8 mg of organic C into a 125-ml Erlenmeyer flask. Add exactly 10 ml of 0.5*N*  $K_2Cr_2O_7$  solution and 15 ml of conc  $H_2SO_4$  ( $H_2SO_4$  may be added by burette). Attach the flask to the West condenser, and place on a preheated electric hot plate. Include a blank in each group of five soil samples to be heated and at least two unboiled blanks (unboiled blanks are unheated mixtures of 10 ml of 0.5*N*  $K_2Cr_2O_7$  and 15 ml of conc  $H_2SO_4$ ) for each day that analyses are performed. The normality of the  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$  solution is determined by titrating the unboiled blank. Gently boil each sample for 30 min, and then insert an asbestos pad between the hot plate and bottom of the Erlenmeyer flask. Allow the flask to cool for about 15 min, and rinse the inside of the condenser with de-

## WALKLEY-BLACK METHOD

### Equipment:

1. 500-mL Erlenmeyer flasks.
2. 10-mL pipette.
3. 10- and 20-mL dispensers.
4. 50-mL burette.
5. Analytical balance.
6. Magnetic stirrer.
7. Incandescent lamp.

### Reagents:

1.  $\text{H}_3\text{PO}_4$ , 85%.
2.  $\text{H}_2\text{SO}_4$ , concentrated (96%).
3. NaF, solid.
4. Standard 0.167M  $\text{K}_2\text{Cr}_2\text{O}_7$ : Dissolve 49.04 g of dried (105°C)  $\text{K}_2\text{Cr}_2\text{O}_7$  in water and dilute to 1 L.
5. 0.5 M  $\text{Fe}^{2+}$  solution: Dissolve 196.1 g of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4) \cdot 6\text{H}_2\text{O}$  in 800 mL of water containing 20 mL of concentrated  $\text{H}_2\text{SO}_4$  and dilute to 1 L. The  $\text{Fe}^{2+}$  in this solution oxidizes slowly on exposure to air so it must be standardized against the dichromate daily.
6. Ferrous indicator: Slowly dissolve 3.71 g of o-phenanthroline and 1.74 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 250 mL of water.

### Procedure:

1. Weigh out 0.10 to 2.00 g dried soil (ground to <60 mesh) and transfer to a 500-mL Erlenmeyer flask. The sample should contain 10 to 25 mg of organic C (17 to 43 mg organic matter). For a 1 g soil sample, this would be 1.2 to 4.3% organic matter. Use up to 2.0 g of sample for light colored soils and 0.1 g for organic soils.
2. Add 10 mL of 0.167 M  $\text{K}_2\text{Cr}_2\text{O}_7$  by means of a pipette.
3. Add 20 mL of concentrated  $\text{H}_2\text{SO}_4$  by means of dispenser and swirl gently to mix. Avoid excessive swirling that would result in organic particles adhering to the sides of the flask out of the solution.
4. Allow to stand 30 minutes. The flasks should be placed on an insulation pad during this time to avoid rapid heat loss.
5. Dilute the suspension with about 200 mL of water to provide a clearer suspension for viewing the endpoint.
6. Add 10 mL of 85%  $\text{H}_3\text{PO}_4$ , using a suitable dispenser, and 0.2 g of NaF. The  $\text{H}_3\text{PO}_4$  and NaF are added to complex  $\text{Fe}^{3+}$  which would interfere with the titration endpoint.
7. Add 10 drops of ferrous indicator. The indicator should be added just prior to titration to avoid deactivation by adsorption onto clay surfaces.

8. Titrate with 0.5 M Fe<sup>2+</sup> to a burgundy endpoint. The color of the solution at the beginning is yellow-orange to dark green, depending on the amount of unreacted Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> remaining, which shifts to a turbid gray before the endpoint and then changes sharply to a wine red at the endpoint. Use of a magnetic stirrer with an incandescent light makes the endpoint easier to see in the turbid system (fluorescent lighting gives a different endpoint color). Alternatively use a Pt electrode to determine the endpoint after step 5 above. This will eliminate uncertainty in determining the endpoint by color change. If less than 5 mL of Fe<sup>2+</sup> solution was required to backtitrate the excess Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> there was insufficient Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> present, and the analysis should be repeated either by using a smaller sample size or doubling the amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>SO<sub>4</sub>.
9. Run a reagent blank using the above procedure without soil. The blank is used to standardize the Fe<sup>2+</sup> solution daily.

10. Calculate %C and % organic matter:

a. % Easily Oxidizable Organic C

$$\%C = \frac{(B-S) \times M \text{ of Fe}^{2+} \times 12 \times 100}{\text{g of soil} \times 4000}$$

where:

B = mL of Fe<sup>2+</sup> solution used to titrate blank  
 S = mL of Fe<sup>2+</sup> solution used to titrate sample  
 12/4000 = milliequivalent weight of C in g.

To convert easily oxidizable organic C to total C, divide by 0.77 (or multiply by 1.30) or other experimentally determined correction factor. To convert total organic C to organic matter use the following equation:

b.  $\% \text{ Organic Matter} = \frac{\% \text{ total C} \times 1.72}{0.58}$

## ROUTINE COLORIMETRIC DETERMINATION OF SOIL ORGANIC MATTER

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### Equipment:

1. Standard 1 g scoop.
2. Glass marbles with a diameter slightly larger than the mouth of a 50 mL Erlenmeyer flask.
3. 50 mL Erlenmeyer flasks.
4. Digestion oven, capable of temperatures to 90°C, with air circulation fan and fume exhaust.
5. 10 and 25 mL pipettes or dispensers.
6. Standard organic matter samples.

### Reagents:

1. Digestion solution:  
 (0.5 M Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> • 2H<sub>2</sub>O in 5 M H<sub>2</sub>SO<sub>4</sub>):  
 Dissolve 140 g Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> • 2H<sub>2</sub>O in 600 mL of distilled water. Slowly add 278 mL of concentrated H<sub>2</sub>SO<sub>4</sub>. Allow to cool and dilute to 1 L with deionized water.

### Procedure:

1. Scoop 1 g of soil into a 50 mL Erlenmeyer flask. See Chapter 2 for details on proper scooping techniques.
2. Pipette 10 mL of dichromate-sulfuric acid digestion solution. Include a reagent blank without soil.

