APPLICATION NOTE 73415

# Routine analysis of purgeable organic compounds in drinking water with ISQ 7000 GC-MS

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Keywords: EPA, VOCs, phthalates, trace analysis, gas chromatography, single quadrupole mass spectrometry, selected ion monitoring, sensitivity, GRO, THM, volatiles, environmental lab, environmental sample analysis, contract labs

## Goal

Demonstration of a routine analytical method that meets the requirements outlined in U.S. EPA Method 524.4 for the quantitation of purgeable organic compounds (POCs) in drinking water, using the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) along with a single software control for the entire system, the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Method linearity, method detection limit (MDL), precision, accuracy, and minimum reporting level (MRL) confirmation were assessed to evaluate method performance.

## Introduction

It is essential that routine environmental laboratories monitor drinking water for the presence of purgeable organic compounds. POCs have the potential to cause negative health effects when consumed. EPA Method 524.4 is used in environmental analysis labs to test water samples for volatile organic compounds (VOCs).[1] It is extremely important that routine laboratories accurately detect and quantitate VOCs to ensure water is safe for the public. This method is a revised version of EPA Method 524.2 on which more details can be found here. Due to technological advances in analytical instrumentation and techniques, this method allows the analyst to modify P&T parameters and GC/MS conditions. This can result in reduced sample run time and increased laboratory throughput in a 12-hour period.

With this method flexibility comes strict quality control (QC) requirements for EPA Method 524.4. Along with MDL and Initial Demonstration of Capability (IDC) calculations, MRL confirmation is required. The MRL is the minimum concentration that can be reported by a lab and can be very difficult to achieve as you have to determine the ±50% limits of the low level standard in the calibration. These limits are used for low level Calibrating Check Standards and determine if the calibration is still valid during routine analysis.

In order to perform EPA Method 524.4, method acceptance criteria must be achieved. These criteria include assessing the linearity and detection limits for a wide range of compounds. The analytical method must produce consistent results and be reproducible from day to day. As the sample matrix is water, it is essential that moisture is not introduced into the analytical column as this could damage the column and affect the results.

The following evaluation describes the use of the ISQ 7000 MS system coupled to the Atomx XYZ P&T for U.S. EPA Method 524.4.

## Experimental

### Sample preparation

A 25 parts per million (ppm) calibration working standard was prepared in methanol from the following Restek standards: 524.3 VOA MegaMix® and 524.3 Gas Calibration Mix. In total, the standards contained 75 compounds.

A nine-point calibration curve was prepared from 0.2 to 50 parts per billion (ppb) for all compounds. The relative response factor (RF) was calculated for each compound using three internal standards: 1,4-difluorobenzene, chlorobenzene-$d_5$, and 1,4-dichlorobenzene-$d_4$. Surrogate standards consisted of methyl-tert-butyl ether-$d_3$, 4-bromofluorobenzene, and 1,2-dichlorobenzene-$d_4$. Internal and surrogate standards were prepared in methanol from Restek standards at a concentration of 12.5 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 12.5 ppb.

Seven 0.5 ppb standards were prepared to calculate the MDL and MRL confirmation calculations. Seven 5 ppb standards were prepared for the assessment of precision and accuracy, and a further twenty 5 ppb standards were prepared for the assessment of method robustness. All calibration, MDL, accuracy, precision, robustness, and MRL standards were analyzed with the Atomx XYZ conditions in Table 1. GC-MS conditions are shown in Table 2.

### Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.2. This software can control both the GC/MS system and the Tekmar Atomx XYZ P&T. This allows a single software to be utilized for the full workflow simplifying the instrument operation. Figure 1 shows the Chromeleon control of the Atomx XYZ P&T. The fully optimized method used within this application note is available for download via Thermo Scientific™ AppsLab. AppsLab contains all the parameters needed to acquire, process, and report the analytical data for EPA Method 524.4.[2]

### GC-MS parameters

A Thermo Scientific™ TRACE™ 1310 GC was coupled to the ISQ 7000 MS system equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite ion source. A Thermo Scientific™ TraceGOLD™ TG-VMS 20 m × 0.18 mm, 1 µm film (P/N 26080-4950) was used for compound separation. The GC run time is under 15 minutes and a 50 to 1 split injection was used. The ISQ 7000 MS system was operated in full scan mode, which gave enough sensitivity to meet the regulatory requirements. Expanded method parameters for the GC-MS system are displayed in Table 2.

**Table 1. Tekmar Atomx XYZ water method parameters**

| Standby | Variable | Desorb | Variable |
|---|---|---|---|
| Valve oven temperature | 140 °C | Methanol needle rinse | Off |
| Transfer line temperature | 140 °C | Methanol needle rinse volume | 0.00 mL |
| Sample mount temperature | 90 °C | Water needle rinse volume | 7.00 mL |
| Water heater temperature | 90 °C | Sweep needle time | 0.25 min |
| Sample vial temperature | 20 °C | Desorb preheat temperature | 245 °C |
| Soil valve temperature | 100 °C | GC start signal | Begin Desorb |
| Standby flow | 10 mL/min | Desorb time | 1.00 min |
| Purge ready temperature | 40 °C | Drain flow | 300 mL/min |
| | | Desorb temperature | 250 °C |
| **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 temperature | N/A | Bake rinse drain time | 0.40 min |
| Pre-purge time | 0.00 min | Bake time | 6.00 min |
| Pre-purge flow | 0 mL/min | Bake flow | 200 mL/min |
| Purge time | 5.50 min | Bake temperature | 280 °C |
| Purge flow | 80 mL/min | Condensate bake temperature | 180 °C |
| Purge temperature | 20 °C | | |
| Condensate purge temperature | 20 °C | | |
| Dry purge time | 0.00 min | Trap | K |
| Dry purge flow | 0 mL/min | Chiller tray | On |
| Dry purge temperature | 20 °C | Purge gas | Nitrogen |

