Analysis and Reporting of Non-Target Semi-Volatile Organic Compounds in Extremely Impaired Water Sources and Recycled Water Using Methods 3510C/8270C

1) Analysis for semi-volatile organic compounds

   a) USEPA approved drinking water methods should be used, as applicable, to analyze for the regulated and unregulated drinking water chemical contaminants listed by the USEPA or the California Department of Health Services (DHS).

   b) When a general semi-volatile organic compound analysis is required, USEPA methods 3510C (Rev. 3, 12/96) and 8270C (Rev. 3, 12/96) should be used instead of USEPA method 525.2 (Rev. 4.1, 1995) for the following reasons.

      i) The liquid-liquid extraction procedure in method 3510C is designed to extract acidic, neutral and basic organic compounds, whereas the liquid-solid phase extraction procedure in method 525.2 is designed to extract primarily acidic and neutral compounds.

      ii) Method 8270C includes 241 target compounds compared to 118 target compounds in method 525.2. It should be noted, however, that some of the compounds listed in methods 8270C and 525.2 should be analyzed for qualitative purposes only, due to poor quantitative performances with these compounds. Also, the extraction efficiency of method 3510C has not been determined for a few of the compounds listed in method 8270C.

   c) When using methods 3510C/8270C:

      i) Calibrate the instrument with as many target compounds, as is practical. However, phenol and benzo(ghi)perylene must be included as analytes because these two compounds are also used to determine the retention time window for data collection by the mass spectrometer detector.

      ii) The analytical and quality control guidelines in USEPA method 8000B (Rev. 2, 12/96) should be employed, unless superseded by the guidelines in method 8270C.

      iii) Non-target compounds detected in the analysis shall be reported as described in this document.

2) Definitions

   a) Non-target compounds are compounds detected in a sample that are not method compounds (*i.e.,* target or calibrated compounds), internal standards, system monitoring compounds, or surrogate compounds. See the Tables 1, 2, and 3 for the list of target compounds, internal standards and surrogate compounds, respectively.

b) Target compounds are the method listed compounds that generally have been demonstrated to be applicable to the method and are used to calibrate the system for retention time and detector response.

c) Tentatively identified compounds (TICs) are non-target compounds, which have been subjected to mass spectral library searches for tentative identifications. Concentration estimates for TICs are determined by the internal standard method.

d) Unknown compounds are non-target compounds whose mass spectra do not adequately match the mass spectra from the mass spectral library searches for tentative identifications.

3) Reporting Requirements for Non-Target Compounds

a) The peak threshold for reporting non-target compounds is a signal to noise ratio of five, or higher. All non-target compounds, which are present in the sample at concentrations sufficient to produce peak signals equal to, or greater than the peak threshold shall be library searched and reported.

b) All non-target compounds that meet the peak threshold criterion and elute after benzo(ghi)perylene shall be library searched and reported. A preliminary GC analysis may be necessary to determine if the sample extract contains late eluting non-target compounds. The GC run time and the mass spectrometer data collection time parameters should be adjusted, as required.

c) All non-target compounds that are suspected to be straight-chain, branched, or cyclic alkanes, alone or part of an alkane series, shall be library searched and reported by class (*e.g.*, series of straight chain, branched, or cyclic alkanes, as applicable).

d) The following conditions do not require reporting:

i) Compounds detected below the peak threshold criterion (Section 3.a).

ii) Compounds eluting 30 seconds prior to the first target compound (phenol).

iii) Volatile compounds reported in the analysis for target and non-target compounds by method 524.2 (provided that the 524.2 analysis was performed).

iv) Semi-volatile compounds reported in the analysis for target compounds by method 525.2 (provided that the 525.2 analysis was performed).

v) Non-target compounds detected in the sample that were also detected in the method blank, including column bleed.

4) Identification of Non-Target Compounds

a) The tentative identifications shall be performed via a forward search of the NIST/EPA/NIH (May 1992 release, or later) and/or Wiley (1991 release, or later), or equivalent, mass spectral library.

b) Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

c) Guidelines for assigning tentative identifications

   i) The mass scan range should be set to 35 to 500 mass/z, as recommended in method 8270C, section 7.3.

   ii) Relative intensities of the major ions in the library reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

   iii) The relative intensities of the major ions should agree within and absolute ± 20%. (Example: For an ion with an abundance of 50% in the library reference spectrum, the corresponding sample ion abundance should be between 30-70%).

   iv) A molecular ion present in the library reference spectrum should be present in the sample spectrum.

