

## Preliminary Investigation of a Range of Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) Applications

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### Introduction

Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) is a form of direct mass spectrometry that uses precisely controlled soft ionisation to enable real-time, quantitative analysis of volatile organic compounds (VOCs) in air, typically at detection limits of parts-per-trillion level (by volume; pptv). This eliminates the need for sample preparation, pre-concentration and chromatography. Figure 1 shows a schematic of the instrumentation.

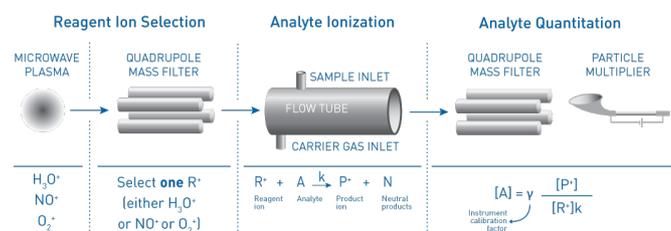


Figure 1 – Schematic representation of the SIFT-MS technique.

**Reagent ion selection** – A microwave discharge through moist air forms the standard SIFT-MS positive ions;  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$ , and these are then selected using a quadrupole mass filter.

**Analyte ionization** – The selected reagent ion is injected into the flow tube and excess energy is removed through collisions with the carrier gas (either nitrogen or helium). The sample is then introduced and an ion-molecule reaction takes place to form well-characterised product ions.

**Analyte quantitation** – Product ions and unreacted reagent ions pass into a second quadrupole mass analyser and the analyte concentration is calculated as a ratio of product ions to reagent ions multiplied by a rate constant,  $k$ , unique to that ion-molecule reaction.

The use of three, selectable reagent ions, coupled with a library of known reaction products and reaction rates enables SIFT-MS to quantify multiple analytes, in real-time, without the need for prior chromatographic separation.



Figure 2 – Syft Technologies' Voice200ultra SIFT-MS instrument.

This application note describes some preliminary analyses, to demonstrate the selectivity of SIFT-MS, and the wide range of potential applications available to it.

### Instrumentation

Syft Technologies' Voice 200ultra running LabSyft software (version 1.4.9)  
Syft Technologies' Sampling Case T0006  
GERSTEL MPS 2 XL-xt and Headspace kit  
Maestro software integrated (version 1.4.25.8/3.5)

### Method

Voice200ultra parameters:

Carrier gas – 99.999+% nitrogen  
Heated inlet temperature – 120°C  
Inlet flow (via restriction capillary) – 22 mL/min  
Flow tube temperature – 110°C

The broad range of sample types that can be analysed using SIFT-MS means that there is no definitive technique for obtaining and analysing samples. The most common approach is either through the use of Tedlar bags, passivated canisters or gas cylinders. Consequently, the sampling details and introduction will be described in the Results Section. Methods were produced using the LabSyft Method editor, with suitable reagent and product ions selected. Where applicable, measured concentrations have been background subtracted prior to reporting.

### Results

Real-time quantitation, without the need for external calibration standards, is possible with SIFT-MS by combining the count rates for both the reagent ions and the products with the known rate constant,  $k$ , for that specific ion-molecule reaction. This information is available from the LabSyft compound library; however, enhanced precision can be obtained by optimising the rate constant using known concentrations of analytes. Once calibrated,  $k$  remains valid for any subsequent measurement.

Calibration of selected compounds using an NPL ozone precursor gas mix

A subset of selected compounds from a certified NPL 30-component ozone precursor mixture was used to optimize the reaction rate ( $k$ ) values for those compounds. Subsequent measurement of this gas mixture confirmed the precision of these measurements. The gas mixture was introduced into the instrument directly from the bottle, using a passive split (via a T-fitting), to ensure the correct sample flow. The reaction rates ( $k$ ) for each compound were calculated, assuming a component concentration of 4 ppbv, and the LabSyft library updated accordingly. Figure 3 show a subsequent

measurement and Table 1 lists the measured concentrations, limits of detection (LOD) and matrix backgrounds for each of the analysed compounds. It should be noted that the concentration of the xylene and ethylbenzene isomers, and the trimethylbenzene isomers, are reported as combined concentrations respectively. SIFT-MS is unable to report these as separate concentrations.

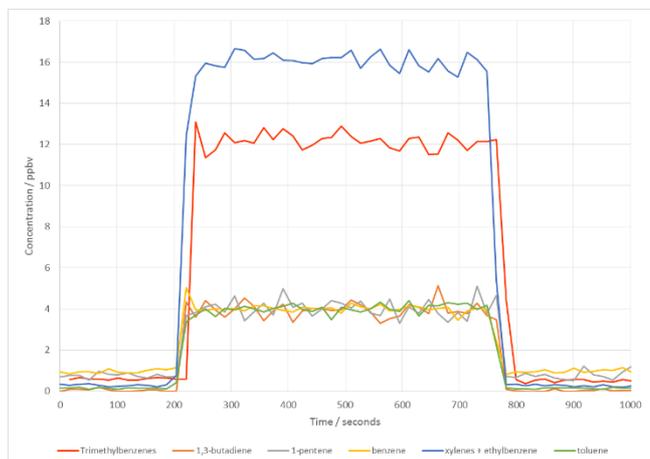


Figure 3 – Real-time plot of selected compounds from an NPL 30-component ozone precursor gas mix.