**Table 2. GC/MS conditions**

| Parameter | Value |
|---|---|
| **TRACE 1310 GC** | |
| Column | TraceGOLD TG-VMS, 20 m x 0.18 mm, 1 µm film<br>Carrier gas: helium @ 1 mL/min |
| Oven temperature program | 35 °C, 3 min, 12 °C/min to 85 °C,<br>25 °C/min to 225 °C, 2 min hold<br>Run time 14.8 min |
| Inlet | 200 °C, 50:1 split<br>Purge flow 0.5 mL/min |
| **ISQ 7000 MS** | |
| | Transfer line 230 °C; Ion source 280 °C |
| Scan mode | Range: 35 amu to 260 amu;<br>Solvent delay: 0.50 min<br>Dwell/scan time: 0.15 s |
| Filament current | Emission current: 25 µA<br>Detector gain: 3.00E+005 |

## Results and discussion

### Chromatography

Excellent chromatography was achieved using the conditions described in Table 2. The moisture transferred onto the analytical column was minimized using the Atomx XYZ P&T, which limits any damage to the analytical column and increases method robustness. Figure 2 displays consistent peak shape and separation of a 5 ppb VOC standard with minimal water interference.

### Linearity and sensitivity

A calibration range of 0.2–50 ppb was assessed for all compounds. Table 3 displays the $R^2$ value, which was ≥0.995 for all compounds across the specified concentration range. The MDL and the MRL were assessed using n=7 replicates of a 0.5 ppb standard. The MDL, which is <0.25 ppb, and the precision data, which is <20 %RSD, are shown in Table 3, alongside the MRL confirmation data, with upper prediction interval of results (PIR) limit ≤150% and lower PIR limit ≥50% for all analytes. Iodomethane was outside these limits because the compound broke down after several injections -- a higher concentration was used. Figure 3 demonstrates the quantitation of bromochloromethane in the 5 ppb standard with very good library spectral matching and calibration curve. Figure 4 shows several compounds at 0.2 ppb that are being detected at a low level with excellent peak shape and minimal water interference.

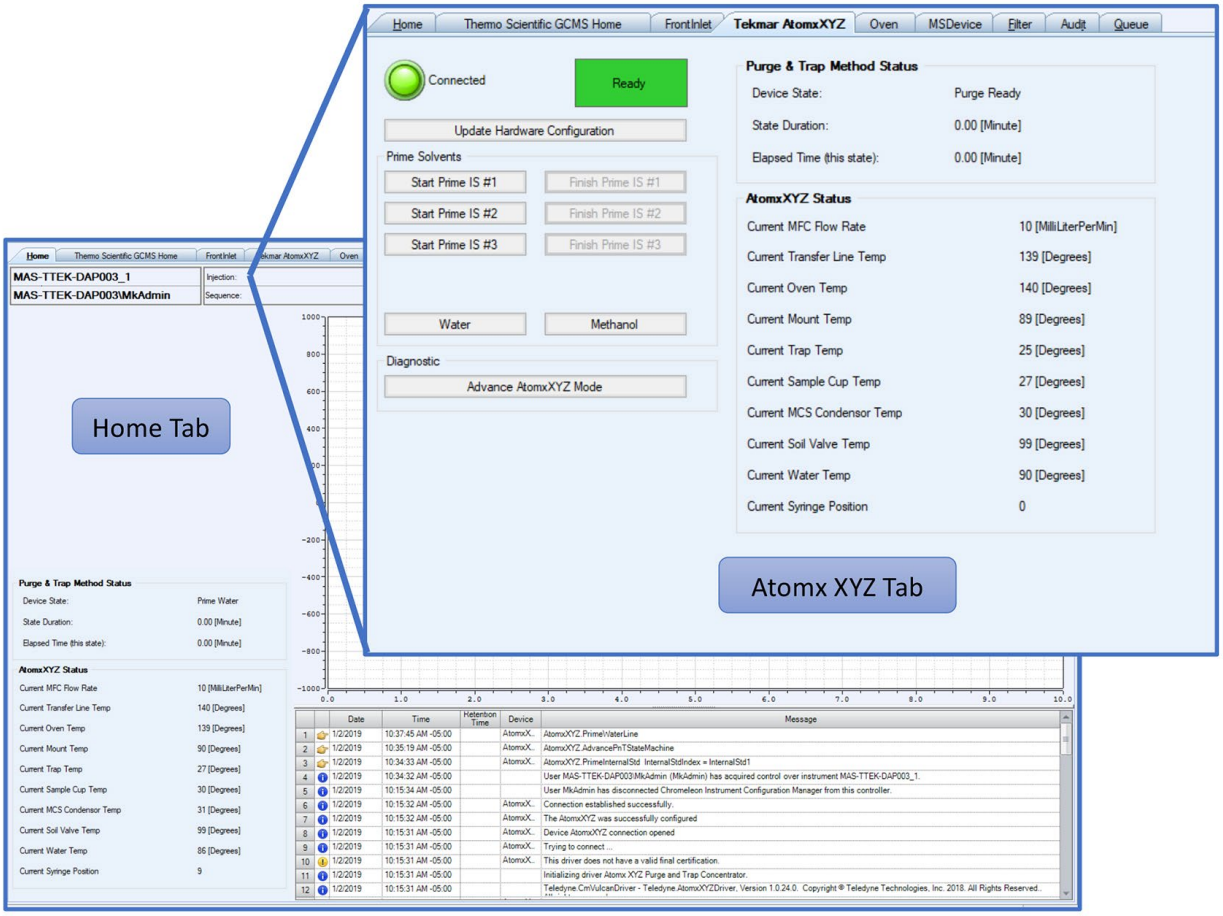


**Figure 1. Chromeleon control of the Atomx XYZ P&T**

Peaks:
19. tert-butyl alcohol
20. tert-butyl ethyl ether
21. trans-1,2-dichloroethene
22. Bromochloromethane
23. Chloroform
24. Carbon tetrachloride
25. Tetrahydrofuran
26.1,1,1-trichloroethane
27. 1,1-dichloropropene
28. 1-chlorobutane
29. Benzene