APPENDIX XXXV. SOP for Data Verification, Validation and Loading to the ILRP SWAMP Comparable Database. (Revision 2, 04/22/10)

# Standard Operating Procedure for Data Verification, Validation and Loading to the ILRP SWAMP Comparable Database

(Revision 2 April 22, 2010 AS)

## 1.0 Purpose

This standard operating procedure (SOP), based on Moss Landing Marine Laboratory's SWAMP Standard Operating Procedure for Data Loading and Verification of SWAMP database v1.1, describes the process used by the Michael L. Johnson, LLC Data Management Team (MLJ-LLC DMT) to verify, validate and load chemistry and bacteria data into the ILRP SWAMP comparable database. The data verification will be performed in accordance with the requirements of the ILRP QAPP (September 25, 2008).

## 2.0 Receipt of New Laboratory Data Files

1. Multiple laboratories send data for MLJ-LLC chemistry and bacteria analysis in SWAMP comparable Excel spreadsheets. These data files are delivered to the MLJ-LLC DMT who files the electronic data to be processed.

## 2.1 Filing and Storage of Laboratory Data Files

1. Data are stored on the "X" drive on the MLJ-LLC server within one of three main folders (New, Working, and Loaded). All new data are stored under the folder *Database\EDDs\New* in the appropriate event category folder. In addition, new data are also stored under the Lab folder in the appropriate coalition, event, agency, and "Original EDDs" category folders and renamed with a "\_OR" after the file name. For example, an inorganics file from coalition Y, event W, and analyzed by laboratory X would be filed in *Database\EDDs\New\EventW* as well as *Lab\Lab EDD\CoalitionY\CoalitionY\_EventW\Laboratory X\Original EDDs*.
2. While a file is being prepared for loading, it is moved from the specific *New* folder into the *Working* folder.
3. After all necessary corrections have been made and the data file is loaded, the file is moved into the *Database\EDDs\Loaded* folder beneath the appropriate analysis, agency and event category. A copy of the loaded file is also saved in the *Final EDDs* subfolder located on the common drive and renamed with "\_Loaded" and the date after the file name (e.g. *\_Loadedmmddyy*). For example, data from laboratory X and coalition Y for event W would be filed in *Lab\Lab EDD\CoalitionY\CoalitionY\_EventW\LaboratoryX\Final EDDs*.

## 3.0 Loading Laboratory Data Files

Verification checklists exist for each labs electronic data files, listing the specific formatting and data verification needed prior to uploading that labs data. Checklists are updated regularly and are used to ensure quality control. Listed below are all manual data formatting and verification checks needed prior to loading any data file into the Data Loader Program.

## 3.1 Manual Verification of Unloaded Laboratory Data Files

1. Verify sample integrity
  - a. Verify all results, MDL and RL values with the hardcopy data report.
  - b. Verify result qualifier code (*ResultQualCode* field).
  - c. Verify dates (*Prep Date*, *DigestExtractDate*, and *AnalysisDate* fields) with the hardcopy data report.



- d. Verify the following fields have been entered correctly: *SampleCode*, *EventType*, *ProtocolCode*, *SampleDate*, *CollectionTime*, *SampleTypeCode*, *Replicate*, *CollectionDepth*, *UnitCollectionDepth*, *ProjectCode*, and *AgencyCode* with the appropriate Sample Details table (see Sample Details SOP).
  - e. Verify that the analytes listed in the appropriate Sample Details table have been analyzed for.
  - f. Verify that the holding times have been met as required by the method or the QAPP.
  - g. Verify the *QACode*.
  - h. Verify that batch requirements are met (as per QAPP).
2. Verify method blanks
- a. Verify the method blanks have met the frequency requirements as stated in the QAPP.
  - b. Verify the *SampleTypeCode* is "*LabBlank*".
  - c. Verify that the method blank is within control limits.
  - d. Verify the *QACode* (data outside of control limits must be flagged with the appropriate code).
3. Verify surrogates
- a. Verify surrogates were reported for all samples, blanks, and QC samples as required by the methods. Surrogates are reported as percents with an expected value of 100.
  - b. Verify percent recovery (PR) values were entered in the *Result* field and "%" was entered into the *UnitName* field.
  - c. Verify the surrogates were within the QC acceptance limits as stated in the QAPP.
  - d. Verify the *QACode* (data outside of control limits must be flagged with the appropriate code). If surrogate is flagged, all samples in the batch receive the QA flag as well.
4. Verify the laboratory QC samples (e.g. MS/MSDs, DUPs, LCSs, and CRMs).
- a. Verify the laboratory QC samples met the frequency requirements of the QAPP.
  - b. Verify the codes in the *SampleTypeCode* field against the "*SampleTypeCode LookUp*" table.
  - c. Verify a value was entered in the *ExpectedValue* field for spiked samples.
  - d. Verify the units in the *UnitName* field.
  - e. Verify the QC samples were within the QC acceptance limits as stated in the QAPP.
  - f. Verify the *QACode* (data outside of control limits must be flagged with the appropriate code).
  - g. Verify that all lab replicates of 2 have an RPD value and a corresponding lab replicate 1 result.
  - h. Verify that all LCS samples have a *MatrixName* of "blankwater."
5. Verify the field QC samples (e.g. travel blanks, equipment blanks, field blanks, field duplicates).
- a. Verify the field QC samples meet the frequency requirements of the QAPP.
  - b. Calculate the FieldDup relative percent difference (FD RPD) and verify the FieldDup results were within the expected range of the native sample as stated in the QAPP (RPD<25).
  - c. Verify the *QACode* is correct if the FieldDup RPD was greater than 25. Both FieldDup and environmental sample receive the flag.
  - d. Verify that the FieldBlanks are within control limits as stated in the QAPP (<RL or <1/5 environmental sample).
  - e. Verify the *QACode* is correct if the FieldBlanks were outside the control limits.
  - f. Verify that the *MatrixName* for FieldBlanks, EquipBlanks and TravelBlanks is "blankwater."
6. Verify the target analytes and target reporting limits (TRLs).
- a. Verify against the QAPP that the required target analytes were reported for each requested method for every sample, QC sample, and blank.

