Lower Detection & Reporting Limits for 1,2,3-Trichloropropane (TCP) in Drinking Water and Source Water

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Presented 5/11/16 to the Environmental Laboratory Technical Advisory Committee (ELTAC), Sacramento

Objectives

- Describe modifications to the California Department of Health Services methods (CDHS, 2002) that can support TCP reporting limits at OEHHA's 2009 PHG of 0.0007 µg/L

PTI-GC/MS

25-mL Water

Purge and trap

GC/MS (SIM)

MDL = 0.9 ppt (5 ppt spike)

P. Hill & W. Steeber (2002)

LLE-GC/MS

1000-mL Water

16 hr LLE CH_2Cl_2

1-mL Extract

2-uL injection

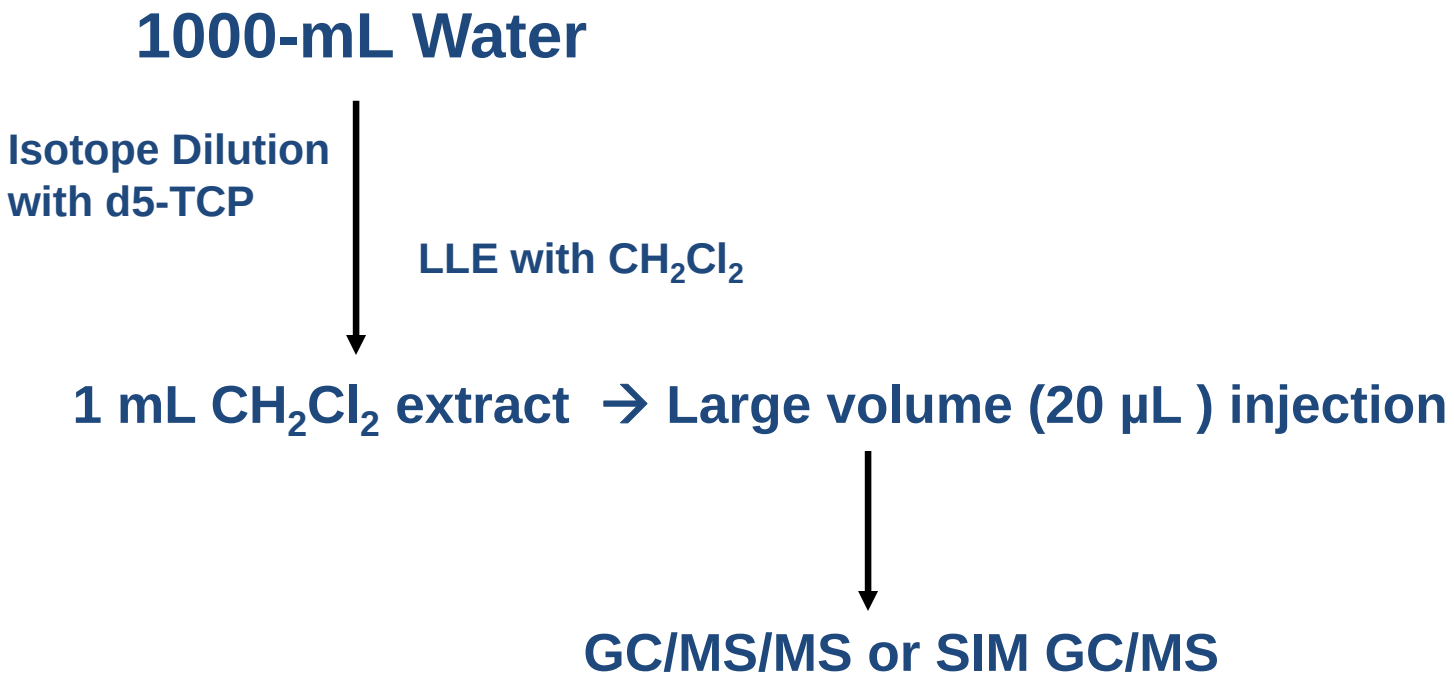
GC/MS (SIS)

MDL = 0.8 ppt (5 ppt spike)

