

HIGH-SPEED FORMALDEHYDE ANALYSIS FOR THE PROCESS-LINE AND LABORATORY: SIFT-MS

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KEY WORDS

Formaldehyde, Process Analytical Technology, High-Throughput Analysis, Real-Time Analysis, SIFT-MS, Mass Spectrometry

ABSTRACT

Reliable, sensitive, and selective analysis of chemically diverse volatile organic compounds (VOCs) and inorganic gases cannot be achieved using traditional chromatographic techniques unless multiple analyses are invoked. A more recent analytical technique – Selected Ion Flow Tube Mass Spectrometry (SIFT-MS)^{1,2} – overcomes this limitation by eliminating chromatography and using highly controlled chemical ionization to achieve broad-spectrum, direct analysis of air and headspace.

In this paper, the SIFT-MS technique will be introduced. Selectivity in SIFT-MS is achieved by coupling mass spectrometry with ultra-soft chemical ionization: eight reagent ions are available and automatically switched by software control of a quadrupole mass spectrometer. The very diverse reaction mechanisms provided by the reagent ions provides detection of a very wide range of compounds, including chromatographically challenging ones such as ammonia, formaldehyde, and hydrogen sulfide. Rapid, direct analysis naturally lends itself to applications both on the process-line and in the laboratory.

The paper will illustrate the unique capabilities of SIFT-MS analysis by focusing on formaldehyde – a chromatographically challenging compound. Various analysis scenarios will be illustrated, including analysis of formaldehyde emissions in candle flames, polymer headspace, and direct air analysis from sample bags.

INTRODUCTION

Formaldehyde is ranked 25th overall in United States chemical production and is predicted to surpass world production of 52 million tons in 2017.¹ Currently 56% of the world's production is in the Asia Pacific region with North America accounting for 15.8%.² About 70% of its production is directed to the manufacture of formaldehyde based resins used in many different applications. The United States' Environmental Protection Agency provides a succinct description of its widespread use and anthropogenic sources:

Formaldehyde is present in a wide variety of products including some plywood adhesives, abrasive materials, insulation, insecticides, and embalming fluids. The major sources of anthropogenic emissions of formaldehyde are motor vehicle exhaust, power plants, manufacturing plants that produce or use formaldehyde or substances that contain it (e.g., glues), petroleum refineries, coking operations, incinerating, wood burning and tobacco smoke.³

Widespread usage, plus its formation as a byproduct of combustion and various industrial processes, means that formaldehyde significantly impacts air quality in workplaces, homes, and the environment.

Much has been written on formaldehyde's role in photochemical smog formation, and its carcinogenic properties, particularly since being categorized as "reasonably anticipated to be a human carcinogen".¹ The combined effects of these concerns and formaldehyde's ubiquity has focused attention on air quality in homes, workplaces and the environment.

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Despite the health and environmental concerns, formaldehyde analysis is not undertaken as frequently as it should be because it is very difficult to analyze at trace levels using conventional chromatographic-based analysis due to its polarity and reactivity. Derivatization is commonly applied to stabilize formaldehyde and convert it to a non-polar form that gas chromatography (GC) or liquid chromatography (LC) can handle (Table I). Furthermore, to achieve low detection limits chromatographic techniques usually require large volumes of air to be sampled and subsequently solvent extracted.

This paper describes how the application of selected ion flow tube mass spectrometry (SIFT-MS) provides a breakthrough in formaldehyde analysis. SIFT-MS analyzes formaldehyde direct from air to sub-part-per-billion-by-volume (ppbv) concentrations within seconds

TABLE I. Comparison of formaldehyde analysis using chromatographic methods and SIFT-MS

CHARACTERISTIC	HPLC	GC – DERIVATIZED	GC – DIRECT	SIFT-MS
<i>Sampling method(s)</i>	Sorbent tube	Headspace	Direct	Direct (incl. headspace), sample bag, canister
<i>Derivatization</i>	Yes (DNPH)	Yes (e.g. pentafluorobenzyl-hydroxyl amine)	No	No
<i>Sample introduction</i>	Solvent extraction, then injection	Injection	Injection	Continuous
<i>Speed / response time</i>	12.5 minutes	>8 minutes	2 – 4 minutes	100 milliseconds
<i>Concentration range</i>	ppb1 to ppm	ppb1 to ppm	ppm	ppt to ppm2
<i>User technical level required</i>	High	High	High	Low3
<i>Consumable costs per sample</i>	High	High	Moderate	Low
<ol style="list-style-type: none"> 1. For high-performance liquid chromatography (HPLC) and gas chromatography (GC) to achieve low detection limits, large volumes of gas need to be sampled. 2. SIFT-MS has a wide linear range with concentration – six orders of magnitude, giving great flexibility for sample introduction. 3. SIFT-MS has the option of simple push button operation for chosen volatiles and is routinely used by personnel in ports with no, or little chemical training. 				

