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RAPID ANALYSIS OF ORGANOCHLORINE COMPOUNDS IN WATER USING AUTOMATED SIFT-MS

Combining the power of direct analysis using selected ion flow tube mass spectrometry (SIFTMS) and GERSTEL automation, headspace analysis of chlorinated volatile organic compounds (VOCs) in water is greatly simplified. This application note demonstrates the linearity and and repeatability achievable with automated SIFT-MS. The sample throughput achievable with SIFTMS is at least three-fold higher than traditional purge-and-trap gas chromatography methods.

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INTRODUCTION

Organochlorine compounds such as chloroform, trichloroethylene (TCE), and tetrachloroethylene (perchloroethylene, PCE) found widespread use in diverse industries in the 20th century. Although usage is now greatly reduced, these compounds continue to be significant contaminants in air, soil, and water.

The purge and trap approach is most commonly applied for analysis of these chlorinated VOCs in water, followed by gas chromatography analysis coupled with either electron capture detection (GC-ECD) or mass spectrometry (GC-MS). Not only are these methods slow, but the GC requires that moisture is removed prior to analysis. The cumulative price paid by the laboratory for these requirements is low sample throughput.

In contrast, application of SIFT-MS accelerates analysis through direct headspace analysis. That is, SIFT-MS eliminates the need to purge, trap, and dry the sample, in addition to significantly reducing sample analysis time. In this application note, we describe the simplified, direct SIFT-MS analysis of chloroform, TCE and PCE in drinking water headspace. Using the approach described here, at least 12 samples per hour can be analyzed.

METHOD

1. The SIFT-MS technique

SIFT-MS[1,2,3] (Figure 1) uses soft chemical ionization (CI) to generate mass-selected reagent ions that can rapidly quantify VOCs to low parts-per-trillion concentrations (by volume, pptv). Eight reagent ions (H_3O^+, NO^+, O_2^+, O^-, OH^-, O_2^-, NO_2^- and NO_3^-) obtained from a microwave discharge of moist or dry air, are now applied in commercial SIFT-MS instruments. These eight reagent ions react with VOCs and other trace analytes in well-controlled ion-molecule reactions, but they do not react with the major components of air (N2, O2 and Ar). This allows for real-time analysis of air samples at trace and ultra-trace levels without pre-concentration, and results compare well with gas chromatography mass spectrometry (GC-M S).[4]

Rapid switching between reagent ions provides high selectivity, because the multiple reaction mechanisms provide additional independent measurements of each analyte. The multiple reagent ions also help to remove uncertainty from isobaric overlaps in mixtures containing multiple analytes.

Analyses were run in Selected Ion Mode (SIM) for the compounds of interest on a Voice200ultra SIFT-MS instrument (Syft Technologies, Christchurch, New Zealand). Instrument methods were created using the Method Editor module in the LabSyft software package from Syft Technologies.

2. Automated SIFT-MS analysis

In SIFT-MS, the capability for rapid direct analysis of a sample provides unique opportunities for high-throughput headspace analysis, irrespective of whether the task is routine VOC monitoring or the analysis of chromatographically-challenging species, such as ammonia and formaldehyde. In contrast to chromatographic techniques that require rapid injection to achieve good peak shapes and temporal separation, SIFTMS simply requires steady sample injection for the
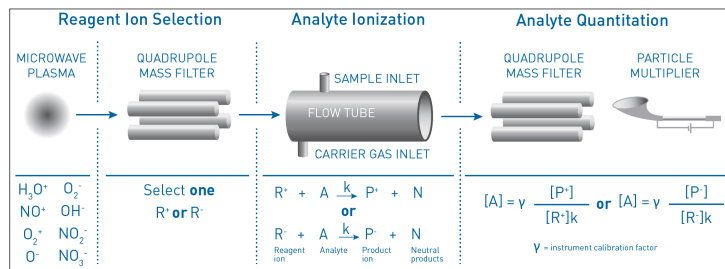
Figure 1. Schematic diagram of SIFT-MS – a direct chemical-ionization analytical technique.
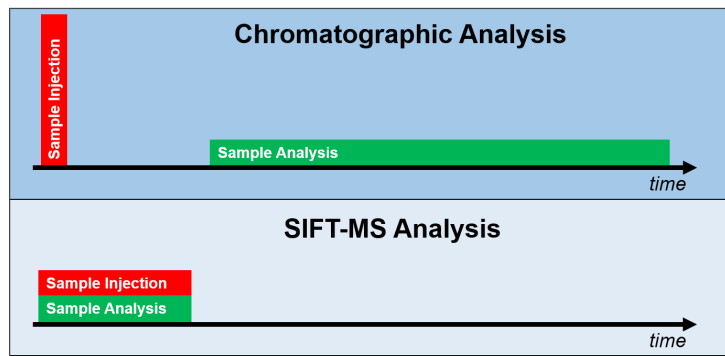