   v) Ions present in the sample spectrum, but not in the library reference spectrum, should be reviewed for possible background contamination, or presence of co-eluting compounds.

   vi) Ions present in the library reference spectrum, but not in the sample spectrum, should be reviewed for possible background subtraction from the sample spectrum because of background contamination, or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

d) If a tentative identification cannot be made by the mass spectroscopist after a careful review of the data, the compound should be reported as follows.

   i) If the library search produces a match at, or above 85%, report that compound.

   ii) If the library search produces more than one compound with a match at, or above 85%, report the first compound with the highest match.

   iii) If the library search produces no matches at, or above 85%, the compound should be reported as unknown. The mass spectroscopist should give additional classification of the unknown compound, if possible (*i.e.* unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound, etc.) The unknown should be reported to the DHS along with the total ion chromatogram and the mass spectrum of the unknown, with and without background subtraction. The

DHS will evaluate if further research by the water system will be necessary to identify the compound.

e) Tentatively identified non-target pesticides (pesticides not listed in Table 1) shall be reported.

5) Quantification of Non-Target Compounds

a) Estimated concentrations for tentatively identified compounds, as well as those identified as unknowns, shall be determined by the internal standard method. Method 8270C recommends six internal standards (Table 2). The internal standards are added to the 1 mL sample extract to produce a final concentration of 20 ng/µL for each internal standard in the extract. Non-target compounds that meet the criteria for reporting (Section 3) shall be quantified using the nearest internal standard that is free from interferences and reported.

b) Total area counts from the total ion chromatograms shall be used for both the compound to be measured and the nearest internal standard free from interferences. A relative response factor (RRF) of one (1) is to be assumed. The resulting concentration shall be qualified as "estimated", due to lack of a compound-specific response factor, and "presumptive evidence of presence", indicating the quantitative and qualitative uncertainties associated with this non-target component.

$$conc.\,(\mu g / L) = \frac{(A_X)(I_S)(V_t)(DF)}{(A_{IS})(RRF)(V_0)(V_i)}$$

Where,

A_X = Area of the total ion current for the compound to be measured.

A_{IS} = Area of the total ion current for the specific internal standard.

I_S = Amount of internal standard added (in ng).

RRF = 1.

V_O = Volume of water extracted (in mL).

Vi = Volume of extract injected (in µL).

Vt = Volume of concentrated final extract (in µL).

DF = Sample dilution factor.

= (µL of conc. extract + µL of dilution solvent)/(µL of conc. extract).

If no dilution is performed, DF = 1.

6) Confirmation of Non-Target Compounds

a) The DHS will review the 8270C analysis results to determine if confirmation will be required for any TIC reported in the non-target analysis.

b) If confirmation of a TIC is required, analyze a reference standard of the TIC, if available, and compare the retention time and mass spectrum of the reference standard with the TIC, as described in method 8270C for target compounds.

i) If a reference standard is not available or cannot be synthesized, the TIC remains unconfirmed.

ii) If a reference standard is available and the TIC is positively identified, perform the following.

(1) Determine the method performance by performing a MDL study and an accuracy and precision study, as described in method 8000B, section 8.4.

(2) If the method performance is determined to be poor, the sample collection, sample preservation, sample extraction conditions, GC/MS parameters, etc. may be optimized to increase the method performance. If a deuterated reference standard is available and if it is necessary to improve quantification accuracy, the isotope dilution method may be used, if applicable. Section 6.b.ii.1 should then be repeated using the modified procedure. Modifications made to the method must be documented and validated.

(3) Quantify the compound against the reference standard using the internal standard approach, as described in methods 8000B/8270C, or by the isotope dilution method, if used.

iii) If the TIC is not positively identified, (*i.e.*, retention time and/or spectrum do not match the retention time and/or spectrum of the reference compound), refer to Section 4.d.

7) References

a) Method 3510C and Method 8270C, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" SW-846, 3rd Edition, USEPA, December 1996.

b) USEPA Contract Laboratory Program Statement of Work for Low Concentration Organic, OLC03.2, December 2000.

