

Analysis of 1, 2, 3-Trichloropropane by Purge and Trap Concentration and Gas Chromatography/Mass Spectrometry (GC/MS)

Introduction

1,2,3-Trichloropropane (TCP) was used in the past as an industrial solvent, a cleaning and degreasing agent, and in the manufacture of soil fumigants. It is currently used as a chemical intermediate in the production of other chemicals such as polysulfone liquid polymers, dichloropropene, and hexafluoropropylene. It is also used as a cross-linking agent in the synthesis of polysulfides. TCP is manufactured for uses in many industries, but may also be an unwanted by-product in the production of other chemicals such as epichlorohydrin, dichloropropene, propylene oxide, propylene chlorohydrin, dichlorohydrin, and glycerol.¹

TCP is a contaminant of interest to the government and private sector because of its persistence in groundwater and its classification as a likely carcinogen by the USEPA. It does not tend to stay in the soil; therefore, it either leaches into the groundwater or evaporates from the soil surface. Once it enters the groundwater, it sinks to the bottom of the aquifer since its density is greater than that of water and because of low degradation rates may remain in groundwater for a long time.²

The State of California recognizes TCP to be a carcinogen and known toxin.³ A maximum contaminant level (MCL) was established at 0.000005 mg/L (5 ppt) effective on December 14, 2017 with initial monitoring to start the first quarter of 2018.⁴ It is possible this low, as well as difficult, limit to achieve will be required by other states and the United States as a whole in the future. This poster will explore the analysis of TCP by purge and trap concentration with separation and detection by gas chromatography/mass spectrometry (GC/MS) using selective ion monitoring (SIM).

Experimentation

The instrumentation used for sample concentration was an OI Analytical 4760 Eclipse Purge and Trap along with a 4100 Sample Processor. An Agilent 7890A/5975C GC/MS was used for chromatographic separation and detection. Data was acquired using selective ion monitoring rather than full scan for greater sensitivity. TCP and trans-1,2-Dichloro-2-butene tend to co-elute or overlap on many columns and share a high abundance of ion 75; therefore, the quant ion used for TCP was 110 even though its relative abundance is lower.



Figure 1. OI Analytical 4100 Autosampler and Eclipse 4760 Purge & Trap and Agilent 7890A/5975C GC/MS

Two sets of data were acquired using modified methods of USEPA Method 524.2 and USEPA Method 8260C. Method 524.2 was modified by using heated purge. In initial tests, the response of TCP doubled by purging at 50° C rather than ambient temperature. Method 8260C was modified by purging 10 mL rather than 5 mL for increased response. Instrument conditions were the same for both methods with the exceptions that 25 mL purge with 4 minute desorb was used for 524.2 and 10 mL purge with 0.5 minute desorb was used for 8260C. Please see Table 1 for instrument parameters.

An injection of 25 ng Bromofluorobenzene (BFB) was performed each day of the study and Table 3 criteria from Method 8260C was met prior to sample analysis. A seven-point calibration from 5 ppt to 500 ppt was analyzed for TCP. All samples were spiked with 5 µL 0.5 ppm internal standard and surrogates. An Initial Demonstration of Capability (IDOC) was run at 100 ppt for TCP. A Method Detection Limit (MDL) study was run over a three day period at 4 ppt. Tap water samples from various locations in the area were also analyzed.

