High-Throughput Analysis of Volatile Compounds in Air, Water and Soil Using SIFT-MS

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Since its introduction in 1995, selected ion flow tube mass spectrometry (SIFT-MS) has found many applications in research and industry, together with a substantial peer-reviewed literature. In this paper, we describe a new application of SIFT-MS that is suited to the contract laboratory, where the direct analysis provided by SIFT-MS may have significant benefits due to its accelerated sample throughput. Using the environmentally significant BTEX compounds (benzene, toluene, ethylbenzene and the xylenes) as a case study, we demonstrate high-throughput analysis from several matrices (air, water and soil). For the BTEX compounds, detection limits in the single-digit part-per-billion concentration range (by volume) are readily achievable within seconds using SIFT-MS, because sample analysis is achieved without chromatography, pre-concentration, or drying. For the first time with SIFT-MS, we also present a calibration approach that enables speciation of ethylbenzene from the xylenes in real time.

Introduction

A number of different technologies have been employed to monitor the aromatic hydrocarbons benzene, toluene, ethylbenzene and xylenes (collectively known as BTEX) for different applications. Benzene, toluene and ethylbenzene have been linked with cancers [1-6], with a common source of exposure being land contaminated by oil spillage [7,8]. The importance of analyzing these species in environmental matrices, including air, water, and soil is high and various reference methods have been developed [9-12].

Chromatographic techniques have been the traditional choice — in particular, gas chromatography (GC) with various detectors (most notably flame ionization detection, FID, photoionization detection, PID, and mass spectrometry, MS). However, GC is usually slow due to the time consuming chromatographic separation of analytes, so direct analysis techniques are frequently being evaluated. Among these, direct mass spectrometry (DMS) techniques have come to prominence because of their ability to analyze samples much more rapidly than GC and with better selectivity than spectroscopic techniques. However DMS techniques have struggled to distinguish ethylbenzene from the xylene isomers, so their measurement has been reported as a total concentration of "ethylbenzene plus xylenes". Where speciation is required, methods using chromatographic separation must be retained, which means off-line analysis. For example, in the European Union — unlike the United States — chromatography would have been essential because

regulators have imposed different occupational exposure limits (OELs) for ethylbenzene and the xylenes (time-weighted averages (TWAs) of 100 and 50 ppm, respectively) [13]. Likewise, recent vehicle interior air quality (VIAQ) regulations from Japan and Korea impose quite different permissible emission limits on these compounds — albeit the inverse of the EU workplace regulations (Table 1).

Table 1. Vehicle interior air quality (VIAQ) regulations for ethylbenzene and the xylenes. Japan and Korea now have significantly different thresholds for the ethyl versus dimethyl isomers.

COMPOUND	Maximum permissible concentrations ($\mu g\ m^{-3}$)		
	CHINA	JAPAN	KOREA
Ethylbenzene	1000	3800	1600
Xylenes (total)	1000	870	870

With the increasing need to rapidly speciate these isomers — whether in the lab or in-process monitoring — enhanced performance of DMS is required, rather than chromatography. Clearly, higher resolution MS is not a solution, because the elemental composition is the same (C_8H_{10}). The need is to utilize an ionization approach that yields different product ions. With a portfolio of eight standard rapidly switchable reagent ions, selected ion flow tube mass spectrometry (SIFT-MS) is the ideal technique with which to seek a solution to distinguishing ethylbenzene from xylenes in real-time.

In this paper, we describe a new approach to resolving ethylbenzene from the xylene isomers, by utilizing their

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different reactivities with the O_2^+ reagent ion of SIFT-MS. Based on calibration, it enables the SIFT-MS technique to achieve direct, real-time speciation of the xylenes from ethylbenzene. We apply this comprehensive approach to BTEX analysis to direct measurement of ambient air, water headspace, and methanolic extraction from soil. We find that it is successful for air and water, whereas for methanolic extraction only a total can be reported due to methanol residues consuming the O_2^+ reagent ion.

Method

1. SIFT-MS

SIFT-MS [14,15] is a real-time analytical technique for direct, comprehensive gas analysis to ultra-trace levels [16]. Data obtained by SIFT-MS instruments compare well with the accepted chromatographic method for volatile organic compound (VOC) analysis [17].

