SIMPLE DETERMINATION

OF FORMALDEHYDE ADSORPTION BY MERINO WOOL, USING SIFT-MS

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Formaldehyde is ubiquitous in the modern built environment, but it is also carcinogenic and so it is desirable to reduce chronic exposure in homes and workplaces. This study demonstrates the ease with which construction materials can be evaluated for their formaldehyde adsorption efficacy, by utilizing direct analysis with selected ion flow tube mass spectrometry (SIFT-MS). With this approach, merino wool is shown to be extremely effective in adsorbing formaldehyde from air.

INTRODUCTION

Formaldehyde was classified as a known human carcinogen by the United States National Toxicology Program in 2011,[1] and was added to the third proposal to the Carcinogens and Mutagens Directive 2004/37/EC by the European Union in 2018.[2] However, the widespread historic use of formaldehyde-containing resins in construction materials, as well as emissions from other sources, means that many are chronically exposed to formaldehyde in their homes and offices.

One approach to reducing chronic exposure to formaldehyde is the use of furnishings in homes and workplaces, that adsorb it from the atmosphere. Wool, because it is composed of a diverse range of proteins and lipids, can bind airborne pollutants such as formaldehyde. However, quantifying formaldehyde adsorption is non-trivial using conventional analytical methods because of its low molecular weight, high polarity, and high reactivity. SIFT-MS, on the other hand, provides simple, direct analysis of formaldehyde in air and headspace via soft chemical ionization, as has been described elsewhere.[3,4]

In this application note, SIFT-MS is utilized to determine the formaldehyde adsorption rates of ten merino wool samples supplied by The New Zealand Merino Company. Formaldehyde adsorption is determined through repeated measurement of headspace formaldehyde concentration, which diminishes more rapidly as a function of time than do blank samples.

Method

1. The SIFT-MS technique

SIFT-MS[11-14] (Figure 1) uses soft chemical ionization (CI) to generate mass-selected reagent ions that can rapidly quantify VOCs to low parts-per-trillion concentrations (by volume, pptv). Eight reagent ions (H_3O^+, NO^+, O_2^+, O^-, OH^-, O_2^-, NO_2^- and NO_3^-) obtained from a microwave discharge of moist or dry air, are now applied in commercial SIFT-MS instruments. These eight reagent ions react with VOCs and other trace analytes in well-controlled ion-molecule reactions, but they do not react with the major components of air (N_2, O_2 and Ar). This allows for real-time analysis of air samples at trace and ultra-trace levels without pre-concentration.

Rapid switching between reagent ions provides high selectivity, because the multiple reaction mechanisms provide additional independent measurements of each analyte. The multiple reagent ions also help to remove uncertainty from isobaric overlaps in mixtures containing multiple analytes.

Analyses were run in Selected Ion Mode (SIM) for the compounds of interest on a Voice200ultra SIFT-MS instrument (Syft Technologies, Christchurch, New Zealand). Analytical methods were created using the Method Editor module in the LabSyft software package from Syft Technologies.

2. Automated SIFT-MS analysis

In SIFT-MS, the capability for rapid direct analysis of a sample provides unique opportunities for high-throughput headspace analysis, irrespective of whether the task is routine VOC monitoring or the analysis of chromatographically-challenging species, such as ammonia and formaldehyde. In contrast to chromatographic techniques that require rapid injection to achieve good peak shapes and temporal separation, SIFT-MS simply requires steady sample injection for the duration of the analysis – that is, sample injection and analysis occur simultaneously (Figure 2).

Automated headspace analysis was carried out using a Syft Technologies Voice200ultra SIFT-MS instrument coupled with a GERSTEL multipurpose sampler (MPS; GERSTEL, Mülheim an der Ruhr, Germany). Samples were first incubated in a GERSTEL agitator prior to sampling of the headspace and injection into the SIFT-MS instrument through a GERSTEL septumless sampling head (maintained at 150 °C).

Table 1. Schematic diagram of SIFT-MS – a direct chemical-ionization analytical technique.