H. Okamoto, K. Perera , J. Remoy & J. Dhoot (2002)

2002 CDHS Methods Supporting
DLR & “Notification Level” of 5 ppt

Large Volume Injection (LVI) & MS/MS Modification of LLE-GC/MS Method



MDL = 0.20 ppt (0.80 ppt spike)

LVI & GC Conditions

Split Event

Time (min)	State	Ratio
initial	on	20
0.50	off	off
2.5	on	100

$C_3H_4Cl_2^+(110) \rightarrow C_3H_4Cl^+(75) + Cl$

$C_3D_4Cl_2^+(114) \rightarrow C_3D_4Cl^+(79) + Cl$

Injector Temperature Program

Temp (°C)	Rate	Hold (min)	Total (min)
35	0	0.50	0.5
250	200	32	33.6

Oven Program

Temp(°C)	Rate	Hold (min)	Total (min)
35	0	2.5	2.5
105	10	0	9.5
215	5.5	0	29.5
255	25	5	36.1

Column: 624ms 60 m x 0.32mmx 1.8 uM, flow 1.4 ml/min
GC: CP3800 and Autosampler CP-8400
MS: Saturn 2000 GC/MS Ion Trap

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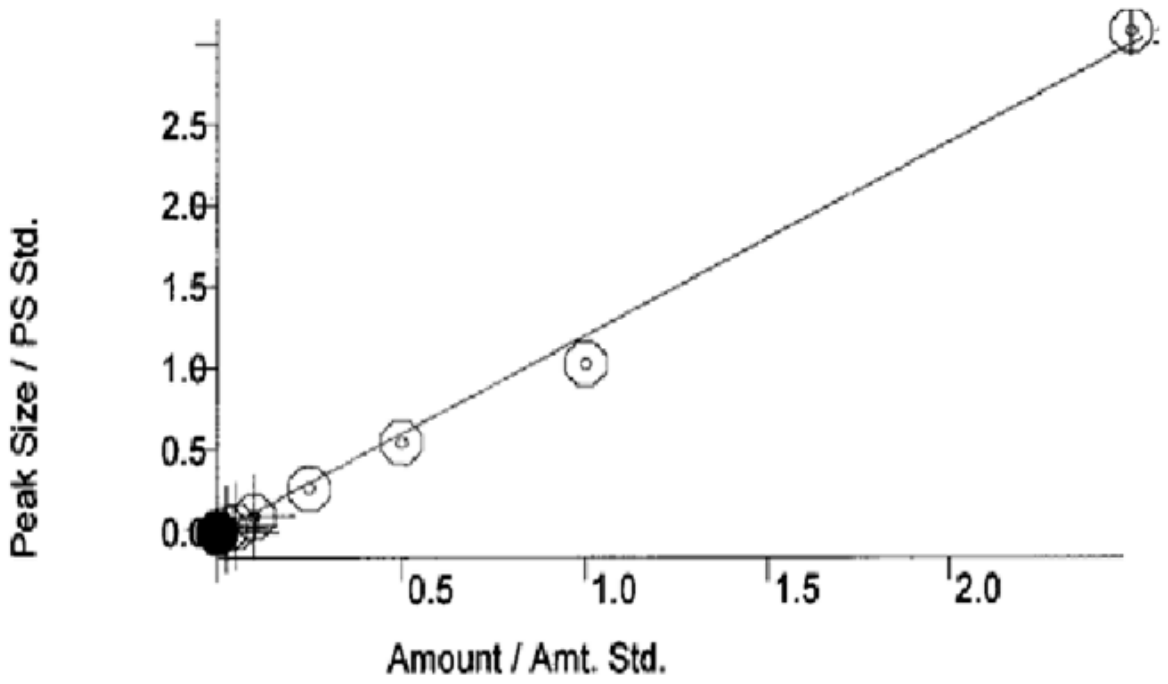
GC/MS/MS Calibration Curve
Linear from 0.5 ug/L to 50 ug/L

1 2 3-Trichloropropane
Curve Fit: Linear
Resp. Fact. RSD: 16.51%, Coeff. Det.(r2): 0.995895
y = +1.1969x