METHODS

A. SELECTED ION FLOW TUBE MASS SPECTROMETRY (SIFT-MS)

SIFT-MS^{4,5} is a real-time analytical technique for direct, comprehensive gas analysis to ultra-trace levels.⁶ Data obtained by SIFT-MS instruments compare well with the accepted chromatographic method for volatile organic compound (VOC) analysis.⁷

SIFT-MS (Figure 1) uses ultra-soft, precisely controlled chemical ionization coupled with mass spectrometric detection to rapidly quantify VOCs – including formaldehyde – and permanent gases to low part-per-trillion concentrations by volume (ppt v/v). Eight chemical ionization agents (reagent ions) are now applied in commercial SIFT-MS instruments: H₃O⁺, NO⁺, O₂⁺, O⁻, O₂⁻, OH⁻, NO₂⁻, and NO₃⁻. The eight SIFT-MS reagent ions react with VOCs and inorganic gases in very well controlled ion-molecule reactions, but they do not react with the major components of air (N₂, O₂, and Ar). This enables SIFT-MS to analyze air at trace and ultra-trace levels without pre-concentration.

Rapid switching of 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, both Voice200 and Voice200ultra model SIFT-MS instruments from Syft Technologies (Christchurch, New Zealand; www.syft.com) were utilized.

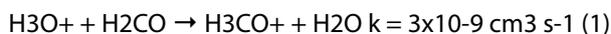
B. AUTOMATED SIFT-MS

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; www.gerstel.com), which has proved the best-suited commercial autosampler system for integration with the SIFT-MS technique. Sampling of Tedlar gas sample bags (SKC, Eighty-Four, PA, USA) was achieved using the GERSTEL sample bag analysis accessory, while headspace analysis was carried out from 20-mL sample vials on a standard GERSTEL vial rack.

C. SIFT-MS-BASED FORMALDEHYDE DETECTION AND CALIBRATION

SIFT-MS selectively detects formaldehyde via the proton-transfer reaction shown in Eqn. 1.9 The H₃CO⁺ product ion is detected at m/z = 31.



Due to the soft ionization process that is characteristic of SIFT-MS and the low m/z of the formaldehyde product ion, this measurement is specific to the detection of formaldehyde.

Formaldehyde is quantified using the standard SIFT-MS approach.⁵ Instruments can be calibrated simply by using

permeation tubes that are readily obtained from commercial suppliers which provide accurate concentrations of formaldehyde in the low ppm v/v and ppb v/v range.

SIFT-MS has a linear concentration range that extends over five orders of magnitude,⁸ with detection limits in the low part-per-trillion by volume (pptv) concentration range. Figure 2 shows a calibration curve for formaldehyde based on a permeation tube reference, appropriate to workplace safety applications, extending from 7 ppb to 4 ppm.

