Highly Sensitive P&T-GCMS Technology is Setting New Standards in Drinking Water Testing

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ABSTRACT

Purpose: This paper illustrates how advanced P&T-GC-MS technology is applied to the analysis of VOCs in drinking water, offering enhanced analytical performance, extended uptime and streamlined workflow.

Methods: A GC-MS system equipped with a highly efficient EI source has been used to enhance the sensitivity of VOCs, especially when full scan acquisition is applied. Additionally, the P&T method has been optimized to minimize the amount of water transferred during desorption, thanks to the effective moisture control system embedded in the instrument.

Results: The linearity of the calibration curve from 0.05 ppb to 100 ppb passed all method requirements with no interference of moisture from the sample. The MDL, precision and accuracy for seven 0.1 and 0.05 ppb standards also indicated no interference from water.
Improvements to the method were tested by combining changes to the chromatography, employing the capabilities of the hardware, and applying a software package developed around routine GC-MS workflows.

INTRODUCTION

Environmental testing laboratories are routinely involved in monitoring water and soils contamination from chemicals commonly found in industrial products or consumer goods, with the aim to control and minimize people exposure to possible toxic compounds. Volatile Organic Chemicals (VOCs) are commonly found as contaminants in the environment and therefore heavily monitored in water and soil under strict regulations. Especially when drinking water or surface water are considered, Maximum Contaminant Levels (MCLs) can be extremely challenging for some target analytes, requiring highly performing instrumentation. State-of-the-art technology is available to push the boundary of sensitivity with significantly lower detection limits. This helps routine laboratories in delivering high-confident results more easily and more efficiently, reducing time waste and keeping costs down.

This paper illustrates how advanced technology is applied to the analysis of VOCs in drinking water, with particular attention to critical compounds as 1,2,3-Trichloropropane and 1,2-Dibromoethane, offering enhanced analytical performance, extended uptime and streamlined workflow.

The analysis of volatile organic compounds (VOCs) has been performed with the Thermo Scientific™ ISQ™ 7000 single quadrupole GC-MS using quality control requirements based on United States Environmental Protection Agency (EPA) methodologies.
This requires integration of a range of instrumentation, from the sample introduction system to the gas chromatograph and mass spectrometer, to the software for data interpretation, analysis and reporting [1]. While the overall process of analyzing VOC is a mature technique, there are continuous innovations that allow laboratories to meet lower detection limits and analyze new compounds to comply with changing regulations, with higher throughput and improved quality.

MATERIALS AND METHODS

Instrumentation

This study has been performed coupling the Teledyne Tekmar Atomx XYZ P&T system to the ISQ 7000 GC-MS equipped with the highly sensitive Advanced Electron Ionization (AEI) source (Figure 1)

Figure 1. Teledyne Tekmar Atomx XYZ P&T coupled to the ISQ 7000 AEI GC-MS

Sample Preparation

A 25 ppm calibration working standard was prepared in 10 mL of methanol from the following Restek® standards: Drinking Water VOA MegaMix™ (Catalog Number, 30601) and 502.2 Calibration Mix (Catalog Number, 30042). In total, the working standard contained 75 compounds.

The calibration curves were prepared from 0.05 to 100 ppb for all compounds, with the following calibration points: 0.05, 0.1, 0.2, 0.5, 1, 5, 20, and 100 ppb.

The 0.05, 0.1, and 0.2 ppb calibration points were made with the appropriate amount of calibration standard for each point in 500 mL volumetric flasks of deionized (DI) water from the Milli-Q® Integral 10 Water Purification System (Millipore Sigma, Burlington, MA). The rest of the calibration standards were made with the appropriate amount of calibration standard for each point in 50 mL of DI water. Each calibration standard was then poured into a 40 mL VOA vial with no headspace and placed into the Atomx XYZ autosampler.

The relative response factor (RF) was calculated for each compound using one internal standard: Fluorobenzene. Surrogate standards consisted of: Bromofluorobenzene and 1,2-Dichlorobenzene-d4. Internal and surrogate standards were prepared in methanol from Restek® standards (Catalog Number, 30201) at a concentration of 25 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Seven 0.1 ppb standards, with a few compounds using seven 0.05 ppb standards, were prepared to calculate the MDL, accuracy, and precision for all compounds. All calibration and MDL standards were analyzed with the Atomx XYZ conditions in **Table 1**. The GC-MS system was equipped with an Instant Connect SSL Injector with a Split Liner (p/n 453A1335). The GC-MS system conditions are shown in **Table 2**.

