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Analysis of VOCs in soil using automated methanol extraction

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Goal

Demonstration of the analysis of volatile organic compounds in soil according to U.S. EPA Method 5035 used in accordance with U.S. EPA Method 8260C. This method employs an automated methanol extraction with 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). Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software was used to fully control the analytical instruments as well as to acquire, process, and report the data. Method linearity, carryover, and Initial Demonstration of Capability (IDC) were assessed to evaluate method performance.

Introduction

It is essential to test for volatile organic compounds (VOCs) in soil due to their potential detrimental health effects on humans. Contaminated soil in which crops are grown and consumed by the populations can cause humans to be exposed to these harmful VOCs. Analytical testing laboratories must monitor soil contaminants to protect the public. U.S. EPA Method 5035 allows for two sample collection options that can be used in accordance with U.S. EPA Method 8260C.[1,2] The first option is to collect 5 grams (g) of soil into a pre-weighed vial containing a prescribed amount of a water miscible solvent (methanol). An aliquot of this sample is taken and purged using U.S. EPA Method 5030.[3]

The second option is to collect a bulk soil sample on site. Once back in the lab, the bulk soil is separated into individual sub-samples containing a water miscible solvent (methanol). Then an aliquot of the sample is taken and purged using U.S. EPA Method 5030.[3]

In this study, spiked baked sand samples were placed in a vial, methanol was added, and the sample agitated to release the VOCs for analysis. The Teledyne Tekmar Atomx XYZ P&T system along with a Thermo Scientific ISQ 7000 MS system coupled with a Thermo Scientific TRACE 1310 GC and Thermo Scientific CDS software were used for the analysis. Method linearity, carryover, and Initial Demonstration of Capability (IDC) were assessed to evaluate method performance.

Experimental

Sample preparation

A 1000 parts per million (ppm) or milligram per liter (mg/L) working calibration standard was prepared in methanol from a 9-compound Restek™ PVOC/GRO Mix (Wisconsin) standard. A 5-point methanol extraction calibration curve was prepared from 200 ppb to 1000 ppb (µg/L). The relative response factor (RF) was calculated for each compound using one of the four internal standards: pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Surrogate standards consisted of: dibromofluoromethane, 1,2-dichloroethane-d_4, toluene-d_8, and 4-bromofluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 25 ppm, after which 5 microliters (µL) were then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Seven, 5 g spiked baked sand samples were prepared for the IDC accuracy and precision calculations. Five grams of baked sand were weighed out and put in a 40 mL VOA vial with a stir bar. These replicates of baked sand were then spiked with the 1000 ppm PVOC/GRO Mix (Wisconsin) standard. The methanol extracted samples were then diluted 1:50 in 5 mL of DI water by the Atomx XYZ for a final concentration of 600 ppb. Atomx XYZ conditions for all calibration and IDC samples are found in Table 1.
A Trace 1310 GC was coupled to the ISQ 7000 mass spectrometer equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite™ ion source. Expanded method parameters for the GC-MS system are displayed in Table 2.

