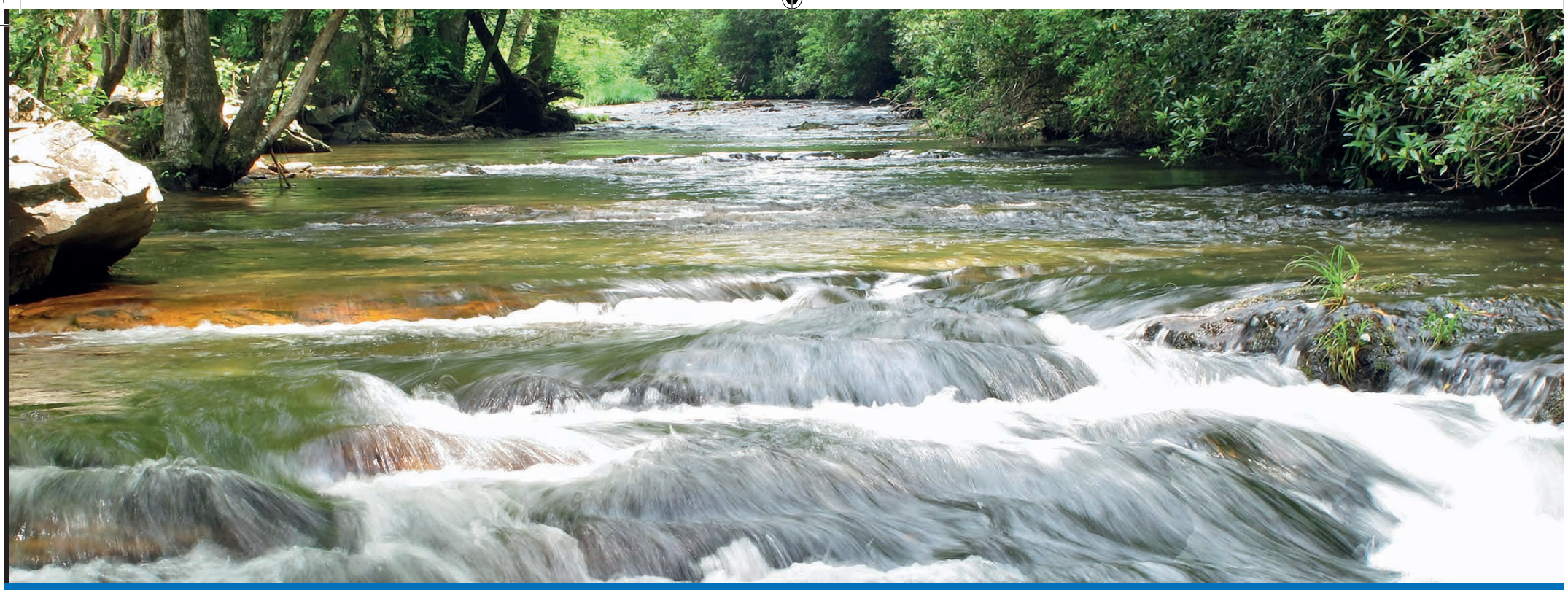


ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN WATER USING PURGE AND TRAP COUPLED TO SINGLE QUADRUPOLE GC-MS

To demonstrate the compliance of the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer coupled to a Thermo Scientific™ TRACE™ 1610 gas chromatograph (GC) and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) for the determination of volatile organic compounds (VOCs) in ground water, surface water, and wastewater according to the Chinese Method HJ 639. Linearity, detection limit, precision and accuracy were assessed to evaluate the method performance. A long-term study was also performed to demonstrate the robustness of the method.

Introduction

Volatile organic compounds (VOCs) are a group of chemicals with different properties that are generated from natural processes, industrial activities, petroleum, and household products. These compounds are of major concern as they are important pollutants contributing to the ground-level ozone formation and thus posing a risk to human health. Regulatory agencies all over the world have published several methods to support analytical testing laboratories dealing with VOCs analysis. Purge and trap coupled to gas chromatography–mass spectrometry (GC-MS) is the method of choice for analysis of VOCs as it offers the advantage of sample pre-concentration combined with water removal, therefore improving sensitivity, increasing column lifetime, and reducing peak interferences that can occur when moisture enters the GC system. Some of the most common methods are defined by the U.S. Environmental Protection Agency (U.S. EPA) and include Method 8260 and Method 524.2.