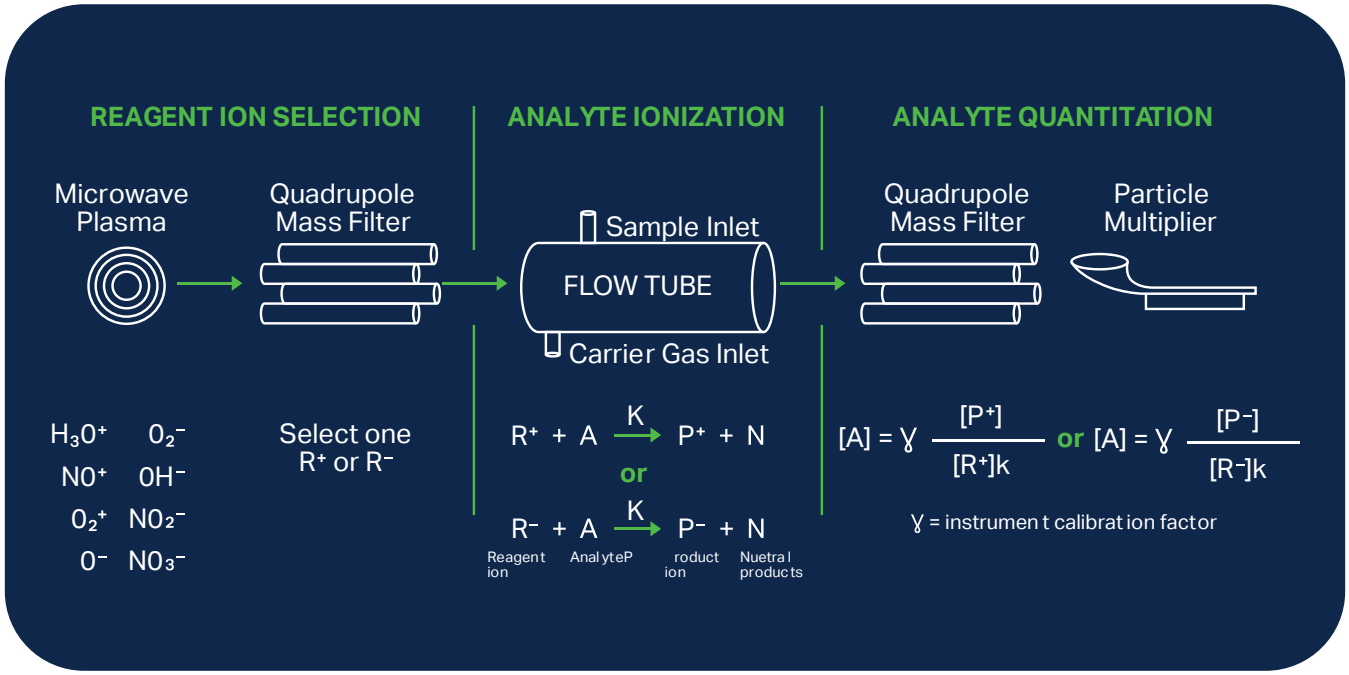
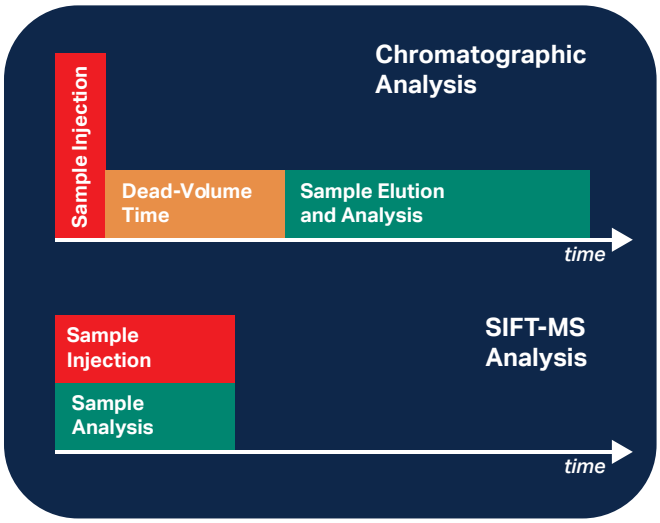


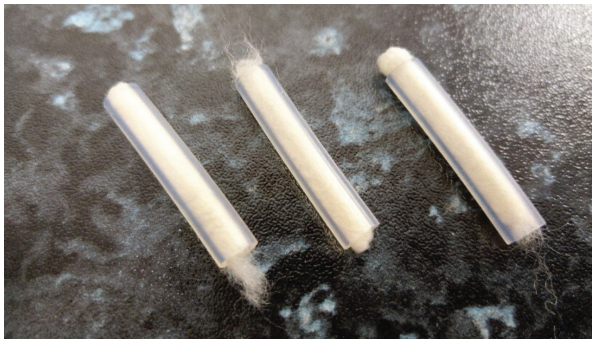
Figure 2. Graphical representation of the different sample-injection and analysis requirements of chromatographic techniques and SIFT-MS.



3. Samples

To ensure different types of wool would have consistent surface area exposure in this experiment, 0.1 g of each sample was inserted into 3-cm lengths of 1/8" PFA tubing (as shown in Figure 3). These tubes were then inserted into 20-mL autosampler vials for testing.

Figure 3. Examples of tube wool filter.



4. Experimental procedure

A standard stock "atmosphere" of formaldehyde in air was generated in 20-mL autosampler vials by incubating paraformaldehyde overnight at 50 °C. The air/formaldehyde mixture was then sampled (0.5 mL) and injected into vials containing empty PFA tubing (blank vials) and into sample vials containing PFA tubing with wool samples.