Table 1. Teledyne Tekmar Atomx XYZ method parameters

Standby	Variable
Valve oven temperature	140 °C
Transfer line temperature	140 °C
Sample mount temperature	90 °C
Water heater temperature.	90 °C
Soil valve temperature	100 °C
Standby flow	10 mL/min
Purge ready temperature	40 °C
Purge	**Variable**
Presweep time	0.25 min
Methanol volume	10.0 mL
Sparge vessel heater	Off
Sample mix speed	Medium
Sample mix time	2.00 min
Sample mix settle time	2.00 min
Sample sweep time	0.25 min
Sample sweep flow	100 mL/min
Purge time	11.00 min
Purge flow	40 mL/min
Purge temperature	20 °C
MCS purge temperature	20 °C
Dry purge time	1.00 min
Dry purge flow	100 mL/min
Dry purge temperature	20 °C
Desorb	**Variable**
Desorb	Variable
Methanol needle rinse	On
Methanol needle rinse volume	2.0 mL
Water needle rinse volume	7.0 mL
Sweep needle time	0.25 min
Desorb preheat temperature	245 °C
GC start signal	Begin desorb
Desorb time	2.00 min
Drain flow	300 mL/min
Desorb temperature	250 °C
Bake	**Variable**
Methanol glass rinse	On
Methanol glass rinse volume	3.0 mL
Number of methanol glass rinses	1
Number of water bake rinses	1
Water bake rinse volume	7.0 mL
Bake rinse sweep time	0.25 min
Bake rinse sweep flow	100 mL/min
Bake rinse drain time	0.40 min
Bake time	2.00 min
Bake flow	200 mL/min
Bake temperature	280 °C
MCS bake temperature	180 °C
Trap	9
Chiller tray	Off
Purge gas	Helium

Table 2. GC-MS conditions

Thermo Scientific TRACE 1310 GC conditions	
Column	Thermo Scientific™ TraceGOLD™ TG-VMS GC, 20 m × 0.18 mm, 1 µm film, P/N 26080-4950 Helium – 0.8 mL/min
Oven profile	35 °C, 3 min, 12 °C/min to 85 °C, 25 °C/min to 225 °C, 2 min hold Run time: 14.767 min
Inlet	200 °C, 50:1 split ratio Purge flow: 0.5 mL/min
SSL mode	Split
Split liner	1.2 mm ID, P/N 453A1335
O-ring	P/N MI-290AA1-0001
ISQ 7000 MS system conditions	
Temperature	Transfer line: 230 °C Ion source: 280 °C
Scan	Range: 35 amu to 260 amu Solvent delay: 0.50 min Dwell/scan time: 0.15 s
Gain	Emission current: 25 µA Detector gain: 3.00E+005

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 CDS 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 8260.[4]

