

ANALYSIS OF A FORMALDEHYDE SCAVENGING COMPOUND USING SELECTED ION FLOW TUBE MASS SPECTROMETRY (SIFT-MS)

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INTRODUCTION

The toxicity, carcinogenicity and ubiquity of formaldehyde is well-known and can impact on air quality in workplaces, homes and the environment. The US EPA states: "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."¹ Within the EU, its carcinogenicity is recognised by its inclusion in the 3rd Proposal to the Carcinogens and Mutagens Directive (2004/37/EU) in 2018, limiting its use in the workplace.

Clearly, levels of formaldehyde in the environment should be monitored, and where possible, controlled. However, formaldehyde is difficult to analyse by traditional chromatography, usually requiring large gas volumes to be sampled, followed by derivitisation. This makes continuous monitoring in real-time highly problematic. From a control perspective, materials that can selectively scavenge volatile organic compounds (VOCs) are of interest, but again, formaldehyde poses a particular challenge. Additionally, to follow the removal process and determine maximum capacities and breakthrough volumes, it is necessary to monitor concentration changes in real-time.

This Application Note presents data on a novel cage-based scavenging material that selectively removes formaldehyde in the presence of other VOCs and water. The removal of formaldehyde is followed, in real-time using Selected Ion Flow Tube Mass Spectrometry (SIFT-MS).

SIFT-MS is a form of direct mass spectrometry that uses precisely controlled soft ionisation to enable real-time, quantitative analysis of VOCs in air, at detection limits as low as 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.

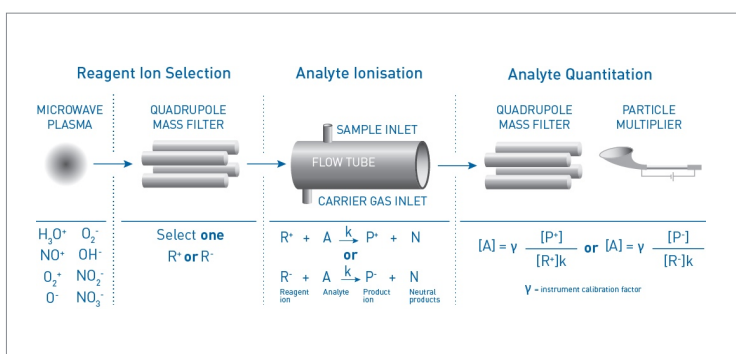


Figure 1: Schematic representation of the SIFT-MS technique.

Reagent ion selection – A microwave discharge through moist air forms the standard SIFT-MS positive and negative ions; H_3O^+ , NO^+ , O_2^+ , OH^- , O_2^- , O^- , NO_2^- and NO_3^- 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 eight, 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

INSTRUMENTATION

Syft Technologies' Voice 200ultra running LabSyft software (version 1.7.1). Helium carrier gas, HPI inlet.



Figure 2: Syft Technologies Voice 200ultra SIFT-MS.

METHOD

Samples of cage material were packed into empty GERSTEL thermal desorption tubes and plugged with a small amount of quartz wool. This was attached to the inlet of the SIFT-MS using a short piece of silicone tubing. A 1 L Tedlar bag containing the required gas mix was attached to the other end of the tube, again using silicone tubing and the tap opened. Figure 3 shows the tube and Tedlar bag used. The uptake of formaldehyde into the cage material was then monitored using the SIFT-MS sampling continuously at 20 mL/min.

Various amounts of sample and gas mixtures were used to assess the uptake and selectivity of the cage material. Additionally, the effectiveness of the material in the presence of water was also assessed by adding 1 mL of water to the Tedlar bag gas mixtures prior to sampling. Details of gas mixtures will be given in the Results section.



Figure 3: Fritted thermal desorption tube, filled with cage material and attached to filled 1 L Tedlar bag.

RESULTS

Dry gas standards testing

Initial testing was carried out using a formaldehyde gas standard passing through 10, 25, 50 and 100 mg of cage material. Figure 4 shows the concentration profiles obtained over 45 minutes of exposure. The sharp spike at this point corresponds to the removal of the packed tube and reattachment of the Tedlar bag to the SIFT-MS, to determine the actual concentration in the gas standard. This is marked as the red dashed line.

