

Interfacing a Markes Unity2™ Thermal Desorber with the Syft Voice200® SIFT-MS

Thermal desorption has become a commonly used technique for transferring volatile and semi-volatile organic compounds into a gas chromatograph, or gas chromatography – mass spectrometer. However, the GC and GC-MS techniques can suffer from long column elution times and poor sensitivity to certain compounds. Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) provides an alternative analytical technology to GC and GC-MS in these circumstances.

The detection and quantitation of several common compounds using Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) was first described some years ago.¹⁻³ In this document we present the results of a study in which a Syft Technologies Voice200® SIFT-MS instrument was interfaced to a Markes Unity2™ thermal desorber.

Experimental

Physical Interfacing

The Unity2 was used in its factory-supplied configuration for this study. The Voice200 simply required removal of the sample head component of the heated inlet extension. The sample output of the Unity2 was directly connected to the end of the Voice200's heated inlet extension with the sample head removed because the sample head contains the flow restriction component, the sample flow into the Voice200 was controlled by the carrier gas from the Unity2. In this work, the sample flow into the Voice200 was 46 standard cubic centimeters per minute (scm) for a nitrogen carrier gas pressure of 10 psi from Unity2.

Compounds Studied and Desorption Parameters

Five separate compounds were chosen for these studies, which span the mass range commonly measured on the Voice200 instrument: isobutane, benzene, ethylbenzene, hexafluorobenzene and octafluorotoluene. Each compound

was loaded onto a 3.5" sorbent tube by passing a constant flow of a calibrated gas standard over the sorbent media for a particular time period. Chromosorb was selected as the sorbent media for this study because it is expected efficiently trap all studied compounds.

To effectively test the lower end of the dynamic range of the Voice200, splits were employed on the Unity2 where the split ratio was commonly 35:1 (2.9% of all analyte directed to Voice200). This method was considered a more accurate way of preparing low concentrations than attempting to load the sorbent media with a very low mass of analyte.

Analytes were desorbed from the Chromosorb sorbent onto the secondary (focusing) trap for 5 minutes at 280°C. Once the primary desorption was completed, the analytes were then desorbed from the secondary focusing trap by ramping the temperature of the focusing trap from -20 to 300°C at 1 °C s⁻¹. Following the temperature ramp, the secondary trap was held at 300°C for 3 minutes to ensure that all analyte was desorbed.

SIFT-MS analysis

SIFT-MS is a powerful analytical technique that utilizes chemical ionization reactions coupled with mass spectrometric detection to rapidly quantify targeted VOCs. VOCs are identified and quantified in real time from whole-gas samples based on the known rate coefficients for reaction of the chemically ionizing species (so-called reagent ions) with the target analytes. The most common reagent ions used are H₃O⁺, NO⁺ and O₂⁺, which react with trace VOCs in well characterized ways but do not react with the major components of air. Generally the soft chemical ionization used in SIFT-MS yields a smaller range of product ions than is common in electron impact mass spectrometry (as used by GC-MS, for example).

These characteristics circumvent the need for chromatographic separation of the sample, speeding sample throughput and providing instantaneous quantification of VOCs. Use of several reagent ions to independently quantify target analytes also greatly reduces interferences, markedly increasing the specificity of SIFT-MS versus competing whole-gas analysis technologies.

In this work, Selected Ion Mode of a Syft Technologies Voice200 SIFT-MS instrument was used to detect and quantify the analytes arising from the sorbent media. Most compounds were quantified using multiple reagent ions and then data from the one that performed best (that is, was not subject to interference effects) were selected for presentation.

SIFT-MS is a real-time analytical technique, but is commonly used to analyze static samples (such as in gas sample bags) over a period of one or two minutes. However, when coupled with a thermal desorber, the analysis time is dependent on the desorber's secondary desorption temperature ramp.

Determining mass loadings using SIFT-MS

The Voice200 generally reports concentrations in units of ppbv (parts-per-billion-by-volume). Concentrations in 'by-volume' units are common when measuring samples in whole air. However, for a thermal desorption application, by-volume units are not meaningful and the mass of analyte adsorbed onto the sorbent must be calculated instead.

The sorbent tube mass loading is calculated by determining the average concentration for the entire desorption envelope (see Figure 1) for each analyte multiplied by the time period. The calculated value is equal to the total area under the curve for that time period, which correlates with the average number of molecules per cubic centimeter found in the flow tube. Therefore, by calculating the total volume of gas that has passed through the Voice200 flow tube, the total number of analyte molecules delivered into the instrument can be calculated. Equations (1) and (2) summarize these calculations.

$$V_{Total} = \frac{t_d \Phi_{Total} T}{P_{FT} 273} \quad (1)$$

$$m_{analyte} = \frac{V_{Total} [A] M_R}{6.023 \times 10^{20}} \quad (2)$$

Here V_{Total} is the volume of gas that passed through the flow tube, t_d is the desorption time in seconds, Φ_{Total} is the total flow tube flow in Torr L s⁻¹, T is the temperature in Kelvin and P_{FT} is the flow tube pressure in Torr, $[A]$ is the average concentration of the analyte in molecules cm⁻³, M_R is the molar mass in g mol⁻¹ and $m_{analyte}$ is the mass of a particular analyte in picograms (pg).

Results and Discussion

Figure 1 below shows a typical desorption profile observed on the Voice200 for the five analytes studied. Since all analytes were loaded onto the tube at similar concentrations (from the gas standard), they have similar area under the curve when they are plotted in the traditional by-volume concentration units used in SIFT-MS. The concentration profiles in Figure 1 show temporal separation because each compound has a different affinity for the Chromosorb sorbent.

