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# USEPA Method 524.4 Using the Teledyne Tekmar Atomx and Thermo Scientific™ GC/MS System with New Helium Saver Module

## Application Note

*Roger Bardsley, Applications Chemist; Teledyne Tekmar*

### Abstract

Increasing concerns over the availability of helium, and its rising cost, has led the United States Environmental Protection Agency (USEPA) to update drinking water Method 524 to USEPA Method 524.4.  This new method affords environmental laboratories increased Purge and Trap (P&T) parameter flexibility and permits the use of nitrogen as a sample purge gas.

For this application note, a Teledyne Tekmar Atomx Automated VOC Sample Prep System was configured with nitrogen sample purge gas and connected to a Thermo Scientific™ TRACE™ 1310 gas chromatograph (GC) and ISQ™ LT mass spectrometer (GC-MS) system equipped with the newly released Thermo Scientific™ Instant Connect™ Helium Saver Module.

This cost-efficient configuration effectively minimized helium consumption and met the calibration curve, Minimum Reporting Level (MRL), precision and accuracy, and Initial Demonstration of Capability (IDC), requirements of USEPA Method 524.4[1]

## Introduction

USEPA Method 524.2 was the standard method for analysis of Volatile Organic Compounds (VOC) in drinking water since 1995.  In 2009, the USEPA released Method 524.3 that allowed laboratories additional P&T parameter flexibility and resulted in reduced total analysis time.  This method specified helium as the purge and GC carrier gas, rather than any inert gas, as allowed in USEPA Method 524.2.

Today, as helium cost continues to increase and the finite supply dwindles, laboratories are increasingly confronted with the decision to switch to a more cost-efficient alternate gas. Consequently, the search for a suitable alternative gas has escalated.

Investigations into alternate gases found that hydrogen was a suitable carrier gas for GC/MS, but not as a purge gas, and its reactivity with VOCs of interest was an additional drawback.  In May of 2013, USEPA Method 524.4 was released and nitrogen was again permitted to purge drinking water samples.

## Experimental Instrumentation

A Teledyne Tekmar Atomx Automated VOC Sample Prep System, with nitrogen as the sample purge gas, was connected to a Thermo Scientific™ TRACE™ 1310 GC/ISQ™ LT MS system equipped with a Thermo Scientific™ Instant Connect™ Helium Saver Module.

Thermo Scientific™ TraceFinder™ EFS software was used to control the GC/MS system parameters and collect the MS data. The GC/MS was tuned so that 4-bromofluorobenzene (BFB) ion abundance criteria met the requirements specified in USEPA Method 524.4.

The Atomx VOC TekLink software was configured to deliver an accurate volume of nitrogen gas, via the electronic Mass Flow Controller (MFC), to purge the VOC compounds onto a #9 trap. The Atomx was also equipped with an optional chiller tray to maintain sample temperatures below 10 °C throughout the analysis, according to USEPA 524.4, Section 8.4.

Table I shows the Atomx instrument parameters for purging the samples and standards.  Table II shows the Thermo Scientific™ TRACE™ 1310 GC/ISQ™ LT MS system instrument parameters for detecting VOCs released from the Atomx trap.

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## Experimental Instrument Conditions

| Table I | Atomx Automated VOC Sample Prep System Instrument Parameter | | |
|---|---|---|---|
| **Purge Variable** | **Value** | **Desorb Variable** | **Value** |
| Valve Oven Temp | 140 °C | Methanol Needle Rinse | Off |
| Transfer Line Temp | 140 °C | Methanol Needle Rinse Volume | 3.0 mL |
| Sample Mount Temp | 90 °C | Water Needle Rinse Volume | 7.0 mL |
| Water Heater Temp | 20 °C | Sweep Needle Time | 0.25 min |
| Sample Vial Temp | 20 °C | Desorb Preheat Temp | 240 °C |
| Sample Equilibrate Time | 0.00 min | GC Start Signal | Start of Desorb |
| Soil Valve Temp | 50 °C | Desorb Time | 0.50 min |
| Standby Flow | 10 mL/min | Drain Flow | 300 mL/min |
| Purge Ready Temp | 40 °C | Desorb Temp | 250 °C |
| Condensate Ready Temp | 45 °C | **Bake Variable** | **Value** |
| Pre-sweep Time | 0.25 min | Methanol Glass Rinse | Off |
| Prime Sample Fill Volume | 3.0 mL | Number of Methanol Glass Rinses | 1 |
| Sample Volume | 5.0 mL | Methanol Glass Rinse Volume | 3.0 mL |
| Sweep Sample Time | 0.25 min | Number of Water Bake Rinses | 1 |
| Sweep Sample Flow | 100 mL/min | Water Bake Rinses | 7.0 mL |
| Sparge Vessel Heater | On | Water Bake Rinse Volume | 0.25 min |
| Sparge Vessel Temp | 40 °C | Bake Rinse Sweep Time | 100 mL/min |
| Pre-purge Time | 0.00 min | Bake Rinse Sweep Flow | 0.40 min |
| Pre-purge Flow | 0 mL/min | Bake Rinse Drain Time | 2.00 min |
| Purge Time | 8.00 min | Bake Time | 400 mL/min |
| Purge Flow | 55 mL/min | Bake Flow | |
| Purge Temp | 20 °C | Bake Temp | 260 °C |
| Condensate Purge Temp | 20 °C | Condensate Bake Temp | 200 °C |
| Dry Purge Time | 1.00 min | | |
| Dry Purge Flow | 100 mL/min | Trap | #9 |
| Dry Purge Temp | 20 °C | | |

