Low-level Drinking Water Analysis of 1,2,3-Trichloropropane by Purge and Trap Concentration and GC/MS

Application Note

Abstract

1,2,3-Trichloropropane (TCP) is a common industrial solvent with applications as a paint and varnish remover, degreasing agent, and an intermediate in pesticides. The California Department of Public Health recognizes TCP as a carcinogen with a notification level of 0.005 µg/L in drinking water.[1] For low level drinking water analysis of volatile organic compounds (VOCs), the USEPA developed Method 524.3, *Measurement of Purgeable Organic Compounds by Capillary Column Gas Chromatography/Mass Spectrometry*. This purge and trap method allows the use of Single Ion Monitoring (SIM) to reach the part-per-trillion (ppt) levels required for the analysis of TCP.[2]

This study uses a Teledyne Tekmar Stratum Purge and Trap Concentrator (PTC) and AQUATek 100 Autosampler coupled to a Thermo ISQ Single Quadrupole GC-MS. A calibration curve and detection limit will be determined for 1,2,3-trichloropropane.

Introduction

1,2,3-trichloropropane is a man-made compound found primarily at industrial or hazardous waste sites, and capable of leaching from soil into ground water. Testing completed by the USEPA has determined that TCP is likely to be carcinogenic in humans.[3] TCP can have toxic effects on many organs, primarily the liver, which can occur within a short period of time. The California Department of Public Health recognizes TCP as a carcinogen and has a notification level of 0.005 µg/L.[1] A notification level is a health-based advisory level established for chemicals in drinking water that lack maximum contaminant levels (MCLs).[1]

USEPA Method 524.3, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*, includes TCP on its analyte list. Using the parameters set in Method 524.3 and SIM scan, TCP can be analyzed at the ppt (ng/L) level.

This study will use a Stratum PTC and AQUATek 100 Autosampler with a Thermo ISQ GC-MS to establish a calibration and detection limit for TCP.

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Experimental-Instrument Conditions

The Stratum PTC and AQUATek 100 autosampler were coupled to the Thermo ISQ GC/MS system for analysis. The Thermo ISQ was configured with a Restek Rtx-624 20 m x 0.18 mm x 1.0 µm column. The GC-MS parameters are outlined in **Table 1** and **2**.

A Tekmar proprietary #9 trap was the analytical trap of choice. **Table 3** outlines the PTC and autosampler conditions.

GC Parameters	
GC:	Thermo Trace GC Ultra
Column:	Restek Rtx®-624 20m x 0.18mm x 1.0µm
Oven Program:	45° C for 4.5 min, to 100 °C at 15 °C/min, for 0 min, to 240 °C at 25 °C/min for 0.33 min
Inlet:	200 °C
Column Flow:	1.0 mL/min
Gas:	Helium
Pressure:	21.76 psi
Split Ratio:	25:1

MS Parameters	
MSD:	Thermo ISQ
Source:	275 °C
Transfer Line Temp:	230 °C
Solvent Delay:	0.5 min
SIM ions:	110, 112, 75
Ionization Mode:	EI+
Emission Current	25 uA

Tables 1 & 2: Thermo ISQ GC/MS Parameters

Stratum PTC and AQUATek 100 Parameters			
Variable	**Value**	**Variable**	**Value**
Pressurize Time	0.25 min	Purge Time	6.00
Sample Transfer Time	0.50 min	Purge Temp	20 °C
Rinse Loop Time	0.50 min	Purge Flow	60 mL/min
Sweep Needle Time	0.30 min	Dry Purge Time	2.00 min
Bake Rinse	On	Dry Purge Temp	30 °C
Bake Rinse Cycles	1	Dry Purge Flow	100 mL/min
Bake Rinse Drain Time	0.50 min	GC Start	Start of Desorb
Presweep Time	0.35 min	Desorb Preheat Temp	250 °C
Water Temp	90 °C	Desorb Drain	On
Valve Oven Temp	150 °C	Desorb Time	1.00 min
Transfer Line Temp	150 °C	Desorb Temp	250 °C
Sample Mount Temp	90 °C	Desorb Flow	300 mL/min
Purge ready Temp	35 °C	Bake Time	2.00 min
Condenser Ready Temp	40 °C	Bake Temp	280 °C
Condenser Purge Temp	20 °C	Bake Flow	400 mL/min
Standby Flow	10 mL/min	Condenser Bake Temp	200 °C
Pre-Purge Time	0.5 min		
Pre-Purge Flow	40.0mL/min		

Table 3: Stratum PTC and AQUATek 100 Parameters (Stratum PTC Parameters are in Blue)

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Calibration Data

A 2 ppm Stock solution of 1,2,3-trichloropropane was prepared in methanol. From this stock solution, a nine-point curve from 2.5-1000 ppt was prepared in de-ionized water. The results of this calibration can be found in **Figure 1**. Thermo Scientific EnviroLab Forms software was used to process the data.