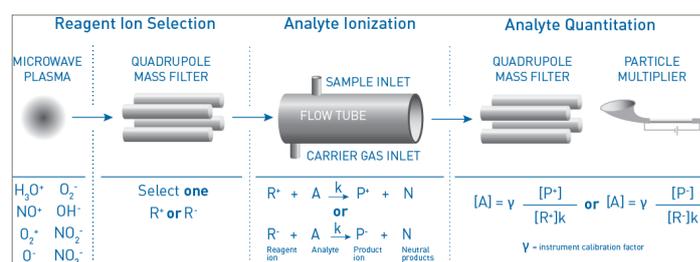


Figure 1. Schematic representation of the SIFT-MS analytical technique

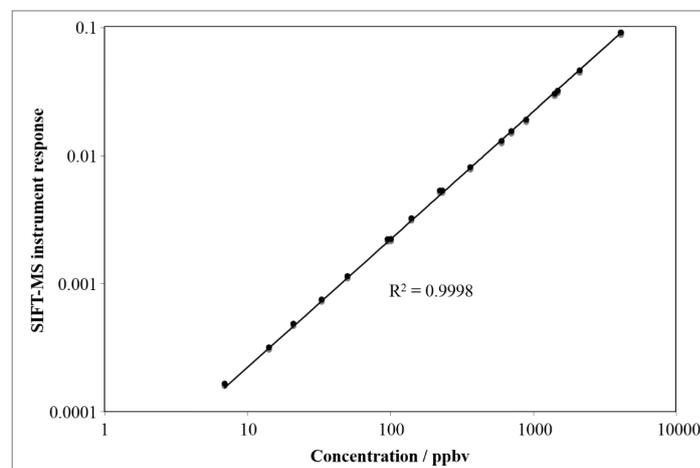


Figure 2. Linear detection of formaldehyde using a SIFT-MS instrument

RESULTS AND DISCUSSION

A. DIRECT ANALYSIS OF FORMALDEHYDE

SIFT-MS instruments quantify formaldehyde at low-ppt v/v concentrations in less than 30 seconds. Figure 3 shows results from an instrument analyzing formaldehyde, demonstrating real-time detection of formaldehyde.

Simple, real-time analysis of formaldehyde at sub-part-per-million concentrations is unique to the SIFT-MS technique and is applicable in industry from in-process monitoring to stack gas analysis, to fenceline monitoring.

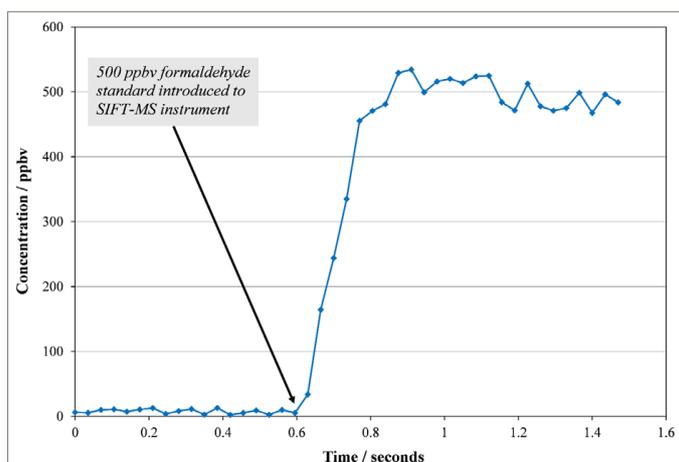


Figure 3. Rapid response of the SIFT-MS instrument to introduction of a 500-PPB v/v formaldehyde standard.

Rapid SIFT-MS analysis has also been applied to discrete sample analysis, providing simple and reliable analysis of formaldehyde and other toxic residues in shipping containers for over a decade⁸. Figure 4 shows instrument screenshots obtained from analysis of Tedlar bag samples taken from shipping containers that had safe and unsafe concentrations of formaldehyde. The instrument raises an alarm when levels exceed regulatory exposure standards.

B. AUTOMATED FORMALDEHYDE ANALYSIS

Prior to mid-2015, all SIFT-MS analysis was manual. Recently SIFT-MS has been automated, providing benefits in sample throughput and also repeatability due to a reduction in operator-related variability. In this paper, automated gas and headspace analyses of formaldehyde have been implemented.

Direct analysis of gas samples: SIFT-MS analyzes formaldehyde directly and repeatedly, as demonstrated by four replicate injections of

a 200-ppb v/v formaldehyde gas standard taken from a Tedlar gas sampling bag (Figure 5). The mean concentration reading was 203 ppb v/v with an RSD of 2.6%