The Chinese Ministry of Ecology and Environment has developed a standard method, HJ 639, to monitor VOCs in ground water, surface water, and wastewater to ensure safety. To perform HJ 639, method acceptance criteria must be achieved. These criteria include demonstrating the method detection limit (MDL) for the compounds in water samples (the lowest MDL being defined as 0.6 ppb (µg/L)). The linearity of the method must show the calibrations results produce R^2 values of >0.99 or Relative Response Factor (RRF) RSD <20%. To ensure the sampling with the purge and trap is satisfactory, the recovery must be between 70 to 130% for the compounds. To assess the entire reproducibility of the method, precision must be less than 25% for two consecutive injections for every compound. In addition to these criteria, analytical testing laboratories must produce consistent results and be reproducible from day to day. In this application note, purge and trap sampling was coupled to GC-MS to demonstrate HJ 639 for analysis of VOCs in water.

Experimental

An ISQ 7610 single quadrupole mass spectrometer equipped with a Thermo Scientific™ ExtractaBrite™ ion source was coupled to a TRACE 1610 GC and a Teledyne Tekmar Atomx XYZ P&T and used to assess the system suitability for the determination on VOCs in water according to the Chinese HJ 639 method. The Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) technology of the ISQ 7610 system allows users to service the ionization source and analytical columns without venting the mass spectrometer, significantly reducing instrument downtime and minimizing sample analysis interruptions. 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. Experimental conditions for the GC-MS system and the purge and trap are displayed in Tables 1 and 2. (Table 1 can be viewed in the application note on Analysis of VOCs in Water at thermofisher.com/GC-MS.)

Table 2. GC-MS operating conditions for analysis of VOCs in water

TRACE 1610 GC conditions	
Column	Thermo Scientific™ TraceGOLD™ TG VMS (P/N 26080-4950), 20 m × 0.18 mm, 1 µm film
Carrier gas	Helium, 0.8 mL/min
Oven temp. 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	SSL, 200 ˚C, 30:1 split, purge flow 0.5 mL/min
ISQ 7610 MS conditions	
Temp.	Transfer line 230 ˚C; ion source 280 ˚C
Scan	Range 40 amu to 270 amu, solvent delay 0.50 min, dwell/scan time 0.20 s
Current	Emission current 25 µA, gain 3.00E+005

Data acquisition, processing, and reporting

Data was acquired, processed, and reported using Chromeleon CDS software, version 7.3. The integrated instrument control of the Atomx XYZ P&T ensures full automation from sequence set-up to data reporting, simplifying the instrument operation. As an example,