SIFT-MS uses soft, precisely controlled chemical ionization coupled with mass spectrometric detection to rapidly quantify VOCs to low part-per-trillion concentrations by volume (pptv). Eight chemical ionization agents (reagent ions) are now available in commercial SIFT-MS instruments: H_3O^+, NO^+, O_2^+, O^-, O_2^-, OH^-, NO_2^-, and NO_3^- [18]. These reagent ions react with VOCs and inorganic gases in well controlled ion-molecule reactions, but they do not react with the major components of air (N_2, O_2, and Ar). This enables SIFT-MS to analyze air at trace and ultra-trace levels without pre-concentration.

Rapid switching between the eight reagent ions provides very high selectivity. The key benefit of the additional ions is not primarily in the number of reagents ions, but in the multiple reaction mechanisms that provide additional independent measurements of each compound, delivering unparalleled selectivity and detection of an extremely broad range of compounds in real time.

In this paper, a Voice200*ultra* SIFT-MS instrument (Syft Technologies, Christchurch, New Zealand; syft.com) was utilized.

2. Automated headspace analysis

Autosampler integration enables the direct gas analysis provided by SIFT-MS to be applied for rapid analysis of discrete samples. Autosamplers have been integrated most commonly with chromatographic analytical techniques, where rapid injection is required to achieve good chromatographic separation. However, SIFT-MS analyzes samples continuously (since chromatography is eliminated), so it requires steady sample injection of the gas sample for the duration of the analysis.

Data presented here were obtained using an integrated GERSTEL Multipurpose Sampler (MPS) (GERSTEL, Mülheim an der Ruhr, Germany; GERSTEL.com), which has proved the best-suited commercial autosampler system for integration with the SIFT-MS technique. Headspace analysis was carried out from 20-mL sample vials on a standard GERSTEL vial rack. GERSTEL's Maestro control software has the ability to overlap parts of the preparation and injection sequence, leading to highly efficient sample scheduling and increased sample throughput.

a. Headspace analysis of water

BTEX and chloroform 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, and then injected into the SIFT-MS instrument at a flow rate of 50 µL s⁻¹.

b. Analysis of soil samples

A methanolic extraction technique was adapted from GC-MS for determination of BTEX in soil [7].

In the first step, linear detection of BTEX in the presence of high methanol concentrations was demonstrated over a range of BTEX concentrations (5 – 2,000 ppbv in solution). Saturated sodium chloride solution (10 mL) was placed in 20-mL headspace vials. Standard solutions were prepared in methanol and 250 µL of these were spiked into the aqueous solutions in sealed vials. Samples were incubated for 15 mins at 60 °C. Then 2.5 mL of headspace was injected at 50 µL s⁻¹. Standard solution dilutions and spiking was carried out by the autosampler. Linearities – as determined from R^2 values – were greater than 0.997 for all compounds in the stated range and recoveries were 77-108% for 20-2,000 ppbv solutions.

Next, soil samples were prepared as follows. Soil samples (2 g) were spiked with known amounts of primary standard and then sonicated with 6 mL of methanol (Merck, LiChrosolv grade), as extraction solvent, in 10-mL headspace vials using GERSTEL's QuickMix shaker for 2 minutes. They were then centrifuged at 4500 rpm for 5 minutes using the Anatune CF200 centrifuge. A 250-µL aliquot of methanol was then taken and spiked into 10-mL saturated sodium chloride solution in a 20-mL headspace vial. Incubation and analysis by SIFT-MS were carried out using the procedure described above. Following the addition of the extraction solvent, the entire sample preparation and analysis was fully automated.
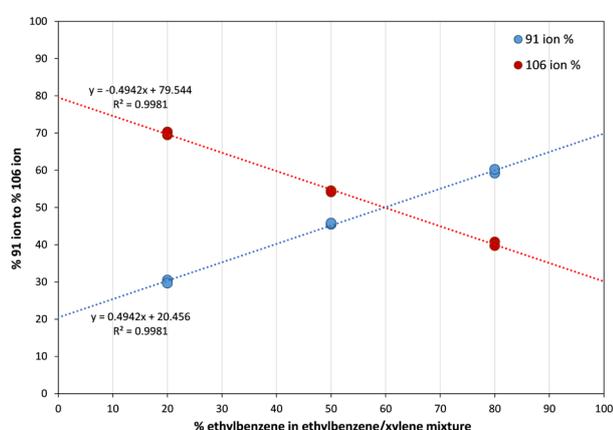
3. Analysis of BTEX using SIFT-MS

Parameters for detection of benzene, toluene, ethylbenzene and the total xylene isomers using the positively charged reagent ions (H_3O^+, NO^+, and O_2^+) of SIFT-MS are summarized in Table 2. Rate coefficients are not shown, but these occur at or near collision rate for all reagent ions [19].