Table 1. Instrument Parameters

Purge-and-Trap	Eclipse 4760 P&T Sample Concentrator	
Trap	#10 trap; Tenax® / Silica gel / CMS	
Purge Gas	Zero grade Helium at 40 mL/min	
Purge Time	11 min	
Sparge Mount Temperature	45 °C	
Sample Temperature (purge)	50 °C	
Sample Temperature (bake)	45 °C	
Desorb Time	4 min (524.2) 0.5 min (8260)	
Bake Time	5 min	
Ol #10 Trap Temperature	Ambient during purge 180 °C during desorb pre-heat 190 °C during desorb 210 °C during bake	
Water Management	120 °C during purge Ambient during desorb 240 °C during bake	
Transfer Line Temperature	140 °C	
Six-port Valve Temperature	140 °C	
Autosampler	4100 Water/Soil Sample Processor	
System Gas	Zero grade nitrogen	
Purge Gas	Zero grade helium	
LV20 Pressure	8.0 psi	
Loop-based Time Settings	Default	
Rinse Water	80 °C	
Soil Sample Transfer	150 °C	
Soil Oven	150 °C	
Soil Lift Station	45 °C	
Sample Loop	25 ml (524.2) 10 ml (8260)	
Gas Chromatograph	Agilent 7890A	
Column	Restek Rxi - 624Sil MS 30 meter, 0.25 mm ID, 1.4 µm	
Carrier Gas	Zero grade helium	
Inlet Temperature	240 °C	
Inlet Liner	Agilent Ultra Inert, 1 mm straight taper	
Column Flow Rate	0.6 mL/min	
Split Ratio	20:1	
Oven Program	Hold at 40 °C for 1.5 min 10 °C/minute to 120 °C Hold 4 min 40 °C/minute to 220 °C Hold 2 min Total GC Run is 18.0 min	
Mass Spectrometer	Agilent 5975 C	
Mode	SIM 100 msec dwell time	
SIM Compounds		
Group 1	Fluorobenzene	m/z 70, 96 6.00 min
Group 2	4-Bromofluorobenzene	m/z 95, 174, 176 13.00 min
Group 3	1,2,3-Trichloropropane-d5	m/z 79, 100, 114 13.40 min
Group 4	1,2,3-Trichloropropane	m/z 75, 110 13.58 min
Group 5	1,2-Dichlorobenzene-d4	m/z 115, 150, 152 15.40 min
Solvent Delay	6.00 min	
Transfer Line Temperature	240 °C	
Source Temperature	300 °C	
Quadrupole Temperature	200 °C	
Draw Out Plate	6 mm	

Results

The %RSD for all compounds was <15%, so both method criteria were easily met. IDOC precision and accuracy as well as MDL results were well within method criteria. No carryover was observed for TCP even after the calibration with 500 ppt being the last standard run. All samples were non-detect for TCP. Please see tables 2 and 3 for results.

Table 2. Results for Modified USEPA Method 524.2

Compound	Quant Ion	RT	RL (ppt)	Avg RF	% RSD	MDL % REC	MDL (ppt)	IDOC Precision (% RPD)	IDOC Accuracy (% REC)
Fluorobenzene(IS)	96	6.93	N/A	N/A	N/A	N/A	N/A	N/A	N/A
4-Bromofluorobenzene(SS)	95	13.14	N/A	0.448	13.63	N/A	N/A	1.98	79.2
1,2,3-Trichloropropane-d5(SS)	79	13.49	N/A	0.124	1.61	N/A	N/A	1.49	98.6
1,2,3-Trichloropropane	110	13.64	5	0.037	9.73	104	1.48	2.37	92.9
1,2-Dichlorobenzene-d4(SS)	150	15.59	N/A	0.507	4.42	N/A	N/A	1.00	99.4

IS - Internal Standard

SS - Surrogate Standard

Table 3. Results for Modified USEPA Method 8260C

Compound	Quant Ion	RT	RL (ppt)	Avg RF	% RSD	MDL % REC	MDL (ppt)	IDOC Precision (% RPD)	IDOC Accuracy (% REC)
Fluorobenzene(IS)	96	6.93	N/A	N/A	N/A	N/A	N/A	N/A	N/A
4-Bromofluorobenzene(SS)	95	13.14	N/A	0.352	2.12	N/A	N/A	1.83	96.3
1,2,3-Trichloropropane-d5(SS)	79	13.49	N/A	0.190	1.62	N/A	N/A	1.15	100.1
1,2,3-Trichloropropane	110	13.64	5	0.071	11.25	115	1.43	1.10	95.4
1,2-Dichlorobenzene-d4(SS)	150	15.59	N/A	0.514	0.68	N/A	N/A	0.59	98.1

IS - Internal Standard

SS - Surrogate Standard

Figure 2. 100 ppt Standard (Modified USEPA Method 524.2)