| Table II | Thermo Scientific™ TRACE™ 1310 GC/ISQ™ LT MS System Instrument Parameters |
|---|---|
| **Variable** | **Value** |
| Column | Thermo Scientific™ TG-VMS, 20m, 0.18mm ID, 1µm; Constant Flow 0.5 mL/min |
| Oven Program | 35 °C for 3 min; 14 °C/min to 100 °C, 25 °C/min to 210 °C, hold for 2.00 min |
| Inlet: | Temp 200 °C; Split Ratio 70:1, Septum Purge Flow 5 mL/min, Thermo |
| Line Pressure | Helium, 110 Psi: Nitrogen 95 psi |
| MS | Ion Source Temp 325 °C; Solvent Delay 1.35 min; Atune; Transfer Line 230 °C |
| Scan Mode | Scan - 35.0 m/z to 260.0 m/z, Scan Time 0.2 sec, Emission Current 25 µA |

## Standard Preparation

The Internal Standard (IS) consisted of a 524.3 Internal Standard/Surrogate mix diluted to 12.5 ppm with P&T methanol.  The Atomx accurately added 5 µL of this solution into each 5 mL sample.

The preservation reagent consisted of deionized water containing approximately 0.625 g/L of ascorbic acid and 5 g/L of maleic acid.

The stock standard consisted of a 524.3 Gas Calibration Mix and a 524.3 VOA MegaMix® diluted to 50 ppm with P&T methanol.

A calibration curve from 0.2 ppb to 100 ppb, seven MRL samples (0.5 ppb) and seven precision and accuracy samples (20 ppb) consisted of dilutions of the stock standard with preservation reagent. Headspace-free 40 mL VOA vials were used to prepare calibration curve standards, MRL standards, and precision and accuracy standards.

## 524.4 Results

Thermo Scientific™ TraceFinder™ EFS software was used for all data collection and processing. The peak shape and height above the noise provided for easy quantification of peak area for adequate detection of a majority of VOCs down to 0.2 ppb.  Methyl acetate, pentachloroethane, 1,2-dibromo-3-chloropropane and hexachlorobutadiene peak areas were sufficient for the 0.5 ppb MRL level only.  No peaks were detectable for these compounds at the 0.2 ppb level.  The 1 ppb level was the lowest detectable peak for t-butyl alcohol.  The MRL level was not calculated for this VOC.

Figure 1 displays the extracted quantitation ion (quant ion) chromatograms for the critical first six gases of a 0.5 ppb MRL standard.  Figure 2 displays a baseline-subtracted TIC chromatogram of this 0.5 ppb MRL standard for the remaining VOCs.

USEPA 524.4 Section 10.1.10 requires that calibration points ≤MRL must calculate to within ±50% of their true value. All other calibration points must calculate to within ±30% of their true value.  All of the VOCs passed this requirement for each calibration point, based on their percent difference from their true value.

USEPA 524.4 IDC Section 9.2.2 and 9.2.3 requires a mid-point accuracy determination where the precision, calculated as percent Relative Standard Deviation (%RSD), is to be ≤20% and the accuracy, calculated as average recovery, is to be ≤20%. Both are to be calculated with seven replicates of a concentration at or near the mid-point of the calibration.  The precision and accuracy data from seven replicate samples at 20 ppb passed these requirements and is shown in Table III.