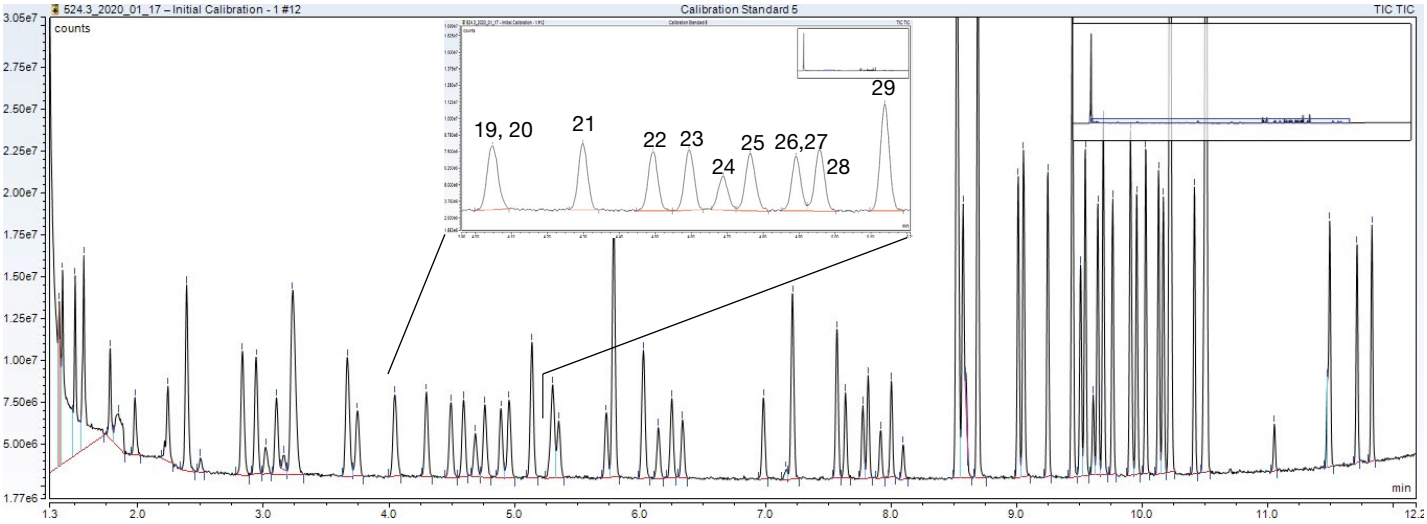


**Figure 2. Total ion chromatogram (TIC) of a water method 5 ppb VOC standard with an inset indicating good peak shape and separation with minimal matrix interference**

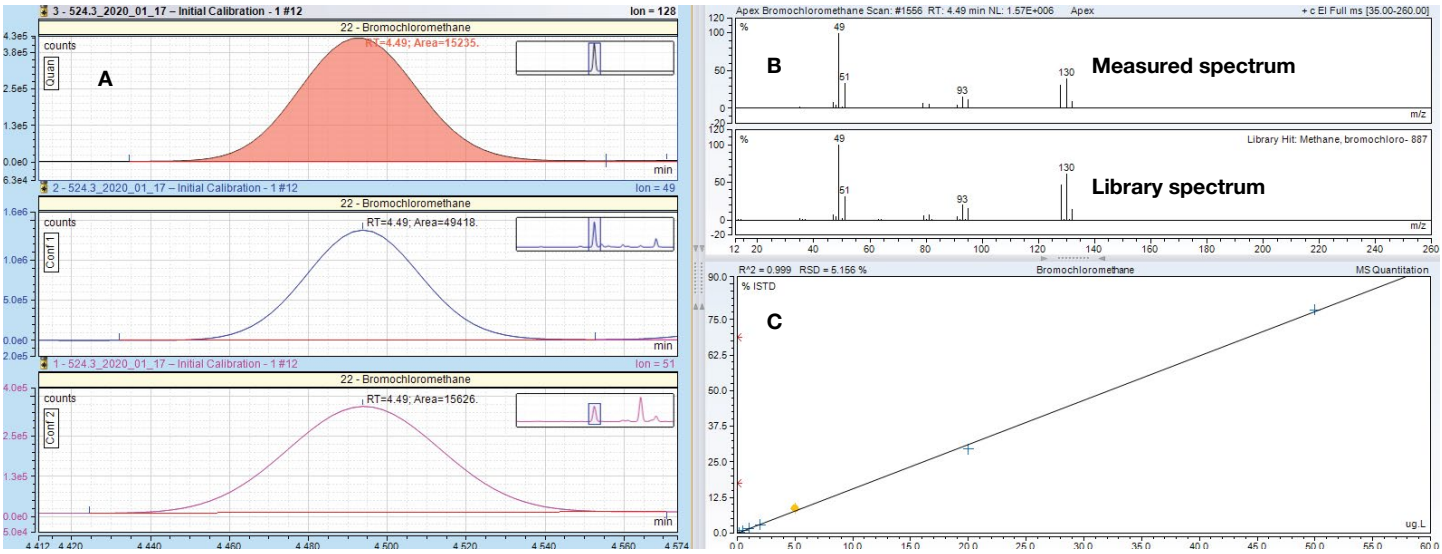


**Figure 3. Chromeleon results browser showing extracted ion chromatograms for bromochloromethane, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B) and a linear calibration over a concentration range of 0.2 ppb to 50 ppb (C)**

