White Paper 051
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Monitoring disinfection by-products in water using thin-film SPME coupled with GC×GC and BenchTOF MS

Thin-film solid-phase microextraction (TF-SPME) with comprehensive two-dimensional gas chromatography and BenchTOF™ time-of-flight mass spectrometry (GC×GC–TOF MS) provides efficient non-target screening of organic pollutants in water. Here, water samples were analysed before, during and after treatment with a water purification system, to determine compositional differences.

Introduction

Water pollution occurs when harmful substances (chemicals or microorganisms) contaminate streams, rivers, lakes or other bodies of water, which can lead to degradation of water quality. As water is able to dissolve more substances than any other liquid, it is uniquely vulnerable to pollution. Although organic pollutants are typically found at low concentration levels, continued exposure to these compounds could have a detrimental effect on living organisms.

A number of different physical, biological and chemical processes are used for removing undesirable substances from water, including filtration, coagulation and disinfection. Chlorine is the most widely used disinfectant for water supplies in many countries;[1] when chlorine or bromine are added to water, compounds such as hypochlorous acid and hypobromous acid can react with naturally occurring organic matter to create halogenated disinfection by-products (DBPs). Investigations into how DBPs affect human health are of significant interest in the US and Europe, making it important to monitor their presence in drinking water.

Several sample preparation techniques can concentrate analytes in water samples, including solid-phase microextraction (SPME), which is favoured as a solvent-free 'green' technique. In recent years, thin-film solid-phase microextraction (TF-SPME) has been shown to provide improved extraction efficiency and sensitivity compared to conventional SPME. The technique uses a substrate, in this case carbon mesh sheets, impregnated with sorbent phase(s) and works on the same principles as conventional fiber-based SPME, but the planar geometry and greater sorbent thickness (>40 µm) result in a significantly greater extraction phase volume and surface area-to-volume ratio. After sampling, TF-SPME membranes are placed inside empty thermal desorption (TD) tubes (Figure 1), where they benefit from trap-based focusing and optional re-collection of the split flow using Markes' TD systems, prior to desorption onto a GC(–MS).

However, improved extraction capability often results in more complex chromatograms. Here, we demonstrate the use of comprehensive two-dimensional gas chromatography coupled with BenchTOF time-of-flight mass spectrometry (GC×GC–TOF MS), which offers enhanced separation of complex water samples, allowing confident identification of compounds that would co-elute in conventional 1D GC.

Finally, streamlined non-target workflows are required to allow fast and efficient comparison of water samples from different sources. In this study, ChromCompare+ chemometrics software was used to automatically identify the key differences between water samples collected before and after filtration processes, to quickly highlight compounds of potential concern.

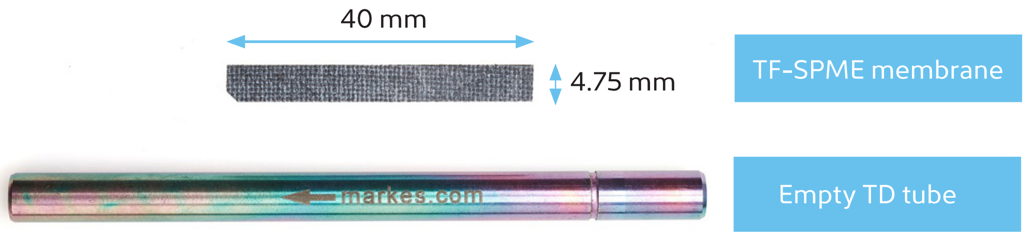


Figure 1
The TF-SPME membrane is desorbed within an empty TD tube using Markes' thermal desorbers.

Experimental

Full analytical procedures are described by Murtada et al.[2]

Samples: Water samples were collected from a house in Waterloo, ON, Canada (May 2021) – raw water (before purification treatment), water after addition of softener (during purification treatment) and drinking water (after purification treatment). Each sample was analysed in replicate (n = 5).

TF-SPME: Hydrophilic-lipophilic balanced/polydimethylsiloxane (HLB/PDMS)-coated TF-SPME membranes (Markes International).

TD: Instrument: UNITY-xr™ (Markes International); Tube desorb: 10 min at 250°C and 50 mL/min trap flow; Focusing trap: Material Emissions (Markes International).

GC×GC: INSIGHT® flow modulator (SepSolve Analytical); Modulation period (P_M) = 5 s.

TOF MS: BenchTOF mass spectrometer (SepSolve Analytical); Mass range: m/z = 30–600.

