Validation of USEPA Method 524.2 Using a Stratum PTC, AQUATek 100 Autosampler, and Perkin-Elmer Clarus 600 GC/MS

Application Note

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Abstract

The US EPA developed Method 524.2[1], "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry", for identifying and measuring purgeable volatile organic compounds (VOC) in surface water, groundwater, and drinking water. Due to the required sensitivity of this method, the use of purge and trap gas chromatography is vital. This study will utilize a Teledyne Tekmar Stratum Purge and Trap Concentrator (PTC) and AQUATek 100 Autosampler in conjunction with a Perkin-Elmer Clarus 600 GC/MS. A linear calibration and Method Detection Limits (MDLs) will be established for Method 524.2[1] compounds.

Introduction

Clean drinking water is something that many of us take for granted. This is due, in part, to the stringent water quality criteria established by the US EPA. Methods such as 524.2[1] allow for detection of a wide-range of VOCs at very low levels. VOCs are known drinking water contaminants with potentially harmful long- and short-term health effects. The reason methods can be created with such precise, low-level performance criteria is through the use of Purge and Trap technology.

For this study, a Stratum PTC was used in conjunction with an AQUATek 100 Autosampler. This set-up allows for complete automation of sample preparation for the analysis of liquid samples for purge and trap. Through the features the AQUATek 100 provides, such as the 100-position sample tray and standard addition vessels, efficiency and throughput can be greatly increased, leading to cost and time savings.

Utilizing a Perkin-Elmer Clarus 600 GC/MS, a linear calibration was performed and percent Relative Standard Deviation (%RSD) and Method Detection Limits (MDLs) were determined for the full list of compounds. A 25mL purge volume was used and all performance criteria of EPA Method 524.2[1] were met.

Experimental-Instrument Conditions

The Stratum PTC and AQUATek 100 Autosampler were coupled to a Perkin-Elmer Clarus 600 GC/MS for analysis. Teledyne Tekmar's proprietary #9 trap was the analytical trap used. The GC was configured with a Perkin-Elmer Elite-624 20m x 0.18mm x 1.0µm column. The GC/MS parameters are outlined in Tables 1 and 2. Table 3 outlines the P&T and autosampler conditions.

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GC Parameters	
GC:	Perkin-Elmer Clarus 600 Gas Chromatograph
Column:	Perkin-Elmer Elite-624 20m x 0.18mm x 1.0µm
Oven Program:	35° C for 2 min, to 200° C at 10° C/min, for 0 min, to 240° C at 50 ° C/min
Inlet:	220° C
Column Flow:	0.8mL/min
Gas:	Helium
Pressure:	16.1 psi
Split Ratio:	80:1

MS Parameters	
MSD:	Clarus 600T Quadrupole Mass Spectrometer
Source:	200° C
Transfer Line Temp:	200°C
Solvent Delay:	0.5 min
Scan Range:	35-300 m/z
Scan Time:	0.2 sec
Inter-scan Delay:	0.1 sec
Ionization Mode:	EI+

Tables 1 & 2: GC and MSD Parameters

Stratum PTC and AQUATek 100 Parameters			
Variable	**Value**	**Variable**	**Value**
Pressurize Time	0.95 min	Purge Time	11.00
Sample Transfer Time	1.25 min	Purge Temp	20°C
Rinse Loop Time	0.85 min	Purge Flow	40mL/min
Sweep Needle Time	0.35 min	Dry Purge Time	0.0 min
Bake Rinse	On	Dry Purge Temp	20°C
Bake Rinse Cycles	1	Dry Purge Flow	100mL/min
Bake Rinse Drain Time	0.60 min	GC Start	Start of Desorb
Presweep Time	0.35 min	Desorb Preheat Temp	245°C
Water Temp	90° C	Desorb Drain	On
Valve Oven Temp	150°C	Desorb Time	2.00 min
Transfer Line Temp	150°C	Desorb Temp	250°C
Sample Mount Temp	90°C	Desorb Flow	300mL/min
Purge ready Temp	35°C	Bake Time	4.00 min
Condenser Ready Temp	40°C	Bake Temp	280°C
Condenser Purge Temp	20°C	Bake Flow	200mL/min
Standby Flow	5mL/min	Condenser Bake Temp	200°C
Pre-Purge Time	0.5 min		
Pre-Purge Flow	40.0mL/min		
Sample Heater	Off		
Sample Preheat Time	1.00 min		
Sample Temp	40°C		