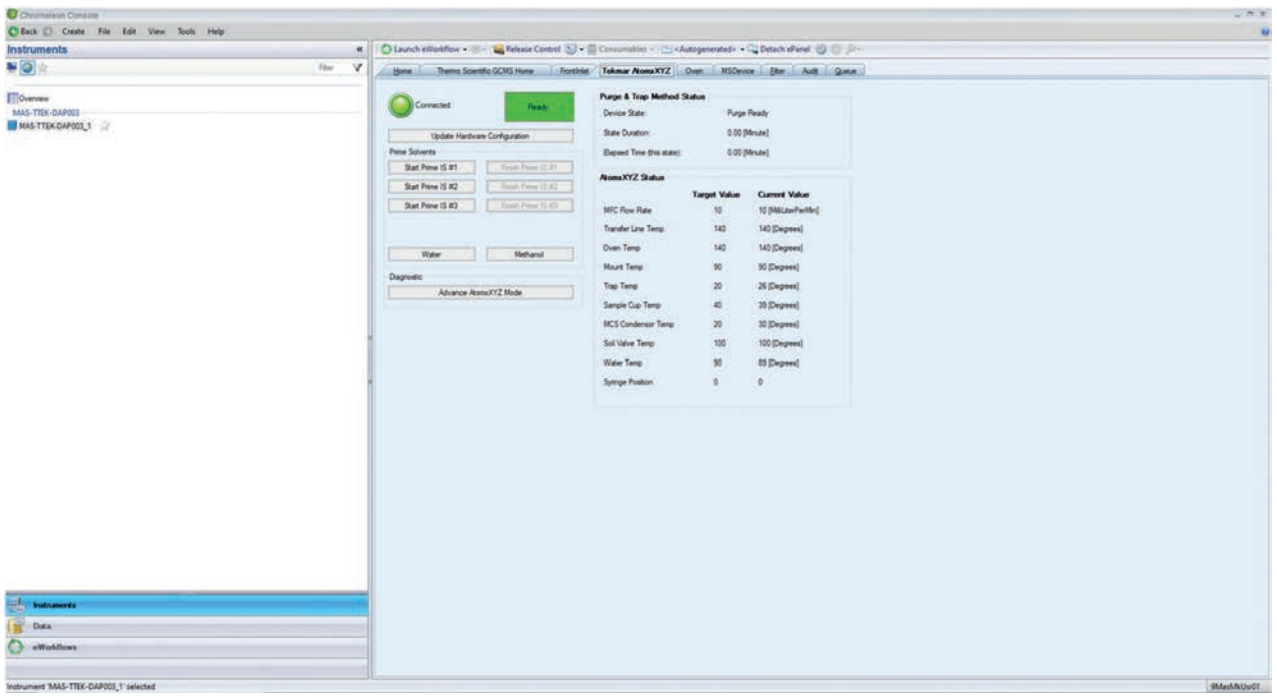


Figure 1. Chromeleon CDS e-panel allowing for direct control of the Atomx XYZ P&T

the Chromeleon CDS e-panel allowing for direct control of the Atomx XYZ P&T is shown in Figure 1. The fully optimized method used within this application note together with the eWorkflow™ are available for download in the Thermo Scientific™ AppsLab application note repository (www.appslab.com). Chromeleon CDS eWorkflow can be easily imported into the CDS allowing the users to start a sequence, process the data, and generate results with only few clicks.

Standard and sample preparation

To produce standards and simulated water samples, standard mixes were spiked into reagent water. 8260B MegaMix® (P/N 30633), VOA (Ketones) (P/N 30006), and 502.2 Calibration Mix (P/N 30042) were purchased from Restek. The three mixes were combined and serially diluted using purge and trap grade methanol (Honeywell/Burdick & Jackson, P/N 232-1L) to obtain three working solutions at 500, 50, and 10 ppm. The full list of analyzed compounds is reported in Appendix 1 (to view this table, please see the application note on Analysis of VOCs in Water at thermofisher.com/GC-MS).

Internal standards, fluorobenzene (P/N 30030), chlorobenzene-d_5 (P/N 30074) and 1,4-dichlorobenzene-d_4 (P/N 30074) as well as surrogates standards dibromofluoromethane (P/N 30240), toluene-d_8 (P/N 30240), and 4-bromofluorobenzenewere (P/N 30240) were purchased from Restek and diluted in methanol to a final concentration of 25 ppm.

A calibration curve was prepared diluting the working solutions with reagent water to obtain nine calibration levels ranging from 0.5 to 200 ppb. Each calibration level (5 mL) was spiked with ISTD and surrogate standards (final concentration 25 ppb). The ISTD and surrogate standards were used to calculate the relative response factor (RRF) for each compound.

Method detection limit (MDL) and peak area repeatability were assessed by using n=7 standards at 0.5 ppb. Water standards (n=7) were prepared for the instrument check (20 ppb) and used to assess method precision and accuracy.

Results and discussion

Chromatography

Chromatographic separation was achieved for the 66 target compounds in 12 minutes. The effective water removal of the Atomx XYZ P&T combined with the superior inertness of the TraceGOLD VMS column allowed for reduced moisture entering the GC system, resulting in good peak shape and adequate peak separation. The excellent peak shape and resolution allowed easier quantitation and helped achieve lower detection limits. An example of chromatography for a 5 ppb VOC standard in water is reported in Figure 2.