Figure 2. Graphical representation of the different sample-injection and analysis requirements of chromatographic techniques and SIFT MS.
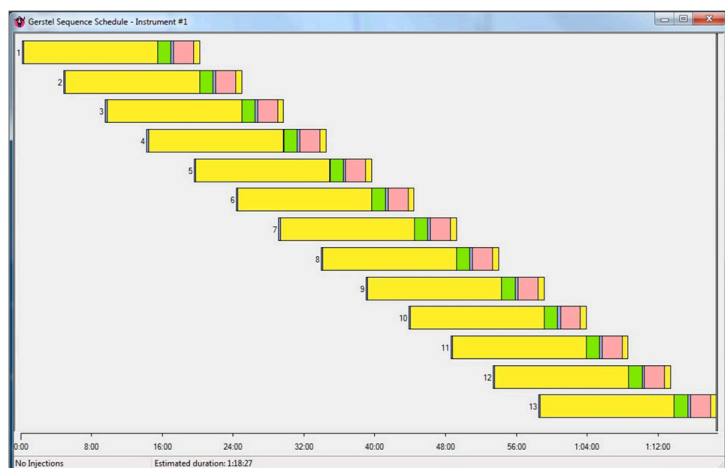

Figure 3. Sequence tables from the GERSTEL Maestro software for analysis of 13 water headspace samples using SIFT-MS. A throughput of at least 12 samples per hour is achieved.

duration of the analysis – that is, sample injection and analysis occursimultaneously (Figure 2).

Automated headspace analysis was carried out at Anatune's laboratory using the above SIFT-MS instrument coupled with a GERSTEL MPS2 autosampler (GERSTEL, Mülheim an der Ruhr, Germany). Samples were first incubated in a GERSTEL agitator prior to sampling of the headspace and injection into the SIFTMS instrument through a GERSTEL septumless sampling head.

The GERSTEL MPS2 autosampler was controlled using GERSTEL's Maestro software. In addition to controlling the injection into the SIFT-MS instrument, the Maestro

software's PrepAhead function allows for optimal scheduling of pre-injection preparation steps, such as syringe flush or incubation. This ensures that the highest sample throughput is achieved for the conditions described in this application note (Figure 3). In this figure, the different colors represent different actions that the autosampler undertakes, including vial movements, incubation, sample injection and syringe flushing. With the hardware and method conditions used here, throughputs of at least 12 samples per hour are achieved with hardware optimized for chromatographic analysis.

3. Samples and analysis conditions

Standards containing chloroform, trichloroethylene, and tetrachloroethylene were prepared from a 1,000-ppm solution in methanol. From this stock solution, 10 μL was transferred into 10 mL of water to make a 1-ppm standard solution. The solutions for linearity and repeatability measurements were prepared by taking 20 μL, 50 μL, 100 μL, 250 μL, 500 μL, 750 μL and 1,000 μL aliquots and filling them to a total of 10 mL in water in 20-mL headspace vials. This yielded solutions ranging in concentration from 2 to 100 ppl.

The solutions were incubated for 15 minutes at 60 ℃. Headspace was sampled using a 2.5-mL headspace syringe (heated to 150 ℃; fill speed of 200 μL s^{-1}) and injected into the SIFT-MS instrument's inlet at a flow rate of 50 μL s^{-1} (together with nitrogen make-up gas, giving a total flow rate of ca. 420 μL s^{-1}).

RESULTS AND DISCUSSION

Figure 4 shows the results obtained when water headspace containing chloroform, trichloroethylene, and tetrachloroethylene is injected into the inlet of the SIFT MS instrument as a function of concentration in solution (2 to 100 ppb). These data illustrate the very stable injection by the autosampler and measurement by the SIFT-MS instrument, since every data cycle is equivalent to a single chromatographic analysis (but with a run time of 3.8 seconds). The error bars are two standard deviations (2 s.d.) of the repeated measurements made during a single sample injection.

Linearity is determined from the data in Figure 4, as shown in the linearity curves of Figure 5. Linearity of the direct SIFT-MS headspace analysis is excellent.