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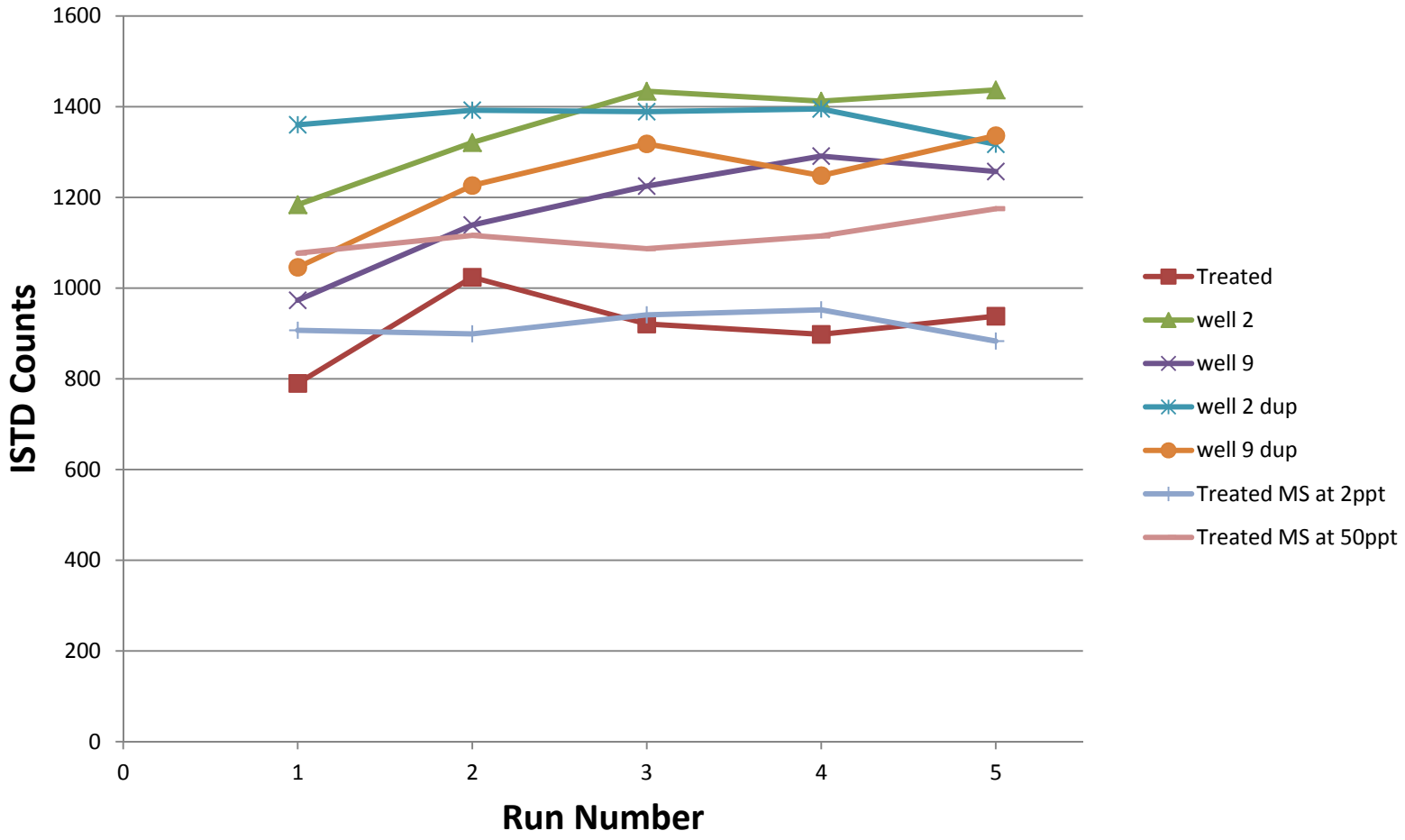
Isotope Dilution LLE-LVI-GC/MS/MS MDL Data

Replicate	0.80 ng/L TCP Formulatiion		2.0 ng/L TCP Formulation	
	TCP Conc. (ng/L)	Recovery (%)	TCP Conc. (ng/L)	Recovery
Blank	ND	N/A	ND	N/A
1	0.69	86	2.4	120
2	0.72	90	2.3	115
3	0.60	75	2.3	115
4	0.68	85	2.3	115
5	0.67	84	2.4	120
6	0.57	71	2.4	120
7	0.57	71	2.5	125
8	N/A	N/A	2.3	115
Mean	0.64	80.3	2.4	118
SD	0.0616	7.78	0.074	3.72
MDL	0.19 ng/L		0.22 ng/L	