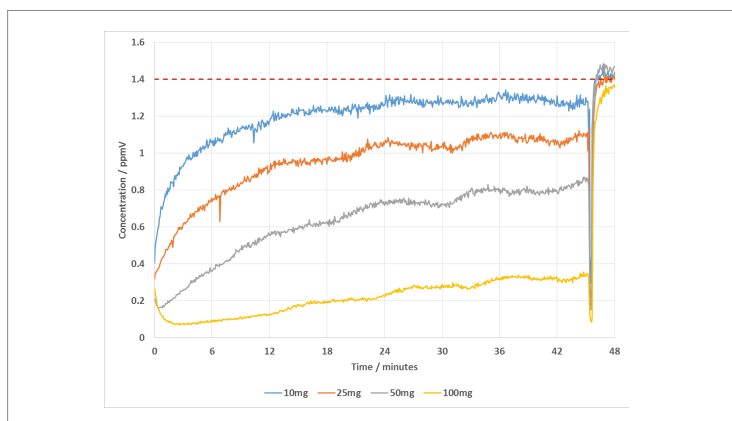


Figure 4: Results for 10, 25, 50 and 100 mg of cage material challenged with formaldehyde.

Table 1: Lowest, end point and actual concentration of formaldehyde, in ppmV, for results shown in Figure 4.

Cage material mass (mg)	Measured concentration (ppmv)		
	Lowest	End Point	Actual
10	0.4	1.2	1.4
25	0.3	1.1	1.4
50	0.2	0.8	1.4
100	0.05	0.3	1.4

Table 1 lists the results obtained, with the lowest concentration measured, the end point concentration – measured just prior to removal of the sample tube, and the actual gas standard concentration measured in the Tedlar bag at the end of the run. As expected, increasing sample mass leads to increased removal of formaldehyde both initially and over the course of the experiment. As the mass of the sample increases, the time taken to reach the minimum concentration also increases. This is probably due to the increased bed size of the sample leading to an increased diffusion length to reach the bulk of the material.

In order to test the selectivity of the cage material, 50 mg of sample was challenged with a gas mixture containing formaldehyde and two similar aldehydes – acetaldehyde and acrolein. Figure 5 and Table 2 shows the results obtained and it can clearly be seen that the material is entirely selective towards formaldehyde, despite structural similarities with the other two aldehydes. Again, the actual formaldehyde concentration is marked as the red dashed line. (This marking is used in all subsequent plots).

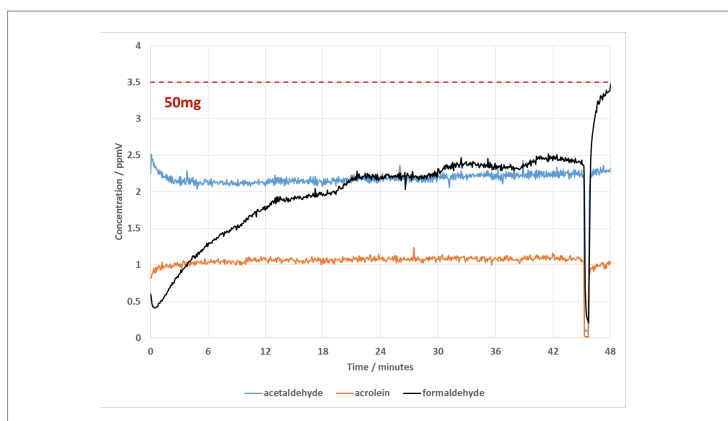


Figure 5: Results for 50 mg of cage material challenged with formaldehyde, acetaldehyde and acrolein.

Table 2: Lowest, end point and actual concentration for formaldehyde, acetaldehyde and acrolein, in ppmV, for results shown in Figure 5.

Compound	Measured concentration (ppmv)		
	Lowest	End Point	Actual
Formaldehyde	0.4	1.2	1.4
Acetaldehyde	0.3	1.1	1.4
Acrolein	0.2	0.8	1.4

In order to test selectivity in the presence of non-polar analytes, a gas mixture containing formaldehyde, trimethylbenzene isomers, xylene isomers, toluene, benzene and isooctane (BTEX+ mix) was prepared. Figure 6 shows the results obtained for 10, 25, 50 and 100 mg samples. As before, the cage material is totally selective to formaldehyde, with the concentration profiles mimicking those seen in Figure 4, with the concentrations scaled to the starting concentration of formaldehyde (4.3 ppmV cf. 1.4ppmV). It is also noticeable that the lower volatility compounds take some time to reach a steady concentration, again, probably due to surface effects and diffusion through the sample bed. The results are tabulated in Table 3 below.