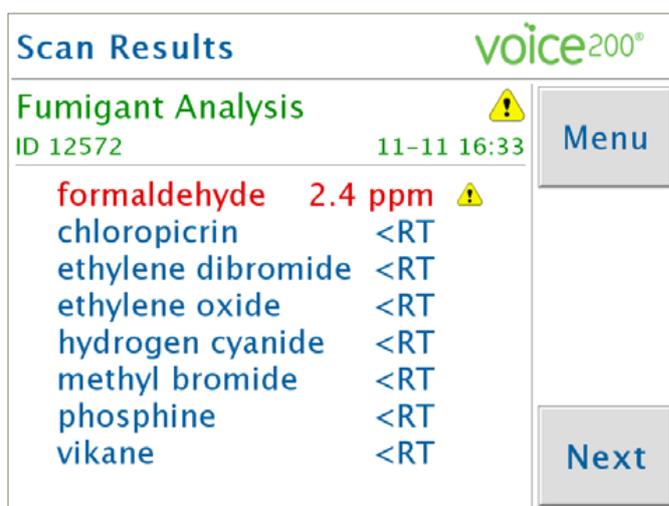
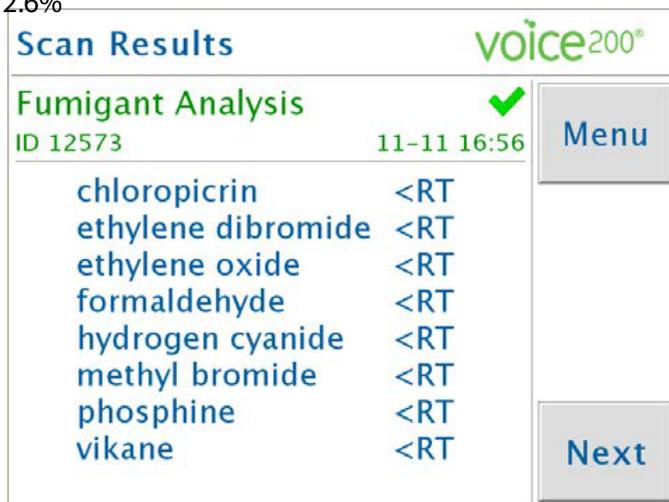


Figure 4. Simple reporting of safe (top) and unsafe (bottom) concentrations of formaldehyde in two shipping containers detected using a sift-ms instrument. note: "<rt" refers to "less than the reporting threshold" (typically half the workplace exposure limit), where the actual concentration is hidden from the non-technical operator.

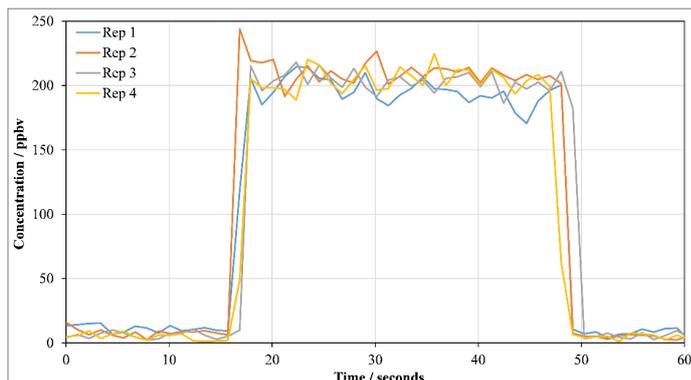


Figure 5. Replicate, rapid analyses of formaldehyde direct from a tedlar sample bag using automated sift-ms.

SIFT-MS analysis is not just limited to formaldehyde. In Figure 6, formaldehyde and the five other saturated linear aldehydes from acetaldehyde to hexanal were analyzed from two sample bags within one minute. Note that HPLC analysis takes about 12.5 minutes and when automated, the analysis itself is the rate-limiting step. For example, analysis of 20 samples takes 4½ hours with HPLC, whereas with SIFT-MS the sample set is analyzed in less than 10 minutes; that is to say, the sample throughput delivered by SIFT-MS is 25 times higher.

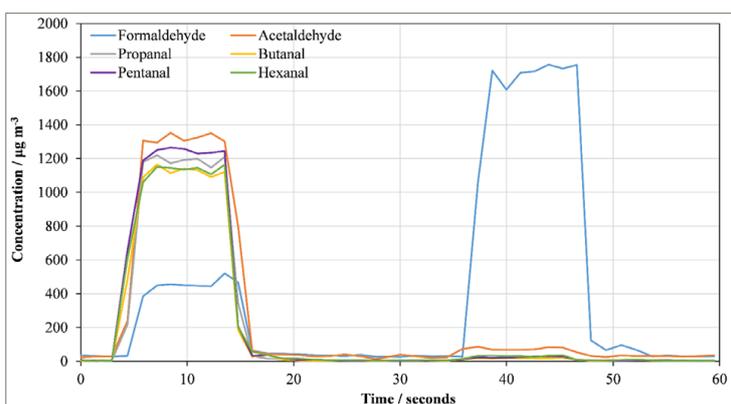


Figure 6. Sift-ms analysis of two tedlar bag samples containing c1 – c6 saturated aldehydes within one minute.