Method Ruggedness Test with Groundwater Samples

d_5-TCP (IS) Response over 35 Injections



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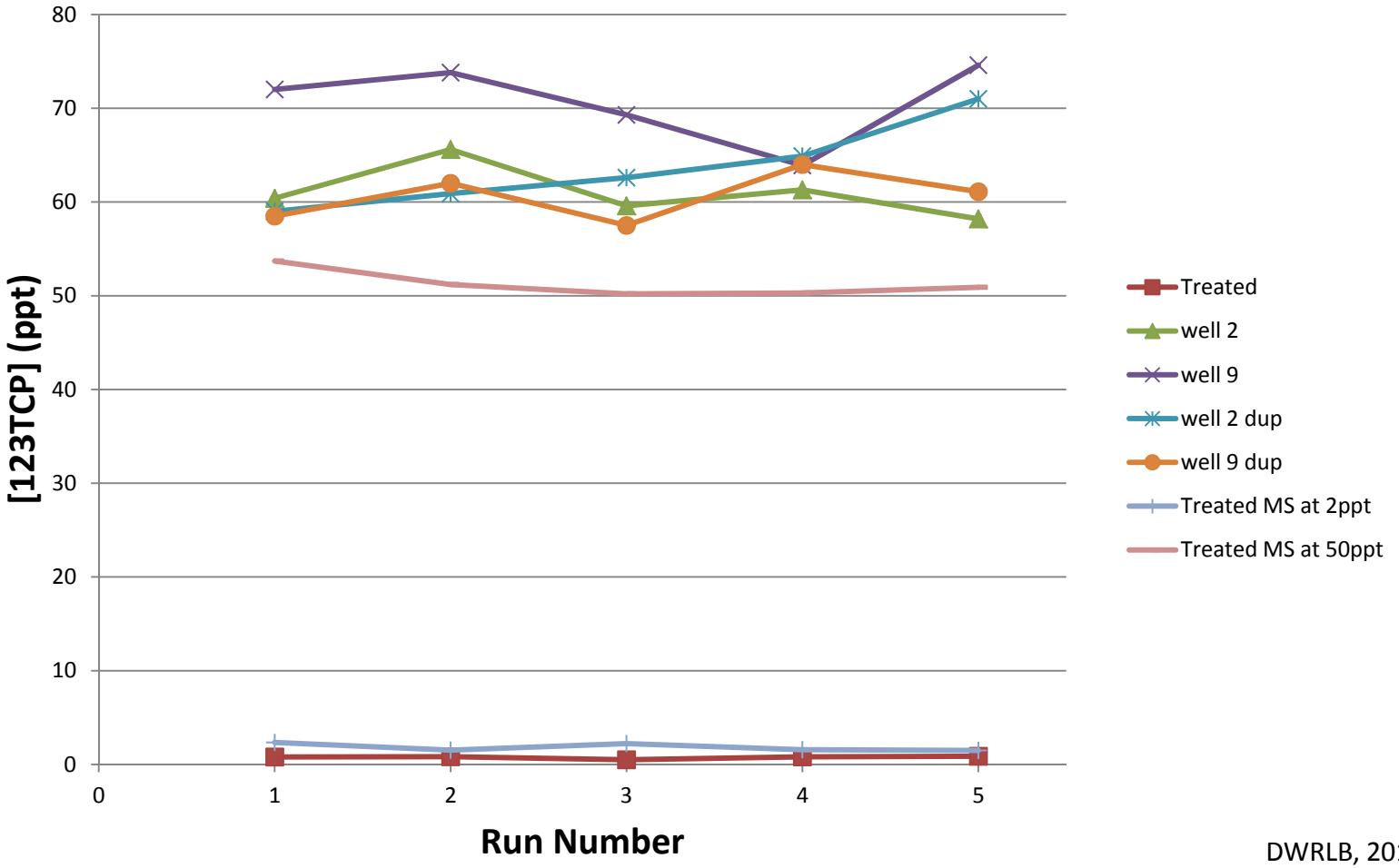
Method Ruggedness Test with Groundwater Samples