Table 1. Target Compounds - Method 8270C

Analyte	CAS No.
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Acetophenone	98-86-2
2-Acetylaminofluorene	53-96-3
1-Acetyl-2-thiourea	591-08-2
Aldrin	309-00-2
2-Aminoanthraquinone	117-79-3
Aminoazobenzene	60-09-3
4-Aminobiphenyl	92-67-1
3-Amino-9-ethylcarbazole	132-32-1
Anilazine	101-05-3
Aniline	62-53-3
o-Anisidine	90-04-0
Anthracene	120-12-7
Aramite	140-57-8
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5
Azinphos-methyl	86-50-0
Barban	101-27-9
Benzidine	92-87-5
Benzoic acid	65-85-0
Benz(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(g,h,i)perylene	191-24-2
Benzo(a)pyrene	50-32-8
p-Benzoquinone	106-51-4
Benzyl alcohol	100-51-6
A-BHC	319-84-6
B-BHC	319-85-7
Δ-BHC	319-86-8
Γ-BHC (Lindane)	58-89-9
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	108-60-1
Bis(2-ethylhexyl) phthalate	117-81-7
4-Bromophenylphenyl ether	101-55-3
Bromoxynil	1689-84-5

Analyte	CAS No.
Butyl benzyl phthalate	85-68-7
Captafol	6/1/2425
Captan	133-06-2
Carbaryl	63-25-2
Carbofuran	1563-66-2
Carbophenothion	786-19-6
Chlordane (NOS)	57-74-9
Chlorfenvinphos	470-90-6
4-Chloroaniline	106-47-8
Chlorobenzilate	510-15-6
5-Chloro-2-methylaniline	95-79-4
4-Chloro-3-methylphenol	59-50-7
3-(Chloromethyl)pyridine•HCl	6959-48-4
1-Chloronaphthalene	90-13-1
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chloro-1,2-phenylenediamine	95-83-0
4-Chloro-1,3-phenylenediamine	5131-60-2
4-Chlorophenyl phenyl ether	7005-72-3
Chrysene	218-01-9
Coumaphos	56-72-4
p-Cresidine	120-71-8
Crotoxyphos	7700-17-6
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Demeton-O	298-03-3
Demeton-S	126-75-0
Diallate (cis or trans)	2303-16-4
2,4-Diaminotoluene	95-80-7
Dibenz(a,j)acridine	224-42-0
Dibenz(a,h)anthracene	53-70-3
Dibenzofuran	132-64-9
Dibenzo(a,e)pyrene	192-65-4
1,2-Dibromo-3-chloropropane *	96-12-8
Di-n-butyl phthalate	84-74-2
Dichlone	117-80-6
1,2-Dichlorobenzene *	95-50-1
1,3-Dichlorobenzene *	541-73-1
1,4-Dichlorobenzene *	106-46-7
3,3'-Dichlorobenzidine	91-94-1
2,4-Dichlorophenol	120-83-2

Table 1. Continued

Analyte	CAS No.
2,6-Dichlorophenol	87-65-0
Dichlorovos	62-73-7
Dicrotophos	141-66-2
Dieldrin	60-57-1
Diethyl phthalate	84-66-2
Diethylstilbestrol	56-53-1
Diethyl sulfate	64-67-5
Dihydrosaffrole	56312-13-1
Dimethoate	60-51-5
3,3'-Dimethoxybenzidine	119-90-4
Dimethylaminoazobenzene	60-11-7
7,12-Dimethylbenz(a)anthracene	57-97-6
3,3'-Dimethylbenzidine	119-93-7
α,α-Dimethylphenethylamine	122-09-8
2,4-Dimethylphenol	105-67-9
Dimethyl phthalate	131-11-3
1,2-Dinitrobenzene	528-29-0
1,3-Dinitrobenzene	99-65-0
1,4-Dinitrobenzene	100-25-4
4,6-Dinitro-2-methylphenol	534-52-1
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Dinocap	39300-45-3
Dinoseb	88-85-7
Dioxathion	78-34-2
Diphenylamine	122-39-4
5,5-Diphenylhydantoin	57-41-0
1,2-Diphenylhydrazine	122-66-7
Di-n-octyl phthalate	117-84-0
Disulfoton	298-04-4
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
EPN	2104-64-5
Ethion	563-12-2
Ethyl carbamate	51-79-6
Ethyl methanesulfonate	62-50-0
Famphur	52-85-7
Fensulfothion	115-90-2

