

High-Throughput Thermal Desorption Analysis of Volatile Compounds Using Selected Ion Flow Tube Mass Spectrometry

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Abstract

Direct mass spectrometry combined with automation has potential to significantly increase sample throughputs in routine laboratory analysis. This article describes the performance of direct-analysis selected ion flow tube mass spectrometry (SIFT-MS) integrated with automated thermal desorption. The performance of thermal desorption-SIFT-MS in several air quality applications of conventional thermal desorption-gas chromatography mass spectrometry is described. Compared to gas chromatography mass spectrometry analysis, one of the most significant advantages of thermal desorption tube analysis using SIFT-MS is that volatiles are analysed as they are desorbed, providing at least four-fold greater throughputs.

Introduction

Thermal desorption tubes (TDTs) are widely used air sampling media because of the convenience of in-built sample preconcentration, robustness, economical shipping, and their re-usability (including low cost of cleaning). Applications that use TDT sampling include environmental monitoring [1,2], indoor air quality [3,4], and breath research [5].

However, sample throughput has been a critical bottleneck for conventional TDT analysis, because of the relatively slow gas chromatography-mass spectrometry (GC/MS) analysis with which thermal desorption has been coupled. Direct analysis techniques eliminate the throughput-limiting step: the chromatographic separation, and in doing so yield significant throughput improvements for routine analysis. Selected ion flow tube mass spectrometry (SIFT-MS) is a technique that directly analyses volatile compounds in air in real time with high sensitivity and selectivity. High selectivity in real-time is provided by application of multiple rapidly switchable, soft chemical ionisation agents (so-called reagent ions) [6].

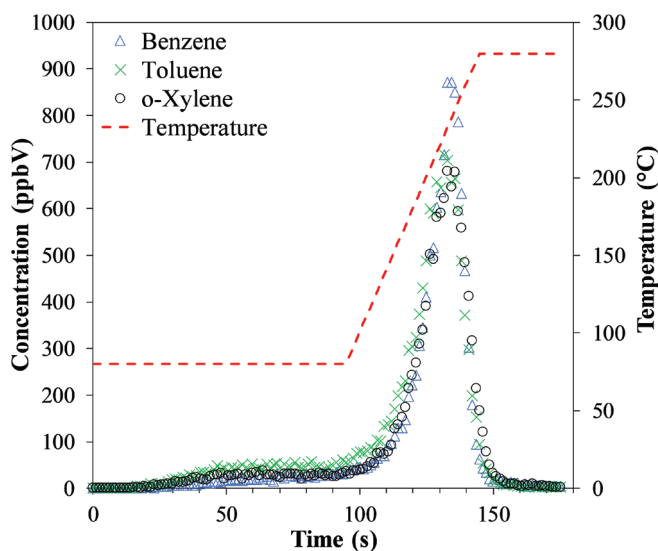


Figure 1. Desorption profile for BTX spiked onto a TDT packed with Carboxpack™ X sorbent (Method 325). Instantaneous concentrations in the SIFT-MS flow tube are shown on the left-hand axis, while the TD temperature ramp is shown in red on the right-hand axis.

Therefore, by coupling thermal desorption with SIFT-MS, there is opportunity to significantly improve analysis throughput for TDTs.

This article describes the initial application of a fully integrated thermal desorption-SIFT-MS (TD-SIFT-MS) system to several important environmental analyses. First, suitability for outdoor monitoring is

considered in terms of ambient and fence-line methods (United States Environmental Protection Agency (US EPA) methods TO-17R [1] and 325 [2], respectively). Second, the application to indoor air quality measurement is demonstrated by vehicle interior air quality (VIAQ) analysis. In these case studies, the analytical performance of TD-SIFT-MS is presented. In practical terms, throughputs

Table 1. Linearity, MDL (in terms of minimum mass detected on the tube for TO-15, and concentration in air for Method 325), precision and recovery for TD-SIFT-MS analysis of BTX. Precision and recovery data are at ca. twice the TO-17 MDL.

| Target Compound | Linearity (R^2) | Method Detection Limit | | Precision (at twice MDL) / % | Recovery (at twice MDL) / % |
|-----------------|---------------------|------------------------|-------------------|------------------------------|-----------------------------|
| | | TO-17 / ng on tube | Method 325 / pptV | | |
| Benzene | 0.9997 | 0.23 | 2.1 | 13.8 | 91 |
| Toluene | 0.9999 | 0.28 | 5.1 | 9.5 | 66 |
| Xylene | 0.9997 | 0.37 | 7.9 | 13.0 | 98 |

of up to 20 TDTs per hour per SIFT-MS instrument can be achieved using this fully integrated system - approximately an order of magnitude higher than the throughput of thermal desorption (TD)-GC/MS.

