

RAPID ANALYSIS OF BTEX IN WATER USING AUTOMATED SIFT-MS

Selected ion flow tube mass spectrometry (SIFT-MS) combined with GERSTEL automation greatly simplifies analysis of benzene, toluene, ethylbenzene and the xylenes (BTEX) in water. This application note demonstrates the linearity, repeatability and sensitivity achievable with automated SIFT-MS. Automated static headspace (SH)-SIFT-MS provides sample throughputs at least three-fold higher than traditional purge-and-trap-gas chromatography methods.

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INTRODUCTION

Various technologies have been employed to analyze the aromatic hydrocarbons benzene, toluene, ethylbenzene and xylenes (collectively known as BTEX) for different matrices. The purge and trap approach is most commonly applied for analysis of BTEX compounds in water, followed by gas chromatography analysis coupled with either flame ionization detection (GC-FID) or mass spectrometry (GC-MS). Not only are these methods slow, but the GC requires that moisture is removed prior to analysis. The result is low sample throughput. In contrast, application of SIFT-MS accelerates throughput through direct headspace analysis. That is, SIFT-MS eliminates the need to purge, trap and dry the sample, plus it analyses the sample within tens of seconds. In this application note, we describe the simplified, direct SIFT-MS analysis of BTEX in the headspace of drinking water.

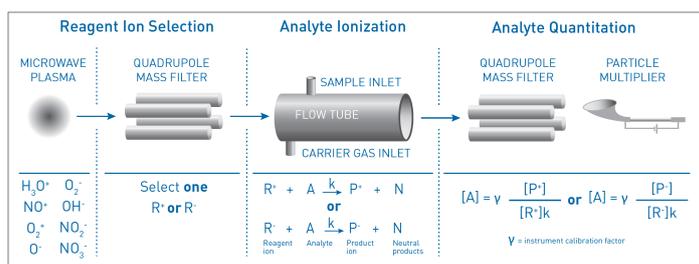


Figure 1. Schematic diagram of SIFT-MS – a direct chemical-ionization analytical technique.

At least 12 samples per hour are analyzed using this approach without compromising the ability to selectively analyze isomeric ethylbenzene and total xylenes.

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 mass-selected reagent ions react with VOCs and other trace analytes in well-controlled ionmolecule reactions, but they do not react with the major components of air (N_2 , O_2 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-MS).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.

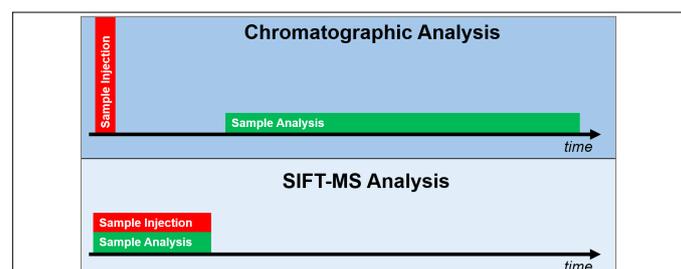


Figure 2. Graphical representation of the different sample-injection and analysis requirements of chromatographic techniques and SIFT-MS.

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 duration of the analysis – that is, sample injection and analysis occur simultaneously (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 preinjection 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 designed and optimized for chromatographic analysis.

3. Samples and analysis conditions

BTEX primary standard solutions were prepared at 1000 ppm in methanol. Working standards were then prepared, via serial dilution, in 10 mL of deionized water in 20 mL headspace vials.

Standard solutions were incubated at 60 °C for 15 minutes. The headspace was sampled using a 2.5-mL headspace syringe (heated to 150 °C; fill speed of 200 $\mu\text{L s}^{-1}$, and then injected into the SIFT-MS instrument at a flow rate of 50 $\mu\text{L s}^{-1}$ (giving a total flow rate of ca. 420 $\mu\text{L s}^{-1}$ when diluent flow is considered).

The analytical approach for BTEX was described in the application note Real-Time Speciation of Ethylbenzene from the Xylenes Using SIFT-MS (application note APN-032).

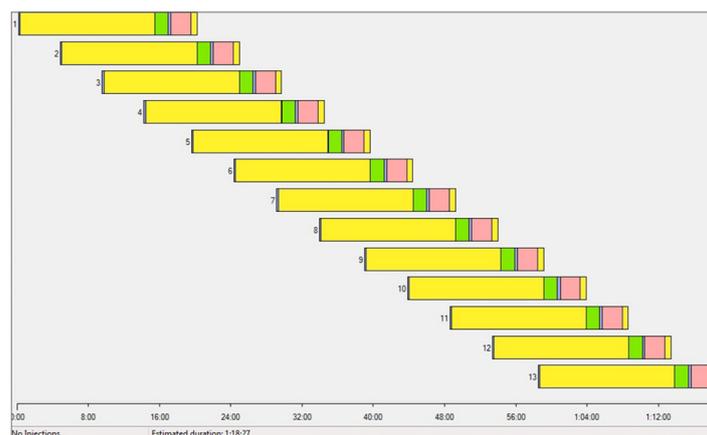


Figure 3. Sequence tables from the GERSTEL Maestro software for analysis of 13 water headspace samples using SIFT-MS. A throughput of at least 12 samples per hour is achieved.