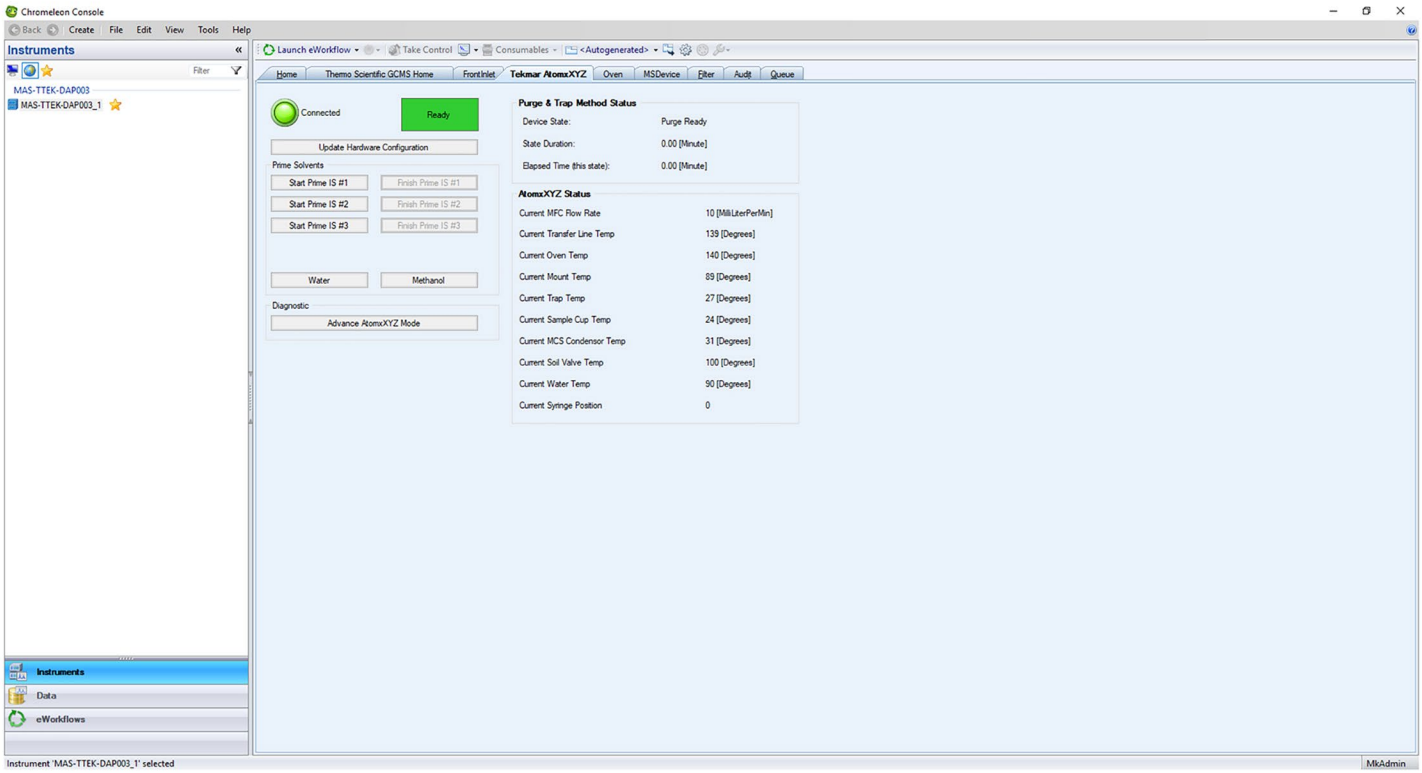

Figure 1. Chromeleon control of the Atomx XYZ P&T

Results and discussion

Chromatography

Excellent chromatographic separation was achieved using the conditions described in Table 2. The chromatography was consistent and unaffected by the matrix, showing consistent peak shape and separation. Figure 2 displays a 200 ppb PVOC/GRO Mix (Wisconsin) (final concentration) standard spiked baked sand sample, methanol extracted and purged by the Atomx XYZ, indicating excellent peak resolution with minimal water interference of all VOCs.

Linearity and sensitivity

The 5-point methanol extraction calibration curve was prepared from 200 ppb to 1000 ppb (µg/L) for all compounds. The average response factor RSD for the calibration solutions was <20% for all compounds. Table 3 shows the calibration and IDC results. The IDC with precision and accuracy were assessed using seven individually extracted standard replicates of a 600 ppb (µg/L) soil standard.