Concentration/ ppbv	Measured concentration	Zero-air background	Limit of detection
Trimethylbenzenes	11.94	0.253	0.043
1,3-butadiene	3.95	0.038	0.022
1-pentene	4.04	2.34	0.150
Benzene	3.99	0.546	0.070
Xylenes + Ethylbenzene	15.92	0.23	0.032
Toluene	3.95	0.098	0.026

Table 1 – Results for measurement of selected compounds at 4 ppbv per component.

**Limit of detection (LOD)** – As the concentration measurements being made by SIFT-MS are continuous (cf. chromatography where narrow analyte peaks are generated), the limit of detection may be calculated as three times the standard deviation of the mean of an equivalent blank matrix sample, e.g. a zero-grade air flow. The standard deviation of the mean is defined as  $\sigma/\sqrt{N}$ , where N = the number of points in the measurement. Clearly, the longer a measurement is made, the lower the LOD becomes (there is a square-root dependency). Consequently, LODs are calculated from a zero-grade air flow through the instrument for the measurement time for that specific method and are quoted accordingly.

#### Preliminary measurement of Vehicle Interior Air Quality (VIAQ)

The measurement of VOC emissions from vehicle interiors is increasingly important for the automotive industry. The range of compounds, and their limits, differ in different parts of the World. However, they all contain common features, for example, the requirement to quantify small aldehydes, BTEX compounds and other volatile hydrocarbons.

The following results show some preliminary measurements from a new car interior made on a summer afternoon after standing in a carpark for the day.

The interior air was sampled using Syft Technologies' Sampling Case, by inserting the sampling hose through a partially opened side window. The sample was collected in a 1L Tedlar bag and analysed for a range of compounds common to a number of global VIAQ standards. Please note that the concentrations shown are indicative only – no attempt was made to relate these to either the car interior volume, ambient temperature or conversion to standard VIAQ reporting units or formats. These were gathered for demonstration purposes only.

Figure 4 shows the sampling process with the resultant real-time plot shown in figure 5. Table 2 lists the results obtained in ppbv.



Figure 4 – Sampling vehicle interior with Sampling Case.

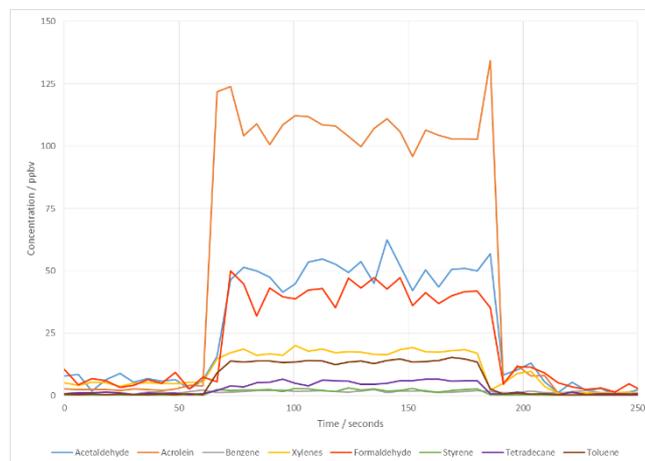


Figure 5 – Real-time plot of selected compounds from new vehicle interior.

Concentration/ ppbv	Measured concentration	Zero-air background	Limit of detection
Acetaldehyde	50.0	20.0	2.11
Acrolein	108.5	1.12	0.247
Benzene	1.79	0.680	0.110
Xylenes	17.5	0.245	0.063
Formaldehyde	41.4	22.4	1.14
Styrene	2.26	0.168	0.060
Tetradecane	5.25	0.244	0.070
Toluene	13.8	0.076	0.059

Table 2 – Results for measurement of selected compounds from new vehicle interior.

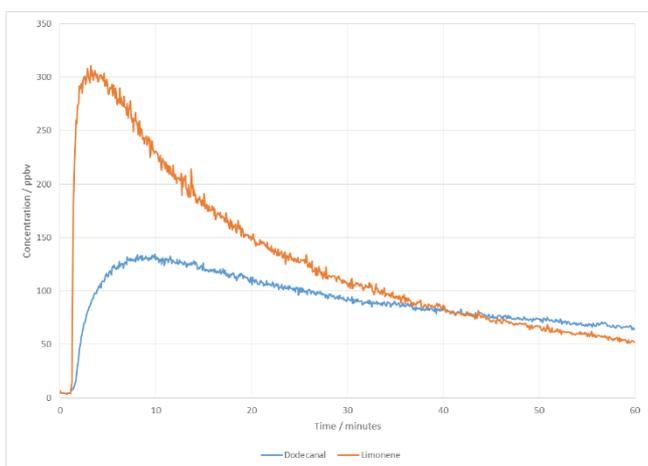
Monitoring of dynamic odour release from a fabric detergent

The ability of SIFT-MS to make measurements without prior sample preparation or preconcentration makes it an ideal technique to continuously monitor dynamic processes, for example, odour and flavour release.