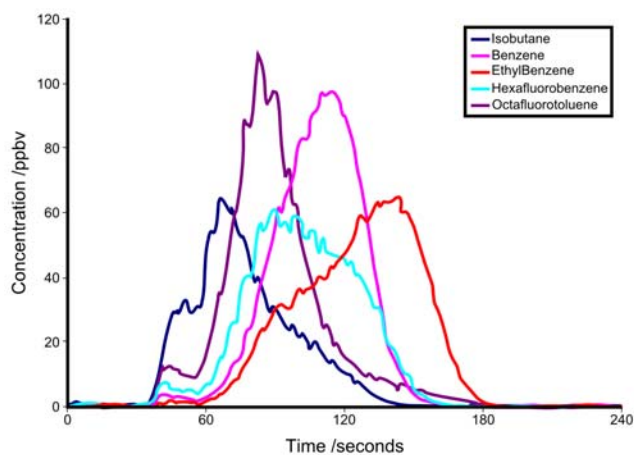


Figure 1. A Voice200 SIM scan showing a typical desorption profile from a Unity2 Thermal Desorber.

The measured concentrations shown in Figure 1 correlate to measured analyte masses of 2 to 8 ng depending on the molar mass of the analyte. Moreover the entire analysis of these five compounds took less than 8 minutes, which is substantially faster than a TD-GC-MS method. With further method optimization there is scope for significantly shorter analyses.

Figure 2 shows the linearity of Voice200® measurements of compounds being desorbed from a Unity2. Linearity is demonstrated down to 1 ng of compound delivered to the Voice200.

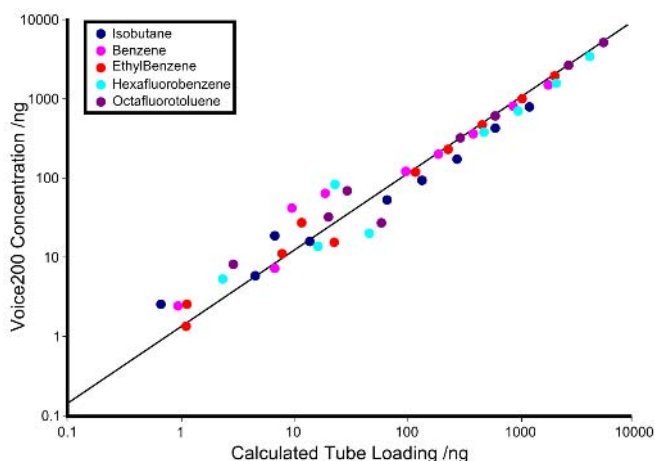


Figure 2. A plot of the linearity of the Voice200 measured concentrations. This plot shows the linear detection of compounds at from 1 ng to approximately 3000 ng.

Limit of detection and limit of quantitation

The limit of detection (LOD) and limit of quantitation (LOQ) on a Voice200 are defined as the minimum concentration detectable at a certain confidence level and the minimal signal with a precision that satisfies an expected value, respectively. Using the method of Milligan *et al.*,⁴ the limits of detection and quantitation for each of the five compounds studied here have been calculated and are given in Table 1. The LODs and LOQs have been calculated by integrating over the time period where analytes were observed, which was approximately 200 seconds. These results were obtained using a $1\text{ }^{\circ}\text{C s}^{-1}$ ramp of the secondary desorber. Increasing the ramp rate will improve the limit of detection on the Voice200.

Analyte	LOD / pg	LOQ / pg
Isobutane	110	190
Benzene	180	310
Ethylbenzene	270	450
Hexafluorobenzene	390	670
Octafluorotoluene	230	420

Table 1. Limits of detection for each of the five studied compounds in picograms.

Conclusion

The data presented here demonstrate that the Syft Technologies Voice200 SIFT-MS instruments can be easily interfaced with Markes Unity2 Thermal Desorbers. Moreover, the combination of these two techniques leads to a fast and effective method for accurately quantifying compounds from sorbent tubes. Thermal desorption-SIFT-MS has the capability to accurately measure compound concentrations at substantially less than 500 pg in less than 8 minutes, and offers great potential to decrease the run time.

For more information about the unique SIFT-MS technology, please contact your nearest Syft Technologies office or visit www.syft.com.

References

1. P. Spanel and D. Smith (1998). "SIFT studies of the reactions of H_3O^+ , NO^+ and O_2^+ with several aromatic and aliphatic hydrocarbons", *Int. J. Mass Spectrom.*, **181**, 1-10.
2. P. Spanel, Y.F. Ji and D. Smith (1997). "SIFT studies of the reactions of H_3O^+ , NO^+ and O_2^+ with a series of aldehydes and ketones", *Int. J. Mass Spectrom. Ion Processes*, **165/166**, 25-37.
3. P. Spanel, J.M. Van Doren and D. Smith (2002). "A selected ion flow tube study of the reactions of H_3O^+ , NO^+ and O_2^+ with saturated and unsaturated aldehydes and subsequent hydration of the product ions", *Int. J. Mass Spectrom.*, **213**, 163-176.
4. D.B. Milligan, G.J. Francis, B.J. Prince and M.J. McEwan (2007). "The first parts-per-trillion detection by SIFT-MS", *Anal. Chem.*, **79**, 2537-2540.