Software: ChromSpace® software (SepSolve Analytical) for full instrument control and processing, with chemometric comparisons by ChromCompare+ (SepSolve Analytical).

Please contact SepSolve for full analytical parameters.

Results and discussion

In this study, GC×GC–TOF MS was used to analyse three classes of different water samples, with the aim of identifying compositional differences before, during and after treatment with a water purification system.

An example GC×GC–TOF MS chromatogram for each class of water is provided in Figure 2. It is clear that GC×GC–TOF MS provides enhanced separation compared to conventional GC analysis.

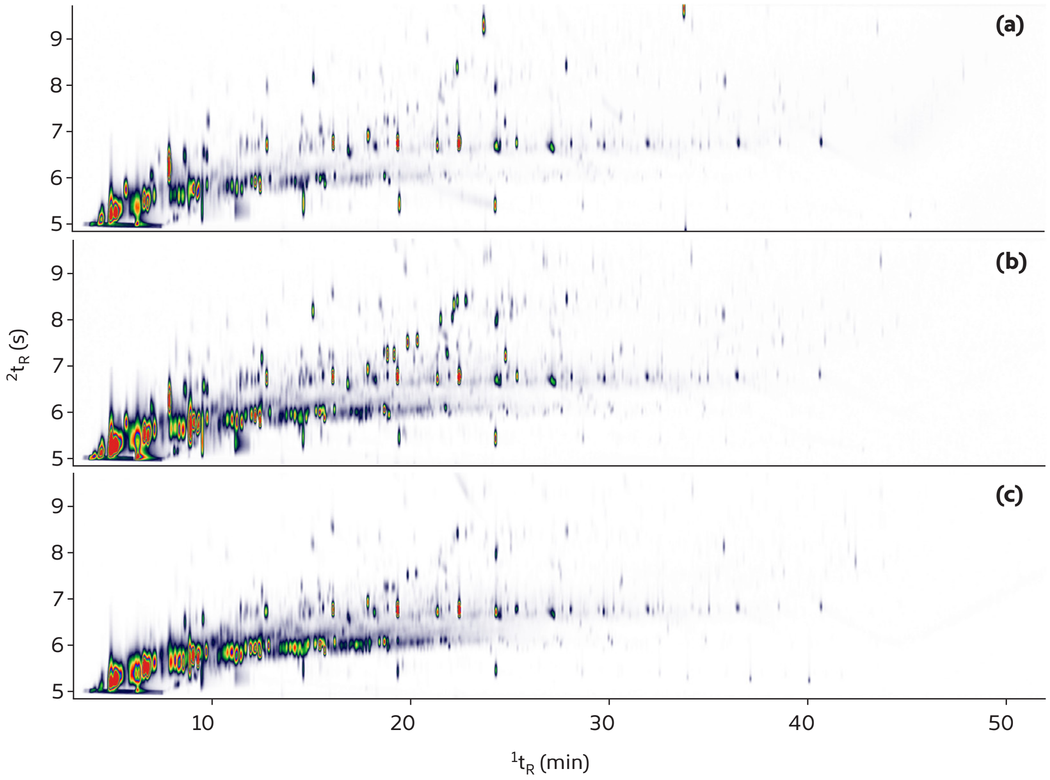


Figure 2

GC×GC–TOF MS colour plot for TF-SPME (a) before, (b) during and (c) after a water purification treatment.

Figure 3 shows an enhanced region of the colour plot for a sample of raw water (before treatment), with multiple co-elutions that would have occurred in 1D GC resolved. The physical separation of peaks provides cleaner spectra, which, when using BenchTOF mass spectrometers, can be directly compared to commercial libraries (such as NIST and Wiley) for confident identification.

