Emerging Applications

First SIFT-MS direct parts per trillion detection

Introduction

Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) is an analytical technique with a normal detection limit in the range of single-digit parts per billion (ppb). This limit can be extended into the ppt range with the use of preconcentration techniques such as sorbent tubes. Unfortunately, costly and relatively slow sorbent tubes are not suitable for use in price-sensitive and time-critical applications.

Detection of phosphine in shipping containers is one example of a price-sensitive and time-critical application that requires reliable ppt sensitivity. Phosphine is commonly used in the fumigation of shipping containers. Exposure to this fumigant is of particular concern to those who work around shipping containers on a regular basis. Exposure limit values for phosphine in air are very low. In many cases limits are less than 100 ppb, depending on country-specific safety standards. To provide a reliable safety margin for workers, this means a method to detect phosphine in ppt concentrations is desirable. Since the freight industry and container ports work to tight deadlines and demand uninterrupted work flows, the method must also be quick and cost effective, which rules out the use of sorbent tubes.

Syft Technologies already provides a system for the rapid and accurate detection of fumigation compounds in containers. This document outlines how SIFT-MS has been adapted so this system can quickly detect phosphine, in ppt concentrations.

Relevant Characteristics of SIFT-MS

SIFT-MS is a chemical ionisation technique ideally suited to the rapid detection and quantification of volatile organic compounds (VOCs) in whole air. SIFT-MS has been used for a wide range of analytical tasks, ranging from breath analysis to environmental monitoring. SIFT-MS detection limits have, however, traditionally been no lower than single-digit ppb.

SIFT-MS uses the three chemical ionisation precursors (precursor ions) H$_3$O$^+$, NO$^+$, and O$_2$$^+$, yielding significant advantages in selectivity over other chemical ionisation techniques such as Proton Transfer Reaction Mass Spectrometry (PTR-MS). For example, prudent selection of precursor combinations allows SIFT-MS to resolve isobaric interferences. The precursors can also be switched rapidly during a scan, giving up to three quantification measurements in parallel.

Experimental

All measurements were made using a Syft Technologies Voice100 SIFT-MS instrument. The instrument used had a modified sample inlet, which allowed manual control of sample introduction to the flow tube. For this work a flow of around twice that of the standard configuration was used.
Figure 1 shows a schematic of the instrument. Ions are formed at the lower left, mass selected by the upstream quadrupole and then passed into the flow tube. The chemical ionisation occurs under kinetic control in a fast flow of inert carrier gas in the flow tube. The product and precursor ions are counted in the downstream end. These ions signals identify the nature and concentration of the VOCs in the sampled air.

SIFT-MS is based on well-defined reaction conditions, which means that once the reaction rate coefficient for a VOC/precursor reaction is known, quantification can be performed without the need for continual calibration. Concentration point samples can be measured as often as every 100 ms. Due to the low signal levels measured in this experiment the sampling time per point was increased to a little over 4 seconds per point. This improves the statistics of counting low signal levels.

The phosphine samples used here were produced by a static dilution method. All phosphine samples were diluted in nitrogen, as phosphine reacts rapidly with oxygen. Sample preparation followed these steps:

- Two sequential dilutions of neat phosphine were used to prepare a parent sample of around 5 ppm. The parent sample was stored in a Tedlar bag.
- Each sample was then prepared by extracting a measured amount of this parent sample from the Tedlar bag and injecting it into a new nitrogen filled bag.
- All extractions from the parent sample were measured using a 1 ml gas syringe.
- The sample bags were filled with dry nitrogen to a volume of 2 litres, using a timed constant flow. A mass flow controller was used to regulate this gas flow.
For verification purposes, the highest concentration sample was also measured on the Voice100’s standard factory-fitted inlet. Good agreement between the concentration results for both inlets was observed. Quantification with the standard inlet has been verified using a phosphine permeation tube (G-Cal type, Vici Metronics).

The phosphine was analysed using the $\text{H}_2\text{O}^+$ precursor.

$$\text{H}_2\text{O}^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{H}_2\text{O}$$

The higher water clusters also react with phosphine to give the same proton transfer product. The ions at mass 19, 37, 55, and 73 (the water clusters) were counted for 100 ms each, and the phosphine product ion (mass 35) was counted for 4 seconds.

**Results and Discussion**

The background-subtracted concentration values for the dilutions are shown in figure 2. The agreement between the measured points and the calculated dilution line is very good. The variation from the line is likely to be a result of the uncertainty in the dilution process. Each point is sampled from a Tedlar bag filled with 2 litres of nitrogen with the appropriate amount of parent sample. The background measurements were the pure nitrogen.

Figure 3 shows an example of an individual measurement point and the low background level.

![Graph showing concentration of phosphine vs. amount of parent sample added to nitrogen](image)

**Figure 2:** Successive dilutions of phosphine, showing good agreement between the calculated dilution line and measured points.
Figure 3: An individual sampling point, showing a clear increase in phosphine concentration when sample enters the flow tube just after 30 seconds.

Through sequential dilutions of phosphine:

- The lowest concentration measured averaged 190 ppt.
- The average instrumental background and any chemical interference with phosphine was 120 ppt.

Excellent linearity has been demonstrated.

**Conclusion**

SIFT-MS is capable of detecting compounds in the ppt concentration range, if point sampling time and sample flow into the flow tube are increased slightly. A series of sequential dilutions has demonstrated the methods linearity and reliability. Preconcentration media such as sorbent tubes are not required, reducing delays and costs of analysis.

Because SIFT-MS can switch sampling times for individual points as well as switch precursor ions, multiple compounds can be detected and quantified in one scan, further enhancing the technique’s flexibility and cost effectiveness.

In this example, quick and reliable direct detection of phosphine in the range of 190 ppt has been demonstrated. This example has specific applications in the commercial application of fumigant detection, as used to protect workers who handle and enter shipping containers. Other applications are being investigated.