**Table 3 (part 1). Calibration, detection limit, and minimum reporting limit results**

| Compound | Calibration | | | MDL (n=7, 0.5 ppb) | | | | IDC (n=7, 5 ppb) | | MRL confirmation (n=7, 0.5 ppb) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Retention Time | Linearity ($r^2$ ≥0.995) | Avg. RF | Avg. Conc. (ppb) | MDL (ppb) | Accuracy (±20%) | Precision (≤20%) | Accuracy (±20%) | Precision (≤20%) | LPIR (≥50%) | UPIR (≤150%) |
| Dichlorodifluoromethane[1] | 1.38 | 0.999 | 0.339 | 0.49 | 0.11 | 89 | 7.9 | 119 | 5.2 | 61 | 117 |
| Chlorodifluoromethane[3] | 1.41 | 0.998 | 0.851 | 0.60 | 0.10 | 120 | 5.1 | 120 | 4.0 | 96 | 144 |
| Chloromethane | 1.51 | 0.999 | 1.27 | 0.44 | 0.14 | 87 | 9.9 | 119 | 4.6 | 53 | 121 |
| Vinyl chloride | 1.57 | 0.998 | 0.470 | 0.60 | 0.11 | 120 | 6.0 | 119 | 4.8 | 91 | 148 |
| 1,3-Butadiene | 1.58 | 0.999 | 0.415 | 0.58 | 0.13 | 116 | 7.0 | 120 | 7.2 | 84 | 149 |
| Bromomethane[1] | 1.79 | 0.997 | 0.416 | 0.43 | 0.13 | 85 | 9.8 | 117 | 6.5 | 52 | 117 |
| Trichlorofluoromethane | 1.99 | 0.999 | 0.481 | 0.58 | 0.11 | 117 | 6.3 | 114 | 5.2 | 88 | 146 |
| Diethyl ether | 2.26 | 0.999 | 0.337 | 0.60 | 0.10 | 119 | 5.1 | 118 | 5.9 | 95 | 144 |
| 1,1-Dichloroethene | 2.4 | 0.999 | 0.374 | 0.59 | 0.11 | 117 | 5.8 | 116 | 5.1 | 90 | 144 |
| Allyl chloride | 2.41 | 0.999 | 1.51 | 0.60 | 0.09 | 120 | 4.6 | 120 | 6.0 | 98 | 142 |
| Iodomethane[2,3,5] | 2.52 | 0.999 | 0.348 | 5.7 | 2.7 | 113 | 14.9 | 113 | 14.9 | 46 | 180 |
| Carbon disulfide | 2.86 | 0.998 | 0.284 | 0.58 | 0.13 | 116 | 7.2 | 115 | 4.2 | 83 | 149 |
| Methylene chloride | 2.97 | 0.997 | 1.02 | 0.59 | 0.10 | 118 | 5.6 | 120 | 3.6 | 91 | 144 |
| *cis*-1,2-Dichloroethene | 3.13 | 0.999 | 0.403 | 0.57 | 0.09 | 114 | 5.3 | 116 | 4.5 | 90 | 138 |
| Methyl acetate | 3.19 | 1.000 | 0.445 | 0.54 | 0.10 | 108 | 5.8 | 108 | 6.9 | 83 | 133 |
| Methyl-t-butyl ether-$d_3$ (surr) | 3.25 | 10.7 | 0.932 | 12.8 | | 102 | 6.4 | 105 | 7.9 | 76 | 128 |
| Methyl tert butyl ether | 3.27 | 0.995 | 0.878 | 0.54 | 0.10 | 109 | 5.6 | 103 | 7.8 | 85 | 133 |
| Diisopropyl ether | 3.68 | 0.997 | 1.71 | 0.57 | 0.05 | 114 | 2.8 | 116 | 3.3 | 101 | 127 |
| 1,1-Dichloroethane | 3.77 | 0.999 | 0.891 | 0.60 | 0.10 | 120 | 5.5 | 118 | 4.2 | 94 | 146 |
| t-Butyl alcohol (TBA) | 4.07 | 0.997 | 1.01 | 0.56 | 0.07 | 112 | 3.7 | 105 | 4.2 | 96 | 129 |
| t-Butyl ethyl ether (ETBE) | 4.07 | 0.997 | 1.01 | 0.56 | 0.07 | 113 | 3.8 | 111 | 4.1 | 96 | 129 |
| *trans*-1,2-dichloroethene | 4.32 | 0.998 | 0.658 | 0.58 | 0.06 | 115 | 3.5 | 120 | 3.0 | 99 | 132 |
| Bromochloromethane | 4.52 | 0.999 | 0.201 | 0.60 | 0.07 | 119 | 3.7 | 113 | 1.6 | 101 | 137 |
| Chloroform | 4.62 | 0.999 | 0.740 | 0.58 | 0.07 | 116 | 3.8 | 118 | 3.1 | 98 | 133 |
| Carbon tetrachloride | 4.71 | 0.999 | 0.376 | 0.52 | 0.10 | 104 | 5.9 | 102 | 6.3 | 79 | 128 |
| 1,1,1-Trichloroethane | 4.79 | 0.999 | 0.492 | 0.55 | 0.10 | 110 | 5.7 | 107 | 5.0 | 85 | 135 |
| Tetrahydrofuran | 4.79 | 1.000 | 0.047 | 0.56 | 0.15 | 112 | 8.3 | 119 | 8.9 | 75 | 149 |
| 1,1-Dichloropropene | 4.91 | 0.995 | 0.432 | 0.54 | 0.07 | 108 | 4.1 | 96 | 6.5 | 91 | 125 |
| 1-Chlorobutane | 4.98 | 0.996 | 0.704 | 0.54 | 0.06 | 108 | 3.7 | 102 | 5.5 | 92 | 124 |
| Benzene | 5.16 | 0.996 | 1.44 | 0.56 | 0.06 | 112 | 3.5 | 105 | 4.2 | 97 | 128 |
| t-Amyl methyl ether (TAME) | 5.33 | 0.998 | 0.866 | 0.57 | 0.06 | 115 | 3.3 | 114 | 3.7 | 100 | 130 |
| 1,2-Dichloroethane | 5.37 | 0.999 | 0.518 | 0.58 | 0.05 | 115 | 2.8 | 116 | 4.1 | 102 | 128 |
| Trichloroethylene | 5.75 | 0.996 | 0.309 | 0.56 | 0.11 | 113 | 6.5 | 100 | 5.6 | 84 | 142 |
| *cis*-1,3-Dichloropropene | 7.65 | 0.996 | 0.503 | 0.55 | 0.06 | 111 | 3.3 | 99 | 3.9 | 96 | 126 |
| 1,1,2-Trichloroethane | 7.79 | 0.996 | 0.224 | 0.57 | 0.07 | 114 | 3.9 | 107 | 6.4 | 96 | 131 |
| Ethyl methacrylate | 7.83 | 0.999 | 0.463 | 0.57 | 0.11 | 115 | 6.2 | 114 | 4.7 | 86 | 143 |
| Dibromochloromethane | 7.93 | 0.996 | 0.261 | 0.53 | 0.10 | 106 | 6.1 | 99 | 5.8 | 80 | 132 |