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

Calibration Data

A 50ppm working calibration standard was prepared in methanol. Calibration standards were prepared in 50mL volumetric flasks filled to volume with de-ionized water over a range of 0.2ppb to 50ppb. Samples were transferred to headspace free 40mL vials for analysis. The Internal Standard (IS) and Surrogate Standards (SS) were prepared in methanol at a 25ppm concentration. After transferring to the standard

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vessel on the AQUATek 100, the IS/SS was added in 5µL volumes to each sample, bringing the final concentration of 5ppb. Perkin-Elmer TuroboMass software was used to process the calibration data. Relative response factors were evaluated for linearity and %RSD with results for all compounds listed in Table 4. Method detection limits were also established for all compounds by analyzing seven replicates at a concentration of 0.2ppb. MDL results for all compounds were below 0.2ppb.

Compound Name	Average RRF	% RSD	Minimum Detection Limit
Dichlorodifluoromethane	0.286	8.6	0.14
Chloromethane	0.559	9.4	0.12
Vinyl Chloride	0.371	6.3	0.13
Bromomethane	0.153	11.2	0.20
Chloroethane	0.228	8.7	0.15
Trichlorofluoromethane	0.283	5.4	0.17
Diethyl Ether	0.143	9.0	0.09
1,1-Dichloroethene	0.223	7.3	0.17
Acetone	0.049	10.4	0.13
Iodomethane	0.137	0.9983*	0.04
Carbon Disulfide	0.681	7.4	0.16
Allyl Chloride	0.180	7.2	0.17
Methylene Chloride	0.220	7.0	0.15
trans-1,2-Dichloroethene	0.241	8.3	0.15
MTBE	0.368	8.1	0.09
Acryl Nitrile	0.041	11.5	0.11
1,1-Dichloroethane	0.476	5.1	0.14
2-Butanone	0.066	14.6	0.06
2,2-Dichloropropane	0.382	7.7	0.13
cis-1,2-dichloroethene	0.273	6.5	0.16
Methyl Acrylate	0.092	9.6	0.10
Propionitrile	0.015	10.8	0.11
Methacrylonitrile	0.045	11.0	0.07
Bromochloromethane	0.078	5.4	0.11
Tetrahydrofuran	0.012	13.3	0.08
Chloroform	0.405	4.6	0.14
1,1,1-Trichloroethane	0.322	5.4	0.15
Carbon Tetrachloride	0.257	4.9	0.13
1-Chlorobutane	0.699	6.4	0.12
1,1-Dichloropropene	0.398	5.1	0.15
Benzene	1.241	4.3	0.15
1,2-Dichloroethane	0.183	6.5	0.11
Trichloroethene	0.262	7.0	0.15
Methyl Methacrylate	0.079	9.3	0.08
1,2-Dichloropropane	0.233	2.3	0.17
Dibromomethane	0.067	6.6	0.15
Ethyl Methacrylate	0.162	8.7	0.04
Bromodichloromethane	0.240	5.0	0.10
2-Nitropropane	0.001	16.5	0.19
Chloroacetonitrile	0.010	13.9	0.12
cis-1,3-Dichloropropene	0.332	3.5	0.09
4-Methyl-2-Pentanone	0.035	7.8	0.08
Toluene	0.685	5.3	0.16