USEPA 524.4 IDC Section 9.2.4 requires the Lower Prediction Interval of Results (LPIR) to be ≥50% and the Upper Prediction Interval of Results (UPIR) to be ≤150% for all VOCs.  The software calculated the concentration of the seven 0.5 ppb MRL samples from the standard curve and then the data was exported to a Microsoft® Excel® spreadsheet.  The spreadsheet was then used to calculate the LPIR and UPIR for all VOCs following the calculations in IDC Section 9.2.4.  Table III presents the LPIR and UPIR data meeting these requirements for all VOCs, with the exception of the surrogate standards and t-butyl alcohol.

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**Figure 1**   Chromatogram of a 0.5 ppb Standard Displaying the Extracted Quantitation Ion Chromatograms for the First Six Gases.
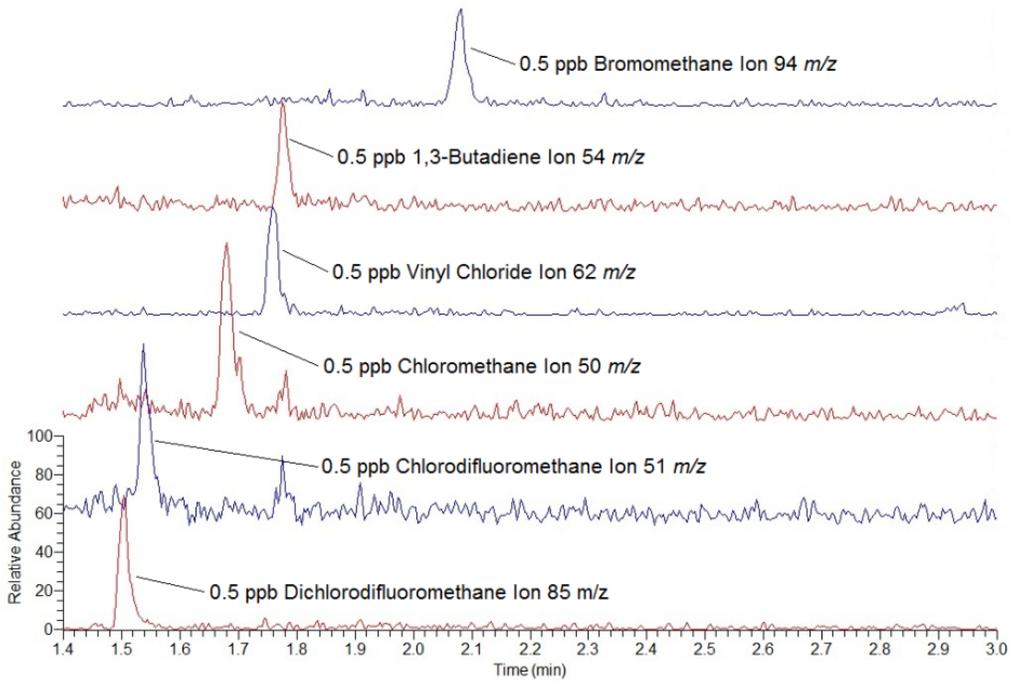