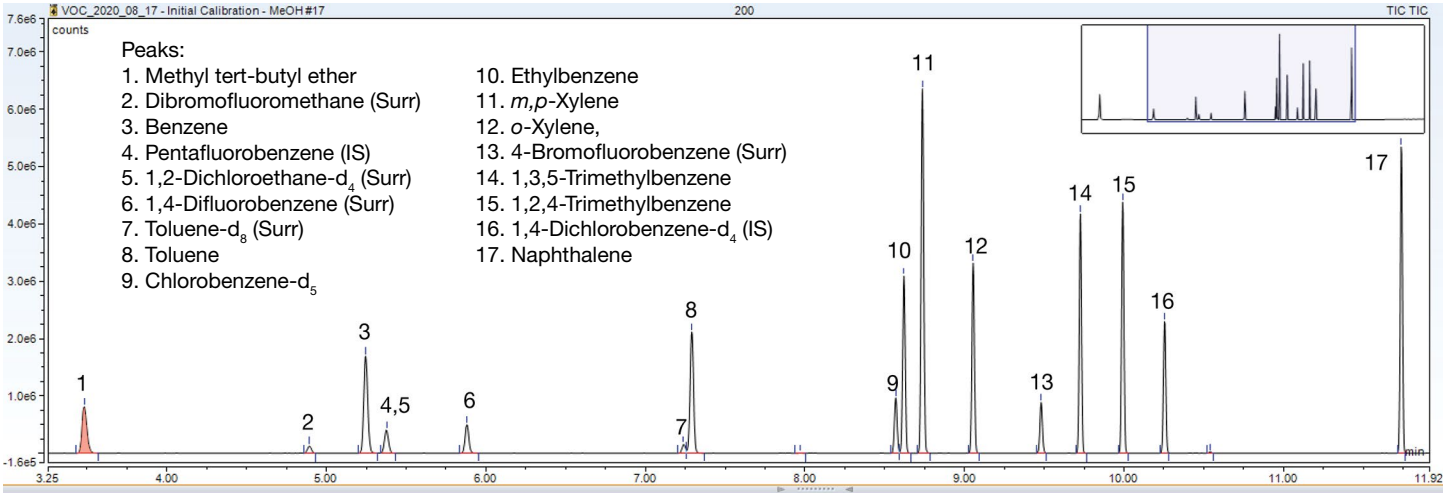

Figure 2. Total ion chromatogram of a methanol extracted 5 g spiked baked sand sample containing a final concentration of 200 ppb (µg/L) PVOC/GRO Mix (Wisconsin)

Table 3. Calibration and IDC results for soil samples

Peak name	Ret. time (min)	Quant ion (*m/z*)	Linearity (AvRF %RSD)	Avg RF	Precision ≤20%	Accuracy ±30%
Methyl tert-butyl ether	3.47	73	6.19	0.254	6.0	114
Dibromofluoromethane (Surr)	4.89	111	16.4	0.130	6.6	85
Benzene	5.25	78	10.3	0.346	4.4	91
Pentafluorobenzene (IS)	5.37	168	–	–	–	–
1,2-Dichloroethane-d_4 (Surr)	5.40	65	12.9	0.061	4.9	82
1,4-Difluorobenzene (IS)	5.88	114	–	–	–	–
Toluene-d_8 (Surr)	7.24	98	8.44	0.431	3.7	103
Toluene	7.29	91	8.84	0.628	6.1	104
Chlorobenzene-d_5 (IS)	8.57	117	–	–	–	–
Ethylbenzene	8.62	91	13.3	0.724	6.4	106
m,p-Xylene	8.74	106	13.8	0.304	8.0	103
o-Xylene	9.06	106	10.8	0.162	8.2	109
1-Bromo-4-fluorobenzene (Surr)	9.48	95	3.13	0.422	2.4	103
1,3,5-Trimethylbenzene	9.73	105	9.69	0.383	4.4	117
1,2,4-Trimethylbenzene	9.99	105	8.81	0.409	5.2	114
1,4-Dichlorobenzene-d4 (IS)	10.26	152	–	–	–	–
Naphthalene	11.74	128	13.6	0.537	6.8	105

Figure 3 shows a total ion chromatogram of (n=7 replicates) 1,2,4-trimethylbenzene in methanol extract of 5 g spiked baked sand sample at a final concentration of 600 ppb (µg/L) PVOC/GRO Mix (Wisconsin), displaying very good reproducibility with a 5.3% RSD and a 114% recovery.

Examples of the linearity for the soil calibration curve are shown in Figures 4 and 5. These figures show the lowest point of the water calibration curve at 200 ppb (equivalent to 200 µg/kg in matrix), producing an excellent response and an average response factor RSD <20%.