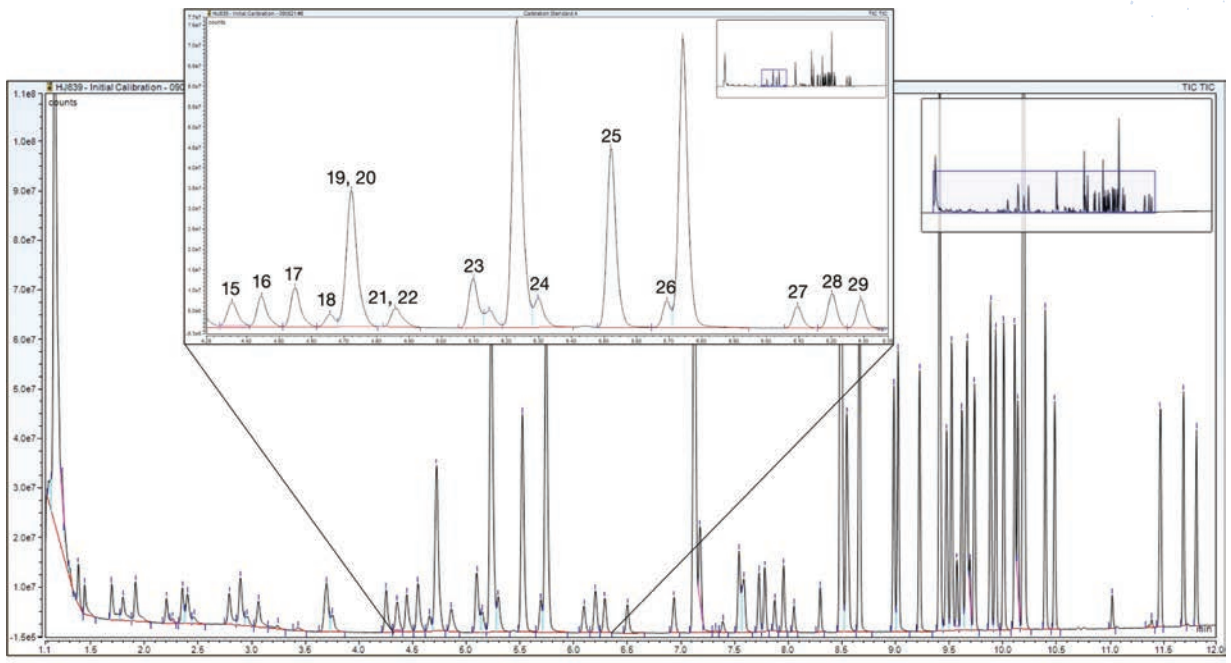
Linearity and sensitivity

Linearity was assessed by injecting nine calibration levels ranging from 0.5 ppb to 200 ppb. Good linearity was obtained with average coefficient of determination (R^2) of >0.99 and average response factor %RSD (AvCF %RSD) <20, confirming the liner trend across the specified concentration range and meeting the method requirements. The MDL and precision were assessed using n=7 reagent water samples spiked at 0.5 ppb. MDLs were <0.27 ppb with the calculated amount within 10% of the expected values. This is below the lowest acceptance criteria 0.6 ppb defined in the method. R^2 as well as AvCF %RSD, calculated MDL, and amounts are reported in Appendix 1.

Figures 3 and 4 show examples of Chromeleon CDS results browser with extracted ion chromatograms for 2-dibromo-3-chloropropane and 1,3,5-trimethylbenzene, respectively, at 0.5 ppb as well as the measured vs. NIST 20 library spectrum comparison and the calibration curve over a concentration range of 0.5 to 200 ppb. Excellent sensitivity and linearity were obtained with S/N >3 at 0.5 ppb (except for methylene chloride, which is a known laboratory contaminate), R^2 value above 0.99, and average response factor RSD <20%. The Thermo Scientific™ XLXR™ detection system on the ISQ 7610 GC-MS provides an extensive linear dynamic range allowing for extended calibration curves. The detector also has an extended lifetime, which significantly reduces the need for replacement.

Precision and accuracy

Precision and accuracy were assessed by using n=7 replicates of reagent water spiked at 20 ppb. For all compounds, the calculated amount was within 20% of the spiked concentration



Peaks:

15. 2,2-Dichloropropane	20. 1,1,1,-Trichloroethane	25. Fluorobenzene (ISTD)
16. Bromochloromethane	21. 1,1-Dichloropropene	26. Trichloroethene
17. Chloroform	22. 2-Butanone (MEK)	27. Dibromomethane
18. Carbon Tetrachloride	23. Benzene	28. 1,2-Dichloropropane
19. Dibromofluoromethane (SURR)	24. 1,2-Dichloroethane	29. Bromodichloromethane

Figure 2. Total ion chromatogram (TIC) obtained for reagent water spiked at 5 ppb. The inset highlights an example of peak shapes and resolution with minimal water interference.