- b. Verify the TRLs in the *RL* field are consistent with the required TRLs in the QAPP.
  - c. Verify that the TRLs have been adjusted to reflect all sample dilutions, concentrations and splits.
  - d. Verify the method detection limit (MDL) results in the *MDL* field are at or below the RL values in the *RL* field.
  - e. Verify the units in the *UnitName* field were correct based on the matrix reported.
7. Verify formatting
- a. Verify that the two worksheets *Results* and *LabBatch* exist and are properly named.
  - b. Verify that the Results and LabBatch header rows are correctly formatted (See Chem Analysis Template).
  - c. Date formats should be dd/mmm/yyyy.
  - d. Time formats should be xx:xx.
  - e. Stations, analytes, methods and qualifiers match values in lookup lists
  - f. Results, MDL and RL values should not be calculated values and only contain numerical values.
  - g. LABQA records have the appropriate format for sample information.
8. Verify record completeness
- a. All required fields are complete in *Results* sheet for all records.
  - b. All required fields are complete in *LabBatch* sheet for all records.
9. Verify that all Lab Batch names are unique and are identified in the LabBatch sheet.
- a. Verify that the *LabSubmissionCode* reflects the batch (i.e. missing QC, no QC or minor deviations). Batches with any flags other require a batch comment.

### 3.2 Corrective Action/Resolution

When errors are found either in the data file which prevent it from being loaded into the database or the hardcopy report the following corrective actions will be performed:

1. The appropriate lab will be contacted regarding the issue(s) requiring resolution and sent a copy of the data file to use as a reference if needed.
2. If the issue requires a resubmission, per the direction of the MLJ-LLC DMT, a revised data file and/or hardcopy report will be requested from the laboratory.
3. All other minor issues will be revised by the DMT and the lab notified of these changes prior to loading the data.

### 3.3 Chemistry Loader Protocol

1. Once verification checks have been completed, the data file is manually loaded into the database following the Chemistry Loader Protocol (file name: Chemistry Loader Protocol\_AS\_MT111609).

## Chemistry Loader Protocol

Name of excel file: \_\_\_\_\_  copy of database

Date: \_\_\_\_\_

Username: \_\_\_\_\_

#Results Sheet \_\_\_\_\_

#Batch Sheet \_\_\_\_\_

**Link loader to current database:** In the switchboard loader form type the UserName of the person loading data and add the suffix "-DL" for data loader (i.e. "mturner-DL"). Then click on the BROWSE DATABASE button under Step 2 on the form. Browse to the current database where data will be entered and click OPEN. Click RE-LINK on the switchboard form.

**Import data:** Click on the BROWSE DATA FILE button under Step 3 on the switchboard form. Browse to the excel file that contains the data to be loaded. Click OPEN. Click IMPORT DATA button. A message confirming all data currently in the two static tables will be overwritten, Click YES. Click OK.

- The Results and LabBatch data from the Excel file have now been imported into two static tables named:
  - 1tblBatch
  - 1tblResults
- Open each table to check that the data looks correct and that the number of records in each matches the original excel file counts.

	Before	After
#LabBatch	_____	_____
#LabCollection_Entry	_____	_____
#LabResult_Entry	_____	_____
#Location_Entry	_____	_____
#Sample_Entry	_____	_____

### Unique queries:

- zBatch Unique
- zResults1 1Samples Unique
- zResults1 2Locations Unique
- zResults1 3Collections Unique
- zResults1 4Results Unique

These queries check the number of unique values in the file to load. Run queries and check that the data looks correct.

**FileChecker Report:** Check the imported data using the switchboard form. Click the RUN REPORT button under Step 4 of the form. A new window will open with the report findings. Review this information and make any necessary changes to the Excel file. If any changes are needed, save the Excel file and re-import the data. Re-run the report until all errors are either corrected or expected.

- Expect to see all LabBatches
- Expect all LABQA and NONPJ to have unmatched Locations, LabCollections, and Results

### Load LabBatches:

- Run select query zBatch. Displays all batches in the static table 1tblBatch, check that the numbers are correct. Close this query.
  - zBatch records \_\_\_\_\_.
- Run select query zBatch WOMatch LabBatch. Displays all batches not currently in the database. Should equal number of batches in zBatch.
- Open append query zBatch WOMatch LabBatch Append in **design view – DO NOT RUN**. \*\*See NOTE below. Click on the datasheet view to display unique batches that will be appended. The number of batches should match the number from zBatch WOMatch LabBatch. Click on the design view and run this query. A window will appear confirming the number of batches to append, click YES if it is the correct number.

### #Batches appended\_\_\_\_\_

\*\*NOTE: The query automatically adds a BatchVerificationCode of "Vac". Use this default ONLY if data has undergone all standard data checking and quality control procedures (usually this applies to all data). IF for some reason the data was not subject to all standard procedures, you MUST change the BatchVerificationCode to Not Recorded (NR). Go to design view, in the Field row of the BatchVerificationCode column change the text from [BatchVerificationCode: "Vac"] to [BatchVerificationCode: "NR"].

- Run query zBatch WOMatch LabBatch again. Query should be blank if all batches were appended properly.

### Load Samples:

- Run select query zResults1 1Samples. Displays all samples in the static table 1tblResults, check that the numbers are correct. Close this query.
  - zResults1 1Samples Records: \_\_\_\_\_.
- Run query zResults1 1Samples WOMatch Sample Entry. Displays all samples not currently in the database. Most often LABQA and NONPJ samples will be the only ones needed to be appended. Close this query.
- Open append query zResults1 1Samples WOMatch Sample Entry Append in **design view – DO NOT RUN**. Click on the datasheet view to display number of unique samples that will be appended. The number should match the number from zResults1 1Samples WOMatch Sample Entry. Click on the design view and run this query. A window will appear confirming the number of samples to append, click YES if it is the correct number.

### #Samples appended\_\_\_\_\_

- Run query zResults1 1Samples WOMatch Sample Entry again. Query should be blank if all samples were appended properly.

### Load Locations:

- Run select query zResults1 2Locations. Displays all samples in the static table 1tblResults, check that the numbers are correct. Close this query.
  - zResults1 2Locations Records: \_\_\_\_\_.
- Run query zResults1 2Locations WOMatch Location Entry. Displays all locations not currently in the database. Most often LABQA and NONPJ locations will be the only ones needed to be appended, and number of results will be the same as the number of Samples previously appended. Close this query.
- Open append query zResults1 2Locations WOMatch Location Entry Append in design view. Click on the datasheet view to display number of unique locations that will be appended. The number should match the number from zResults1 2Locations WOMatch Locations Entry. Click on the design view and run this query. A window will appear confirming the number of locations to append, click YES if it is the correct number.

### #Locations appended\_\_\_\_\_

- Run query zResults1\_2Locations\_WOMatch\_Location\_Entry again. Query should be blank if all locations were appended properly.