**Figure 2**   TIC Chromatogram of a 0.5 ppb Standard.  The TIC chromatogram is background subtracted, which removes the internal standard and surrogate peaks.
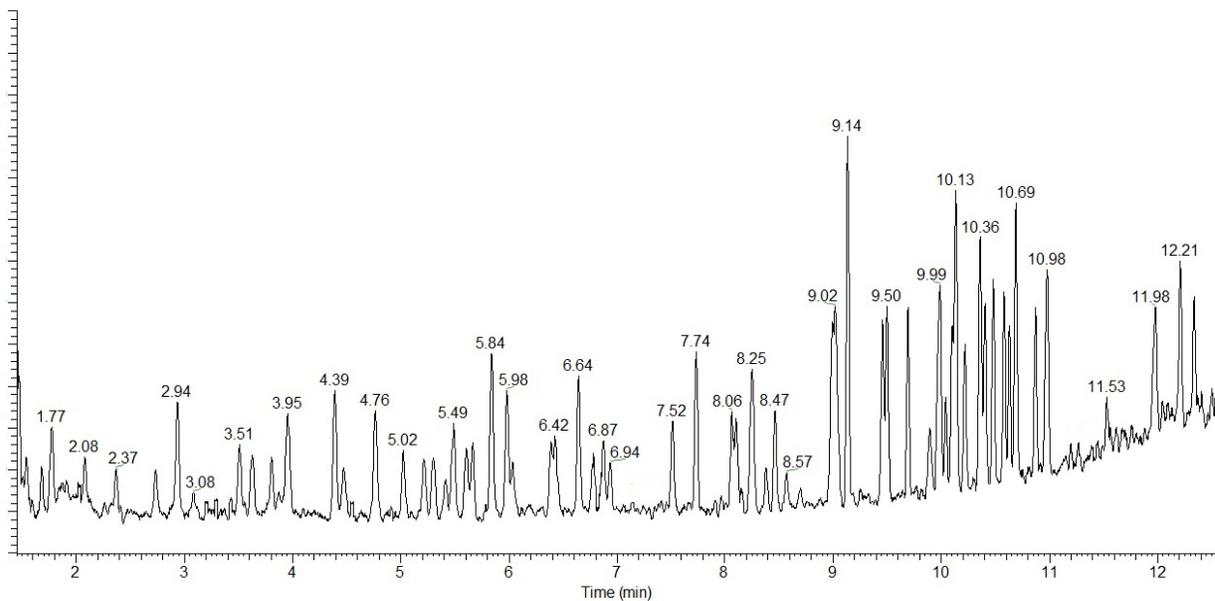
## Table III Initial Demonstration of Capability (IDC) (Section 9.2.2, 9.2.3, 9.2.4)