For ethylbenzene and the xylene isomers, the between-compound variability is less than 10% (i.e. within experimental uncertainty), so that for H_3O^+ and NO^+ the rate coefficients provide a valid sum of all C_8H_{10} isomers. The NO^+ reagent ion was utilized to quantify the total concentration of ethylbenzene and the three xylene isomers. To differentiate ethylbenzene from the total xylene isomers, the O_2^+ reagent

ion was utilized because of the different product ion branching behaviors. Separation of the isomers was achieved through calibration of the 91 to 106 ratios using 20/80, 50/50 and 80/20 ethylbenzene/xylene mixtures carried out at two nominal concentrations (150 ppbv and 10 ppmv). The calibration results are summarized in Figure 1, where the two points for a given ratio arise from ratio determinations at the two concentrations, showing excellent agreement. Notice the linear response and the y-axis intercepts for 0% and 100% agree very well with the branching ratios shown in Table 2 for xylene and ethylbenzene, respectively [19].

Figure 1. Calibration of relative abundance ratios (expressed as percentages) for the m/z 91 and 106 product ions formed when O_2^+ reacts with different mixtures of ethylbenzene and the xylenes. More details are given in the text.

Results and Discussion

1. Direct air analysis

Continuous air analysis demonstrates the speed of BTEX analysis using SIFT-MS. For a semi-controlled environment, the Anatune Limited laboratory proved ideal. This laboratory is used actively for demonstration and application development activities, both for conventional chromatographic methods as well as SIFT-MS, so the air is a relatively complex matrix of trace analytes (typical concentrations in the 10s to 100s of ppbv).

With the SIFT-MS instrument analyzing the laboratory air continuously (a measurement for each compound being acquired approximately every 3 s), various combinations of m-xylene and ethylbenzene (pure samples of each, and a mixture) were introduced from 20 mL headspace vials. Vials were shaken and then uncapped and recapped after a few minutes. After a few minutes, the laboratory windows were opened to ventilate the room before the next sample was opened.

Figure 2 shows the results obtained for ethylbenzene and m-xylene. The total concentration of ethylbenzene and m-xylene was measured using the NO^+ reagent ion, while speciated ethylbenzene and xylenes concentrations were obtained using O_2^+. It is clear that the first exposure was xylenes, followed by ethylbenzene and then a 50/50 mixture of the two. Note that an additional eleven compounds (including benzene and toluene) were monitored concurrently, but these are not shown here for clarity.

Figure 2. Separation of ethylbenzene and xylenes concentrations using O_2^+ with the total concentration (ethylbenzene + xylenes) superimposed.
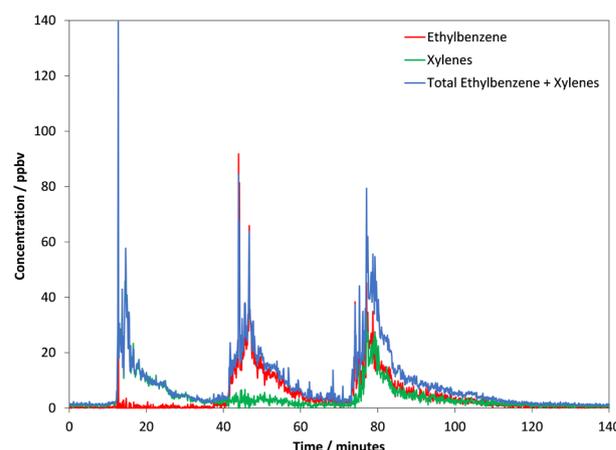
2. Water headspace

The high robustness of SIFT-MS analysis to humidity enables the technique to be applied to direct headspace analysis of BTEX and other hydrophobic volatiles (e.g. chloroform) without any need for water stripping (e.g. no purging, trapping, and drying).

Table 2. Detection parameters for the target compounds using the positively charged SIFT-MS reagent ions [19]. Product ions from reaction with named analyte are shown as ion formula (m/z, in Daltons), and product ion branching ratio as a percentage.

| Reagent Ion	Benzene[1]	Toluene	Ethylbenzene	Xylenes[2]
H_3O^+	$C_6H_6.H^+$ (79); 100%	$C_7H_8.H^+$ (93); 100%	$C_8H_{10}.H^+$ (107); 100%	$C_8H_{10}.H^+$ (107); 100%
NO^+	$C_6H_6^+$ (78); 76% $C_6H_6^+$ (108); 24%	$C_7H_8^+$ (92); 100%	$C_8H_{10}^+$ (106); 100%	$C_8H_{10}^+$ (106); 100%
O_2^+	$C_6H_6^+$ (78); 100%	$C_7H_8^+$ (92); 100%	$C_7H_7^+$ (91); 70% $C_8H_{10}^+$ (106); 30%	$C_7H_7^+$ (91); 20% $C_8H_{10}^+$ (106); 80%

1. The NO^+ branching ratio used here differs from the referenced article due to the differing flow tube conditions used in modern instruments, which see more adduct formation at m/z=108 than was observed in early research instruments.