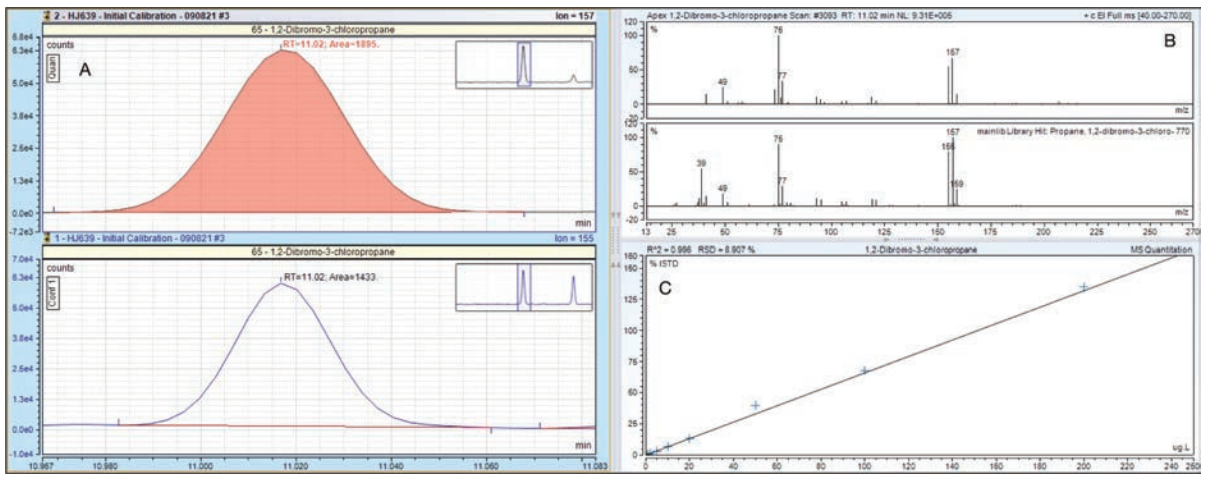


Figure 3. Chromeleon CDS results browser showing extracted ion chromatograms for 2-dibromo-3-chloropropane in the 0.5 ppb water standard, quantitation ion (m/z= 157) and one confirming ion (m/z = 155) (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.5 ppb to 200 ppb (C)