1. Calibration curve 0.5 ppb-50 ppb.
2. Calibration curve 1 ppb-50 ppb.
3. Compounds were quadratic regressed.
4. Analyte is a poor purger and broke down after several injections.
5. 5 ppb MDL.

Table 3 (part 2). Calibration, detection limit, and minimum reporting limit results

| Compound | Calibration | | | MDL (n=7, 0.5 ppb) | | | | IDC (n=7, 5 ppb) | | MRL confirmation (n=7, 0.5 ppb) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Retention Time | Linearity ($r^2$ ≥0.995) | Avg. RF | Avg. Conc. (ppb) | MDL (ppb) | Accuracy (±20%) | Precision (≤20%) | Accuracy (±20%) | Precision (≤20%) | LPIR (≥50%) | UPIR (≤150%) |
| 1,3-Dichloropropane | 8.02 | 0.996 | 0.503 | 0.58 | 0.04 | 116 | 2.2 | 102 | 5.2 | 106 | 126 |
| 1,2-Dibromoethane | 8.11 | 0.997 | 0.248 | 0.54 | 0.08 | 109 | 4.5 | 107 | 5.4 | 89 | 128 |
| Chlorobenzene-$d_5$ (ISTD) | 8.54 | | | 12.5 | | | | | | | |
| Chlorobenzene | 8.55 | 0.999 | 0.920 | 0.57 | 0.11 | 114 | 5.9 | 112 | 4.2 | 87 | 140 |
| Ethylbenzene | 8.58 | 0.998 | 1.72 | 0.58 | 0.09 | 115 | 4.9 | 109 | 5.0 | 93 | 138 |
| 1,1,1,2-Tetrachloroethane | 8.61 | 0.999 | 0.239 | 0.55 | 0.06 | 111 | 3.6 | 108 | 5.4 | 95 | 127 |
| m,p-Xylene | 8.7 | 0.998 | 1.50 | 1.13 | 0.15 | 113 | 4.3 | 107 | 5.0 | 93 | 132 |
| o-Xylene | 9.02 | 0.997 | 1.53 | 0.56 | 0.08 | 112 | 4.4 | 107 | 3.8 | 92 | 131 |
| Styrene | 9.06 | 0.999 | 1.15 | 0.55 | 0.07 | 110 | 4.1 | 104 | 4.7 | 93 | 128 |
| Bromoform | 9.07 | 0.999 | 0.211 | 0.54 | 0.10 | 108 | 6.2 | 102 | 5.2 | 82 | 134 |
| Isopropylbenzene | 9.26 | 0.999 | 1.63 | 0.54 | 0.09 | 108 | 5.0 | 105 | 5.5 | 87 | 130 |
| 4-Bromofluorobenzene (surr) | 9.45 | 4.8 | 0.863 | 12.9 | | 103 | 3.8 | 99 | 1.3 | 88 | 119 |
| Bromobenzene | 9.52 | 0.998 | 0.847 | 0.60 | 0.06 | 119 | 3.2 | 112 | 4.1 | 104 | 135 |
| n-Propylbenzene | 9.55 | 1.000 | 3.02 | 0.54 | 0.14 | 109 | 8.1 | 111 | 6.2 | 74 | 143 |
| 1,1,2,2-Tetrachloroethane | 9.62 | 1.000 | 0.530 | 0.58 | 0.10 | 116 | 5.3 | 116 | 8.4 | 92 | 141 |
| 2-Chlorotoluene | 9.65 | 0.999 | 1.88 | 0.54 | 0.12 | 108 | 7.2 | 111 | 6.0 | 78 | 139 |
| 1,3,5-Trimethylbenzene | 9.7 | 0.999 | 1.93 | 0.56 | 0.14 | 112 | 7.8 | 106 | 5.8 | 77 | 146 |
| 1,2,3-Trichloropropane | 9.7 | 0.999 | 0.498 | 0.59 | 0.10 | 119 | 5.5 | 117 | 8.2 | 93 | 145 |
| 4-Chlorotoluene | 9.77 | 0.999 | 1.96 | 0.57 | 0.12 | 114 | 6.7 | 109 | 5.8 | 84 | 144 |
| p-Isopropyltoluene | 9.91 | 0.999 | 1.75 | 0.52 | 0.14 | 103 | 8.7 | 101 | 5.2 | 68 | 139 |
| tert-Butylbenzene | 9.91 | 0.999 | 1.77 | 0.52 | 0.15 | 104 | 9.2 | 101 | 5.3 | 66 | 142 |
| Pentachloroethane[3,4] | 9.92 | 0.995 | 0.153 | 0.49 | 0.18 | 98 | 11.9 | 75 | 27.7 | 52 | 144 |
| 1,2,4-Trimethylbenzene | 9.96 | 0.999 | 1.96 | 0.56 | 0.13 | 112 | 7.4 | 108 | 5.7 | 79 | 145 |
| sec-Butylbenzene | 10.03 | 0.999 | 2.50 | 0.53 | 0.13 | 106 | 8.0 | 106 | 6.2 | 72 | 139 |
| 1,3-Dichlorobenzene | 10.18 | 0.999 | 1.44 | 0.59 | 0.13 | 117 | 6.8 | 112 | 5.4 | 86 | 149 |
| 1,4-Dichlorobenzene-$d^4$ (ISTD) | 10.23 | | | 12.5 | | | | | | | |
| 1,4-Dichlorobenzene | 10.24 | 0.999 | 1.47 | 0.57 | 0.14 | 114 | 7.9 | 110 | 6.6 | 78 | 150 |
| n-Butylbenzene | 10.42 | 0.999 | 1.92 | 0.59 | 0.13 | 118 | 6.9 | 107 | 6.0 | 85 | 150 |
| Hexachloroethane | 10.5 | 0.998 | 0.317 | 0.6 | 0.13 | 112 | 7.1 | 115 | 6.2 | 80 | 143 |
| 1,2-Dichlorobenzene (surr) | 10.51 | 2.0 | 0.927 | 12.7 | | 101 | 1.7 | 102 | 2.1 | 95 | 108 |
| 1,2-Dichlorobenzene | 10.52 | 0.999 | 1.41 | 0.56 | 0.14 | 112 | 7.7 | 110 | 6.0 | 77 | 146 |
| 1,2-Dibromo-3-chloropropane | 11.06 | 0.997 | 0.137 | 0.55 | 0.13 | 109 | 7.8 | 118 | 7.5 | 76 | 143 |
| Hexachlorobutadiene | 11.48 | 0.999 | 0.051 | 0.58 | 0.12 | 115 | 6.7 | 112 | 6.6 | 84 | 146 |
| 1,2,4-Trichlorobenzene | 11.5 | 0.995 | 0.922 | 0.58 | 0.19 | 116 | 10.2 | 117 | 2.4 | 86 | 147 |
| Naphthalene | 11.72 | 0.996 | 1.85 | 0.58 | 0.12 | 116 | 6.6 | 119 | 6.4 | 82 | 143 |
| 1,2,3-Trichlorobenzene | 11.84 | 0.995 | 0.887 | 0.56 | 0.15 | 112 | 8.5 | 120 | 5.7 | 74 | 149 |