### Load Collections:

- Run select query zResults1\_3Collections. Displays all samples in the static table 1tblResults, check that the numbers are correct. Close this query.
  - zResults1\_3Collections Records:\_\_\_\_\_.
- Run query zResults1\_3Collections\_WOMatch\_Collection\_Entry. Displays all collections not currently in the database. Most often LABQA and NONPJ collections will be the only ones needed to be appended. Close this query.
- Open append query zResults1\_3Collections\_WOMatch\_Collection\_Entry\_Append in **design view – DO NOT RUN**. Click on the datasheet view to display number of unique collections that will be appended. The number should match the number from zResults1\_3Collections\_WOMatch\_Collection\_Entry. Click on the design view and run this query. A window will appear confirming the number of collections to append, click YES if it is the correct number.

### #Collections appended\_\_\_\_\_

- Run query zResults1\_3Collections\_WOMatch\_Collection\_Entry again. Query should be blank if all collections were appended properly.

### Load Collection Comments:

- Run select query zResults1\_4CollectionsComments. Displays all collection comments in the static table 1tblResults. **If there are no collection comments to append, skip ahead to Load Results.**

### Load Results:

- Open make table query zResults1\_5Collections\_MakeTable in **design view – DO NOT RUN**. This query creates a static table of unique collections in the database. Run this query. Click YES to the first window confirming that the data in the table tblSampleCollectionTemp will be deleted, and then click YES to the window confirming that the certain number rows will be added to the static table. Close the query.
  - zResults1\_5Collections\_MakeTable Records:\_\_\_\_\_.
- Run select query zResults1\_5Results. Displays all results in the static table 1tblResults, check that the numbers are correct. Close this query.
  - zResults1\_5Results Records:\_\_\_\_\_.
- Run query zResults1\_5Results\_WOMatch\_Results. Displays all results not currently in the database. The number of results in query zResults1\_5Results and this query **should** be identical. Close this query.
- Open append query zResults1\_5Results\_WOMatch\_Results\_Append in **design view – DO NOT RUN**. \*\*See NOTE below. Click on the datasheet view to display the number of unique results that will be appended. The number should match the number from zResults1\_5Results\_WOMatch\_Results. Click on the design view and run this query. A window will appear confirming the number of results to append, click YES if it is the correct number.

### #Results appended\_\_\_\_\_

\*\*NOTE: The query automatically adds a ComplianceCode of compliance (Com). Use this default ONLY if data has undergone all standard data checking and quality control procedures (usually this applies to all data). IF for some reason the data was not subject to all standard procedures, you MUST change the ComplianceCode to Not Recorded (NR). Go to design view, in the Field row of the ComplianceCode column change the text from [ComplianceCode: "Com"] to [ComplianceCode: "NR"].

- Run query zResults1\_5Results\_WOMatch\_Results again. Query should be blank if all results were appended properly.

**Check Loaded Data:** Use *qry4SampleResults\_Entry* to compare the records in the Excel file to those in the database. Filtering by the LastUpdateDate will allow you to see the number of records that were uploaded on any particular day. Check that the number of records in the excel file equal the number of records uploaded.

**Record number of records uploaded in excel data tracker**

APPENDIX XXXVI. SOP for Creating Sample Detail Excel Files (Revision 2, 05/04/10)

# Standard Operating Procedure for Creating Sample Detail Excel Files

(Revision 2 May 04, 2010 AS)

## 1.0 Purpose

This standard operating procedure (SOP) describes the process used by the Michael L. Johnson, LLC Data Management Team (MLJ-LLC DMT) to create excel files for laboratories that outline the details of the samples collected in the field. The sample detail files aid the laboratories in formatting their electronic deliverable data (EDDs) to be SWAMP comparable and are verified against the Chain of Custody (COC) forms.

## 2.0 Retrieval of Data from the Database

1. After all the desired field data has been entered into the Access database (see Field Data Entry SOP), open qrySampleDetailsExpanded in the most recent version of the Report\_QryDatabase\_121608\_AS.
  - a. In the Design View set the "SampleDate" criteria to the desired sampling event date, and the "SamplePurposeCode" to FieldMeasure.
  - b. Switch back to Table View.
  - c. Copy and paste the table from Access into the SampleDetails\_Template\_2.5 "Database" tab, found in the *Sample Details* folder on the "X" drive on the MLJ-LLC server.
2. To obtain the data for the individual lab tabs open qrySampleDetails in the most recent version of the Report\_QryDatabase\_121608\_AS.
  - a. In the Design View set the "SampleDate" criteria to the desired sampling event date.
  - b. Switch back to Table View.
  - c. Copy and paste the table from Access into the SampleDetails\_Template\_2.5 "APPL" tab.

## 3.0 Verify Field Data Entry

1. Copy and paste all the sampled site rows from the APPL worksheet into each of the individual lab worksheets.
  - a. Delete station names and replace with the SampleIDs found on the Chain of Custody forms (COCs).
2. For each lab, verify that the *StationCode* of the sites in the database match those listed on their respective COCs.
3. Verify the *EventCode* is "WQ" for all samples.
4. Verify the *ProtocolCode* is "MLJ\_FieldSOP\_031309", unless using a different protocol or technique (i.e. clean hands/dirty hands), for all samples.
5. Verify the location that each site was sampled by checking the *LocationCodes* against the locations listed on the field sheets.
6. Verify that the *CollectionTime* of the sites in the database match those listed on the COC, and that the time has been formatted as text.
7. Verify *CollectionMethodCode*.
  - a. The code should be "Water\_Grab" for all water samples and "Sed\_Grab" for sediment samples.



- b. The code should be “Not Applicable” for all blank samples.
8. Verify *SampleTypeCode*.
    - a. All field duplicate samples are now listed as “Grab” with a *Replicate* of “2”.
    - b. MS are now “MS1”.
  9. Verify that all *Replicates* are “1”, with the exception of field duplicate Grab samples which are “2”.
  10. Verify *CollectionDepth*.
    - a. “0.1” for all water samples and “2” for sediment samples.
  11. Verify *UnitCollectionDepth*.
    - a. “m” for all water samples and “cm” for sediment samples.
  12. Verify that the correct project is listed in the *ProjectCode* column ( “ESJWQC\_08” for the East San Joaquin Water Quality Coalition, “SJCDWQC\_08” for the San Joaquin County and Delta Water Quality Coalition, and “TMDL\_SJR\_OP” for the San Joaquin River TMDL sampling).
  13. Verify that “MLJ-LLC” is listed as the *AgencyCode*.