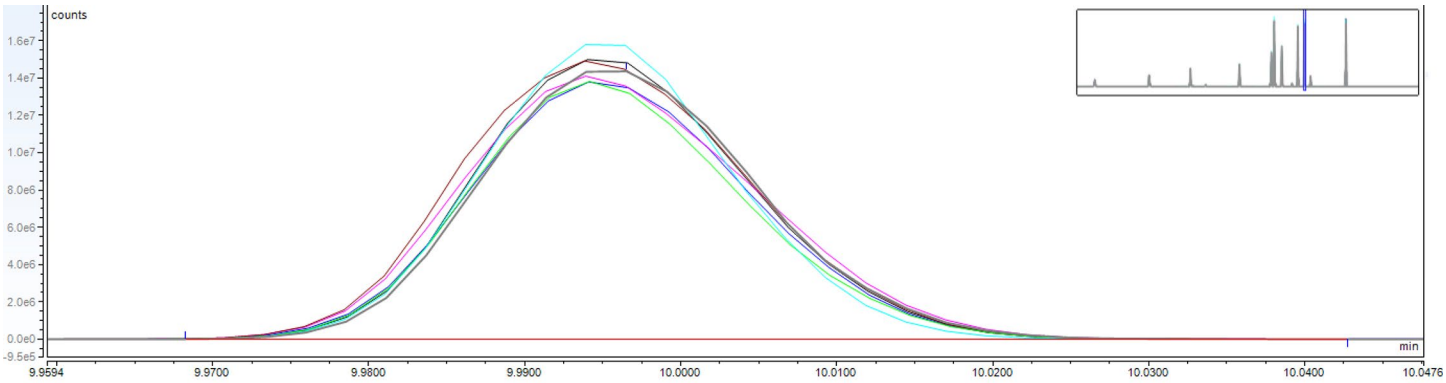

Figure 3. Total ion chromatogram of (n=7 replicates) of 1,2,4-trimethylbenzene in methanol extract of 5 g spiked baked sand sample, containing a final concentration of 600 ppb PVOC/GRO Mix (Wisconsin), displaying good reproducibility with a 5.3% RSD and a 114% recovery

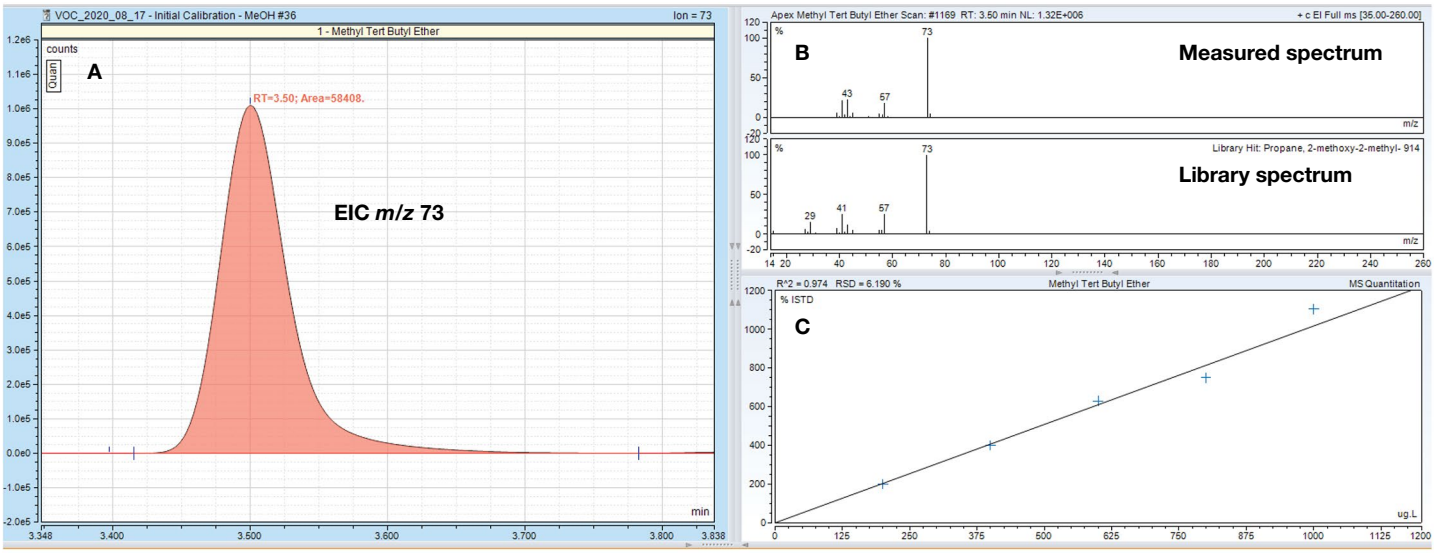

Figure 4. Chromeleon CDS results browser showing extracted ion chromatogram for methyl tert-butyl ether (MTBE) (*m/z* 73) in the methanol extract of 5 g baked sand sample containing a final concentration of 200 ppb PVOC/GRO Mix (Wisconsin) standard, quantitation ion (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 200 ppb to 1000 ppb(C)