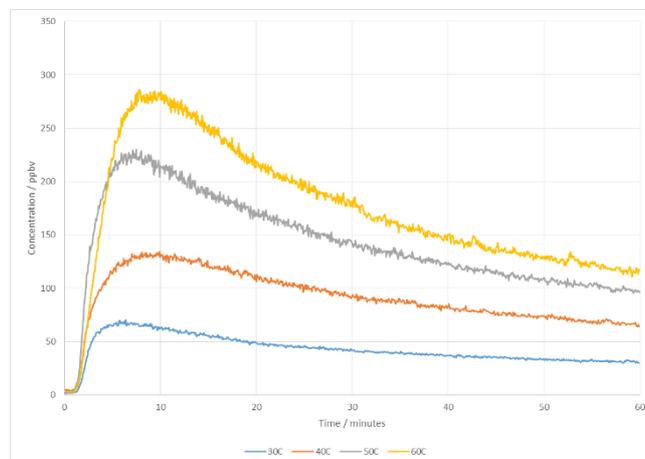
The following results show the release of two fragrance compounds from a more complex fabric detergent – dodecanal and limonene. Initially, dodecanal did not appear in the LabSyft library, however, the process of entering new compounds is straightforward. Information regarding its ion-molecule chemistry and reaction rate,  $k$ , is required. Using data for decanal, suitable product ions and well-estimated reaction rates were entered. To enhance the precision of measurement, a known concentration of dodecanal should be analysed and the reaction rates amended.

A 2 cm x 2 cm square of fabric was inserted in the bottom of a 20 mL headspace vial, 1 mL of detergent added and the headspace vial was capped. The vial was inserted in the headspace incubator, at a specified temperature and the release of compounds was measured for 1 hour, at 200 msec intervals using a needle inserted in the vial septum and attached to the instrument inlet. Four samples were analysed at 30, 40, 50 and 60°C respectively. As the instrument sample rate is 22 mL/min, it was necessary to insert a second needle into the vial septum to allow flow into the vial from the surrounding atmosphere.

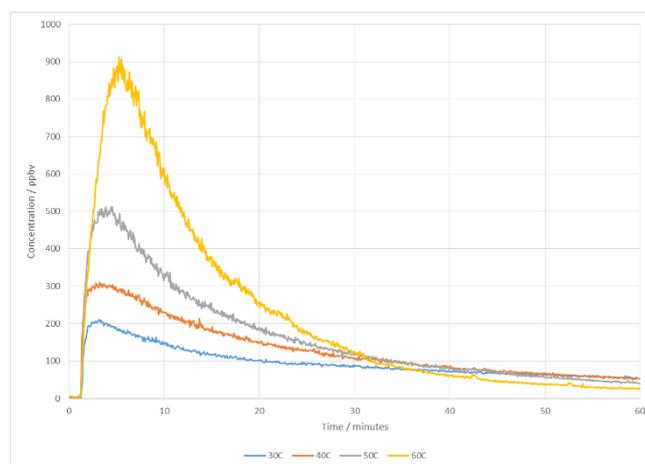
Figure 6 shows the fragrance release for both compounds at 40°C, demonstrating the different profiles obtained. Figure 7 and 8 show the release of limonene and dodecanal respectively at the four different incubation temperatures.



**Figure 6 – Fragrance release profile for dodecanal and limonene from a fabric detergent at 40°C.**



**Figure 7 – Fragrance release for dodecanal from a fabric detergent at 30, 40, 50 and 60°C.**



**Figure 8 – Fragrance release for limonene from a fabric detergent at 30, 40, 50 and 60°C.**

As expected, there is a direct correlation between sample temperature and initial concentration of fragrance in the headspace. Additionally, the decay in headspace concentration is faster at higher temperatures.

An interesting point to note is the rather different concentration decay profile for dodecanal compared to limonene. It suggests that whilst the predominant fragrance would initially be limonene, dodecanal would dominate in the longer term. The volatilities of these compounds are different (the boiling point of dodecanal is 80°C higher than limonene) but dodecanal is also more polar than limonene. Given the complex nature of modern detergent formulations, there are clearly more complex interactions taking place than simple relative boiling points when considering the fragrance release properties of this sample.

## Discussion

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This application note is a brief overview of SIFT-MS and shows the diverse nature of analyses that are amenable to this instrument. Without the need for chromatographic separation, it is a technique capable of simultaneous measurement of difficult and diverse chemical species, e.g. being able to analyse both small aldehydes and BTEX compounds, whilst also being highly sensitive (LODs in the low parts-per-trillion – pptv). Additionally, the continuous monitoring capabilities enable it to make measurements from seconds to hours in length.