1. Calibration curve 0.5 ppb-50 ppb.
2. Calibration curve 1 ppb-50 ppb.
3. Compounds were quadratic regressed.
4. Analyte is a poor purger and broke down after several injections.
5. 5 ppb MDL.

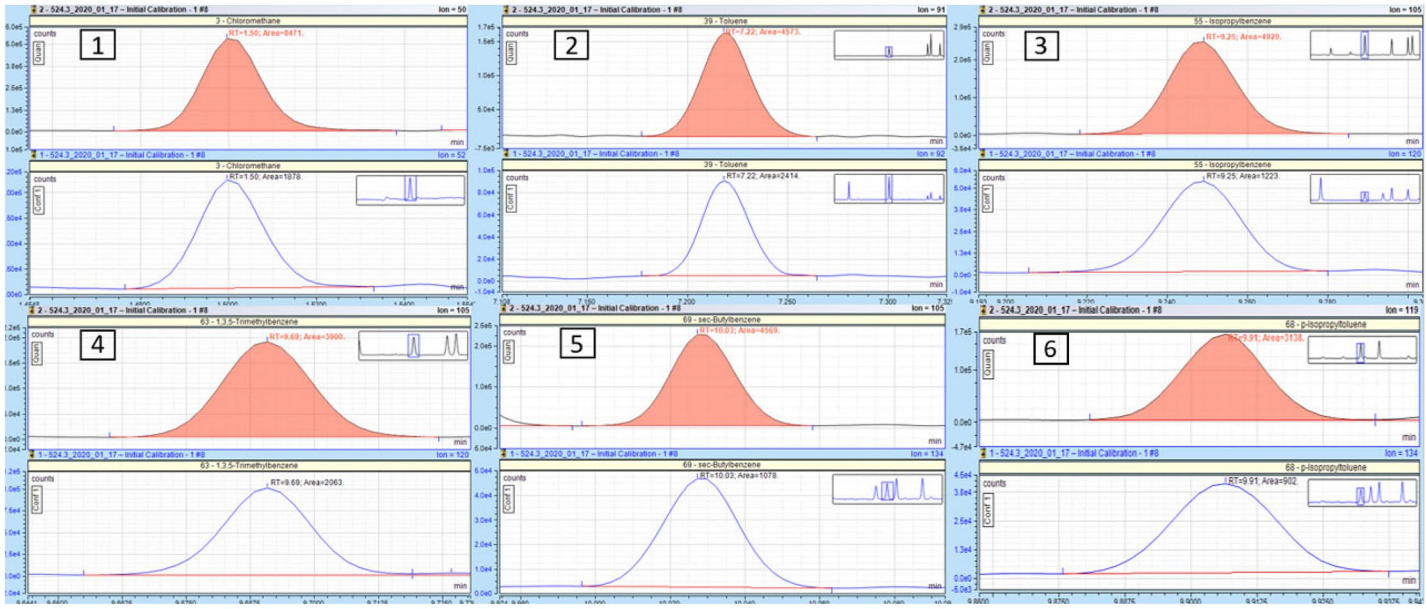


**Figure 4. Example of chromatography (extracted quantitation and confirmatory ions) from the calibration level 0.2 ppb for several compounds (1. chloromethane 2. toluene 3. isopropylbenzene 4. 1,3,5-trimethylbenzene 5. sec-butylbenzene 6. p-isopropyltoluene)**

## Precision and accuracy

Precision and accuracy were assessed by analyzing n=7 replicates of a 5 ppb standard. The results are displayed in Table 3. For all compounds assessed, the %RSD of the calculated concentration is 20% and the mean recovery is within ±20% of the true value meeting the requirements of EPA Method 524.4 for initial demonstration of capability (IDC). Pentachloroethane broke down during the IDC and recovery was just under ±20%.