| Compound | RT (min) | Quant Ion | Precision (≤ 20%) | Accuracy (± 20%) | MRL Confirmation (0.5 ppb) | |
|---|---|---|---|---|---|---|
| | | | | | LPIR (> 50%) | UPIR (< 150%) |
| Dichlorodifluoromethane | 1.50 | 85 | 5.6 | -10.9 | 75.8 | 117.9 |
| Chlorodifluoromethane | 1.54 | 51 | 5.5 | -7.2 | 77.8 | 145.9 |
| Chloromethane | 1.68 | 50 | 5.0 | -8.7 | 54.7 | 135.6 |
| Vinyl Chloride | 1.75 | 62 | 5.2 | 1.7 | 69.8 | 144.3 |
| 1,3-Butadiene | 1.77 | 54 | 5.3 | 1.7 | 92.3 | 145.0 |
| Bromomethane | 2.08 | 94 | 5.8 | -4.6 | 75.1 | 145.7 |
| Trichlorofluoromethane | 2.36 | 101 | 4.5 | -6.3 | 85.0 | 126.1 |
| Diethyl Ether | 2.72 | 59 | 5.2 | -4.1 | 72.6 | 147.3 |
| 1,1-Dichloroethene | 2.93 | 96 | 5.6 | -7.9 | 81.3 | 124.1 |
| Carbon Disulfide | 2.93 | 76 | 5.8 | -9.4 | 88.7 | 130.9 |
| Iodomethane | 3.08 | 142 | 5.4 | -8.5 | 64.7 | 105.0 |
| Allyl Chloride | 3.51 | 76 | 3.8 | -6.3 | 83.4 | 133.3 |
| Methylene Chloride | 3.63 | 84 | 4.0 | -5.6 | 81.1 | 113.1 |
| trans-1,2-Dichloroethene | 3.80 | 96 | 5.8 | -6.4 | 80.3 | 131.9 |
| Methyl Acetate | 3.87 | 43 | 5.7 | -10.0 | 78.9 | 148.6 |
| Methyl-tert-Butyl Ether-d3 (surrogate 1) | 3.93 | 76 | 2.4 | -12.1 | | |
| Methyl-tert-Butyl Ether (MtBE) | 3.96 | 73 | 3.8 | -5.1 | 78.2 | 107.4 |
| tert-Butyl Alcohol (TBA) | 4.12 | 59 | 11.1 | 0.4 | Note[1] | Note[1] |
| Diisopropyl Ether (DIPE) | 4.39 | 45 | 4.7 | -6.4 | 80.6 | 119.5 |
| 1,1-Dichloroethane | 4.47 | 63 | 5.1 | -3.5 | 80.4 | 126.6 |
| tert-Butyl Ethyl Ether (ETBE) | 4.76 | 59 | 4.4 | -2.2 | 82.3 | 114.9 |
| cis-1,2-Dichloroethene | 5.02 | 61 | 3.9 | -2.5 | 82.8 | 119.9 |
| Bromochloromethane | 5.21 | 128 | 4.6 | -4.4 | 81.7 | 148.5 |
| Chloroform | 5.30 | 83 | 5.2 | -4.2 | 80.9 | 109.1 |
| Carbon Tetrachloride | 5.41 | 117 | 4.2 | -3.4 | 84.0 | 131.9 |
| Tetrahydrofuran | 5.47 | 72 | 5.7 | -10.4 | 58.7 | 143.3 |
| 1,1-Dichloropropene | 5.61 | 110 | 5.6 | -3.3 | 83.8 | 149.4 |
| 1,1,1-Trichloroethane | 5.48 | 97 | 6.5 | -8.5 | 88.4 | 114.6 |
| 1-Chlorobutane | 5.66 | 56 | 5.8 | -5.7 | 86.8 | 122.4 |
| Benzene | 5.84 | 78 | 5.2 | -6.9 | 84.4 | 116.0 |
| tert-Amyl Methyl Ether (TAME) | 5.98 | 73 | 5.3 | -6.2 | 76.4 | 119.6 |
| 1,2-Dichloroethane | 6.03 | 62 | 4.8 | 1.9 | 76.8 | 109.2 |
| Trichloroethene | 6.39 | 132 | 5.2 | -5.3 | 79.1 | 137.5 |
| 1,4-Difluorobenzene (IS 1) | 6.43 | 114 | 4.7 | | | |
| tert-Amyl Ethyl Ether (TAEE) | 6.64 | 59 | 4.2 | -2.9 | 96.0 | 110.9 |
| Dibromomethane | 6.77 | 93 | 4.0 | -5.3 | 75.4 | 110.3 |
| 1,2-Dichloropropane | 6.88 | 63 | 5.2 | -3.6 | 90.6 | 109.3 |
| Bromodichloromethane | 6.94 | 83 | 4.7 | -5.3 | 79.2 | 113.2 |
| cis-1,3-Dichloropropene | 7.51 | 75 | 5.5 | -6.6 | 86.8 | 125.2 |
| Toluene | 7.73 | 92 | 5.4 | -6.2 | 82.2 | 109.6 |
| Tetrachloroethene | 8.06 | 166 | 5.6 | -2.3 | 67.0 | 134.9 |
| trans-1,3-Dichloropropene | 8.11 | 75 | 4.6 | -5.6 | 83.9 | 125.5 |
| 1,1,2-Trichloroethane | 8.24 | 83 | 4.9 | -5.9 | 66.8 | 127.9 |
| Ethyl Methacrylate | 8.26 | 69 | 4.3 | -9.1 | 84.3 | 117.3 |
| Dibromochloromethane | 8.38 | 129 | 4.8 | -5.0 | 82.0 | 130.1 |
| 1,3-Dichloropropane | 8.46 | 76 | 4.4 | -4.7 | 87.9 | 122.8 |
| 1,2-Dibromoethane (EDB) | 8.57 | 107 | 4.5 | -4.1 | 81.1 | 133.9 |
| Chlorobenzene-d5 (IS 2) | 8.98 | 117 | 4.7 | | | |
| Chlorobenzene | 8.99 | 112 | 4.6 | -3.4 | 93.6 | 110.3 |
| Ethylbenzene | 9.02 | 91 | 5.2 | -4.4 | 84.8 | 130.5 |