Direct analysis of formaldehyde simplifies R&D and facilitates novel research that is exceedingly difficult to undertake using traditional methods. For example, formaldehyde can be sampled directly from a candle flame using a syringe, injected into a sample bag, and then analyzed instantly using SIFT-MS. A formaldehyde concentration of 235 ppb v/v, or 6.4 mg/m³, was measured in less than a minute.

Headspace analysis: SIFT-MS provides very rapid and highly sensitive quantitation of formaldehyde from headspace samples. Figure 7 shows rapid screening of three ground polymer samples for residual monomers. Significant formaldehyde emissions are detected from the polyoxymethylene (POM) sample on a timescale of seconds without any derivatization, pre-concentration, or any other pre-treatment. This speed of analysis can be utilized for very high throughput screening to provide rapid warning of quality issues and greatly reduces the cost per analysis.

Multiple Headspace Extraction (MHE).¹¹ The residual monomer concentrations shown in Figure 7 represent the amount of monomer that has partitioned from the polymer material into the headspace and it is possible

that a significant amount of monomer remains within the bulk of the material. The ratio of monomer retained to monomer released into the headspace is related to the partition coefficient of these compounds. Without knowing these values for the analytes in these matrices, and under these experimental conditions, it is not possible to calculate the total amount of residual monomer in the sample. Additionally, complete equilibrium of the headspace may not have been reached, further complicating the measurement.

If multiple headspace measurements could be made and a total concentration calculated from all measurements, the actual concentration of residual monomer within the solid could be found. However, this would require a significant number of measurements to ensure total removal of all monomer within the polymer.

The multiple headspace extraction (MHE) technique is a headspace technique that calculates the total concentration from a limited number of consecutive headspace analyses by recognizing that the decrease in concentration over multiple headspace measurements is exponential. A headspace concentration is generated, the concentration measured and then flushed or vented and a new headspace generated. Figure 8 shows sequential MHE measurements of formaldehyde emitted from ground POM polymer. The concentration data are summarized in Table II.

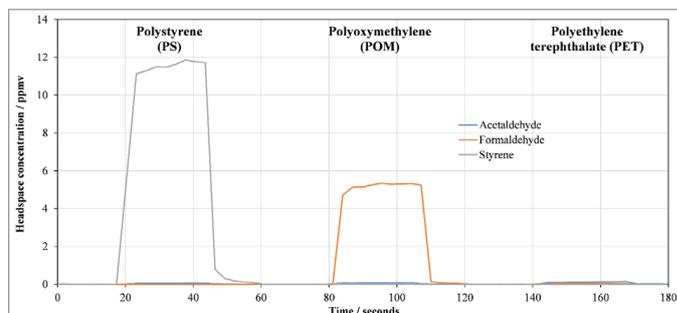


Figure 7. Residual monomer analysis of three ground polymers, including formaldehyde from pom polymer.

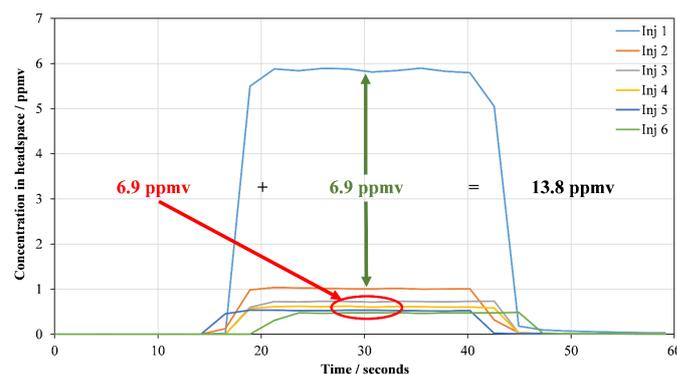


Figure 8. MHE analysis of formaldehyde from pom polymer using automated sift-ms. see table ii for full data summary. the green data are the sum of injections 1 and 2, while the red data are calculated from extrapolation of points 3 – 6 (table iii).

TABLE II. Concentration data for sequential injections of headspace during MHE analysis.