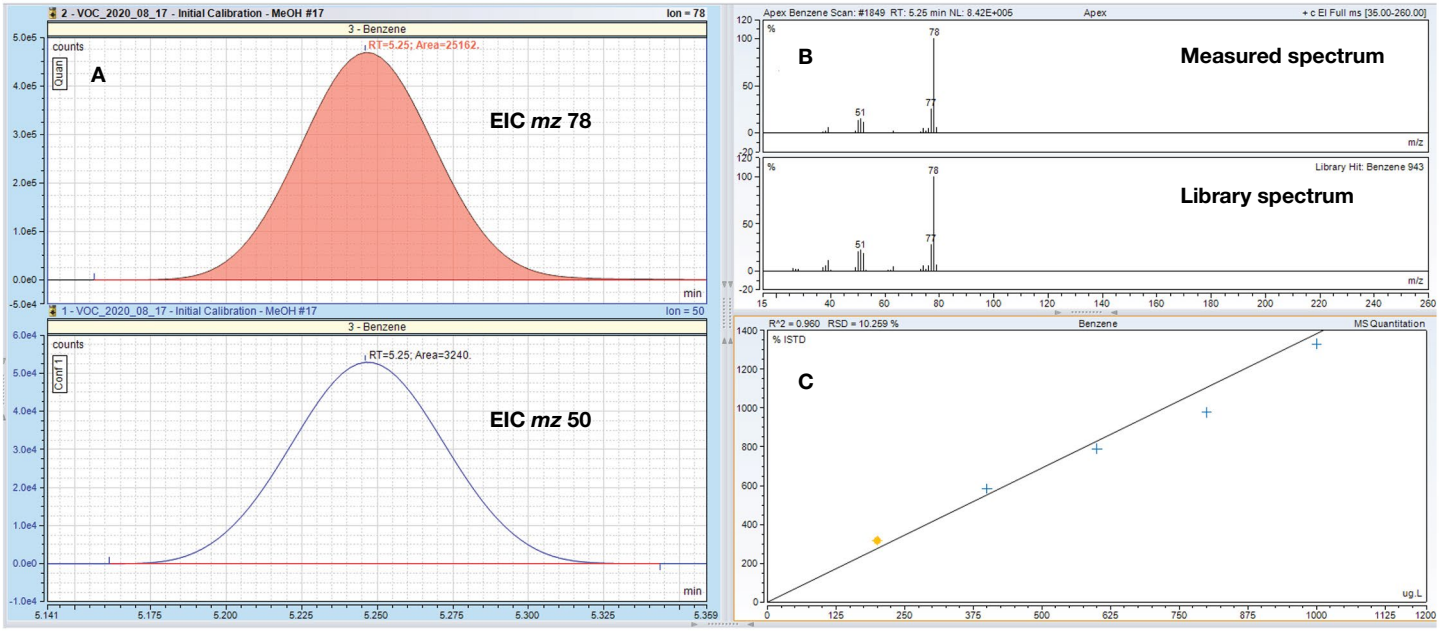

Figure 5. Chromeleon CDS results browser showing extracted ion chromatograms (quan ion *m/z* 78, confirmatory ion *m/z* 50) for benzene in the methanol extract of 5 g baked sand sample containing a final concentration of 200 ppb PVOC/GRO Mix (Wisconsin) standard, quantitation ion and one confirming ion (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 200 ppb to 1000 ppb (C)

Assessment of carryover

When analyzing high-level soil samples, system carryover can be a concern. Within the EPA regulation an exact number is not assigned to carryover. The method does, however, state repeat blanks with organic-free reagent water until you are confident there will be no carryover into the next sample. Carryover below 2% is an acceptable level. Carryover from the Atomx XYZ's automated methanol extraction method (Table I) was evaluated with two replicates of blanks analyzed directly after a 5 g spiked baked sand sample with a final concentration of 1000 ppb. Table 4 shows carryover even with high-level samples is minimal.