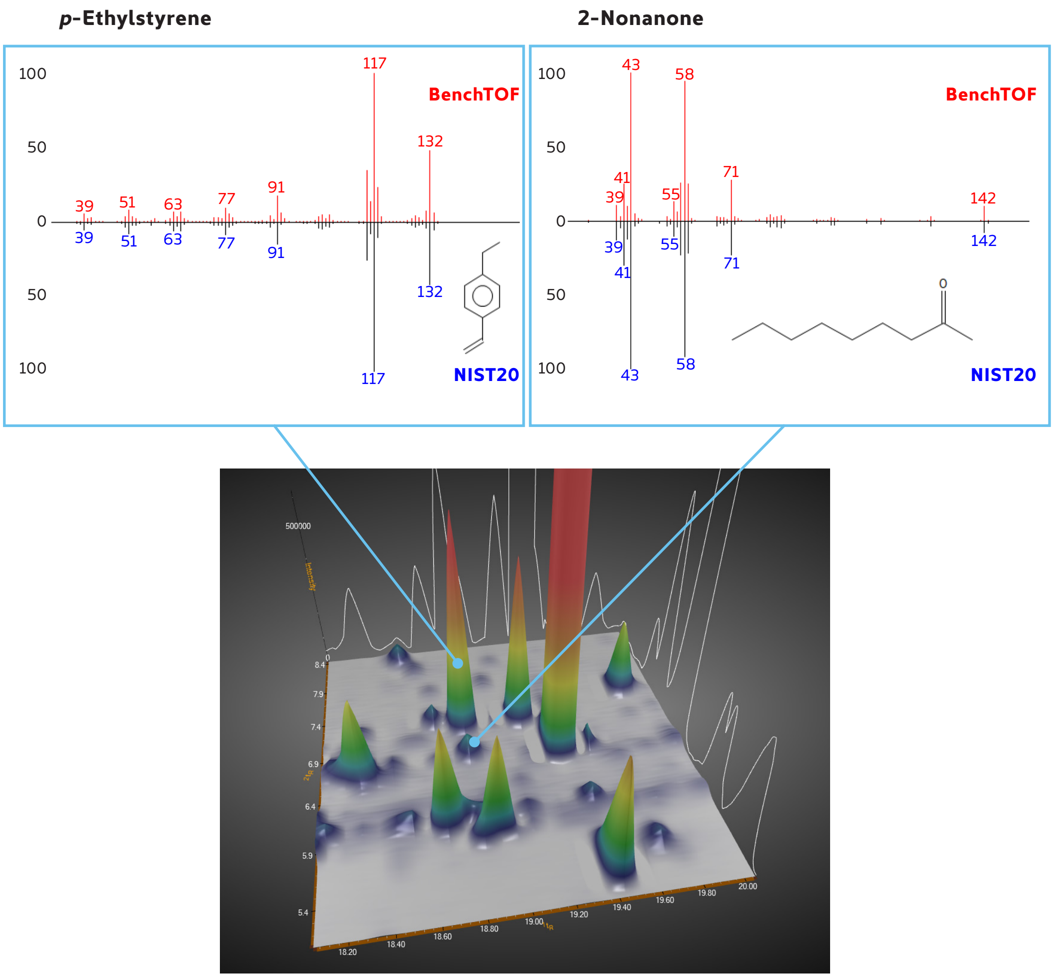


Figure 3
Surface chart showing an enhanced region of the chromatogram for a raw water sample, highlighting the improved separation and identification capability of GC×GC–TOF MS.

In fact, over 1000 individual peaks were detected in each GC×GC–TOF MS chromatogram. Despite this, analysis of a blank TF-SPME membrane showed minimal carryover, with only a series of siloxanes evident in the blank chromatogram (Figure 4). This indicates efficient desorption of the analytes from both the TF-SPME and the focusing trap within the thermal desorber.

Due to the sample complexity, automated data processing was also an imperative part of the workflow. To determine the significant differences between each class of water, non-target workflows were used in ChromCompare+ software to compare all of the raw data.