Analyte	CAS No.
Fenthion	55-38-9
Fluchloralin	33245-39-5
Fluoranthene	206-44-0
Fluorene	86-73-7
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorobutadiene *	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane *	67-72-1
Hexachlorophene	70-30-4
Hexachloropropene	1888-71-7
Hexamethylphosphoramide	680-31-9
Hydroquinone	123-31-9
Indeno(1,2,3-cd)pyrene	193-39-5
Isodrin	465-73-6
Isophorone	78-59-1
Isosafrole	120-58-1
Kepone	143-50-0
Leptophos	21609-90-5
Malathion	121-75-5
Maleic anhydride	108-31-6
Mestranol	72-33-3
Methapyrilene	91-80-5
Methoxychlor	72-43-5
3-Methylcholanthrene	56-49-5
4,4'-Methylenebis(2-Chloroaniline)	101-14-4
4,4'-Methylenebis(N,N-dimethylaniline)	101-61-1
Methyl methanesulfonate	66-27-3
2-Methylnaphthalene	91-57-6
Methyl parathion	298-00-0
2-Methylphenol	95-48-7
3-Methylphenol	108-39-4
4-Methylphenol	106-44-5
Mevinphos	7786-34-7
Mexacarbate	315-18-4
Mirex	2385-85-5
Monocrotophos	6923-22-4
Naled	300-76-5
Naphthalene	91-20-3
1,4-Naphthoquinone	130-15-4
1-Naphthylamine	134-32-7
2-Naphthylamine	91-59-8

Table 1. Continued

Analyte	CAS No.
Nicotine	54-11-5
5-Nitroacenaphthene	602-87-9
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6
5-Nitro-o-anisidine	99-59-2
Nitrobenzene *	98-95-3
4-Nitrobiphenyl	92-93-3
Nitrofen	1836-75-5
2-Nitrophenol	88-75-5
4-Nitrophenol	100-02-7
5-Nitro-o-toluidine	99-55-8
Nitroquinoline-1-oxide	56-57-5
N-Nitrosodi-n-butylamine	924-16-3
N-Nitrosodiethylamine	55-18-5
N-Nitrosodimethylamine	62-75-9
N-Nitrosomethylethylamine	10595-95-6
N-Nitrosodiphenylamine	86-30-6
N-Nitrosodi-n-propylamine	621-64-7
N-Nitrosomorpholine	59-89-2
N-Nitrosopiperidine	100-75-4
N-Nitrosopyrrolidine	930-55-2
Octamethyl pyrophosphoramide	152-16-9
4,4'-Oxydianiline	101-80-4
Parathion	56-38-2
Pentachlorobenzene	608-93-5
Pentachloronitrobenzene	82-68-8
Pentachlorophenol	87-86-5
Phenacetin	62-44-2
Phenanthrene	85-01-8
Phenobarbital	50-06-6
Phenol	108-95-2
1,4-Phenylenediamine	106-50-3
Phorate	298-02-2
Phosalone	2310-17-0

Analyte	CAS No.
Phosmet	732-11-6
Phosphamidon	13171-21-6
Phthalic anhydride	85-44-9
2-Picoline (2-Methylpyridine)	109-06-8
Piperonyl sulfoxide	120-62-7
Pronamide	23950-58-5
Propylthiouracil	51-52-5
Pyrene	129-00-0
Pyridine	110-86-1
Resorcinol	108-46-3
Safrole	94-59-7
Strychnine	57-24-9
Sulfallate	95-06-7
Terbufos	13071-79-9
1,2,4,5-Tetrachlorobenzene	95-94-3
2,3,4,6-Tetrachlorophenol	58-90-2
Tetrachlorvinphos	961-11-5
Tetraethyl dithiopyrophosphate	3689-24-5
Tetraethyl pyrophosphate	107-49-3
Thionazine	297-97-2
Thiophenol (Benzenethiol)	108-98-5
Toluene diisocyanate	584-84-9
o-Toluidine	95-53-4
Toxaphene	8001-35-2
1,2,4-Trichlorobenzene *	120-82-1
2,4,5-Trichlorophenol	95-95-4
2,4,6-Trichlorophenol	88-06-2
Trifluralin	1582-09-8
2,4,5-Trimethylaniline	137-17-7
Trimethyl phosphate	512-56-1
1,3,5-Trinitrobenzene	99-35-4
Tris(2,3-dibromopropyl) phosphate	126-72-7
Tri-p-tolyl phosphate	78-32-0
O,O,O-Triethyl phosphorothioate	126-68-1

Notes:
Compounds denoted by italicized and bold print are also analytes listed in method 525.2.
Compounds denoted with an asterisk (*) are also analytes listed in method 524.2.

Table 2. Internal Standards - Method 8270C

1,4-Dichlorobenzene-D_4
Naphthalene-D_8
Acenaphthene-D_{10}
Phenanthrene-D_{10}
Chrysene-D_{12}
Perylene-D_{12}

Table 3. Surrogate Standards - Method 8270C

Phenol-D_6
2-Fluorophenol
2,4,6-Tribromophenol
Nitrobenzene-D_5
2-Fluorobiphenyl
p-Terphenyl-D_{14}