Experimental

1. SIFT-MS

SIFT-MS [7,8] is a real-time analytical technique for direct, comprehensive gas analysis to ultra-trace levels [9]. Data obtained by SIFT-MS instruments compare well with the accepted chromatographic method for volatile organic compound (VOC) analysis [10].

SIFT-MS uses soft, precisely controlled chemical ionisation coupled with mass spectrometric detection to rapidly quantify VOCs to low part-per-trillion concentrations by volume (pptV). Eight chemical ionisation 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^- [6]. 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 analyse 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 reagent 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 Voice200ultra SIFT-MS instrument (Syft Technologies, Christchurch, New Zealand; www.syft.com) was utilised. Parameters for detection of benzene, toluene, and xylene isomers (BTX) using the positively charged reagent ions (H_3O^+ , NO^+ , and O_2^+) of SIFT-MS are from Ref. 11. Styrene and 1,3-butadiene parameters are from Ref. 12.

2. Automated thermal desorption-SIFT-MS

Autosampler integration enables the rapid, direct gas analysis provided by SIFT-MS to be applied to high-throughput TDT analysis. In contrast to chromatographic techniques that require cryo-focusing of thermally desorbed volatiles to provide optimal chromatographic resolution, the continuous, direct analysis provided by SIFT-MS means that volatiles are measured as they are desorbed.

Data presented here were obtained using an integrated Gerstel Multipurpose Sampler (MPS) (Gerstel, Mülheim an der Ruhr, Germany; www.gerstel.com). Addition of the Gerstel TD 3.5+ thermal desorption unit and the Gerstel CIS4 transfer line options facilitates simplified, rapid analysis of thermally desorbed volatile compounds. Additionally, Gerstel hardware is controlled using Gerstel's powerful Maestro software, which allows for optimal scheduling of sample transport, temperature ramp and cooling steps. This ensures that the highest sample throughput is achieved for the conditions required for a given method.

The final concentrations were determined from the total integrated mass of each analyte (in environmental samples, xylene and ethylbenzene are reported as a combined total) released during desorption, and the tube loading parameters.

3. Standards and spiking of TDTs

Validation work follows procedures given in United States Environmental Protection Agency (US EPA) Method TO-17R [1]. Stock solutions of concentration $0.3 \mu\text{L mL}^{-1}$ were prepared by dissolving $30 \mu\text{L}$ each of benzene, toluene, and o-xylene in 100 mL methanol. These samples were stored in a sealed volumetric flask from which working solutions were prepared at five concentrations (0.00015 , 0.00150 , 0.00750 , 0.01500 , $0.03750 \mu\text{L mL}^{-1}$), by diluting the stock solution with methanol.

Unless otherwise noted, Tenax® TA tubes were spiked manually with $4 \mu\text{L}$ working solution of benzene, toluene and o-xylene at the working concentrations. At each level, three repeats were prepared to demonstrate precision. Blanks were prepared by spiking $4 \mu\text{L}$ of MeOH onto Tenax® tubes. Solvent purging was conducted by flowing nitrogen at 100 standard cubic centimetres per minute (sccm) for 15 minutes after liquid spiking.

For the VIAQ study described later, a custom gas standard was procured that contained ca. 1 ppmV of each of the eight Chinese-regulated compounds in nitrogen.

4. Thermal desorption parameters

Thermal desorption conditions for the TD-SIFT-MS analysis of TDTs for each study were as follows. In all cases, nitrogen was used as the gas for tube desorption and the transfer line temperature was 200°C .