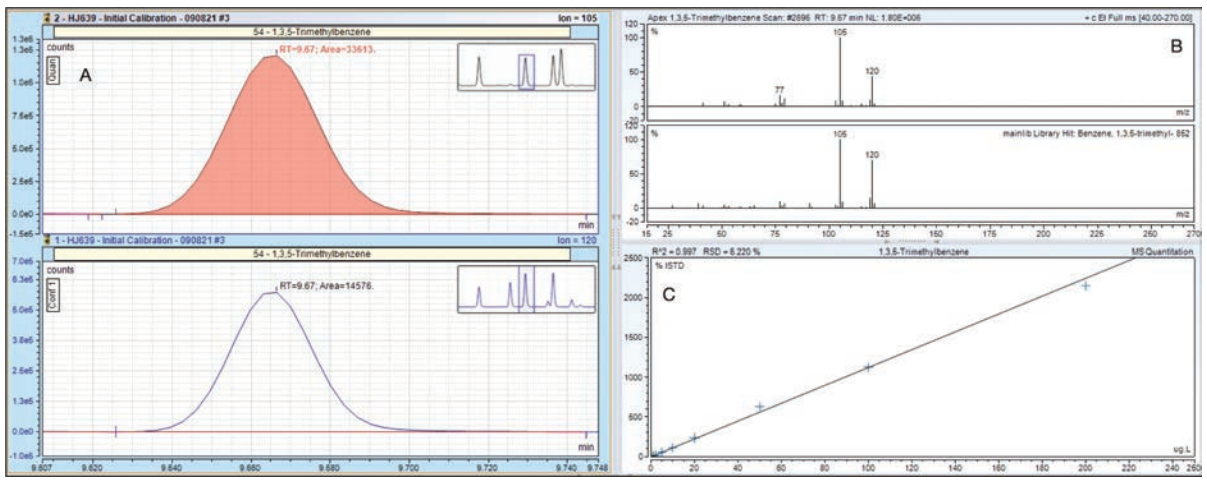


Figure 4. Chromeleon CDS results browser showing extracted ion chromatograms for 1,3,5-trimethylbenzene in the 0.5 ppb water standard, quantitation ion (m/z =105) and one confirming ion (m/z = 120) (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.5 ppb to 200 ppb (C)

with a mean recovery ±30% of the true value, which is an acceptance criterion for HJ 639. Results are detailed in Appendix 1. Figure 5 shows a cross section of compounds in the water standard at 20 ppb, demonstrating good accuracy and precision.

Method robustness

For use as an analytical testing method, it is extremely important that the analytical method is stable and reproducible. To demonstrate this, QC standards (n=22) at 20 ppb were injected at intervals over a 137-sample injection sequence which ran over four days. The samples were acquired with no user intervention on the P&T, GC, or MS system, and the absolute peak areas were plotted to demonstrate the stability of the results. Figure 6 shows the repeatabilty of five of the compounds of the 22 QC standards injected over the 137-sample injection sequence with excellent percentage RSDs. The accuracy and precision for every compound in the 22 QCs ran over 137 injections are shown in Appendix 2 (to view this table, please see the application note on Analysis of VOCs in Water at thermofisher.com/GC-MS).

Conclusion

The results shown in this study demonstrate that the TRACE 1610 GC coupled to the ISQ 7610 single quadrupole MS and the Atomx XYZ P&T provides a suitable tool for analytical testing laboratories analyzing environmental water samples in compliance with the HJ 639 method.

- The ISQ 7610 VPI coupled with the Teledyne Tekmar Atomx XYZ P&T exceeds all the requirements outlined in the HJ 639 method for analysis of VOCs in water.
- Excellent chromatography was obtained with good peak shape and baseline resolution for most of the compounds due to the effective water management of the Atomx XYZ P&T and the high inertness of the TraceGOLD TG-VMS column.
- The XLXR electron multiplier detector on the ISQ 7610 GC-MS provided a wider linear dynamic range allowing for extended calibration curves (0.5–200 ppb) and excellent linearity for all compounds with R^2 >0.99 and AvCF %RSD <10, confirming a good linear trend.
- Calculated MDLs for n=7 reagent water samples spiked at 0.5 ppb were <0.25 ppb for most of the compounds with no interference from unwanted water entering the system.
- Precision and accuracy for n=7 reagent water samples spiked at 20 ppb showed excellent results with calculated amounts ±20% the spiked concentrations and mean recovery of 97% for the compounds.
- System robustness was demonstrated by acquiring 22 QC water spikes at 20 ppb at regular intervals over 137 consecutive injections of water samples corresponding to four days unattended operation with no user intervention. The average %RSD of the calculated concentration was 7.9% with an average compound recovery of 98%.

References

1. Method 8260 Measurement of Volatile Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry https://www.epa.gov/sites/production/files/2017-04/documents/method_8260d_update_vi_final_03-13-2017.pdf
2. Thermo Scientific AppsLab Library (https://appslab.thermofisher.com/)