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trans-1,3-Dichloropropene	0.227	5.9	0.10
1,1,2-Trichloroethane	0.115	8.3	0.08
Tetrachloroethene	0.433	9.7	0.19
2-Hexanone	0.077	9.7	0.08
1,3-Dichloropropane	0.249	6.4	0.11
Dibromochloromethane	0.109	5.7	0.11
1,2-Dibromoethane	0.098	8.7	0.09
Chlorobenzene	0.648	4.8	0.14
1,1,1,2-Tetrachloroethane	0.172	4.9	0.14
Ethylbenzene	1.263	4.9	0.16
m,p-Xylene	1.004	3.6	0.31
o-Xylene	0.988	4.4	0.14
Styrene	0.673	2.2	0.15
Nitrobenzene	0.004	9.6	0.15
Bromoform	0.045	15.9	0.06
Isopropylbenzene	1.255	4.1	0.14
Bromobenzene	0.192	3.6	0.15
1,1,2,2-Tetrachloroethane	0.089	8.8	0.07
trans-1,4-Dichloro-2-butene	0.028	6.0	0.05
1,2,3-Trichloropropane	0.084	5.9	0.10
n-Propylbenzene	1.440	3.5	0.16
2-Chlorotoluene	0.871	3.4	0.14
4-Chlorotoluene	0.977	3.9	0.14
1,3,5-Trimethylbenzene	1.002	3.5	0.13
tert-Butylbenzene	0.837	3.5	0.15
1,2,4-Trimethylbenzene	0.950	4.0	0.12
sec-Butylbenzene	1.331	3.6	0.14
1,3-Dichlorobenzene	0.436	2.8	0.14
p-Isopropyltoluene	0.953	6.9	0.14
1,4-Dichlorobenzene	0.420	2.8	0.14
1,2-Dichlorobenzene	0.360	4.7	0.13
n-Butylbenzene	0.896	6.3	0.14
Hexachloroethane	0.113	0.9999*	0.14
1,2-Dibromo-3-chloropropane	0.012	0.9955*	0.10
1,2,4-Trichlorobenzene	0.237	6.1	0.13
Hexachlorobutadiene	0.109	8.6	0.14
Naphthalene	0.348	10.5	0.07
1,2,3-Trichlorobenzene	0.180	8.1	0.12
Average	0.376	7.0	0.13

* Indicates compounds using correlation coefficients from linear regression (r^2).

Table 4: Calibration and MDL Data for EPA Method 524.2

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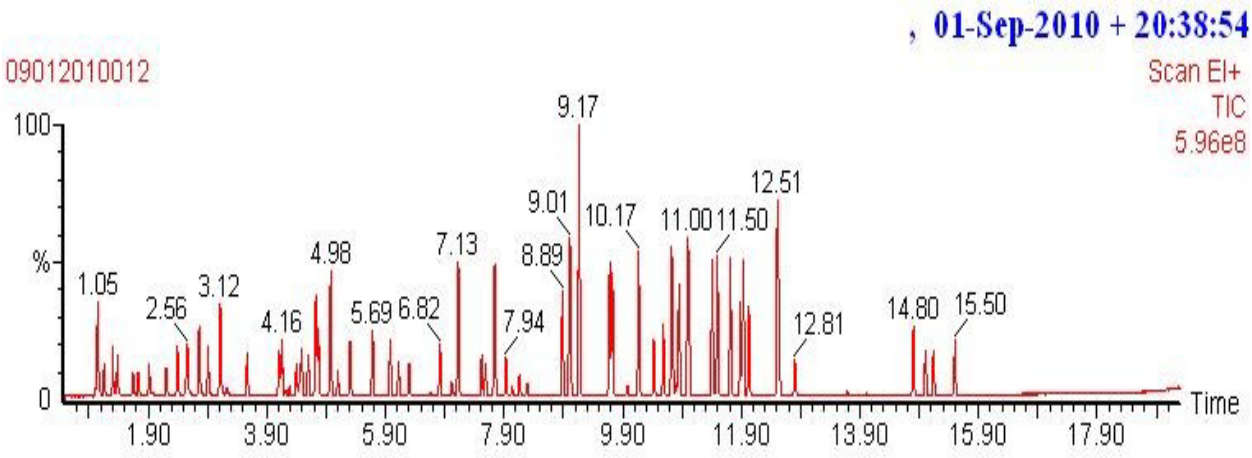

Figure 1: Total Ion Chromatogram of a 10ppb Calibration Standard for Method 524.2

Conclusions

Accuracy and precision are critical when dealing with drinking water analyses because of the impact on public health and safety. This study demonstrates the capabilities of the Teledyne Tekmar Stratum PTC and AQUATek 100 Autosampler coupled with a Perkin-Elmer Clarus 600 system, which met all performance criteria outlined in US EPA Method 524.2[1]. By completely automating the sample preparation, without compromising sensitivity, efficiency and throughput can be greatly increased while saving time and money.

References

1. USEPA Method 524.2, "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)," Revision 4.1, 1995.

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