## Method robustness

For use as a routine testing method, it is extremely important that the analytical method is stable and reproducible. In order to demonstrate this, 5 ppb standards (n=20) were injected at intervals over a 120-sample injection sequence. The samples were acquired without user intervention. Figure 5 shows the reproducibility of six of the compounds over 120 injections with excellent percentage RSDs. Accuracy and precision data are displayed in Table 4.

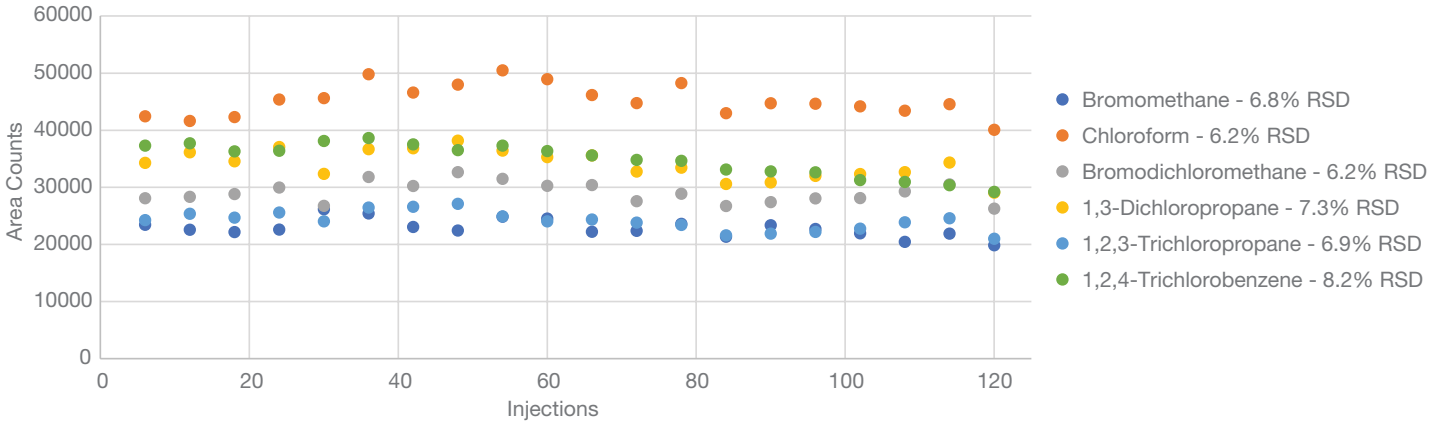


**Figure 5. Repeatability of a 5 ppb VOC standard (as absolute peak area counts) assessed over n=120 consecutive injections**

Table 4. Accuracy and precision data for n=20 injections of a 5 ppb standard

| Compound | Quant. ion | Analyte recovery (n=20) | | |
|---|---|---|---|---|
| | | Avg. conc. (ppb) | Accuracy | Precision |
| Dichlorodifluoromethane | 85 | 5.3 | 106 | 17.5 |
| Chlorodifluoromethane | 51 | 6.6 | 133 | 18.1 |
| Chloromethane | 50 | 7.0 | 140 | 13.8 |
| Vinyl chloride | 62 | 6.1 | 122 | 16.0 |
| 1,3-Butadiene | 54 | 5.8 | 117 | 16.6 |
| Bromomethane | 94 | 6.8 | 136 | 8.3 |
| Trichlorofluoromethane | 101 | 5.5 | 110 | 16.2 |
| Diethyl ether | 59 | 6.1 | 121 | 5.7 |
| 1,1-Dichloroethene | 96 | 5.7 | 113 | 15.2 |
| Allyl chloride | 76 | 6.1 | 121 | 14.4 |
| Iodomethane | 142 | 5.6 | 112 | 20.1 |
| Carbon disulfide | 76 | 5.2 | 105 | 7.3 |
| Methylene chloride | 49 | 7.1 | 143 | 9.0 |
| *cis*-1,2-Dichloroethene | 96 | 5.6 | 113 | 10.5 |
| Methyl acetate | 43 | 6.8 | 137 | 7.3 |
| Methyl-t-butyl ether-$d_3$ (surr) | 76 | 12.1 | 97 | 6.9 |
| Methyl tert butyl ether | 73 | 4.8 | 95 | 5.9 |
| Diisopropyl ether | 45 | 5.7 | 115 | 4.4 |
| 1,1-Dichloroethane | 63 | 6.4 | 127 | 9.3 |
| t-Butyl alcohol (TBA) | 59 | 5.2 | 103 | 3.2 |
| t-Butyl ethyl ether (ETBE) | 59 | 5.2 | 103 | 3.2 |
| *trans*-1,2-dichloroethene | 61 | 5.9 | 118 | 5.7 |
| Bromochloromethane | 128 | 6.0 | 119 | 5.9 |
| Chloroform | 83 | 6.0 | 120 | 7.2 |
| Carbon tetrachloride | 117 | 4.6 | 92 | 13.9 |
| 1,1,1-Trichloroethane | 72 | 5.1 | 101 | 11.8 |
| Tetrahydrofuran | 97 | 5.1 | 103 | 7.9 |
| 1,1-Dichloropropene | 75 | 4.3 | 85 | 11.4 |
| 1-Chlorobutane | 56 | 4.8 | 95 | 11.7 |
| Benzene | 78 | 5.2 | 103 | 8.3 |
| t-Amyl methyl ether (TAEE) | 73 | 5.0 | 100 | 4.2 |
| 1,2-Dichloroethane | 62 | 6.1 | 122 | 4.6 |
| Trichloroethylene | 95 | 5.1 | 101 | 17.4 |
| 1,4-Difluorobenzene (ISTD) | 114 | | | |
| t-Amyl ethyl ether (TMEE) | 59 | 5.1 | 101 | 3.5 |
| Dibromomethane | 93 | 5.8 | 116 | 4.4 |
| 1,2-Dichloropropane | 63 | 5.6 | 111 | 7.1 |
| Bromodichloromethane | 83 | 5.3 | 106 | 6.4 |
| *trans*-1,3-Dichloropropene | 75 | 4.2 | 84 | 7.3 |
| Toluene | 91 | 4.8 | 95 | 6.5 |