The Teledyne Tekmar Teklink™ control SW allows for an easy and intuitive operation of the P&T system while Thermo Scientific™ Chromeleon™ 7.2 CDS software was used for data acquisition and reporting, exploiting the dedicated tools specifically developed for routine environmental GC-MS workflows.

Table 1. Teledyne Tekmar Atomx XYZ Water Method Conditions

Standby	Variable	Desorb	Variable
Valve Oven Temp	140ºC	Methanol Needle Rinse	Off
Transfer Line Temp	140ºC	Methanol Needle Rinse Volume	0.00 mL
Sample Mount Temp	90ºC	Water Needle Rinse Volume	7.00 mL
Water Heater Temp	90ºC	Sweep Needle Time	0.25 min
Sample Vial Temp	20ºC	Desorb Preheat Temp	245ºC
Soil Valve Temp	100ºC	GC Start Signal	Begin Desorb
Standby Flow	10 mL/min	Desorb Time	2.00 min
Condensate Ready Temp	45ºC	Drain Flow	300 mL/min
Purge Ready Temp	40ºC	Desorb Temp	250ºC
Purge	**Variable**	**Bake**	**Variable**
Sample Equilibrate Time	0.00 min	Methanol Glass Rinse	Off
Pre-sweep Time	0.25 min	Number of Methanol Glass Rinses	0
Prime Sample Fill Volume	3.00 mL	Methanol Glass Rinse Volume	0.00 mL
Sample Volume	5.00 mL	Water Bake Rinses	1
Sweep Sample Time	0.25 min	Water Bake Rinse Volume	7.00 mL
Sweep Sample Flow	100 mL/min	Bake Rinse Sweep Time	0.25 min
Sparge Vessel Heater	Off	Bake Rinse Sweep Flow	100 mL/min
Sparge Vessel Temp	20ºC	Bake Rinse Drain Time	0.40 min
Pre-purge Time	0.00 min	Bake Time	30.00 min
Pre-purge Flow	0 mL/min	Bake Flow	200 mL/min
Purge Time	11.00 min	Bake Temp	260ºC
Purge Flow	40 mL/min	Condensate Bake Temp	200ºC
Purge Temp	20ºC		
Condensate Purge Temp	20ºC	**Device**	**Variable**
Dry Purge Time	2.00 min	Trap	9
Dry Purge Flow	100 mL/min	Chiller Tray	Off
Dry Purge Temp	20ºC	Purge Gas	Nitrogen

Table 2. Thermo Scientific™ TRACE™ 1310 GC and ISQ 7000 MS System Conditions

Thermo Scientific TRACE 1310 GC Conditions	
Column	Rtx® VMS, 20 m x 0.18 mm, 1µm Film, Helium – 0.8 mL/min
Oven Profile	35 ºC, 2 min, 12ºC/min to 85 ºC, 20ºC/min to 225 ºC, 2 min Hold, Run Time 15.167 min
Inlet	230 ºC; 60:1 Split
Thermo Scientific ISQ 7000 MS Conditions	
Temp	Transfer Line 230 ºC; Ion Source 300 ºC
Scan	Range 35 amu to 260 amu, Solvent Delay 0.10 min, Dwell/Scan Time 0.15 sec.
Current	Chrom. Filter Peak Width (sec) 1.000, Emission Current 50 µA, Gain 5.00E+005

RESULTS

Figure 2 displays a 50 ppb standard, indicating excellent peak resolution with no water inference for all VOCs. The relative standard deviation (%RSD) of the RFs for the calibration curve, MDL, accuracy, and precision data for the AEI source are shown in Table 3.