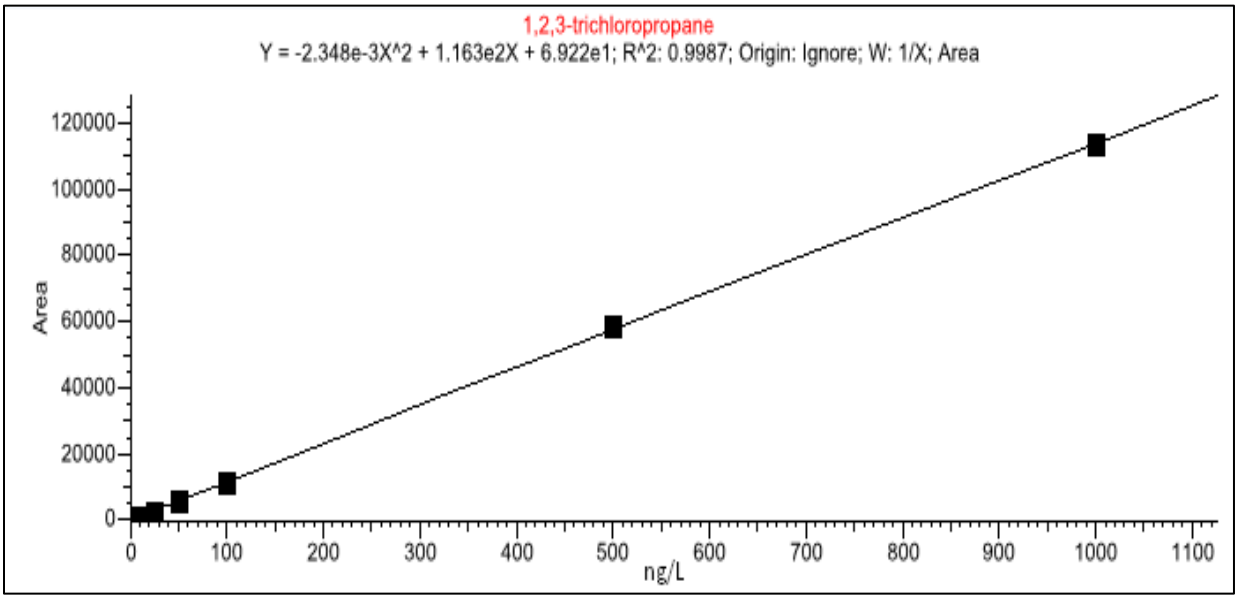

Figure 1: Calibration Curve from 2.5 - 1000ppt for 1,2,3-Trichloropropane
$y = -2.384e^{-3}X^2 + 1.1636e^2X + 6.9221e^2$, $R^2 = 0.9987$

Method Detection Limit

In order to complete analysis at low levels, a SIM scan was used. As recommended by the USEPA, the ions utilized for TCP analysis were 110 m/z as the quantification ion, and 112 m/z and 75 m/z. **Figures 2 and 3** are images from Thermo Scientific EnviroLab Forms software illustrating the quantification ions (110 m/z), the confirming ions(112 m/z, 75 m/z), and an overlay of the ions.