RESULTS AND DISCUSSION

The high robustness of SIFT-MS analysis to humidity enables the technique to be applied to direct headspace analysis of BTEX without any need for water stripping (e.g. no purging, trapping, and drying). Linear detection of BTEX in the headspace of standard aqueous solutions (2.5 to 1,000 ppbv in solution) is shown in Figure 4. These data were generated without using an internal standard and exhibit excellent repeatability (see Table 1 and Figure 5), with RSDs better than 4% for solutions prepared at 250 nL L^{-1} (250 ppbv) concentrations. For this method, the limit of detection (LOD) is 0.3 nL L^{-1} and the limit of quantitation (LOQ) is 1 nL L^{-1} . This is equivalent to a LOD of 0.26 $\mu\text{g L}^{-1}$ and a LOQ of 0.87 $\mu\text{g L}^{-1}$.

Ethylbenzene and the xylenes are very effectively differentiated in these headspace measurements (Figure 4). Notice that the ethylbenzene headspace concentrations are slightly higher than those of m-xylene, despite the standard being a 50/50 mixture. This is a combination of water solubility and boiling point (benzene: 1.8 g L^{-1} , b.p. = 80 °C; toluene: 0.5 g L^{-1} , b.p. = 110 °C; ethylbenzene: 0.15 g L^{-1} , b.p. = 136 °C; m-xylene: 0.16 g L^{-1} , b.p. = 139 °C). The order of BTEX compounds is therefore exactly as predicted from their physicochemical properties.

Even with current automation technology optimized for GC-MS applications, a 3.5-fold increase in sample throughput for SHSIFT-MS is obtained compared to the standard headspace or purge-and-trap GC-MS methods.

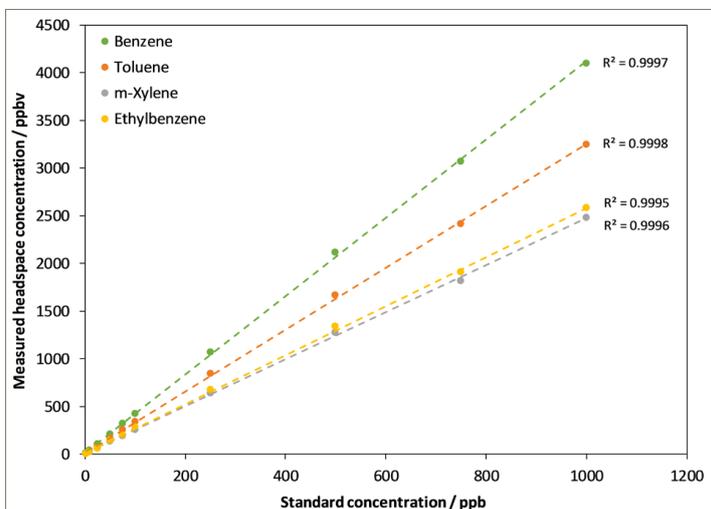


Figure 4. SIFT-MS measurement linearity for direct water headspace analysis of benzene, toluene, ethylbenzene, and m-xylene

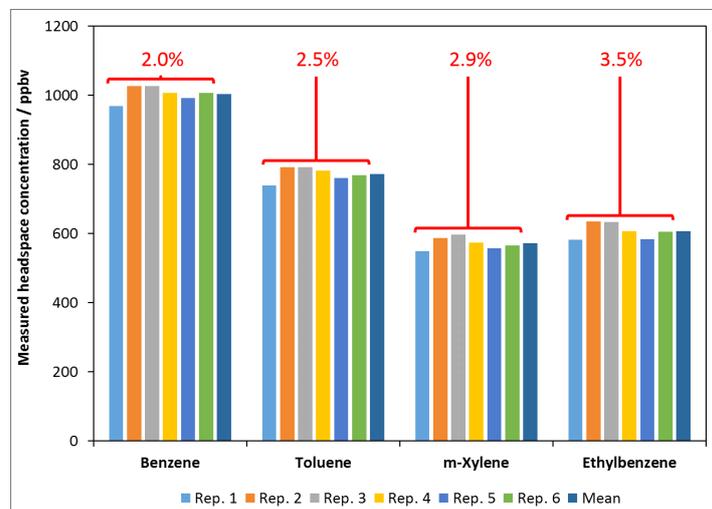


Figure 5. SIFT-MS measurement repeatability (six replicates) for direct water headspace analysis of 250-ppb solutions of benzene, toluene, ethylbenzene, and m-xylene. The mean concentration is also shown.

PARAMETER	Benzene	Toluene	m-Xylene	Ethylbenzene
Rep. 1 / ppbv	968	738	550	582
Rep. 2 / ppbv	1026	793	587	638
Rep. 3 / ppbv	1026	793	598	634
Rep. 4 / ppbv	1006	783	574	607
Rep. 5 / ppbv	992	761	558	584
Rep. 6 / ppbv	1006	767	567	605
Mean / ppbv	1004	773	572	608
SD / ppbv	20.1	19.2	16.4	21.1
%RSD	2	2.5	2.9	3.5

Figure 4. SIFT-MS measurement repeatability (six replicates) for direct water headspace analysis of 250-ppb solutions of benzene, toluene, ethylbenzene, and m-xylene. The mean concentration is also shown.

CONCLUSIONS

This study demonstrates that SIFT-MS is a very powerful new technique for rapid determination of BTEX in water to subng L⁻¹ concentrations via direct headspace analysis. SIFT-MS simplifies and speeds analysis by eliminating preconcentration and drying steps due to its high sensitivity and robustness to humidity. In doing so, SIFT-MS provides substantial throughput increases over traditional purge and trap-GC methods.

REFERENCES

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