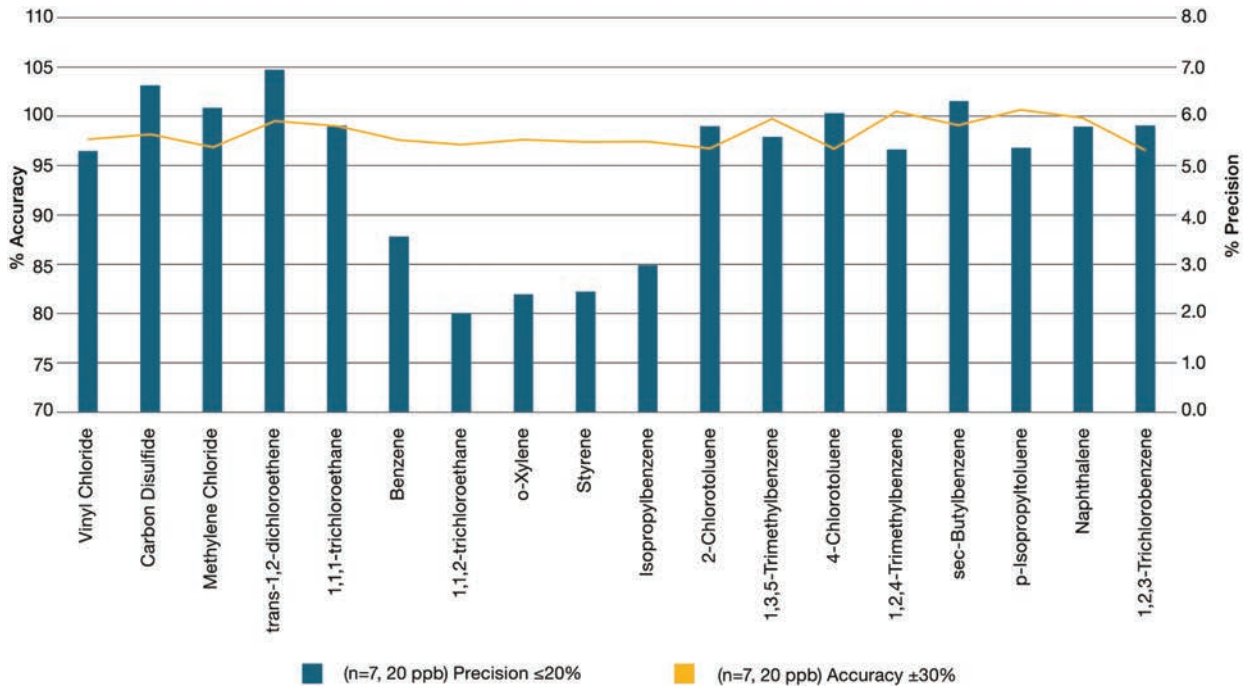


Figure 5. Accuracy (% recovery) and precision obtained by analyzing n=7 replicates of water standard at 20 ppb

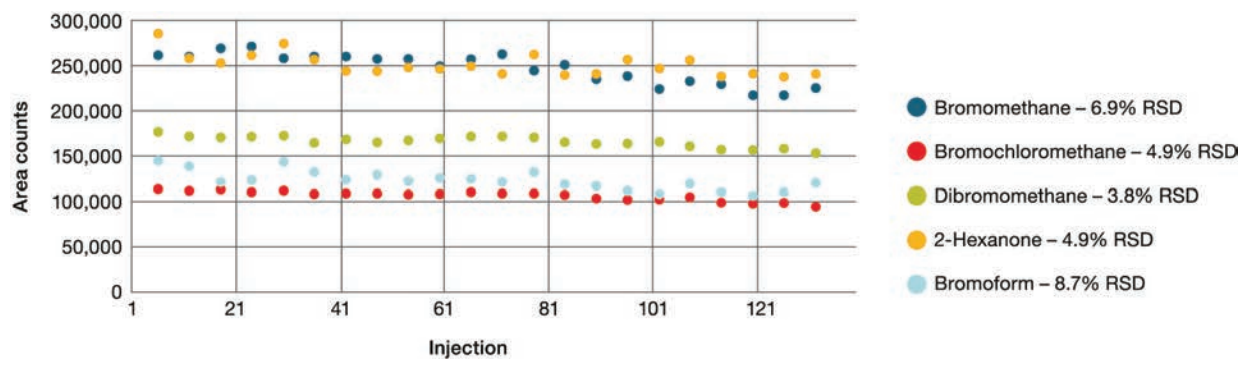


Figure 6. Repeatability (absolute peak area) of 22 QC 20 ppb water standards assessed at regular intervals over n=137 consecutive sample injections corresponding to four days of analysis

Author Contact Details

Terry Jeffers[1], Adam Ladak[2], and Amy Nutter[3]

[1]Thermo Fisher Scientific, USA, [2]Thermo Fisher Scientific, UK, [3]Teledyne Tekmar, Mason, OH, USA

• Email: CMD.APACMarketing@thermofisher.com • **Web: thermofisher.com/GC-MS**