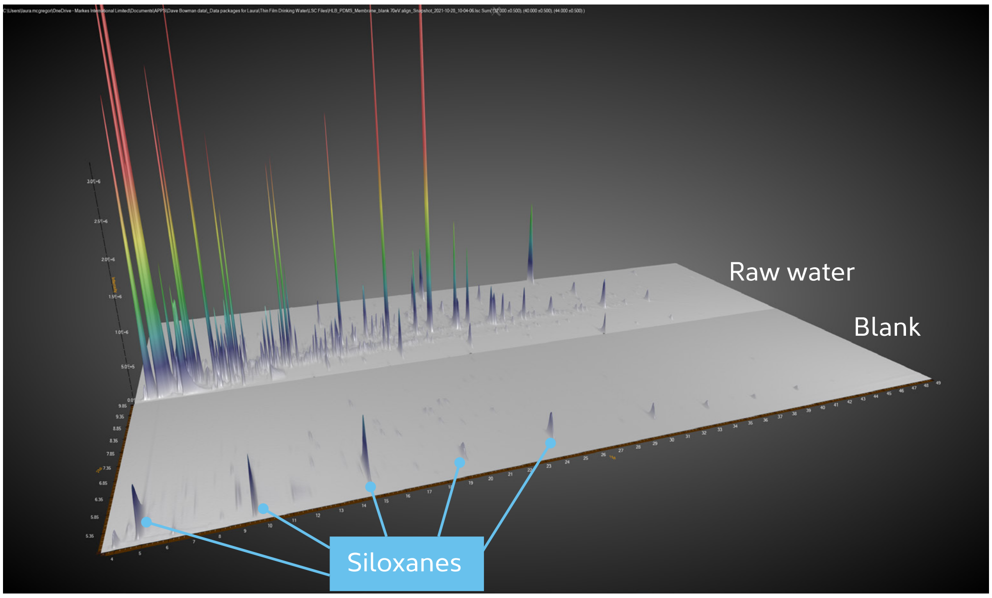
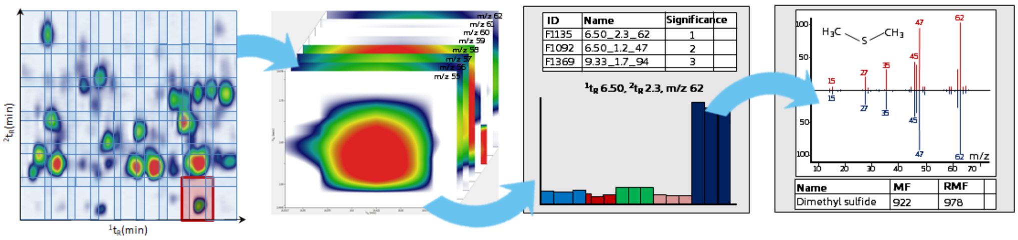


Figure 4

Comparison of the GC×GC–TOF MS surface charts for analysis of a raw water sample (top) and a blank TF-SPME membrane (bottom).

Firstly, the chromatograms were automatically aligned to a user-defined reference chromatogram. A tile-based approach was then used to compare the datafiles (Figure 5). Here, the software splits each chromatogram into small tiles and compiles all of the analytical features present within each tile, by examining the signal for every m/z channel in every tile across every chromatogram. By using all of the raw data in these automated workflows, data processing is accelerated, while also reducing the chance of missing important details. Finally, the Feature Discovery tool was used to find the most significant differences between the sample classes, enabling these differences to be identified based on the retention times and m/z channel of the tile they were found in.



ID	Name	Significance	
F1135	6.50_2.3_62	1	
F1092	6.50_1.2_47	2	
F1369	9.33_1.7_94	3	

Name	MF	RMF	
Dimethyl sulfide	922	978	

Aligned chromatograms are automatically split into small (overlapped) tiles

Every m/z channel is automatically compared for every tile of every datafile

Feature Discovery highlights the key differences between sample classes

The key features can then be reviewed and identified, minimising manual steps

Figure 5

The untargeted, tile-based workflow used in ChromCompare+ software.

The resulting principal components analysis (PCA) score plot in Figure 6 shows distinct clusters between the different classes of drinking water samples, indicating that there are compositional differences.

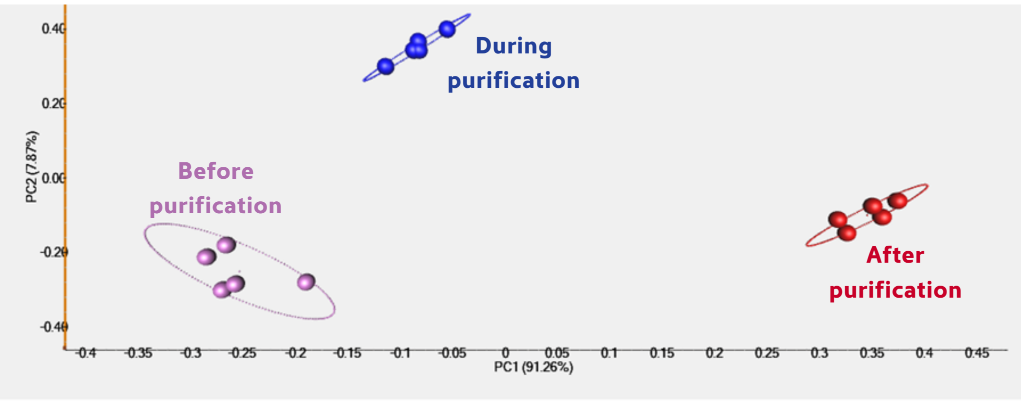


Figure 6

Principal components analysis (PCA) score plot in ChromCompare+ showing the differentiation between water classes.