Due to constraints in the laboratory, Semi-volatile Organic Compounds (SVOC) analysis was occurring at the same time as this analysis. Therefore, calibration, accuracy and precision data for Methylene Chloride have been compromised due to its role in SVOC extraction. Carbon Disulfide was also affected by this Methylene Chloride contamination in the lab, resulting in high %RSDs and accuracy.
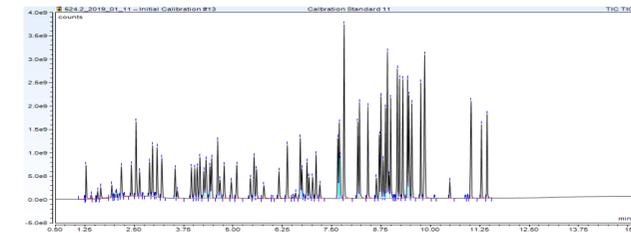

Figure 2. Total Ion Chromatogram of a Water Method 50 ppb VOC Standard Analyzed by the AEI Source Indicating Consistent Peak Shapes for all Compounds with Minimal Water Interference.

Table 3. US EPA Method 524.2 Calibration, Accuracy, and Precision Data

Compound	Calibration				Accuracy and Precision (n=7, 0.1 ppb)[1]		
	RT (min)	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Conc. (ppb)	Accuracy (±30%)	Precision (≤20%)
Dichlorodifluoromethane[2]	1.41	19.7	0.008	0.150	0.036	73	7.19
Chloromethane[3]	1.57	0.996	0.022	0.399	0.099	99	6.97
Vinyl Chloride[2]	1.65	17.2	0.020	0.419	0.039	78	16.4
Bromomethane	1.93	74.2	0.027	0.935	0.12	119	7.18
Chloroethane	2.04	11.4	0.033	0.430	0.11	105	9.85
Trichlorofluoromethane[2]	2.16	16.6	0.005	1.33	0.044	88	3.91
Diethyl Ether	2.43	18.4	0.014	0.644	0.090	90	4.91
1,1-Dichloroethene	2.54	15.8	0.020	0.778	0.099	99	6.59
Carbon Disulfide	2.54	33.5	0.015	2.94	0.091	91	5.34
Iodomethane[2,3]	2.63	0.998	0.014	0.472	0.045	90	9.85
Allyl Chloride	2.89	13.3	0.021	0.878	0.11	107	9.27
Methylene Chloride	2.96	53.1	0.014	1.75	0.13	133	3.41
cis-1,2-Dichloroethene	3.08	16.2	0.009	1.27	0.11	108	2.76
Methyl-tert-Butyl Ether	3.20	11.8	0.012	0.891	0.094	94	3.92
1,1-Dichloroethane	3.53	14.6	0.007	1.33	0.098	98	2.38
Acrylonitrile	3.59	10.9	0.005	0.252	0.11	106	10.4
Propionitrile	3.59	10.0	0.008	0.250	0.093	93	2.88
trans-1,2-Dichloroethene	3.95	8.73	0.008	0.833	0.093	93	2.88
2,2-Dichloropropane	4.03	11.0	0.011	0.604	0.091	91	3.96
Bromochloromethane	4.09	10.1	0.017	0.270	0.097	97	5.43
Chloroform	4.16	10.9	0.008	1.22	0.10	102	2.53
Carbon Tetrachloride	4.26	8.13	0.012	0.564	0.090	90	4.27
1,1,1-Trichloroethane	4.31	10.4	0.014	0.710	0.010	101	4.33
1,1-Dichloropropene	4.41	10.2	0.017	0.425	0.099	99	5.54
1-Chlorobutane	4.45	12.9	0.007	0.800	0.093	93	2.44
Benzene	4.61	6.75	0.009	1.75	0.10	102	2.79
Methacrylonitrile	4.67	9.47	0.061	0.300	0.11	109	17.7
1,2-Dichloroethane	4.78	8.88	0.013	1.22	0.096	96	4.40
Fluorobenzene (IS)	4.96						
Trichloroethylene	5.09	10.0	0.027	0.522	0.11	114	7.53
Dibromomethane	5.44	10.2	0.020	0.435	0.099	99	6.41
1,2-Dichloropropane	5.53	6.09	0.008	0.549	0.10	103	2.32
Bromodichloromethane	5.59	7.49	0.010	0.698	0.094	94	3.52
Methyl Methacrylate	5.78	8.54	0.021	0.359	0.11	106	6.26
cis-1,3-Dichloropropene	6.16	7.68	0.013	0.504	0.093	93	4.31
Toluene	6.37	9.13	0.010	1.42	0.094	94	3.47
Chloroacetonitrile	6.51	9.67	0.042	0.024	0.11	111	12.0
2-Nitropropane	6.58	17.8	0.026	0.113	0.11	111	7.57
Tetrachloroethene	6.70	13.8	0.022	0.734	0.12	118	5.78
trans-1,3-Dichloropropene	6.74	6.37	0.033	0.527	0.098	98	10.7
1,1,2-Trichloroethane	6.87	8.30	0.022	0.424	0.11	107	6.52