TCP Results over 35 Injections



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SPE Modification of the PTI-GC/MS Method

500-mL Water

↓ SPE with Supelco ENVI-Carb Plus

2.5-mL CH_2Cl_2 extract -- Solvent Exchange -- 5-mL water

↓ Purge & Trap (PTI)

GC/MS (SIM)

MDL = 0.11 ppt (0.25 ppt spike) or 0.19 (0.5 ppt spike)

W. Liao, M. Ghabour, W. Draper & E. Chandrasena

SPE-PTI-GC/MS Method Details

Chemicals/Supplies.

A Millipore Milli-Q-Plus water purification system supplied laboratory reagent water for all experiments. Analytical standards of TCP (5,000 ug/mL in methanol) and Supelco Supelclean ENVI-Carb Plus cartridges (400 mg) were obtained from Supelco. The deuterium-labeled internal standard (IS), d5-TCP, was obtained from Cambridge Isotope Laboratories.

Instruments & Operating Conditions.

An Agilent 5973 MSD mass spectrometer (a 10+ year old diffusion pump model) interfaced to an Agilent 6890 gas chromatograph was used. This system was equipped with a Tekmar 3000 automated purge and trap sampler. Operating conditions: electron ionization (EI) mode; ionization energy, 70 eV; autotuned and EM voltage was increased by 300 V; selected ion monitoring (SIM); two ions were monitored, m/z 75 (10 ms dwell time) and m/z 79 (5 ms dwell time). The GC column used was a J & W DB-5.625 column (30 m X 0.25 mm, 1 micron) with the following operating conditions: split interface split ratio/temp. (20:1/200^{o}C); helium carrier gas (0.90 mL min^{-1}); oven temp. program (35^{o}C, 5 min; 4^{o}C min-1 to 100^{o}C; 30^{o}C min^{-1} to 170^{o}C); and transfer line (220^{o}C). The PTI conditions were: sample volume (5 mL); purge vessel (25 mL fritted sparger); purge time/temp./He flow rate (11 min/40^{o}C/20 mL min^{-1}); dry purge (2 min). A Tenax trap was used: desorb preheat (245^{o}C); desorb (4 min at 250^{o}C); desorb gas (20 mL min^{-1} He); bake out (8 min at 270^{o}C). The retention times were: d_5-TCP (20.35 min) and TCP (20.56 min) and a filament delay of 19 min was used.

Analytical Procedure.

Samples were extracted manually using ENVI-Carb Plus SPE cartridges mounted on an extraction manifold. The SPE cartridges were conditioned by washing with 3 mL of dichloromethane, 2 mL of methanol, and a second aliquot of 2 mL of methanol followed by 2 mL of laboratory reagent water. The sorbent was not allowed to run dry during conditioning. Water samples (500 mL) were fortified with 10 ng/L of the IS, d_5-TCP, by transferring 10 uL of a 500 ng/mL methanolic solution. Water samples were then loaded onto the cartridge with a flow rate of ~10 mL/min. The receiver was removed and air was drawn through the cartridge for 2 min. To elute retained analytes, the cartridges were inverted, the cartridge reservoir was filled with methylene chloride, and the sorbent was soaked in the solvent for ~1 min without vacuum. Methylene chloride was then eluted dropwise under a low vacuum. Methylene chloride was dried by percolation through 0.4 g of anhydrous sodium sulfate in a small column and the extract was combined with 50 uL of diethylene glycol-methylene chloride (1:1, v/v). The sample was concentrated under of gentle stream of nitrogen in a room temperature water bath to a final volume of 50-75 µL prior to addition of 5 mL of laboratory reagent water. The sample was vortexed to disperse the solvent “keeper” thoroughly prior to transfer of the sample to a purge vessel.