#### **4.0 Laboratory Analysis**

1. Following *AgencyCode*, each laboratory worksheet lists the constituents or group of constituents analyzed for at their respective labs.
  - a. From the COC, mark with an “X” the constituents each lab is supposed to analyze for at each station. (Note: not every constituent or group of constituents is analyzed for at every station).

#### **5.0 Sample Detail Submission/Data Tracking**

1. When each lab's sample details worksheet has been completed, save the excel file in the SampleDetails folder under the “X” MLJ-LLC common drive in the appropriate coalition and group folder. Name the file “*CoalitionY\_SampleDetails\_GroupX\_date*.” For example an ESJWQC, Irrigation1 sampling event that occurred on April 23, 2008 would have a sample details file named “ESJWQC\_SampleDetails\_Irrigation1\_042308.”
2. After saving, submit the excel file by email to the appropriate laboratories.
3. The final three columns in the lab sample detail worksheets are filled out once the associated EDD has been received by the MLJ-LLC DMT. The dates the EDD is received, uploaded, and filed in pdf format should be noted in the *Received Data in SWAMP format*, and *Uploaded into Database* columns respectively.

APPENDIX XXXVII. SOP for Toxicity Data Verification, Validation and Loading to the ILRP SWAMP Comparable Database (Revision 2, 04/22/10)

# Standard Operating Procedure for Toxicity Data Verification, Validation and Loading to the ILRP SWAMP Comparable Database

(Revision 2 April 22, 2010 AS)

## 1.0 Purpose

This standard operating procedure (SOP), based on Moss Landing Marine Laboratory's SWAMP Standard Operating Procedure for Toxicity Data Verification of the SWAMP database v3.1, describes the process used by the Michael L. Johnson, LLC Data Management Team (MLJ-LLC DMT) to verify, validate and load toxicity data into the ILRP SWAMP comparable database. The data verification will be performed in accordance with the requirements of the most recent project specific QAPP.

## 2.0 Receipt of New Laboratory Data Files

1. Toxicity data are delivered electronically in SWAMP approved Excel spreadsheets to the MLJ-LLC DMT who file and process the data.

## 2.1 Filing and Storage of Laboratory Data Files

4. Data are stored on the "X" drive on the MLJ-LLC server within one of three main folders (New, Working, and Loaded). All new data are stored under the folder *Database\EDDs\New* in the appropriate event category folder. In addition, new data are also stored under the Lab folder in the appropriate coalition, event, agency, and "Original EDDs" category folders and renamed with a "\_OR" after the file name. For example, a toxicity file from coalition Y, event W, and analyzed by laboratory X would be filed in *Database\EDDs\New\EventW* as well as *Lab\Lab EDD\CoalitionY\CoalitionY\_EventW\Laboratory X\Original EDDs*.
5. While a file is being prepared for loading, it is moved from the specific *New* folder into the *Working* folder.
6. After all necessary corrections have been made and the data file is loaded, the file is moved into the *Database\EDDs\Loaded* folder beneath the appropriate analysis, agency and event category. A copy of the loaded file is also saved in the *Final EDDs* subfolder located on the common drive and renamed with "\_Loaded" and the date after the file name (e.g. *\_Loadedmmddyy*). For example, data from laboratory X and coalition Y for event W would be filed in *LaVLab EDD\CoalitionY\CoalitionY\_EventW\LaboratoryX\Final EDDs*.

## 3.0 Verifying and Loading Laboratory Data Files

Verification checklists exist for each labs electronic data files, listing the specific formatting and data verification needed prior to uploading that labs data. Checklists are updated regularly and are used to ensure quality control. Listed below are manual data formatting and verification checks needed prior to loading any toxicity data file.

## 3.1 Manual Verification of Unloaded Laboratory Data Files

1. Verify sample integrity
  - a. Verify *Mean*, *PctControl*, and *SigEffect* values in the *Summary* sheet with the hardcopy report.
  - b. Verify the following fields have been entered correctly: *StationCode*, *EventType*, *ProtocolCode*, *LocationCode*, *SampleDate*, *CollectionTime*, *CollectionMethodCode*,

- SampleTypeCode, Replicate, CollectionDepth, UnitCollectionDepth, ProjectCode* and *AgencyCode* with the appropriate Sample Details table (see Sample Details SOP).
- c. Verify that the correct toxicity species have been analyzed for at each sample site based on the Sample Detail sheet.
  - d. Verify that the holding times have been met as required by the method or the QAPP.
  - e. Verify the *TestQACode*.
  - f. Verify that the *SummaryComments* include an explanation for the following if they occur: Resample, or dilution.
  - g. Verify that the *TIENarrative* includes an explanation for a TIE if one is needed.
  - h. Verify that each batch has one control (CNEG) sample.
2. Verify toxicity and water quality measurement results
    - a. Verify values in the *Results* sheet with the hardcopy report.
    - b. Verify the correct number of replicates is reported as required by the QAPP.
    - c. Verify that the following fields have been entered correctly: *StationCode, EventType, ProtocolCode, LocationCode, SampleDate, CollectionTime, CollectionMethodCode, SampleTypeCode, Replicate, CollectionDepth, UnitCollectionDepth, ProjectCode* and *AgencyCode*.
    - d. Verify the correct water quality measurements are reported as required by the QAPP.
    - e. Verify that the water quality measurements meet the QC limits required by the QAPP.
    - f. Verify the values for *TimePoint*.
    - g. Verify that the evaluation thresholds meet QAPP requirements.
    - h. Verify the units in the *UnitAnalyte* field are correct based on the matrix reported.
  3. Verify laboratory QC samples (i.e. Control samples)
    - a. Verify that the laboratory QC samples meet the frequency requirements of the QAPP.
    - b. Verify the codes in the *SampleTypeCode* field against the *SampleTypeCode LookUp* table.
    - c. Verify the *Mean, PctControl, and StdDev* fields based on the hardcopy report.
    - d. Verify the units in the *UnitAnalyte* field.
    - e. Verify that the QC samples are within the QC acceptance limits as stated in the QAPP.
    - f. Verify the *TestQACode* which should reflect any QC limit exceedances.
  4. Verify field QC samples (i.e. Field duplicates)
    - a. Verify that the field QC samples meet the frequency requirements of the QAPP.
    - b. Verify the codes in the *SampleTypeCode* field against the *SampleTypeCode LookUp* table.
    - c. Calculate the FieldDup relative percent difference (RPD) and verify the FieldDup results are within the expected range of the native sample as stated in the QAPP (RPD<25).
    - d. Verify that the *TestQACode* is correct if the FieldDup RPD was greater than 25. Both FieldDup and environmental sample receive the flag.
  5. Verify formatting
    - a. Verify that the three worksheets *Results, Summary* and *ToxBatch* exist and are properly named.
    - b. Verify that the *Results, Summary* and *ToxBatch* header rows are correctly formatted (See Toxicity Template).
    - c. Date formats should be dd/mmm/yyyy.
    - d. Time formats should be xx:xx.
    - e. Station IDs, sample types, matrix, methods, species name, and qualifiers should match values in lookup lists.
    - f. *Result* and *PctControl* values should not be calculated values.
    - g. LABQA records have the appropriate format for sample and toxicity summary information.