2. The three xylene isomers (m-, o-, and p-) all react similarly with these reagent ions within 5% relative product abundance.

Linear detection of BTEX and chloroform in the headspace of standard aqueous solutions (2.5 to 1,000 ppbv in solution) is shown in Figure 3. Note that these data were generated without using an internal standard and exhibit excellent repeatability (Table 3), 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 µg L^{-1} for BTEX and 0.45 µg L^{-1} chloroform and a LOQ of 0.87 µg L^{-1} for BTEX and 1.5 µg L^{-1} chloroform.

Figure 3. Linear detection of benzene, toluene, ethylbenzene, m-xylene, and chloroform from 2.5 to 1,000 ppbv by volume in solution.
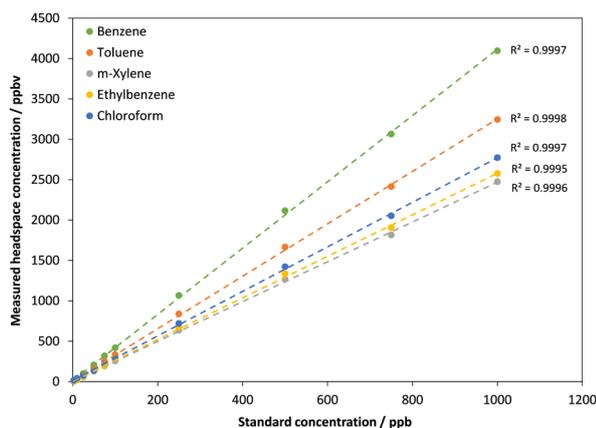
Ethylbenzene and the xylenes are very effectively differentiated in these headspace measurements (Figure 3). Notice that the ethylbenzene headspace concentrations are slightly higher than those of m-xylene, despite the standard being a 50/50 mixture. This is a combination of water solubility and boiling 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; chloroform: 8 g L^{-1}, b.p. = 60 °C). The order of BTEX compounds is therefore exactly as predicted on the basis of their physicochemical properties, while the position of chloroform arises due to its higher water affinity, despite its lower boiling point.

With current automation technology, which was optimized for GC-MS, we see a 3.5-fold increase in sample throughput when compared to the standard headspace GC-MS methods.
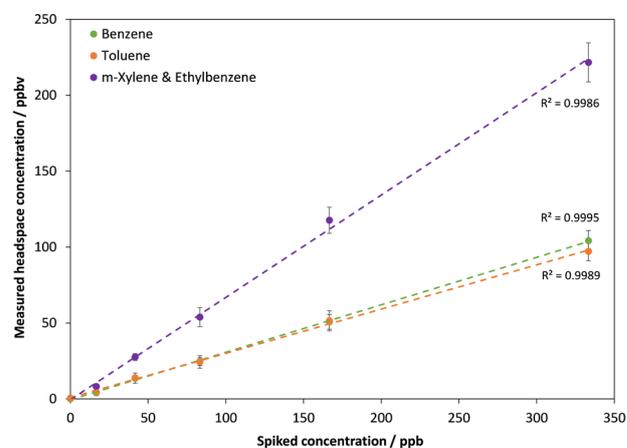
3. Soil headspace

Significant levels of benzene, toluene and the xylenes (BTEX) can be found in soil due to pollution events — gasoline spills and leakage of underground storage tanks are some common causes. Different extraction approaches have been tried in the past, such as vapor partitioning. However, methanolic extractions are far more robust for extraction and recovery of VOCs from soil [7].

Methanolic extraction can also be applied with SIFT-MS when the NO$^+$ reagent ion can be utilized for detection of target compounds, due to the slow reaction rate for the NO$^+$ + methanol reaction. This constraint arises because H$_3$O$^+$ and O$_2^+$ both react rapidly with methanol, whereas NO$^+$ reacts much more slowly (over 100-fold slower). All of the BTEX compounds are sensitively detected with NO$^+$ (see Table 2); benzene has two product ions with NO$^+$, whereas toluene and the sum of ethylbenzene and the xylenes have one product ion. Because O$_2^+$ cannot be used with methanolic extraction, only a total concentration of ethylbenzene plus xylenes can be achieved.