INJECTION NUMBER	MEAN CONCENTRATION / PPM V/V	ln (MEAN)	3 X STANDARD DEVIATIONS	INJECTION NUMBER
1	5.95	1.783	0.0978	1
2	0.95	-0.0513	0.0327	2
3	0.695	-0.364	0.02718	3
4	0.584	-0.53785	0.02124	4
5	0.515	-0.66359	0.02301	5
6	0.454	-0.78966	0.01668	6

It has been suggested that the first point of any MHE measurement can be prone to experimental error.¹² Possible sources include the change in gas matrix from measurement 1 to 2 due to the flush cycle and excessively long standing time for the first headspace generation. It can clearly be seen in Figure 8 that the first concentration measured is significantly higher than the subsequent measurements. This is probably due to the relatively high extraction temperature used in this experiment for this polymer type (80 °C), which causes a significant release of formaldehyde from the top layers of the polymer particles compared to the slower release from the internal bulk. Further analysis also showed the second concentration measurement to be higher than expected (Figure 8). Since the MHE technique relies on adding all concentrations together, the total concentration is calculated from the sum of the first two injections and the extrapolated fit to injection 3 onward (Figure 9). Equation 2 gives the fit equation¹² and Table III summarizes the parameters, where “Extrapolated injection 3” in the table refers to the injection 1 value recalculated from the linear fit.

$$\text{Total HCHO concentration} = \text{Conc. (Inj. 1)} + \text{Conc. (Inj. 2)} + \text{Conc. (Extrapolated Inj. 3)} / (1 - \text{slope})$$

This gives a total residual monomer concentration of 13.8 ppm v/v formaldehyde (as annotated on Figure 8).

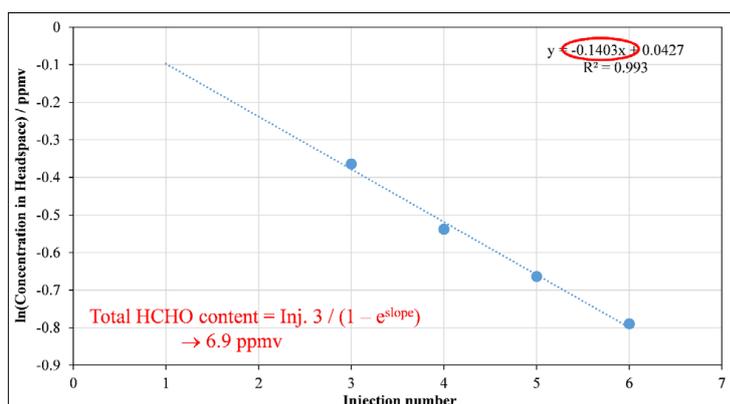


Figure 9: Residual monomer analysis of formaldehyde from a ground pom polymer using MHE.

TABLE III. Parameters used for the MHE calculation.

PARAMETER	VALUE
<i>Slope (injections 3 – 6)</i>	-0.140
<i>Intercept (injections 3 – 6)</i>	0.0427
<i>Extrapolated injection 3</i>	0.907
<i>Exp(slope)</i>	0.869
<i>Calculated HCHO from injection 3 onward / ppm v/v</i>	6.93
<i>Sum of injections 1 and 2 / ppmv</i>	6.9

CONCLUSIONS

Formaldehyde is a very important compound industrially, and public exposure to formaldehyde is widespread through combustion, industrial and material emissions. It is crucial that methods are available to analyze potential sources to low ppb v/v concentrations. Traditional methods based on GC and LC can be used to analyze formaldehyde, but they are off-line and require highly skilled laboratory personnel.

By applying soft chemical ionization coupled with mass spectrometric detection, SIFT-MS provides new opportunities for formaldehyde detection in multiple applications, including process monitoring, fenceline monitoring, and emissions from polymers. SIFT-MS analysis is rapid, selective and sensitive, and can be carried out by non-technical personnel.

The advantages of the SIFT-MS technique stem from the fact that almost any gaseous analyte will undergo reactions with the available reagent ions. Typical exothermic ion-molecule reactions exhibit rate coefficients in the range 1×10^{-9} to 3×10^{-9} molecules $\text{cm}^{-3} \text{ s}^{-1}$. Rate coefficients of this magnitude enable analyte concentrations in gas mixtures from ppt v/v up to around 50 ppm v/v to be monitored in real time. A mass spectrometer with a mass resolution of slightly less than 1 atomic mass unit (amu) is sufficient for most samples. Problems arising from overlapping isobaric compounds can largely be overcome by utilizing multiple reagent ions to analyze the sample. These reagent ions (which can be switched instantly using the first quadrupole mass filter) have different reaction mechanisms that give different products and enable effective separation.

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