6. Verify record completeness
  - a. All required fields are complete in *Results* sheet for all records.
  - b. All required fields are complete in *Summary* sheet for all records.
  - c. All required fields are complete in *ToxBatch* sheet for all records.
  
7. Verify that all Tox Batches are unique and are identified in the *ToxBatch* sheet.
  - a. Verify that if *TestQACode* in the *Summary* sheet is anything other than "None", the batch has a batch comment to explain the minor deviation (MD) and the *LabSubmissionCode* is "A,MD."
  - b. Verify that all *ToxBatchComments* which have no comments are labeled as "NR."
  - c. Verify that all *ToxBatchComments* are less than 250 characters.

### **3.2 Corrective Action/Resolution**

When errors are found either in the data file which prevent it from being loaded into the database or the hardcopy report the following corrective actions will be performed:

4. The appropriate lab will be contacted regarding the issue(s) requiring resolution and sent a copy of the data file to use as a reference if needed.
  
5. If the issue requires a resubmission, per the direction of the MLJ-LLC DMT, a revised data file and/or hardcopy report will be requested from the laboratory.
  
6. All other minor issues will be revised by the DMT and the lab notified of these changes prior to loading the data.

### **3.3 Toxicity Loader Protocol**

2. Once verification checks have been completed, the data file is manually loaded into the database following the Tox Loader Protocol (file name: Toxicity Loader Protocol\_041910SH).

**Tox Loader Protocol**

Name of excel file: \_\_\_\_\_

☐ copy of database

Date: \_\_\_\_\_

Username: \_\_\_\_\_

#Summary Sheet \_\_\_\_\_

#Results Sheet \_\_\_\_\_

#ToxBatch Sheet \_\_\_\_\_

**Link loader to current database:** In the switchboard loader form type the UserName of the person loading data and add the suffix “-DL” for data loader (i.e. “mturner-DL”). Then click on the BROWSE DATABASE button under Step 2 on the form. Browse to the current database where data will be entered and click OPEN. Click RE-LINK on the switchboard form.

**Import data:** Click on the BROWSE DATA FILE button under Step 3 on the switchboard form. Browse to the excel file that contains the data to be loaded. Click OPEN. Click IMPORT DATA button. A message confirming all data currently in the three static tables will be overwritten, Click YES. Click OK.

- The Summary, Results and ToxBatch data from the Excel file have now been imported into three static tables named:
  - 1tblToxBatch
  - 1tblToxResults
  - 1tblToxSummary
- Open each table to check that the data looks correct and that the number of records in each matches the original excel file counts.
- Go through the 1tblToxResults and **delete all -88 Result values** (if there are any), cells should be left blank.
- Import Summary data from Excel file into 1tblSummary\_import. Go to design view and **change the CollectionTime data type from TEXT to DATE/TIME & the PctControl data type from NUMBER to TEXT.**

	Before	After
#LabCollection_Entry	_____ / _____	_____ / _____
#Location_Entry	_____ / _____	_____ / _____
#Sample_Entry	_____ / _____	_____ / _____
#ToxBatch	_____ / _____	_____ / _____
#ToxPoint_Entry	_____ / _____	_____ / _____
#ToxPointSummary_Entry	_____ / _____	_____ / _____
#ToxResult_Entry	_____ / _____	_____ / _____
#ToxTest_Entry	_____ / _____	_____ / _____

**Unique queries, Part I of II:**

- zTox00Batch Unique

This query checks the number of unique values in the file to load. Run the unique batch query and check that the data looks correct. (The other unique queries will be run after imported data constituents are linked with rowIDs.)

**FileChecker Report:** Check the imported data using the switchboard form. Click the RUN REPORT button under Step 4 of the form. A new window will open with the report findings. Review this information and make any necessary changes to the Excel file. If any changes are needed, save the Excel file and re-import the data. Re-run the report until all errors are either corrected or expected.

- Expect to see all LabBatches
- Expect all LABQA to have unmatched Samples, Locations, and Collections.

#### Load ToxBatches:

- Run select query zTox00Batch. Displays all batches in the static table 1tblToxBatch, check that the numbers are correct. Close this query.
  - zTox00Batch records \_\_\_\_\_.
- Run select query zTox00Batch WOMatch ToxBatch. Displays all batches not currently in the database. Should equal number of batches in zTox01Batch.
- Open append query zTox00Batch WOMatch ToxBatch Append in **design view – DO NOT RUN**. Click on the datasheet view to display unique batches that will be appended. The number of batches should match the number from zTox00Batch WOMatch ToxBatch. Click on the design view and run this query. A window will appear confirming the number of batches to append, click YES if it is the correct number.

#### #Batches appended \_\_\_\_\_

- Run query zTox00Batch WOMatch ToxBatch again. Query should be blank if all batches were appended properly.