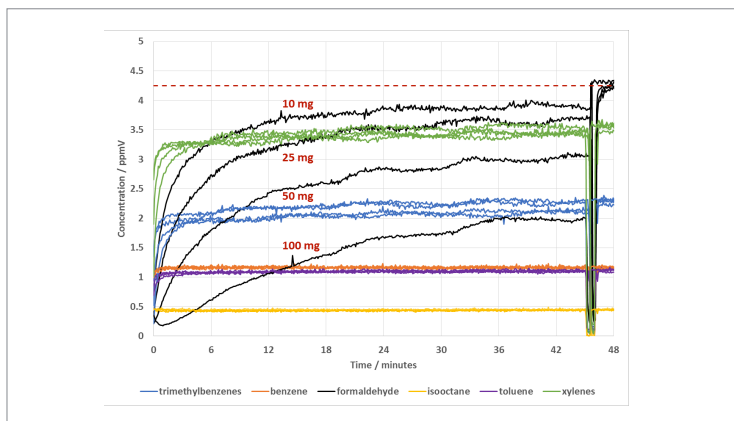


Figure 6: Fritted thermal desorption tube, filled with cage material and attached to filled 1L Tedlar bag.

Table 3: Lowest, end point and actual concentration for the BTEX+ mix, in ppmV, for results shown in Figure 6.

Compound	Measured concentration (ppmv)		
	Lowest	End Point	Actual
Formaldehyde (10mg)	0.6	3.9	4.3
Formaldehyde (25mg)	0.4	3.7	4.3
Formaldehyde (50mg)	0.3	3.1	4.3
Formaldehyde (100mg)	0.2	2.0	4.3
Trimethylbenzenes	2.3	2.3	2.3
Benzene	1.2	1.2	1.2
Isooctane	0.4	0.4	0.4
Toluene	1.1	1.1	1.1
Xylenes	3.5	3.5	3.5

The final challenge mixture using dry gas standards was a “megamix” containing formaldehyde, the BTEX+ mix used above and acetaldehyde, acrolein, methacrolein and crotonaldehyde. A sample mass of 50 mg was used for this analysis. Figure 7 shows the results obtained with the concentration values tabulated in Table 4. As expected, the concentration profiles follow those seen with the previous gas mixtures, with all compounds unaffected by the cage material apart from formaldehyde.

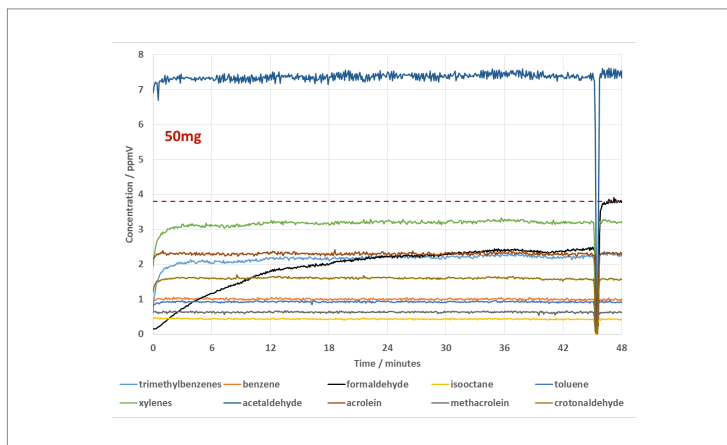


Figure 7: Results for 50 mg of cage material challenged with the “megamix”, as described above.

Table 4: Lowest, end point and actual concentration for the “megamix”, in ppmV, for results shown in Figure 7.

Compound	Measured concentration (ppmv)		
	Lowest	End Point	Actual
Formaldehyde	0.1	2.5	3.8
Acetaldehyde	7.3	7.3	7.5
Acrolein	2.2	2.2	2.3
Methacrolein	0.6	0.6	0.6
Crotonaldehyde	1.6	1.6	1.6
Trimethylbenzenes	2.2	2.2	2.2
Benzene	1.0	1.0	1.0
Isooctane	0.4	0.4	0.4
Toluene	0.9	0.9	0.9
Xylenes	3.2	3.2	3.2

Wet gas standards testing

Following analysis using gas standards prepared with dry matrix gas, a series of standards were prepared in moist air. This was achieved by adding 1 mL of water to the inflated Tedlar bag prior to the analysis.

In addition to sample tubes containing the cage material, a blank tube was used to assess the level of formaldehyde uptake into the water, as it is known that formaldehyde has a significant affinity for water. Figure 8 shows the results from the blank tube and 10, 25, 50 and 100 mg of cage material being challenged with formaldehyde, with the results tabulated in Table 5.

It is clear from the light blue trace in the plot that a significant amount of formaldehyde is removed from the gas phase by the water present, with the gas phase concentration dropping from 2.7 ppmV to 0.5 ppmV after 45 minutes exposure. However, the cage material still removes significant amounts of formaldehyde from the gas stream.