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Isotope Dilution SPE-PTI-GC/MS MDL Data

Replicate	0.25 ng/L TCP Formulatiion		0.5 ng/L TCP Formulation	
	TCP Conc. (ng/L)	Recovery (%)	TCP Conc. (ng/L)	Recovery
Blank	ND	N/A	ND	N/A
1	0.29	116	0.46	92
2	0.27	108	0.55	110
3	0.23	92	0.53	106
4	0.21	84	0.62	124
5	0.25	100	0.53	106
6	0.21	84	0.45	90
7	0.20	80	0.46	92
Mean	0.237	94.9%	0.514	103%
SD	0.0340	13.6%	0.0619	12.4%
MDL	0.11 ng/L		0.19 ng/L	

SPE-PTI-GC/MS Groundwater Data: Historically Contaminated Wells

Sample No.	Location/Sample Point	TCP Conc. (ng/L)
Los Angeles Co./Monterey Park		
11-3021-01	Well 12	3.06
11-3021-02	Well 15	3.02
11-3021-03	LPGAC Com Effluent	2.93
Los Angeles DWP/Pollock Wells Treatment Plant		
11-3030-01	Granular Activated Carbon (GAC) 50% Port	<0.30
11-3030-02	Granular Activated Carbon (GAC) Effluent	<0.30
11-3030-03	4 ANDG Combined Raw	5.82
11-3030-04	Well 4 Raw	1.99
11-3030-05	Well 6 Raw	12.1
San Bernardino Co./Chino Desalting Authority		
11-3035-01	Well 9	0.47
San Diego Co./City of Oceanside		
11-3037-01	Well 2	105.6
11-3037-02	Well 9	79.7
11-3037-03	MBDF	2.53
Fresno Co./City of Fresno		
11-3041-01	Well Head	68.04
11-3041-02	Well Head	45.27
11-3041-03	Well Head	45.64
11-3041-04	Well Head	38.40
Merced Co./City of Livingston		
11-3043-01	Well 15 #1	22.36
11-3043-02	Well 15 #2	22.52
11-3043-03	Well 14 #1	>250
11-3043-04	Well 14 #2	>250
Merced Co./City of Delhi		
11-3042-01	Well 6 #1	40.26

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Conclusions

- Two isotope dilution methods are described for determination of TCP with reporting limits below the 0.0007 µg/L PHG
- LLE-LVI-GC/MS(/MS) uses a large volume inlet (LVI) to increase sample size
- SPE-PT-GC/MS couples solid phase extraction (SPE) to purge and trap sample introduction

Acknowledgements

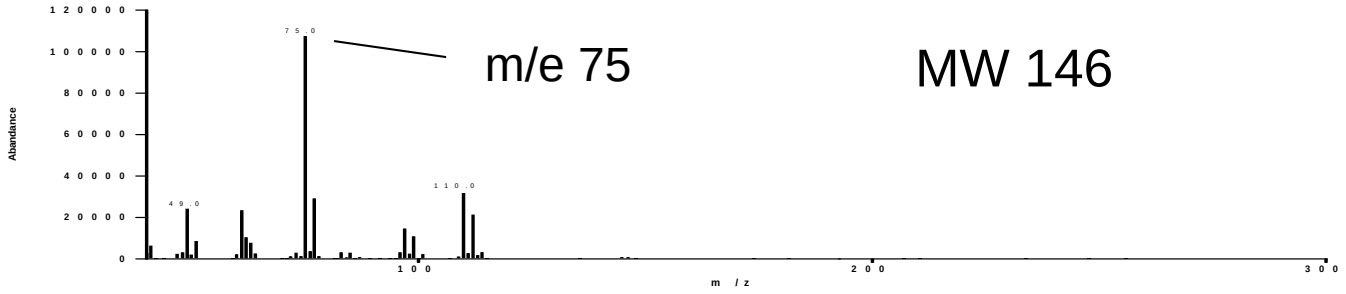
- The LVI method was developed by Jagdev Dhoot, Mario Estrada, Dadong Xu and Raimund Roehl
- The SPE-PT method was developed by Wenta Liao, Miriam Ghabour, and Esala Chandrasena
- David Chang, Sean McCarthy, Jeff O'Keefe, and Oliver Pacifico of the SWRCB Division of Drinking Water provided groundwater samples