The formaldehyde concentrations in the vials were then measured at time intervals of 2, 5, 10, 30 and 45 min using the SIFT-MS instrument. To ensure results were consistent, five replicates of each type of wool were analyzed.

Results and Discussion

Figure 4 shows the average concentrations of formaldehyde measured at different time intervals in the presence of wool samples with different fiber diameters. These are shown relative to the "blank" vials which contained no wool. Similarly, Figure 5 shows the results obtained for the samples with different degrees of processing and different end-product formats. In all cases, replicate measurements are very consistent for this type of measurement, as indicated by the one-standard-deviation error bars on the concentration measurements.

Figure 4. Formaldehyde absorption characteristics of merino wool fibers of various diameters.

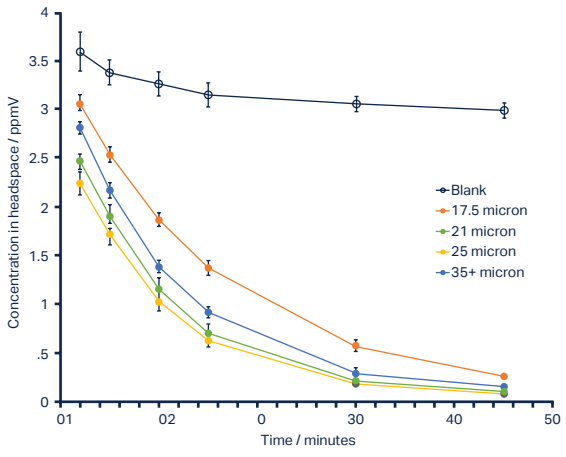
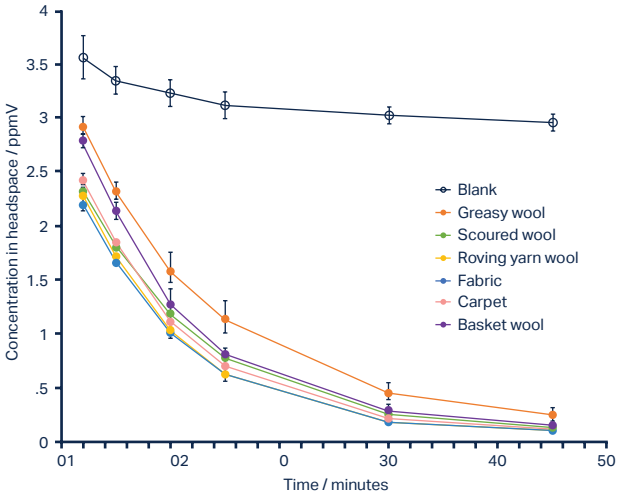


Figure 5. *Formaldehyde absorption characteristics of merino wool fibers that have undergone different processing or have different end uses.*



All wool samples gave more than 90% formaldehyde removal within 45 min, but the rate of removal was dependent on the type of wool. Table 1 summarizes the formaldehyde removal rates over time relative to the blank vials. A comparison of fiber diameters showed that the 25-micron wool has the fastest formaldehyde removal rate. For the differently-processed wools, the fabric had the fastest formaldehyde removal rate.

Again, the products gave more than 90% formaldehyde removal within 45 min, but removal rates depend on processing and application.

Conclusions

This study shows that New Zealand merino wool rapidly removes formaldehyde at room temperature (22 °C), with over 90% formaldehyde absorption within 45 min. Of the wool samples with different fiber diameters, the 25-micron wool has the fastest formaldehyde removal rate, whereas for the wools that have undergone different processing, the fabric has the fastest formaldehyde removal rate.

Formaldehyde adsorption studies such as this one are greatly simplified using automated SIFT-MS.

Acknowledgement

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References

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Table 1. *Comparisons of formaldehyde removal rates for different wool fibers and stages of fiber processing.*

	Formaldehyde removal rates at 22°C					
	2 min	5 min	10 min	15 min	30 min	45 min
17.5 Micron	14.5%	24.9%	42.5%	56.5%	81.5%	91.2%
21 Micron	31.5%	43.8%	64.7%	77.7%	93.2%	96.6%
25 Micron	37.5%	49.1%	68.4%	79.9%	93.9%	96.9%
35+ Micron	21.8%	35.6%	57.4%	71.2%	90.6%	94.8%
Greasy	21.8%	35.6%	57.4%	71.2%	90.6%	94.8%
Scoured	34.9%	45.3%	63.2%	75.0%	91.7%	95.7%
Roving/Yarn	35.7%	48.2%	68.2%	80.3%	94.0%	96.7%
Carpet	32.0%	44.5%	64.9%	77.5%	92.7%	96.1%
Fabric	38.1%	49.9%	68.6%	79.9%	93.6%	96.7%
Basket	22.5%	36.3%	60.4%	73.9%	90.6%	94.8%

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