Figure 7 shows two key differences identified between the water classes. Firstly, an increased abundance of bromodichloromethane was found in raw water prior to purification treatment. Bromodichloromethane is typically a by-product of water disinfection and an important difference to identify as the compound is designated as 'likely to be carcinogenic to humans'.[3]

Benzothiazole was also found at significantly increased levels in the raw water. Benzothiazole is a heterocyclic aromatic that is used in a wide variety of industrial applications and consumer products, and has been reported as a ubiquitous contaminant in waste water and drinking water.[4]

A number of other visualisations can be used in ChromCompare+ to display trends and differences between samples, such as volcano plots (Figure 8). Here, the drinking water samples are compared to the water samples collected before and during purification treatment. A number of halogenated species were found to be in increased levels in both the 'before' and 'during' samples (blues), such as trichloroethylene and dibromomethane. Trichloroethylene is a widely used industrial solvent, while dibromomethane is a potential disinfectant by-product. On the other hand, the features found in increased levels in the drinking water only were simple hydrocarbons such as 4-octene.

These results clearly show that robust sampling by TF-SPME combined with TD–GC×GC–TOF MS and smart software tools is an effective approach for comparing water samples from different sources to find DBPs or other pollutants.

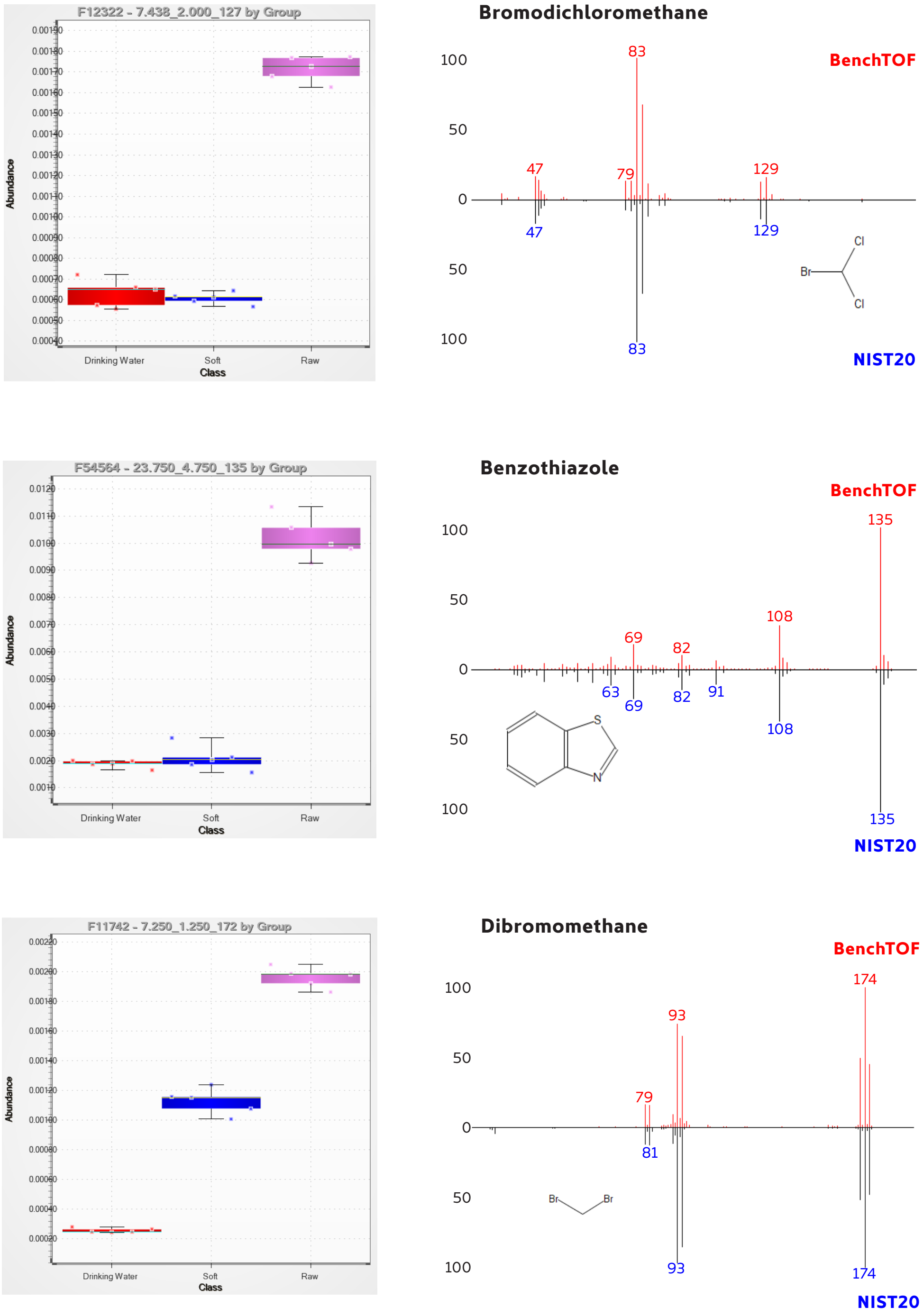


Figure 7