#### Link Imported Data Constituents with RowIDs:

- Open the make table query zTox00Result xWalk MethodDetail MT in **design view – DO NOT RUN**. This query creates a static table that helps to link the constituents to the needed rowIDs for the data you are trying to import. Run this query. Click YES to the first window confirming that the data in table tblXLResultsRecordID MethodDetailRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxResults). Close the query.
  - zTox00Result xWalk MethodDetail MT Records: \_\_\_\_\_.
- Open the make table query zTox00Result xWalk ConstituentRowID MT in **design view – DO NOT RUN**. This query creates a static table that helps to link the constituents to the needed rowIDs for the data you are trying to import. Run this query. Click YES to the first window confirming that the data in table tblXLResultRecordID ConstituentRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxResults). Close the query.
  - zTox00Result xWalk ConstituentRowID MT Records: \_\_\_\_\_.
- Open the make table query zTox00Summary xWalk ConstituentRowID MT in **design view – DO NOT RUN**. This query creates a static table that helps to link the constituents to the needed rowIDs for the data you are trying to import. Run this query. Click YES to the first window confirming that the data in table tblXLSummaryRecordID ConstituentRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxSummary). Close the query.
  - zTox00Summary xWalk ConstituentRowID MT Records: \_\_\_\_\_.
- Open the make table query zTox00Summary xWalk MethodDetail MT in **design view – DO NOT RUN**. This query creates a static table that helps to link the constituents to the needed rowIDs for the data you are trying to import. Run this query. Click YES to the first window confirming that the data in table tblXLSummaryRecordID MethodDetailRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxSummary). Close the query.
  - zTox00Summary xWalk MethodDetail MT Records: \_\_\_\_\_.

#### Unique queries, Part II of II:

- zTox02Results 1Samples Unique
- zTox02Results 2Locations Unique
- zTox02Results 3Collections Unique
- zTox02Results 4ToxTest Unique
- zTox02Results 5ToxPoint Unique
- zTox02Results 6ToxResult Unique
- zTox02Summary 7ToxSummary Unique

These queries check the number of unique values in the file to load. Run queries and check that the data looks correct.

### Load Samples:

- Run select query zTox03Results\_Samples. Displays all samples in the static table 1tblToxResults, check that the numbers are correct. Close this query.
  - zTox03Results\_Samples Records: \_\_\_\_\_.
- Run query zTox03Results\_Samples\_WOMatch\_Sample\_Entry. Displays all samples not currently in the database. Most often LABQA samples will be the only ones needed to be appended. Close this query.
- Open append query zTox03Results\_Samples\_WOMatch\_Sample\_Entry\_Append in **design view – DO NOT RUN**. Click on the datasheet view to display number of unique samples that will be appended. The number should match the number from zTox03Results\_Samples\_WOMatch\_Sample\_Entry. Click on the design view and run this query. A window will appear confirming the number of samples to append, click YES if it is the correct number.

### #Samples appended

- Run query zTox03Results\_Samples\_WOMatch\_Sample\_Entry again. Query should be blank if all samples were appended properly.
- Open the make table query zTox03Results\_Samples\_xWalk\_SampleRowID\_MT in **design view – DO NOT RUN**. This query creates a static table that links the SampleRowID from the database to the data in the 1tblToxResults table and makes comparison of data in the database quicker. Run this query. Click YES to the first window confirming that the data in table tblXLResultsRecordID\_SampleRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxResults). Close the query.
  - zTox03Results\_Samples\_xWalk\_SampleRowID\_MT Records: \_\_\_\_\_.

### Load Locations:

- Run select query zTox04Results\_Locations. Displays all samples in the static table 1tblToxResults, check that the numbers are correct. Close this query.
  - zTox04Results\_Locations Records: \_\_\_\_\_.
- Run query zTox04Results\_Locations\_WOMatch\_Location\_Entry. Displays all locations not currently in the database. Most often LABQA locations will be the only ones needed to be appended, and number of results will be the same as the number of Samples previously appended. Close this query.
- Open append query zTox04Results\_Locations\_WOMatch\_Location\_Entry\_Append in **design view-DO NOT RUN**. Click on the datasheet view to display number of unique locations that will be appended. The number should match the number from zTox04Results\_Locations\_WOMatch\_Locations\_Entry. Click on the design view and run this query. A window will appear confirming the number of locations to append, click YES if it is the correct number.

### #Locations appended

- Run query zTox04Results\_Locations\_WOMatch\_Location\_Entry again. Query should be blank if all locations were appended properly.
- Open the make table query zTox04Results\_Locations\_xWalk\_LocationRowID\_MT in **design view – DO NOT RUN**. This query creates a static table that links the LocationRowID from the database to the data in the 1tblToxResults table and makes comparison of data in the database quicker. Run this query. Click YES to the first window confirming that the data in table tblXLResultsRecordID\_LocationRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxResults). Close the query.
  - zTox04Results\_Locations\_xWalk\_LocationRowID\_MT Records: \_\_\_\_\_.

### Load Collections:

- Run select query zTox05Results\_Collections. Displays all samples in the static table 1tblToxResults, check that the numbers are correct. Close this query.
  - zTox05Results\_Collections Records: \_\_\_\_\_.
- Run query zTox05Results\_Collections\_WOMatch\_Collection\_Entry. Displays all collections not currently in the database. Most often LABQA collections will be the only ones needed to be appended. Close this query.
- Open append query zTox05Results\_Collections\_WOMatch\_Collection\_Entry\_Append in **design view – DO NOT RUN**. Click on the datasheet view to display number of unique collections that will be appended. The number should match the number from



zTox05Results\_Collections\_WOMatch\_Collection\_Entry. Click on the design view and run this query. A window will appear confirming the number of collections to append, click YES if it is the correct number.

### #Collections appended

- Run query zTox05Result\_Collections\_WOMatch\_Collection\_Entry again. Query should be blank if all collections were appended properly.
- Open the make table query zTox05Results\_Collections\_xWalk\_LabCollectionRowID\_MT in **design view – DO NOT RUN**. This query creates a static table that links the LabCollectionRowID from the database to the data in the 1tblToxResults table and makes comparison of data in the database quicker. Run this query. Click YES to the first window confirming that the data in table tblXLResultsRecordID\_LabCollectionRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxResult). Close the query.
  - zTox05Results\_Collections\_xWalk\_LabCollectionRowID\_MT Records: \_\_\_\_\_.

### Load Collection Comments:

- Run select query zTox06Results\_CollectionsComments. Displays all collection comments in the static table 1tblToxResults. **If there are no collection comments to append, skip ahead to Load ToxTests.**

### Load ToxTests:

- Run select query zTox07Results\_ToxTest. Displays all results in the static table 1tblToxResults, check that the numbers are correct. Close this query.
  - zTox07Results\_ToxTest Records: \_\_\_\_\_.
- Run query zTox07Results\_ToxTest\_WOMatch\_ToxTest\_Entry. Displays all results not currently in the database. The number of results in query 1tblToxSummary and this query **should** be identical. Close this query.
- Open append query zTox07Results\_ToxTest\_WOMatch\_ToxTest\_Entry\_Append in **design view – DO NOT RUN**. Click on the datasheet view to display the number of unique results that will be appended. The number should match the number from zTox07Summary\_ToxTest\_WOMatch\_ToxTest. Click on the design view and run this query. A window will appear confirming the number of results to append, click YES if it is the correct number.