Compound	Calibration				Accuracy and Precision (n=7, 0.1 ppb)[1]		
	RT (min)	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Conc. (ppb)	Accuracy (±30%)	Precision (≤20%)
Ethyl Methacrylate	6.92	10.4	0.014	0.256	0.092	92	4.89
Dibromochloromethane	7.02	7.22	0.011	0.388	0.091	91	3.90
1,3-Dichloropropane	7.10	7.52	0.010	0.761	0.093	93	3.49
1,2-Dibromoethane	7.20	9.32	0.022	0.412	0.097	97	7.20
Chlorobenzene	7.65	9.12	0.016	1.04	0.10	101	4.89
Ethylbenzene	7.69	11.5	0.011	1.28	0.086	86	4.00
1,1,1,2-Tetrachloroethane	7.71	6.02	0.010	0.338	0.11	105	3.17
m-, p-Xylene[2,3]	7.81	1.00	0.014	0.503	0.089	89	4.96
o-Xylene	8.16	20.0	0.008	0.480	0.09	79	3.27
Bromoform	8.20	0.999	0.017	0.785	0.088	88	6.05
Styrene[2,3]	8.20	9.65	0.010	0.222	0.044	87	7.06
Isopropylbenzene	8.41	18.9	0.008	1.06	0.076	76	3.15
4-Bromofluorobenzene (SURR)	8.63	13.3		0.431	21.0	84	2.69
Bromobenzene	8.70	11.5	0.015	1.11	0.093	93	5.28
n-Propylbenzene	8.75	14.4	0.019	1.63	0.01	81	7.35
1,1,2,2-Tetrachloroethane	8.80	14.5	0.016	0.493	0.076	76	6.81
2-Chlorotoluene	8.86	10.1	0.012	1.27	0.085	85	4.25
1,2,3-Trichloropropane	8.90	11.1	0.018	0.755	0.095	95	6.06
1,3,5-Trimethylbenzene[2]	8.91	1.00	0.012	1.06	0.040	79	9.91
trans-1,4-Dichloro-2-butene[3]	8.95	1.00	0.022	0.222	0.088	88	7.91
4-Chlorotoluene[3]	8.99	0.997	0.010	1.24	0.072	72	4.59
tert-Butylbenzene[2]	9.16	19.9	0.010	0.809	0.057	113	5.91
1,2,4-Trimethylbenzene[2,3]	9.21	0.999	0.008	1.02	0.037	74	6.51
sec-Butylbenzene[2,3]	9.30	0.999	0.009	1.27	0.047	94	6.39
p-Isopropyltoluene[3]	9.41	1.00	0.007	0.882	0.038	75	5.70
1,3-Dichlorobenzene	9.45	15.2	0.014	0.988	0.092	92	4.71
1,4-Dichlorobenzene	9.52	15.9	0.014	0.869	0.090	90	5.08
n-Butylbenzene	9.75	18.7	0.019	1.09	0.084	84	7.03
Hexachloroethane	9.84	19.1	0.013	0.140	0.084	84	5.06
1,2-Dichlorobenzene-d4 (SURR)	9.85	23.6		0.476	19.4	77	2.72
1,2-Dichlorobenzene	9.86	13.2	0.013	1.08	0.091	91	4.57
1,2-Dibromo-3-Chloropropane	10.49	12.0	0.037	0.137	0.10	100	11.6
Hexachlorobutadiene	10.90	11.0	0.047	0.002	0.10	103	14.5
Nitrobenzene	10.94	12.4	0.056	0.005	0.099	99	18.0
1,2,4-Trichlorobenzene	11.03	4.15	0.019	0.493	0.092	92	6.67
Naphthalene	11.29	18.3	0.016	1.01	0.084	84	6.03
1,2,3-Trichlorobenzene	11.43	13.2	0.011	0.546	0.095	95	3.84