For validation of TD-SIFT-MS, the nitrogen desorption gas was at a constant pressure of 60 kPa and desorption flow of 19.9 sccm in splitless mode. The sample flow into the SIFT-MS instrument was 16.9 sccm. The initial TD temperature (held for 30 seconds) was 60°C for Tenax® TA (Method TO-17R) and 80°C for

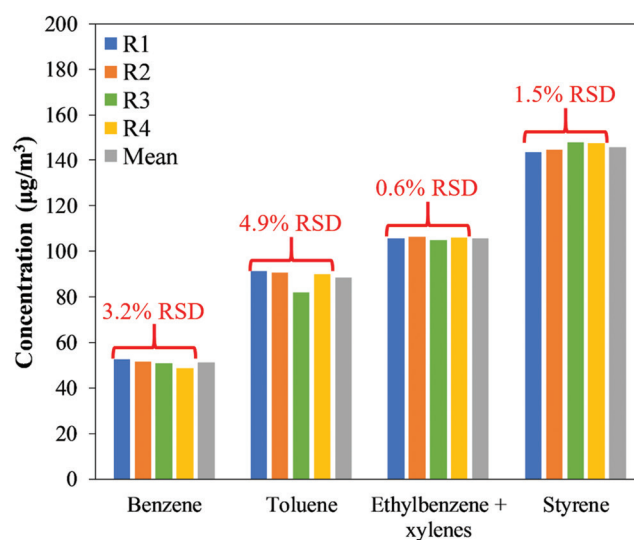


Figure 2. Replicate TD-SIFT-MS analysis of tubes loaded from a gas standard containing BTEX + styrene.

Table 2. Recoveries and breakthroughs determined using direct analysis- and TD-SIFT-MS for the Chinese-regulated VIAQ compounds using TDTs packed with Carbotrap® 300 sorbent.

| Compound | Recovery | % Breakthrough |
|-----------------------|---------------|----------------|
| Acetaldehyde | 1.05 ± 0.07 | 11% ± 3% |
| Acrolein | 1.03 ± 0.01 | 3.0% ± 0.6% |
| Benzene | 0.96 ± 0.03 | 0.07% ± 0.01% |
| Ethylbenzene + Xylene | 0.916 ± 0.001 | 0.37% ± 0.06% |
| Formaldehyde | 0.21 ± 0.02 | 71% ± 9% |
| Styrene | 0.880 ± 0.009 | 0.21% ± 0.07% |
| Toluene | 0.837 ± 0.004 | 0.29% ± 0.01% |

Carbopack™ X (Method 325). The temperature was then ramped from 60 to 280°C at 120°C min⁻¹, where it was held for 120 seconds.

In the environmental monitoring case study, the nitrogen desorption gas was utilised at a flow rate of 41 mL min⁻¹, a constant pressure of 54 kPa. The thermal desorption split was 1:1. The initial TD temperature was 60°C for 60 s, followed by a ramp rate of 240°C min⁻¹, and a hold temperature of 300°C for 30 s. This more optimised desorption program enabled a total runtime of less than 3 min.

For the VIAQ study, the custom gas standard was loaded onto TDTs packed with Carbotrap® 300 at a flow rate of 80 sccm for 60 seconds. The program used with the thermal desorber had an initial temperature of 20°C with a 30-s hold time, followed by a ramp to 220°C at 60°C min⁻¹, and a 2-min hold time at 220°C. The TD operating pressure was 4 kPa which gave a sample flow rate of 30.7 sccm.

Results and Discussion

This section first presents a brief summary of performance of TD-SIFT-MS in the context of a regulatory environmental method, before presenting data that demonstrate application to measurement of volatiles in outdoor and indoor environments.

1. Validation of TD-SIFT-MS

In this section, benchmarking of the analytical performance of TD-SIFT-MS is conducted by comparison with acceptance criteria for two GC-based US EPA thermal desorption methods: (i) Compendium Method TO-17R (active sampling of the more volatile organic components of the hazardous air pollutant (HAP) list [1]), and (ii) Method 325 (passive sampling for benzene over a two-week period at the fence line of oil refineries [2]).

Figure 1 shows an example desorption profile for TD-SIFT-MS corresponding to a

loading of 52 ng of each target compound. The SIFT-MS instrument measures the target compounds in real-time as they are desorbed from the TDT - there is no cryofocusing step. This means that concentration is calculated and plotted initially in volume-to-volume units as a function of time. This desorption 'envelope' is integrated by software to determine the mass of target compound on the sorbent tube. Note that desorption is completed in less than three minutes. With rapid cooling of the thermal desorption unit, throughputs of up to 20 tubes per hour can be realised.