Repeatability was investigated using six replicate samples at a concentration of 50 ppb in solution (Figure 6). The error bars shown on the individual replicate
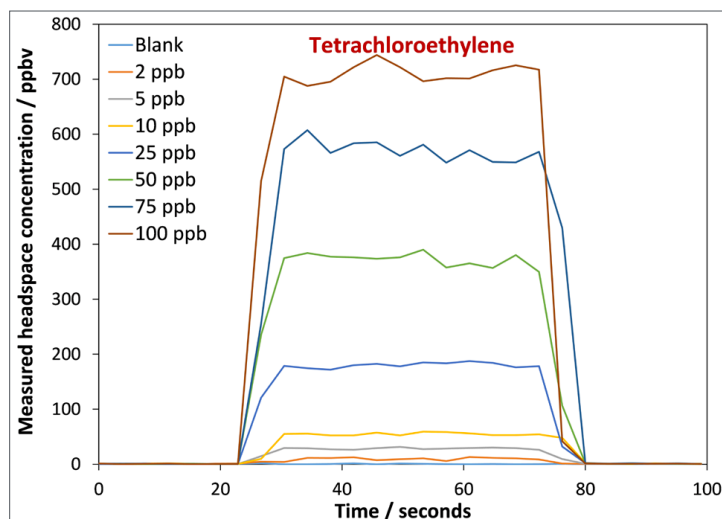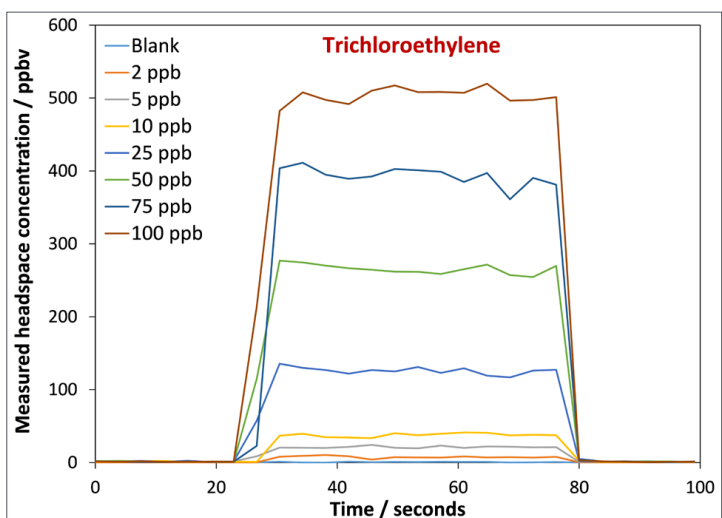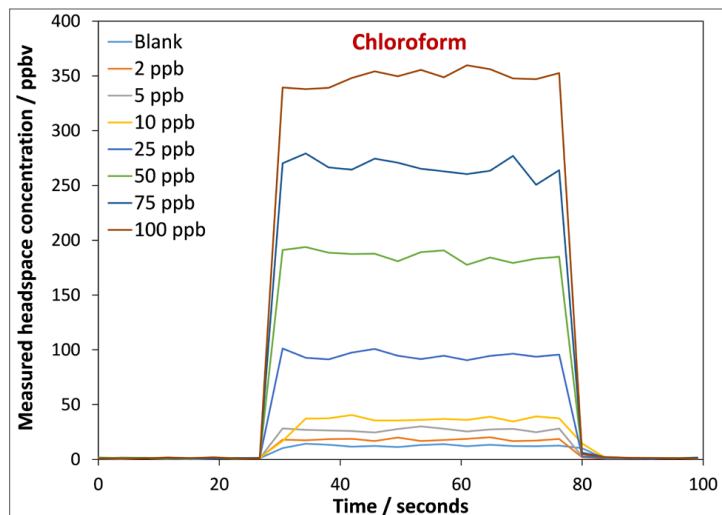
Figure 4. SIFT-MS selected ion mode analysis of (a) chloroform, (b) trichloroethylene (TCE), and (c) tetrachloroethylene (PCE) from water headspace injected continuously into the instrument inlet.

measurements are 2 s.d. of the individual data points measured during sample injection (c.f. Figure 4). The relative standard deviations (RSDs) determined from the six replicate injections were 3.3%, 1.8%, and 1.5% for chloroform, trichloroethylene, and tetrachloroethylene, respectively (Table 1), which easily meets standard industry method acceptance criteria.