| Compound | Quant. ion | Analyte recovery (n=20) | | |
|---|---|---|---|---|
| | | Avg. conc. (ppb) | Accuracy | Precision |
| Tetrachloroethylene | 164 | 5.9 | 118 | 16.1 |
| *cis*-1,3-Dichloropropene | 75 | 4.3 | 86 | 6.2 |
| 1,1,2-Trichloroethane | 83 | 5.5 | 110 | 5.8 |
| Ethyl Methacrylate | 69 | 4.6 | 92 | 9.5 |
| Dibromochloromethane | 129 | 4.7 | 94 | 6.0 |
| 1,3-Dichloropropane | 76 | 5.2 | 104 | 5.2 |
| 1,2-Dibromoethane | 107 | 5.3 | 105 | 5.1 |
| Chlorobenzene-$d_5$ (ISTD) | 117 | | | |
| Chlorobenzene | 112 | 5.3 | 106 | 5.2 |
| Ethylbenzene | 91 | 4.5 | 91 | 7.0 |
| 1,1,1,2-Tetrachloroethane | 131 | 5.3 | 106 | 5.6 |
| m,p-Xylene | 91 | 8.8 | 88 | 6.6 |
| o-Xylene | 91 | 4.3 | 86 | 5.6 |
| Styrene | 104 | 4.3 | 85 | 5.4 |
| Bromoform | 173 | 4.8 | 96 | 5.8 |
| Isopropylbenzene | 105 | 4.2 | 84 | 7.2 |
| 4-Bromofluorobenzene (surr) | 95 | 11.9 | 95 | 3.9 |
| Bromobenzene | 77 | 5.3 | 106 | 5.8 |
| n-Propylbenzene | 91 | 4.5 | 90 | 8.2 |
| 1,1,2,2-Tetrachloroethane | 83 | 6.0 | 120 | 15.6 |
| 2-Chlorotoluene | 91 | 4.8 | 96 | 6.9 |
| 1,3,5-Trimethylbenzene | 105 | 4.5 | 90 | 7.7 |
| 1,2,3-Trichloropropane | 75 | 6.3 | 125 | 8.5 |
| 4-Chlorotoluene | 91 | 4.7 | 94 | 7.3 |
| p-Isopropyltoluene | 119 | 3.9 | 79 | 8.0 |
| tert-Butylbenzene | 119 | 3.9 | 79 | 8.1 |
| Pentachloroethane[1] | 167 | 2.9 | 89 | 35.8 |
| 1,2,4-Trimethylbenzene | 105 | 4.6 | 93 | 8.0 |
| sec-Butylbenzene | 105 | 4.4 | 88 | 9.1 |
| 1,3-Dichlorobenzene | 146 | 5.3 | 106 | 7.0 |
| 1,4-Dichlorobenzene-$d_4$ (ISTD) | 152 | | | |
| 1,4-Dichlorobenzene | 146 | 5.3 | 105 | 6.9 |
| n-Butylbenzene | 91 | 4.3 | 86 | 8.7 |
| Hexachloroethane | 201 | 5.0 | 101 | 10.0 |
| 1,2-Dichlorobenzene (surr) | 152 | 13.1 | 105 | 2.2 |
| 1,2-Dichlorobenzene | 146 | 5.4 | 107 | 7.0 |
| 1,2-Dibromo-3-chloropropane | 75 | 6.0 | 120 | 7.8 |
| Hexachlorobutadiene | 225 | 4.8 | 95 | 8.6 |
| 1,2,4-Trichlorobenzene | 180 | 5.4 | 107 | 7.7 |
| Naphthalene | 128 | 4.9 | 98 | 10.1 |

1. Analyte is a poor purger and broke down after several injections.

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## Conclusion

The combined solution of the TRACE 1310 GC coupled with the ISQ 7000 system and the Atomx XYZ P&T system provides clear advantages for EPA Method 524.4.

- The ISQ 7000 VPI coupled with the Tekmar Atomx XYZ P&T exceeds all the requirements outlined in EPA Method 524.4 for analysis of purgeable VOCs in water.
- Excellent linearity for all compounds was demonstrated with the $R^2$ of the calibration response factors passing all method requirements.
- MDL, precision, and MRL confirmation for n=7, 0.5 ppb standards showed no interference from excessive water and produced very reproducible results.
- Precision and accuracy for n=7, 5 ppb standards showed excellent results with average %RSD <9% and recovery values between 96% and 120%.
- The analytical method was demonstrated to be stable and reproducible over 120 injections ensuring consistent results can be obtained.

Further information on VOC analysis using the ISQ 7000 system and the Atomx XYZ P&T can be found in the application note entitled: *Routine Analysis of Volatile Organic Compounds in Drinking Water with ISQ 7000 GC-MS.*[3]

### References


1. Method 524.4 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100J7EE.TXT
2. Thermo Fisher Scientific AppsLab Library https://appslab.thermofisher.com/
3. Thermo Scientific Application Note 65632: Routine analysis of volatile organic compounds in drinking water with ISQ 7000 GC-MS https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-65632-gc-ms-volatile-organic-compounds-drinking-water-an65632-en.pdf


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