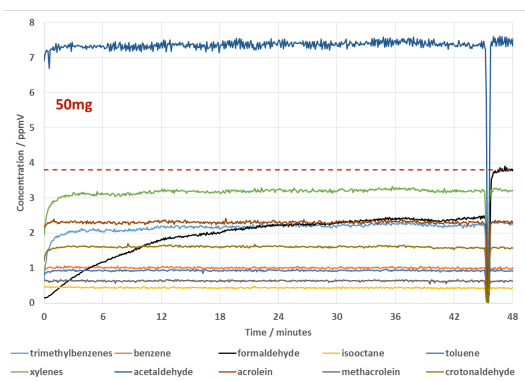


Figure 8: Results for 0, 10, 25, 50 and 100 mg of cage material challenged with formaldehyde in the presence of water.

Table 5: Lowest, end point and actual concentration of formaldehyde, in ppmV, for results shown in Figure 8.

Cage material mass (mg)	Measured concentration (ppmv)		
	Lowest	End Point	Actual
No cage	0.5	0.5	2.7
10	0.3	0.6	2.7
25	0.1	0.7	2.7
50	0.05	0.6	2.7
100	0.05	0.8	2.7

Following the initial tests with formaldehyde, 50 mg of cage material was challenged with both an aldehyde mix and the BTEX+ mix. Figures 9 and 10 show the results of this, with the data listed in Tables 6 and 7. As previously seen, the material is highly selective to formaldehyde. It is worth noting that the aldehyde compounds all have some degree of loss over the 45 minute run, but the measured concentrations after removal of the sample tube match those just before removal, suggesting that the loss is probably due to the water present in the Tedlar bag. This is not the case with the non-polar BTEX+ compounds.

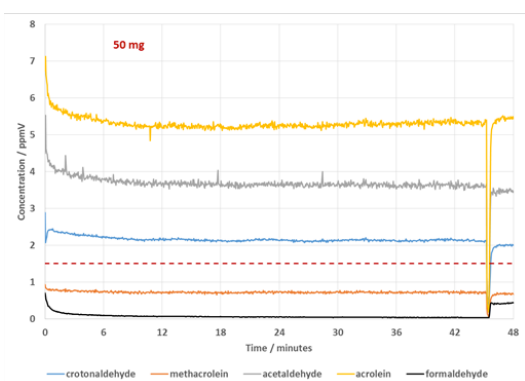


Figure 9: Results for 50 mg of cage material challenged with an aldehyde mix in the presence of water, as described above.

Table 6: Lowest, end point and actual concentration of aldehydes, in ppmV, for results shown in Figure 9.

Compound	Measured concentration (ppmv)		
	Lowest	End Point	Actual
Formaldehyde	0.03	0.4	1.5
Acetaldehyde	3.5	3.5	4.5
Acrolein	5.4	5.4	6.7
Methacrolein	0.7	0.7	0.9
Crotonaldehyde	2.1	2.1	2.8

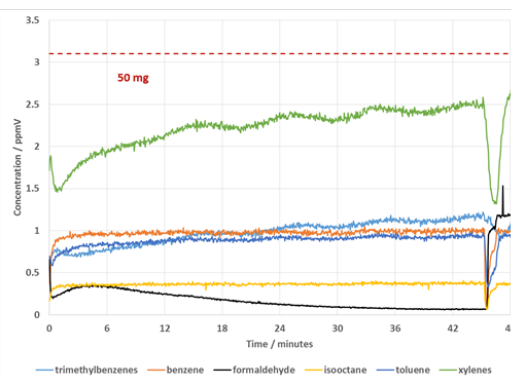


Figure 10: Results for 50 mg of cage material challenged with the BTEX+ mix in the presence of water, as described above.

Table 7: Lowest, end point and actual concentration for the BTEX+ mix, in ppmV, for results shown in Figure 10.

Compound	Measured concentration (ppmv)		
	Lowest	End Point	Actual
Formaldehyde	0.06	1.2	3.1
Trimethylbenzenes	1.2	1.2	1.2
Benzene	1.0	1.0	1.0
Isooctane	0.4	0.4	0.4
Toluene	0.9	0.9	0.8
Xylenes	2.5	2.5	2.5

DISCUSSION

In this Application Note we present data on a novel cage-based material that selectively removes formaldehyde from the gas phase. It is highly selective, even in the presence of similar aldehydes, such as acetaldehyde and acrolein. Additionally, the presence of water does not affect its ability to remove formaldehyde.

The use of SIFT-MS, and its ability to easily detect formaldehyde, without the need for prior derivatization, continuously in real-time was critical to making the above measurements and demonstrates the novel analytical methodology that can be developed with this technique. These include monitoring of VOC release from in-line process control applications.

REFERENCES

1 – US EPA “IRIS Toxicological Review of Formaldehyde” – http://cfpub.epa.gov/ncea/iris_drafts/recordisplay.cfm?deid223614

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