1. Data from seven 0.1 ppb samples.   2. Data from seven 0.05 ppb samples.   3. Compounds were linear regressed
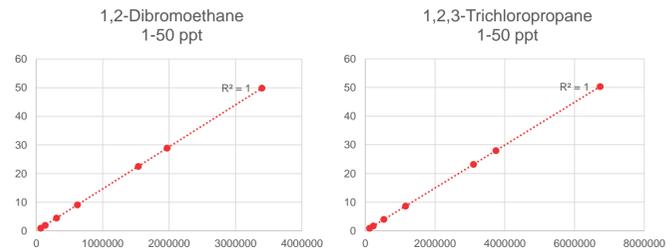

Figure 3. GC-MS linearity and sensitivity assessment through direct injection

The GC-MS method has been optimized through direct injection, before moving to the P&T method set up, obtaining excellent linearity and sensitivity down to 1 ppt.

Achieving low level VOC analysis is traditionally done with a 25 milliliter (mL) sample sparge. This application displays analysis as low as 0.05 ppb or 50 ppt with only a 5 mL sample sparge, greatly reducing sample waste and moisture transferred to the GC during desorb.

The EPA 524.4 method allows flexibility in the dry purge and desorb time of the analytical trap to reduce the large volumes of water to the GC-MS system which would lead to poor chromatography for early eluting gases. Extra measures for moisture control are used in this application, but simply adjusting dry purge or bake times could reduce sample time and increase laboratory throughput in a 12 hour period.
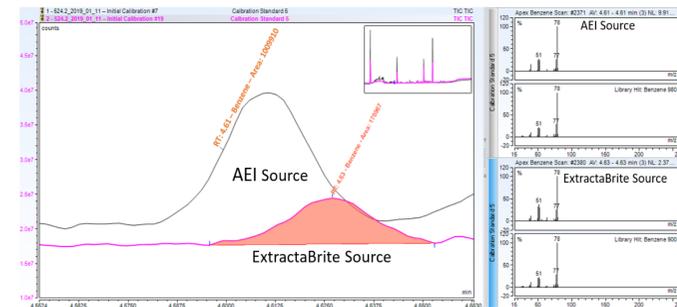

Figure 4. Comparison of AEI Source and ExtractaBrite Source for 1 ppb response of Benzene and NIST Library Match Comparison

The enhanced sensitivity offered by the AEI source compared to the standard ExtractaBrite ion source is particularly advantageous when working in full scan mode, delivering high-confident results more easily. A higher S/N ratio of the TIC peaks helps in achieving high quality spectra with excellent matching with NIST library.

CONCLUSIONS

The Atomx XYZ P&T connected with the ISQ 7000 AEI is providing a sensitive and reliable solution for the analysis of VOCs in drinking water, especially when lower detection limits are required.

The concentrator's efficient trap cooling design reduces sample cycle time by as much as 14% over the previous model. Combined with its 84-position soil and water autosampler, the result is more samples tested per 12-hour period.

An innovative moisture control system improves water vapor removal by as much as 60%. Thereby reducing peak interference and increasing GC column lifespan. In addition to other refinements, the Atomx XYZ incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust.

The Advanced Electron Ionization (AEI) source offers higher ionization efficiency combined to enhanced robustness,

Improvements to the method were tested by combining changes to the chromatography, employing the capabilities of the hardware, and applying a software package developed around routine GC/MS workflows. Laboratories can reduce the analyst review time combined with an increased number of samples that can be analyzed during a 12-hour time period while also attaining lower MDLs. The ISQ 7000 single quadrupole GC-MS equipped with the AEI source was evaluated and found to provide high sensitivity, spectral purity, and linear dynamic range for the method.

The investigation of the full capabilities of the system to push the limits down to sub-ppt levels for critical compounds like 1,2-Dibromoethane and 1,2,3-Trichloropropane is still on-going involving fine tuning of the MS and P&T enrichment conditions.

REFERENCES

1. Method 524.4 - Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry Using Nitrogen Purge Gas; US EPA, Office of Water, May 2013.

TRADEMARKS/LICENSING