All 13 samples in this study (linearity and repeatability) were analyzed within 80 minutes (Figure 3). This equates to a throughput of 12 samples per hour, including sample preparation (incubation) and analysis, which is at least threefold faster than purge and trap-GC-MS.
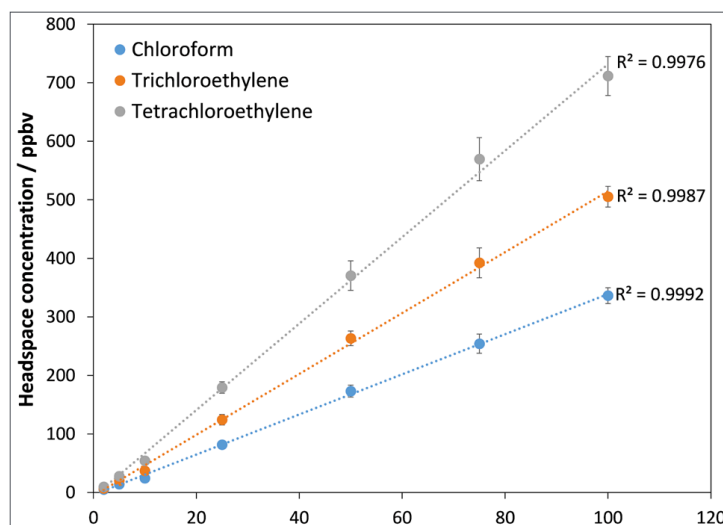

Figure 5. SIFT-MS measurement linearity for direct water headspace analysis of chloroform, trichloroethylene (TCE), and tetrachloroethylene (PCE).
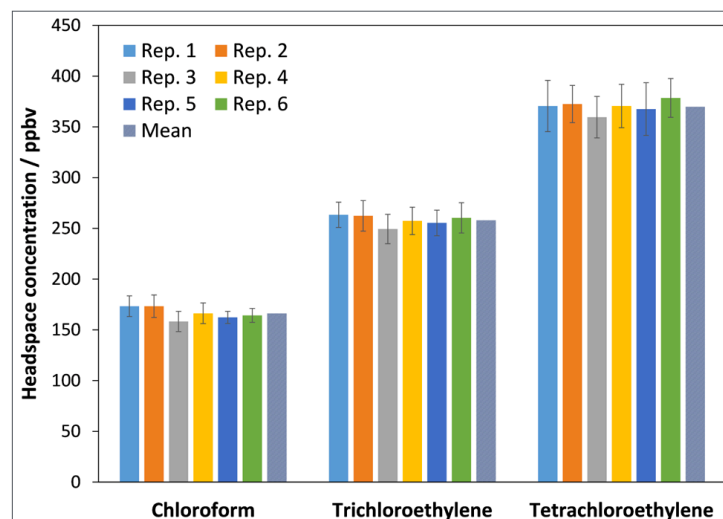

Figure 6. SIFT-MS measurement repeatability for direct water headspace analysis of 50-ppb solutions of chloroform, trichloroethylene, and tetrachloroethylene. Error bars are 2 s.d. of the individual data points measured during sample injection (Figure 4).

PARAMETER	MEASURED CONCENTRATION / PPBV			2 X STANDARD DEVIATIONS / PPBV		
	Chloroform	Trichloroethylene	Tetrachloroethylene	Chloroform	Trichloroethylene	Tetrachloroethylene
Rep. 1	173	263	371	10.2	12.5	25.2
Rep. 2	173	262	373	11.1	15.1	18.3
Rep. 3	158	249	360	9.96	14.5	20.4
Rep. 4	166	257	371	10.2	13.5	21.4
Rep. 5	162	255	368	5.96	12.6	26
Rep. 6	164	260	379	6.84	14.9	19.1
Mean	166	258	370			
SD	5.5	4.7	5.7			
%RSD	3.3	1.8	1.5			

Table 1. Measured headspace concentrations (in ppbv) for the six replicate analyses of 50-ppb aqueous solutions and relative standard deviations (RSDs).

CONCLUSIONS

This study demonstrates that SIFT-MS is a very powerful new technique for rapid determination of chlorinated VOCs in water. Direct headspace analysis using automated SIFT-MS is possible because of the robustness to humidity, providing sensitive, linear, and repeatable quantitation. SIFT-MS provides substantial throughput increases over traditional purge and trap-GC methods, since no preconcentration or drying is required.

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