Box and whisker plots in ChromCompare+ showing increased levels of bromodichloromethane, benzothiazole and dibromomethane in raw water samples (‘before’ purification treatment) compared to ‘during’ and ‘after’ treatment.

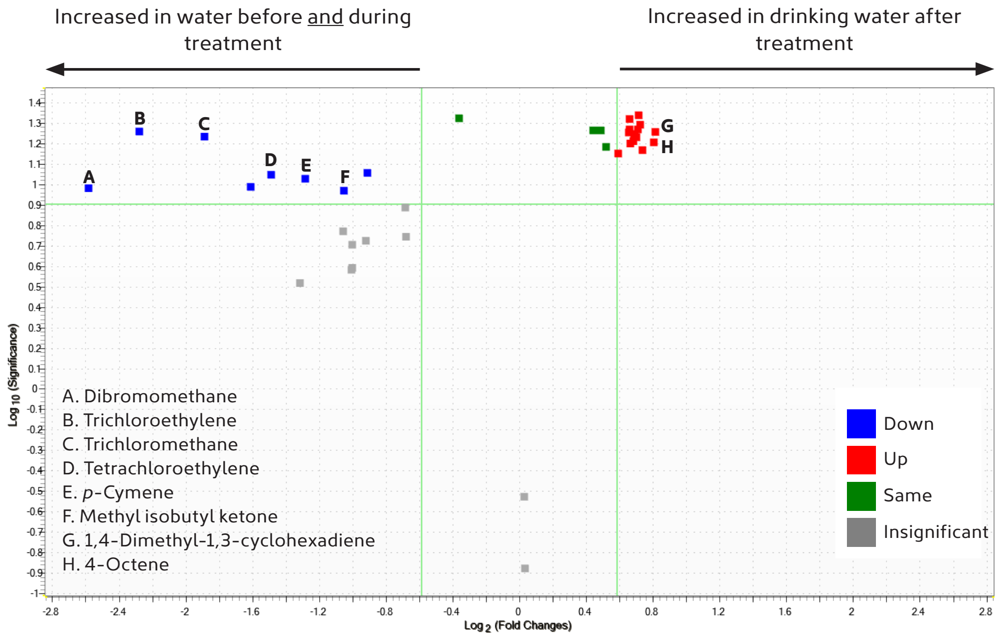


Figure 8

Volcano plot in ChromCompare+ showing features increased in the water samples obtained before and during treatment (blue) and those increased in the drinking water samples after treatment (red). Identifications are provided for a selection of the features. Note that some features represented the same compounds found in adjacent/overlapped tiles.

Conclusions

This study has shown that the TF-SPME–GC×GC–TOF MS system provides:

- Efficient and sensitive extraction of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) from water samples by TF-SPME, while desorption by Markes' thermal desorbers provides secondary refocusing for excellent chromatographic performance and optional split re-collection.
- Enhanced separation by GC×GC using INSIGHT consumable-free flow modulation for improved discovery of sample composition.
- Confident identification of organic compounds in water through the sensitive detection and excellent spectral quality of BenchTOF mass spectrometers.
- Easy-to-use, automated workflows in ChromCompare+ software for fast comparison of complex water samples.

For more information on this application, or any of the techniques or products used, please contact SepSolve Analytical.

Acknowledgements

SepSolve Analytical kindly acknowledges Dr Khaled Murtada and Prof. Janusz Pawliszyn from the Department of Chemistry at the University of Waterloo (Canada) for their collaboration on this study.

References

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