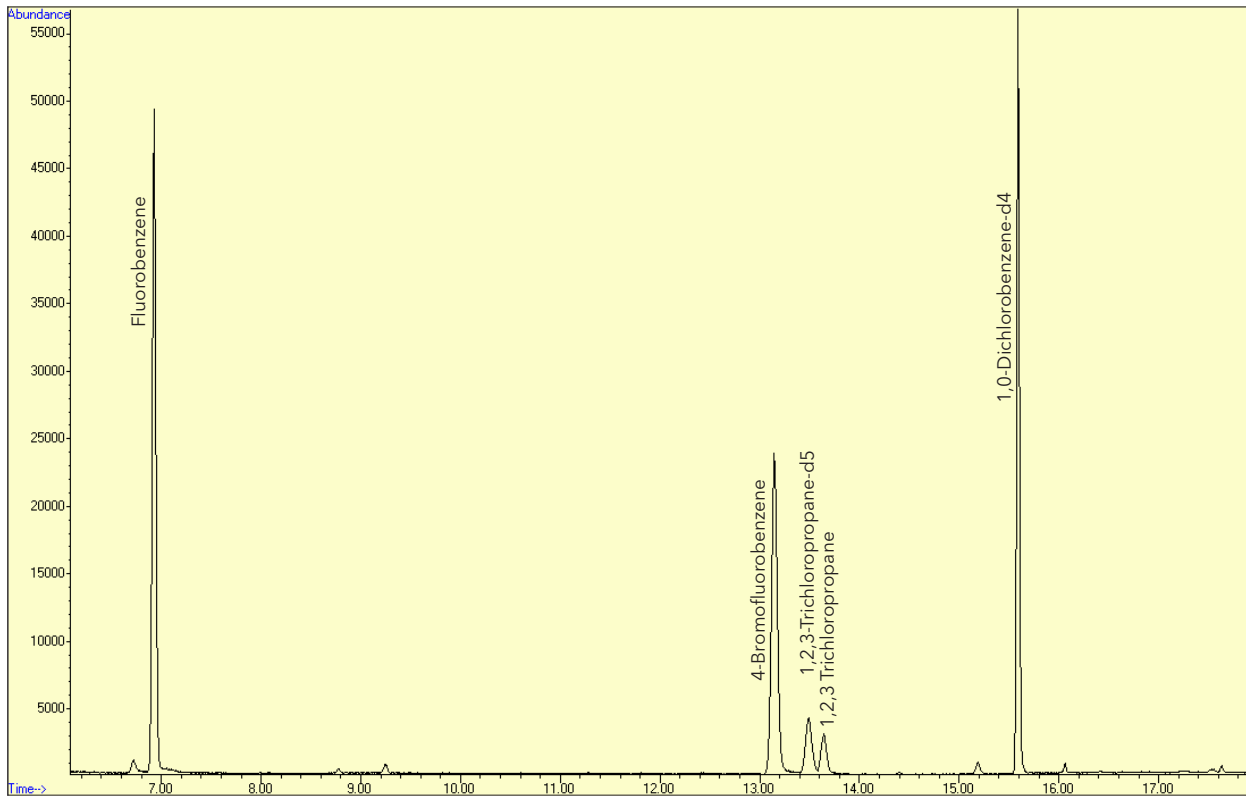


Figure 3. 100 ppt Standard (Modified USEPA Method 8260C)



Conclusion

The consistency of results was very good as shown by daily calibration stability, surrogate recoveries, and multiple sets of IDOC's. Using SIM and purging more than 5 mL of sample at elevated temperature allowed the detection of a very low level of TCP, 5 ppt. If possible, the preferred method would be modified Method 8260C. Using a 10 mL purge instead of 25 mL purge resulted in greater purge efficiency. The 0.5 minute desorb gives equivalent results to 4 minute desorb, but has the advantage of not overloading the system with water, which is best for long-term instrument performance.

References

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151 Graham Road
PO Box 9010
College Station, Texas
77842-9010

(979) 690-1711
(800) 653-1711 USA/Canada
FAX (979) 690-0440

www.oico.com
E-mail: oi-info@xyleminc.com