Questions for ELTAC & ELAP

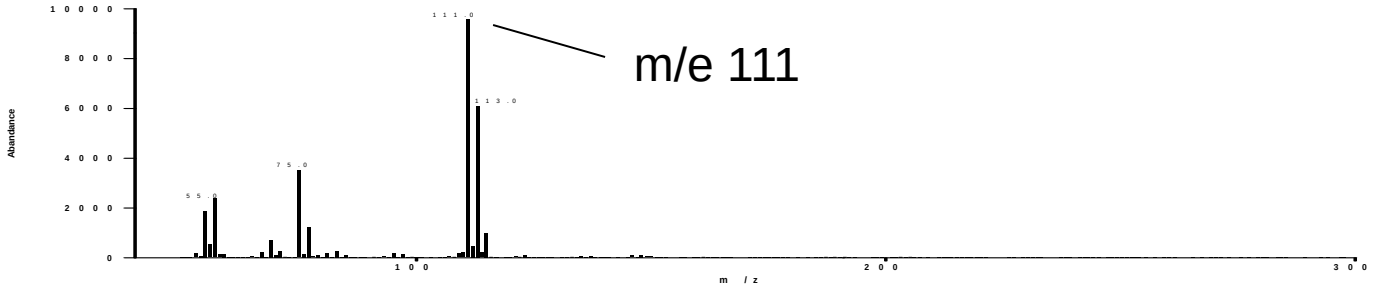
- Which TCP method(s) are labs using now?
- Preservation & Holding Times
- MDL data and Reporting Limits
- Demand, capacity and costs (?)
- Preference/interest in current methods
- Availability of instrumentation
- Are labs interested in multilab validation (e.g., MDL, MRL, single or multi lab LCMRL)?

1,2,3-Trichloropropane
EI & CI GC/MS Spectra

Electron Ionization (EI) Spectrum



Chemical Ionization (CI) Spectrum



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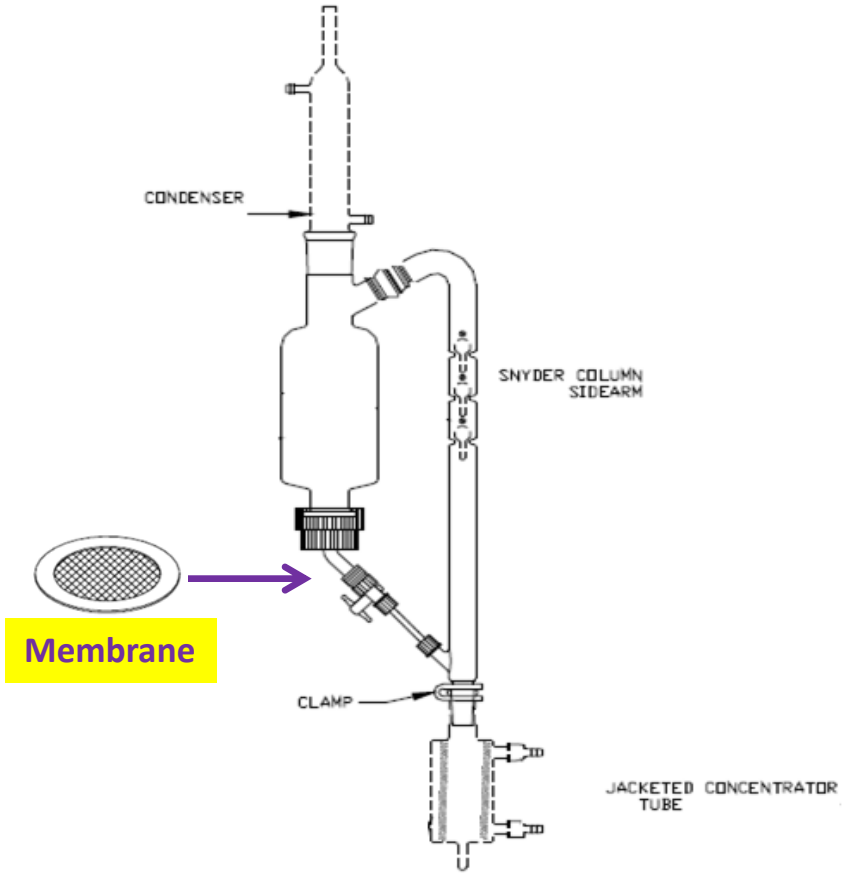
Continuous LLE Apparatus with Hydrophobic Membrane

Corning® Accelerated One-Step® Extractor/Concentrator



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