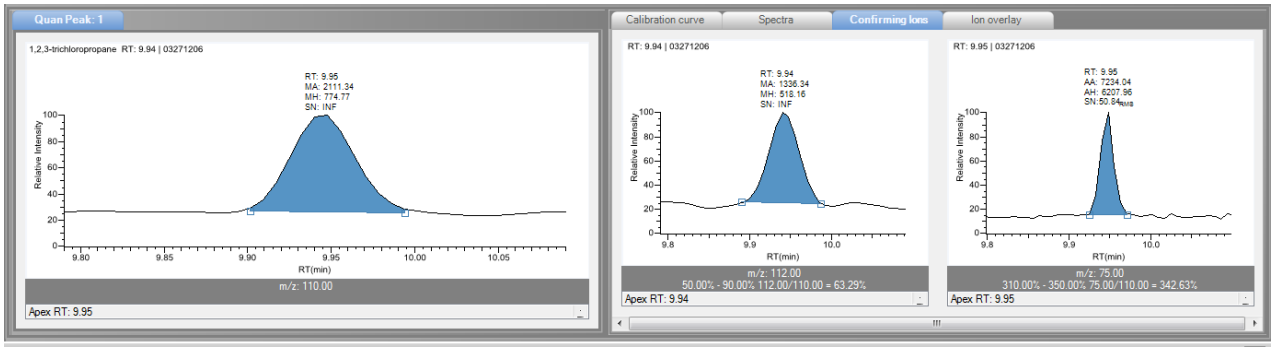

Figure 2: Quantification Ion (110 m/z) and Confirming Ions (112 m/z and 75 m/z)

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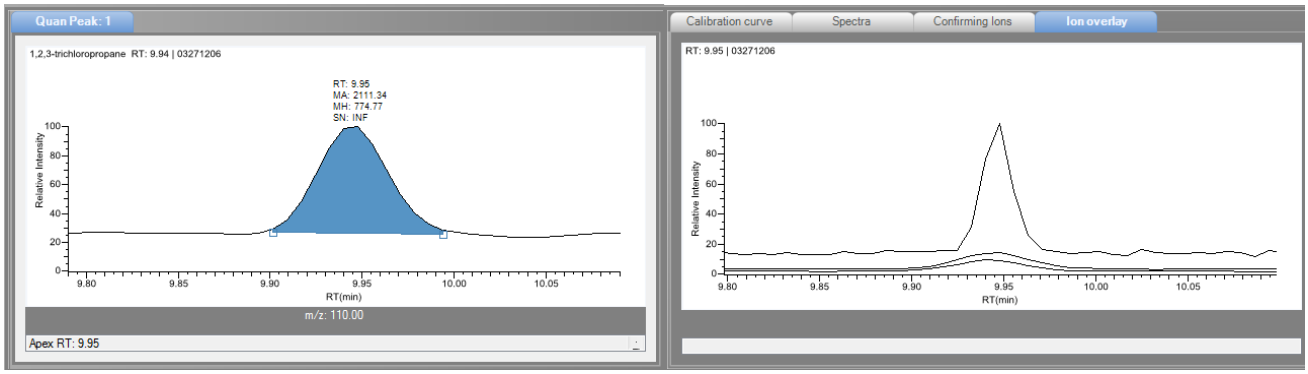

Figure 3: Ion Overlay of the Quantification Ion (110 m/z) and Confirming Ions (112, 75 m/z) for TCP

The method detection limit (MDL) for TCP was established by analyzing seven replicate samples at a concentration of 10 ppt. The detection limit is a statistical determination which identifies the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the concentration is greater than zero.[1]

The detection limit is determined with the following equation, where S is the standard deviation and t is the t value for the 99% confidence level. For seven replicates, the t value is 3.143.[1]

$$DL = S * t_{(n-1,1-\alpha=0.99)}$$

Table 4 illustrates the replicate data and MDL results for TCP.

Spike Level	1 (ppt)	2 (ppt)	3 (ppt)	4 (ppt)	5 (ppt)	6 (ppt)	7 (ppt)	Average (n=7)	Stdev	MDL (ppt)
10ppt	9.592	9.744	9.476	9.745	9.850	9.999	9.609	9.72	0.17	0.543

Table 4: MDL data for 1,2,3-Trichloropropane

Conclusions

The California Department of Public Health has decreased the notification level for 1,2,3-trichloropropane to 5ppt(ng/L) due to its carcinogenic properties. With concerns for public health and safety, notification levels of harmful compounds are being pushed lower and lower, driving the demand for more sensitive instrumentation. This study validates the capability of Teledyne Tekmar Stratum PTC and AQUATek 100 Autosampler coupled with a Thermo ISQ for low-level detection of TCP. Using a SIM scan, as permitted in USEPA method 524.3, an MDL was established for TCP at 0.543 parts-per-trillion, proving purge and trap to be a superb analytical tool for this analysis.

References

1. California Department of Public Health. http://www.cdph.ca.gov/certlic/drinkingwater/Pages/123tcp.aspx
2. USEPA Method 524.3, “Measurement of Purgeable Organic Compounds by Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS),” Revision 1, 2009.
3. Emerging Contaminant -1,2,3-Trichloropropane (TCP. United State Environmental Protection Agency. December 2010. Fact Sheet. http://www.epa.gov/fedfac/documents/emerging_contaminant_tcp.pdf

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