| Compound | RT (min) | Quant Ion | Precision (≤ 20%) | Accuracy (± 20%) | MRL Confirmation (0.5 ppb) LPIR (> 50%) | UPIR (< 150%) |
|---|---|---|---|---|---|---|
| 1,1,1,2-Tetrachloroethane | 9.05 | 131 | 5.2 | -4.1 | 51.0 | 140.0 |
| m- , p-Xylene | 9.14 | 106 | 5.0 | -3.7 | 93.1 | 121.3 |
| o-Xylene | 9.46 | 106 | 4.6 | -6.4 | 83.2 | 120.1 |
| Styrene | 9.50 | 104 | 5.0 | -6.6 | 78.4 | 112.1 |
| Bromoform | 9.51 | 173 | 5.5 | -3.4 | 81.4 | 134.8 |
| Isopropylbenzene | 9.69 | 105 | 4.8 | -4.4 | 104.2 | 117.8 |
| 4-Bromofluorobenzene (Surrogate 2) | 9.89 | 95 | 1.9 | -4.3 | | |
| Bromobenzene | 9.96 | 156 | 4.9 | -4.6 | 88.3 | 125.6 |
| Propylbenzene | 9.99 | 91 | 5.1 | -6.7 | 96.7 | 117.4 |
| 1,1,2,2-Tetrachloroethane | 10.04 | 83 | 4.4 | -9.1 | 76.5 | 122.6 |
| 2-Chlorotoluene | 10.10 | 126 | 5.9 | -8.2 | 84.7 | 134.6 |
| 1,3,5-Trimethylbenzene | 10.13 | 105 | 4.4 | -3.8 | 96.6 | 112.0 |
| 1,2,3-Trichloropropane | 10.14 | 110 | 5.8 | -5.9 | 67.1 | 147.4 |
| 4-Chlorotoluene | 10.22 | 91 | 4.0 | -6.0 | 91.8 | 114.4 |
| tert-Butylbenzene | 10.36 | 134 | 5.3 | -7.4 | 53.8 | 137.1 |
| Pentachloroethane | 10.37 | 167 | 6.0 | -6.6 | 70.1 | 148.5 |
| 1,2,4-Trimethylbenzene | 10.40 | 105 | 5.3 | -5.9 | 92.2 | 126.2 |
| sec-Butylbenzene | 10.48 | 105 | 5.1 | -7.7 | 82.2 | 109.2 |
| 4-Isopropyltoluene | 10.58 | 119 | 4.6 | -6.8 | 102.0 | 119.5 |
| 1,3-Dichlorobenzene | 10.63 | 146 | 5.2 | -5.3 | 87.2 | 132.1 |
| 1,4-Dichlorobenzene-D4 (IS 3) | 10.68 | 152 | 4.4 | | | |
| 1,4-Dichlorobenzene | 10.69 | 146 | 4.2 | -5.7 | 88.3 | 130.8 |
| Butylbenzene | 10.87 | 134 | 4.9 | -9.1 | 83.6 | 131.5 |
| Hexachloroethane | 10.96 | 166 | 4.8 | -1.5 | 54.7 | 134.7 |
| 1,2-Dichlorobenzene-d4 (Surrogate 3) | 10.98 | 146 | 1.8 | -0.6 | | |
| 1,2-Dichlorobenzene | 10.98 | 152 | 3.9 | -5.0 | 84.2 | 125.6 |
| 1,2-Dibromo-3-chloropropane | 11.53 | 157 | 4.2 | -10.1 | 66.5 | 149.4 |
| Hexachlorobutadiene | 11.96 | 225 | 6.6 | -0.5 | 104.0 | 147.6 |
| 1,2,4-Trichlorobenzene | 11.98 | 180 | 5.6 | -5.8 | 98.5 | 141.2 |
| Napthalene | 12.21 | 128 | 5.1 | -11.2 | 86.0 | 112.2 |
| 1,2,3-Trichlorobenzene | 12.34 | 180 | 4.8 | -7.6 | 81.4 | 137.1 |

Table III Initial Demonstration of Capability (IDC) (Section 9.2.2, 9.2.3, 9.2.4)

Note 1 – This compound was not detectable at the 0.5 ppb level. The 1 ppb level was detectable and the precision and accuracy data was calculated for the curve from 1 to 100 ppb.

## Conclusion

The Teledyne Tekmar Atomx Automated VOC Sample Prep System using nitrogen as the sample purge gas, was used to purge and trap 76 VOCs from preserved reagent water according to USEPA Method 524.4.  These desorbed compounds were separated and quantified using a Thermo Scientific™ TRACE™ 1310 gas chromatograph (GC) and ISQ™ LT mass spectrometer (GC-MS) system with the Thermo Scientific™ Instant Connect™ Helium Saver Module to significantly reduce helium use.  The optional chiller for the Atomx maintained the samples below 10 °C while awaiting sampling from the autosampler tray to the sparge vessel.  The Atomx accurately dispensed three surrogate standards and three internal standards during sample transfer.

All 76 VOCs met the precision and accuracy requirements of USEPA Method 524.4.  75 of the VOCs met the LPIR and UPIR requirements for a MRL at 0.5 ppb.  One VOC, t-butyl alcohol, provided no detectable peak at the 0.5 ppb, but a peak was present at the 1 ppb level.  This VOC passed the initial calibration requirement for the 1 ppb to 100 ppb calibration range.

## References

1.  USEPA Method 524.4, Measurement of Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry using Nitrogen Purge Gas, May 2013

Special thanks to Terry Jeffers of Thermo Fisher Scientific for technical assistance with the Instant Connect™ Helium Saver Module.