Table 4. Assessment of carryover for PVOC/GRO Mix (Wisconsin) methanol extraction

Compounds	First blank carryover (%)	Second blank carryover (%)	Average carryover (%)
Methyl tert-butyl ether	0.008	0.001	0.005
Benzene	0.05	0.005	0.03
Toluene	0.06	0.03	0.05
Ethylbenzene	0.12	0.04	0.08
m,p-Xylene	0.13	0.06	0.10
o-Xylene	0.07	0.02	0.04
1,3,5-Trimethylbenzene	0.15	0.05	0.10
1,2,4-Trimethylbenzene	0.20	0.07	0.13
Naphthalene	0.66	0.15	0.40

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Conclusion

The combined analytical solution with the TRACE 1310 GC coupled with the ISQ 7000 single quadrupole MS and the Atomx XYZ P&T system provides clear advantages for analytical testing laboratories that analyze soil samples following the U.S. EPA Method 5035 in accordance with U.S. EPA Method 8260C. The Atomx XYZ concentrator's efficient trap-cooling design reduces sample cycle time and allows for increased sample throughput. The moisture control system improves water vapor removal, thereby reducing peak interference and increasing GC column life span. The modularity of the TRACE 1310 GC and the ISQ 7000 VPI system with the ExtractaBrite ion source allows users to easily service the injection ports and to exchange ionization sources and analytical columns without venting the mass spectrometer, significantly reducing instrument downtime and minimizing sample analysis interruptions.

The experiments performed clearly demonstrate the suitability of this analytical configuration for the analysis of VOCs in soil samples with automated methanol extraction.

- The average linearity (AvRF %RSD) for all the compounds was 10.5% over a 5-point calibration curve from 200 to 1000 ppb.
- Precision and accuracy (assessed from n=7 repeated injections of a 600 ppb soil standard) showed excellent values with all compounds having RSD <9% for the calculated concentration.
- The automated methanol extraction allowed for compounds recovery values between 82% and 117% with an average value of 91%.
- The Atomx XYZ allowed for <0.4% average (n=2 blank replicates) system carryover as determined from high level soil samples spiked with 1000 ppm PVOC/GRO Mix (Wisconsin) standard to a final concentration of 1000 ppb.
- Combined, these technologies effectively address the challenges of VOC analysis in environmental samples and provide a robust, sensitive solution needed for ensuring maximized instrument output and regulatory method compliance.

Further information on VOC analysis using the ISQ 7000 system and the Atomx XYZ P&T can be found in the Thermo Fisher Scientific AppsLab library[4]. Further information on the analysis of VOCs in accordance to EPA Method 8260 can be found here.

References

1. United States Environmental Protection Agency, Office of Solid Waste, SW-846 Method 8260C, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Revision 3, August 2006.
2. United States Environmental Protection Agency, Office of Soil Waste, Method 5035, Closed-System Purge-And Trap and Extractions for Volatile Organics in Soil and Waste Samples; Revision 1, July 2002.
3. United States Environmental Protection Agency, Office of Soil Waste, SW-846 Method 5030B, Purge and Trap for Aqueous Samples; Revision 2, December 1996.
4. Thermo Scientific AppsLab Library. https://appslab.thermofisher.com/
5. Thermo Scientific Application Note 73769: Analysis of VOCs according to EPA Method 8260. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-73769-gc-ms-vocs-epa-method-8260-an73769-en.pdf

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