Measurement linearity is summarised in Table 1 for TD-SIFT-MS measurements made over the concentration range required by the US EPA TO-17R method (0.5 to 100 ppbV). These results easily meet acceptance criteria, with correlation coefficients (R²) in the high 0.999 range.

Table 1 also gives the method detection limits (MDLs) in terms of minimum detectable mass on the Tenax® TA sorbent tube (in nanograms). Assuming that one litre of air is sampled, the data correspond to MDLs of 70.8, 73.1, and 83.8 pptV for benzene, toluene, and xylene, respectively. This is well below the TO-17R requirement of <500 pptV.

MDLs for Method 325, which involves two weeks of passive sampling of benzene onto specified TDTs at oil refinery boundaries yields MDLs shown in Table 1 (these are based on Carbopack™ X uptake volumes for passive sampling over two weeks). In addition to benzene, results for toluene and xylene performance are included. Again, for Method 325 TD-SIFT-MS easily meets the MDL requirement of <50 pptV. On the tube itself, these concentrations correspond to benzene, toluene, and xylene MDLs of 0.09, 0.21, and 0.33 ng, respectively.

Finally, Table 1 summarises the precision and preliminary recovery data determined as part of the study at about double the MDL for the TO-17 method. A question for further work is why some recoveries are poor (lower than 80%).

Overall, the performance of TD-SIFT-MS meets the criteria in Section 14 of US EPA Method TO-17R [1].

2. Environmental monitoring

In this section, results are presented that apply the TD-SIFT-MS technique to environmental monitoring - in this case, using the active sampling approach given in US EPA Compendium Method TO-17. In addition to BTX, styrene and 1,3-butadiene were targeted in this campaign.

Prior to undertaking the sampling campaign, the repeatability of TD-SIFT-MS for analysis of environmental pollutants was assessed by desorption of replicate tubes loaded from the gas standard containing benzene, toluene, ethylbenzene, xylene (BTEX) and styrene in nitrogen. The results are summarised in Figure 2. It is evident that TD-SIFT-MS analysis is highly repeatable, with RSD values less than 5% for all compounds.

Environmental air samples which

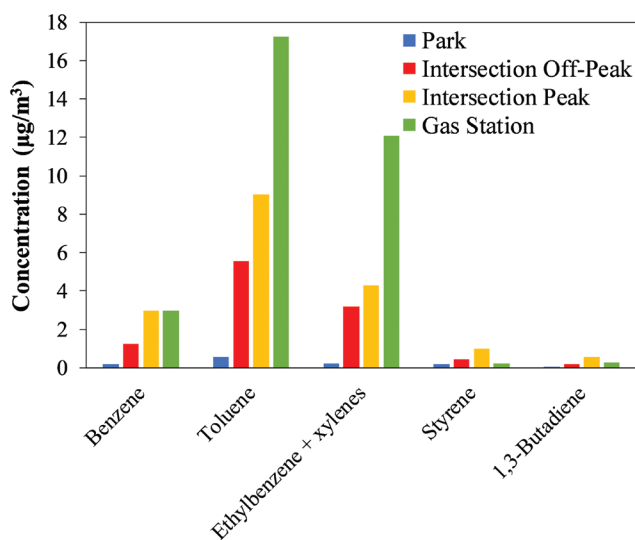


Figure 3. Environmental pollutant concentrations at four sampling sites determined using TD-SIFT-MS.

Table 3. Results obtained for two vehicle cabins using TD-SIFT-MS and targeting the Chinese VIAQ compound suite.

| Compound | Tube 1 / $\mu\text{g m}^{-3}$ | Tube 2 / $\mu\text{g m}^{-3}$ |
|------------------------|-------------------------------|-------------------------------|
| Acetaldehyde | 1.6 | 1.7 |
| Acrolein | 1.9 | 1.4 |
| Benzene | 0.043 | 0.37 |
| Formaldehyde | 0.20 | 0.63 |
| Styrene | 4.8 | 3.5 |
| Toluene | 2.0 | 1.4 |
| Xylenes + ethylbenzene | 9.5 | 8.7 |

were expected to give a range of VOC concentrations, were collected at several sites around Christchurch, New Zealand: a park, a petrol station, and a busy intersection at 9:30 am (peak) and 7:30 pm (off-peak).