Results for SIFT-MS headspace analysis following automated methanolic extraction of BTEX from spiked soil samples are shown in Figure 4. Linear detection is achieved using

Figure 4. . Linear detection of benzene, toluene, and the sum of ethylbenzene and the xylenes in spiked soil over the range 16-340 ppb) following methanolic extraction. See the text for more details.

Table 3. Repeatability of six injections of headspace from the 250-ppbv aqueous standard using automated SIFT-MS headspace analysis.

Parameter	Benzene	Toluene	m-Xylene	Ethylbenzene	Chloroform
Rep 1 / ppbv	968	739	550	582	801.5
Rep 2 / ppbv	1026	793	587	638	850.5
Rep 3 / ppbv	1026	793	598	634	846.5
Rep 4 / ppbv	1006	783	574	607	822.5
Rep 5 / ppbv	992	761	558	584	811.5
Rep 6 / ppbv	1006	767	567	605	792.5
Mean / ppbv	1004	773	572	608	821
SD / ppbv	20.1	19.2	16.4	21.1	21.6
%RSD	2.0	2.5	2.9	3.5	2.6

SIFT-MS — even in the presence of over 1,000 ppmv of methanol in the headspace. Note that for clarity Figure 4 is plotted in terms of the spiked individual concentrations of ethylbenzene and m-xylene, but only the total is measured here due to residual methanol overwhelming the O_2^+ reagent ion signal, so speciation cannot be achieved.

Table 4 shows the results obtained for calibration standards and the various spiked soil samples in the sequence that they were run. Spike levels in ppb are applicable to all samples; the indicative mass per gram is calculated for each compound. RSDs for the calibrations are excellent and recoveries of 75-111% are all acceptable. For the experimental conditions used here, the LOQ and LOD are 40 ng g^{-1} and 12 ng g^{-1}, respectively. There is potential to achieve lower LOQs and LODs through better optimized extraction conditions.

This study has achieved a two-fold increase in sample throughput for SIFT-MS when compared with GC-MS analysis using the current sequential sample preparation/analysis method. It may be possible to further increase this by utilizing the multiple positions available with the GERSTEL modules and by batch-preparing the samples.

Conclusions

Monitoring isomers of aromatic hydrocarbons at low concentrations has traditionally been the domain of chromatographic methods to first achieve separation between the isomers followed by flame ionization or mass spectrometric detection. We have shown in this work that the direct mass spectrometric technique of SIFT-MS has enabled excellent differentiation of the ethylbenzene isomer from the xylene isomers using known O_2^+ reagent ion chemistry for both air and water. This approach can be applied in real time and in high throughput applications both in testing and contract laboratories through to continuous process monitoring applications.

Future work will include fully validation of air, aqueous and soil methods over the full linear range accessible to the SIFT-MS technique. It will also investigate multiple headspace extraction (MHE) as a means to directly analyze volatiles from soil without solvent extraction, thus overcoming the current impediment to resolving ethylbenzene and xylenes: methanol residue consuming the reagent ion.

Table 4. Concentrations for replicate calibration standards and then spiked soil samples (including recoveries) analyzed using automated methanolic extraction and SIFT-MS. Data are organized per the sequence table for the run. See the text for more details.

Parameter	Headspace concentrations / ppbv			Recoveries / %		
	Benzene	Toluene	m-X + ETB*	Benzene	Toluene	m-X + ETB*
Calibration 1	63.9	58.8	131			
Calibration 2	64.9	60.6	135			
Calibration 3	67.5	61.0	136			
Mean	65.4	60.1	134			
SD	1.5	0.96	2.2			
%RSD	2.3%	1.6%	1.6%			
Soil blank	0.14	0.58	0.00			
Spike: 16.7 ppb (43 ng g^{-1})	4.34	4.67	8.46	79.6	93.3	75.9
Spike: 41.7 ppb (108 ng g^{-1})	13.6	13.9	27.6	99.8	110.6	99.0
Spike: 83.3 ppb (216 ng g^{-1})	24.6	24.4	53.9	90.3	97.3	96.7
Spike: 167 ppb (432 ng g^{-1})	50.7	51.5	118	93.0	102.8	105.6
Spike: 333 ppb (864 ng g^{-1})	104	97.2	222	95.5	97.0	99.5
Crosscheck calibration	66.2	60.3	134			

* "m-X + EtB" is the sum of m-xylene and ethylbenzene.

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