### #ToxTests appended

- Run query zTox07Results\_ToxTest\_WOMatch\_ToxTest\_Entry again. Query should be blank if all results were appended properly.
- Open the make table query zTox07Results\_ToxTest\_xWalk\_ToxTestRowID\_MT in **design view – DO NOT RUN**. This query creates a static table that links the ToxTestRowID from the database to the data in the 1tblToxResults table and makes comparison of data in the database quicker. Run this query. Click YES to the first window confirming that the data in table tblXLResultsRecordID\_ToxTestRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxResults). Close query.
  - zTox07Results\_ToxTest\_xWalk\_ToxTestRowID\_MT Records: \_\_\_\_\_.
- Open the make table query zTox07Summary\_ToxTest\_xWalk\_ToxTestRowID\_MT in **design view – DO NOT RUN**. This query creates a static table that links the ToxTestRowID from the database to the data in the 1tblToxSummary table and makes comparison of data in the database quicker. Run this query. Click YES to the first window confirming that the data in table tblXLSummaryRecordID\_ToxTestRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxSummary). Close the query.
  - zTox07Summary\_ToxTest\_xWalk\_ToxTestRowID\_MT Records: \_\_\_\_\_.
- Open the make table query zTox07Summary\_ToxTest\_QACode\_Update in **design view – DO NOT RUN**. This query creates a static table that links the QACodes from the database to the data in the 1tblToxSummary table and makes comparison of data in the database quicker. Run this query. Click YES to the window confirming that the certain number of rows will be updated in the static table (The number should match the number from 1tblToxSummary). Close the query.
  - zTox07Summary\_ToxTest\_QACode\_Update Records: \_\_\_\_\_.

### Load ToxPoints:

- Run select query zTox08Results\_ToxPoint. Displays all results in the static table 1tblToxResults, check that the numbers are correct. Close this query.
  - zTox08Results\_ToxPoint Records: \_\_\_\_\_.

- Run query zTox08Results\_ToxPoint\_WOMatch\_ToxPoint. Displays all results not currently in the database. Note: "Survival" and "Total Cell Count" tox points will only be counted once for each collection. Close this query.
- Open append query zTox08Results\_ToxPoint\_WOMatch\_ToxPoint\_Append in **design view – DO NOT RUN**. Click on the datasheet view to display the number of unique results that will be appended. Click on the design view and run this query. A window will appear confirming the number of results to append, click YES if it is the correct number.

### #ToxPoints appended

- Run query zTox08Results\_ToxPoint\_WOMatch\_ToxPoint again. Query should be blank if all results were appended properly.
- Open the make table query zTox08Results\_ToxPoint\_xWalk\_ToxPointRowID\_MT in **design view – DO NOT RUN**. This query creates a static table that links the ToxPointRowID from the database to the data in the 1tblToxResults table and makes comparison of data in the database quicker. Run this query. Click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxResults). Close the query.
  - zTox08Results\_ToxPoint\_xWalk\_ToxPointRowID\_MT Records: \_\_\_\_\_.
- Open the make table query zTox08Summary\_ToxPoint\_xWalk\_ToxPointRowID\_MT in **design view – DO NOT RUN**. This query creates a static table that links the ToxPointRowID from the database to the data in the 1tblToxSummary table and makes comparison of data in the database quicker. Run this query. Click YES to the first window confirming that the data in table tblXLSummaryRecordID\_ToxPointRowID will be deleted, and then click YES to the window confirming that the certain number of rows will be added to the static table (the number should match the number from 1tblToxSummary). Close the query.
  - zTox08Summary\_ToxPoint\_xWalk\_ToxPointRowID\_MT Records: \_\_\_\_\_.

### Load ToxResults:

- Run select query zTox09Results\_ToxResult. Displays all results in the static table 1tblToxResults, check that the numbers are correct. Close this query.
  - zTox09Results\_ToxResult Records: \_\_\_\_\_.
- Run query zTox09Results\_ToxResult\_WOMatch\_ToxResult\_Entry. Displays all results not currently in the database. The number of results in query zTox09Results\_ToxResult and this query **should** be identical. Close this query.
- Open append zTox09Results\_ToxResult\_WOMatch\_ToxResult\_Entry\_Append in **design view – DO NOT RUN**. \*\*See NOTE below. Click on the datasheet view to display the number of unique results that will be appended. The number should match the number from zTox09Results\_ToxResult\_WOMatch\_ToxResult\_Entry. Click on the design view and run this query. A window will appear confirming the number of results to append, click YES if it is the correct number.

### #ToxResults appended

NOTE: The query automatically adds a ComplianceCode of compliance (Com). Use this default ONLY if data has undergone all standard data checking and quality control procedures (usually this applies to all data). IF for some reason the data was not subject to all standard procedures, you MUST change the ComplianceCode to Not Recorded (NR). Go to design view, in the Field row of the ComplianceCode column change the text from [ComplianceCode: "Com"] to [ ComplianceCode: "NR"].

- Run query zTox09Results\_ToxResult\_WOMatch\_ToxResult\_Entry again.

### Load ToxPointSummary:

- Run select query zTox10Summary\_ToxSummary. Displays all results in the static table 1tblToxSummary, check that the numbers are correct. Close this query.
  - zTox10Summary\_ToxSummary Records: \_\_\_\_\_.
- Run query zTox10Summary\_ToxSummary\_WOMatch\_ToxPointSum\_Entry. Displays all results not currently in the database. The number of results in query zTox10Summary\_ToxSummary and this query **should** be identical. Close this query.
- Open append query zTox10Summary\_ToxSummary\_WOMatch\_ToxPointSum\_Entry\_Append in **design view – DO NOT RUN**. Click on the datasheet view to display the number of unique results that will be appended. The number should match the number from zTox10Summary\_ToxSummary\_WOMatch\_ToxPointSum\_Entry. Click on the design view and run this query. A window will appear confirming number of results to append, click YES if it is correct number.

**#ToxPointSummary appended**

- Run query zTox10Summary\_ToxSummary\_WOMatch\_ToxPointSum\_Entry again. Query should be blank if all results were appended properly.

**Record number of records uploaded in excel data tracker**