Figure 3 compares the concentrations of various environmental pollutants determined following one-hour active sampling on Carbotrap® 300 thermal desorption tubes at various sites (a local park, peak and off-peak intersection, and a gas station). Concentration measurements to sub- $\mu\text{g m}^{-3}$ are readily achievable using TD-SIFT-MS.

3. Vehicle interior air quality (VIAQ)

Thermal desorption tubes are the standard sampling approach for determination of VOC emissions in motor vehicle cabins - to assess the so-called vehicle interior air quality (VIAQ).

Although VIAQ assessments have been made for many years, the need to analyse automobile interiors on a much wider scale was prompted by a Chinese government guideline standard implemented on 1 March 2012, which regulates the VIAQ of new vehicles [13]. This standard outlines stricter limits on eight harmful substances in the vehicle cabin: formaldehyde, acetaldehyde, acrolein, benzene, ethylbenzene, xylene, styrene, and toluene.

Larger testing volumes arising from legislative changes result in significant cost increases for manufacturers when conventional laboratory-based technologies (high-performance liquid chromatography (HPLC) and GC/MS) are used. Additionally, because analysis is offline and turnaround time is slow, failed product is identified too late.

In contrast, SIFT-MS can greatly reduce turnaround through comprehensive analysis and reduced testing time. SIFT-MS can also be integrated into production processes. There are several advantages resulting from

coupling TD with SIFT-MS for VIAQ testing: (i) TDTs are the standard sampling approach to whole cabin testing, together with sub-assemblies and components, (ii) distributed sampling is facilitated, and (3) with suitable sorbent beds, a wider range of compounds can be analysed from one tube.

Formaldehyde, in particular, is a challenge for retention on most sorbents, so recoveries were investigated early in this work. Recovery for all compounds was determined from the ratio of the TD-SIFT-MS results to that of VIAQ standard measured with direct whole-air analysis of the gas standard. Table 2 shows that all compounds, except formaldehyde, have acceptable and reproducible recoveries.

Breakthrough was evaluated by connecting two TDTs in series and loading at an 80-sccm flow rate for 60 s. The results calculated based on the ratio between the second and first tubes is shown in Table 2. The aromatic compounds have breakthrough values < 1%; this small breakthrough is likely due to differing backgrounds between individual tubes. Acetaldehyde and acrolein breakthrough tubes do not show typical desorption profiles but an apparent step in concentration during the 220°C hold time. Formaldehyde showed very high breakthrough and even the second tube likely had further breakthrough, as the combined recovery from the two tubes is still only ca. 40%. Future work will focus on utilising a more suitable sorbent for formaldehyde if one can be identified.

Linearity was investigated by varying the VIAQ standard concentration loaded at a consistent flow rate (80 sccm for 60 s) from dynamically diluted standard (using nitrogen as the make-up gas) to give each concentration level. Linearity (i.e. R^2) results ranged from 0.95 for formaldehyde to 0.995 for acrolein. Interestingly, all compounds show linear response, including formaldehyde with its poor recovery/high breakthrough. This indicates that the formaldehyde is still in equilibrium with

the gas stream, despite the adsorption sites being readily saturated (based on the insensitivity to loading time). Future work will identify and evaluate other sorbents for improved formaldehyde recovery.

Table 3 summarises data obtained for two samples taken from passenger car cabins (3 L of cabin air was sampled volume).

TD-SIFT-MS provides rapid, highly sensitive analysis for VIAQ applications, with potential to cover the full eight compounds required by Chinese regulations in one analysis (sorbent permitting).

Conclusions

By analysing thermal desorption tubes as volatiles are desorbed, TD-SIFT-MS eliminates the throughput-limiting step for conventional TD-GC/MS analysis: the chromatographic separation. Since, for example, key performance criteria for the US EPA Compendium Method TO-17R [1] are achieved by TD-SIFT-MS, it can be applied with confidence to routine TDT analysis, but with results delivered at significantly higher sample throughputs than the conventional method.

Furthermore, TD-SIFT-MS can potentially further reduce costs through its ability to analyse a wider range of compounds in a single analysis. As illustrated by the VIAQ case study, detection of low molecular weight aldehydes, in addition to more routine VOCs (e.g. BTX), means that one analysis is required, rather than separate analyses for VOCs from TDTs by TD-GC/MS and aldehydes from DNPH tubes by HPLC-ultra violet analysis.

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