Automated Selected Ion Flow Tube Mass Spectrometry (SIFT-MS)

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Introduction

Traditionally, analysis with SIFT-MS has relied on either passive ambient monitoring or manual introduction of large volume gas and headspace samples, for example canister or Tedlar bag sampling. Whilst this is an effective means of analysis, it is labour intensive. In this application note, we demonstrate a fully automated SIFT-MS system coupled to GERSTEL's MultiPurpose Sampler, with a range of initial applications showing the utility of this automated approach.

Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) is a form of direct mass spectrometry that uses precisely controlled soft ionisation to enable real-time, quantitative analysis of volatile organic compounds (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.
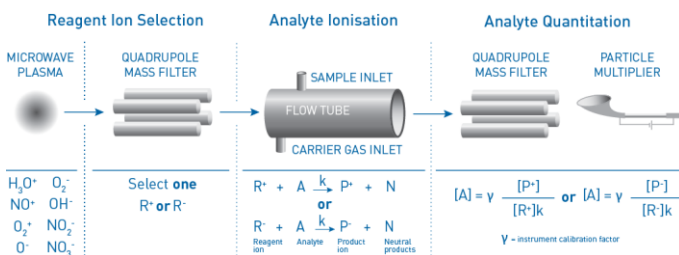

Figure 1: Schematic representation of the SIFT-MS technique.

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 200*ultra* running LabSyft software (version 1.6.2).
Helium carrier gas, Injectable Inlet @ 150°C
GERSTEL MPS xt Dual Head autosampler
- Large capacity 20mL headspace tray, Tedlar bag tray
- Agitator, purge tool
- 2.5mL heated headspace syringe

Figure 2 – Automated SIFT-MS system in Anatune Applications Laboratory.

Method

To enable measurements to be made using SIFT-MS, analytes have to be in the gas phase, consequently automated SIFT-MS relies on headspace analysis. Unlike traditional HS-GC-MS analysis, where samples should be introduced onto the column as quickly as possible to minimise peak broadening, SIFT-MS requires a continuous, steady flow of sample for measurement to take place. For this reason, slow injection of the gas phase analytes into the instrument is needed and GERSTEL's syringe based approach offers the control needed. The inlet flow of the Voice 200*ultra* is fixed at approximately 25 mL/min, consequently a make-up gas flow is needed at these slow injection rates. This is supplied via a passive flow control (open Swagelok T-piece). This will have the effect of diluting the injected concentration, proportional to the ratio of injection speed to total inlet flow.
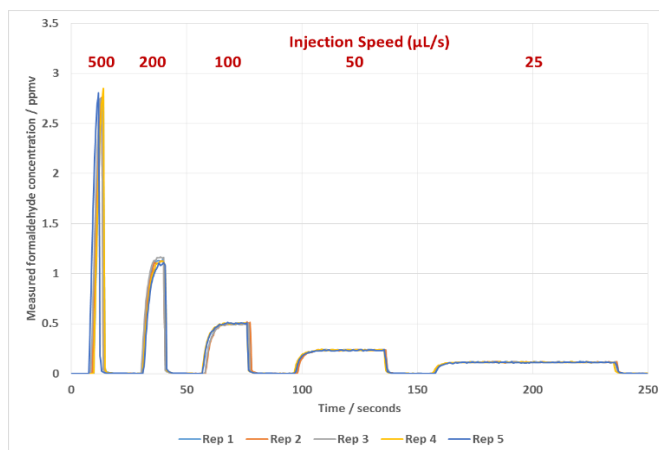

Figure 3 – Formaldehyde analysis from a 1L Tedlar bag, demonstrating variable injection speeds.

Figure 3 shows the effect of reducing the injection speed from 500 − 25 µL/sec (30 − 1.5 mL/min) for a 2.5mL headspace injection of formaldehyde. As the injection speed is decreased, the measurement time increases but the measured concentration decreases. Multiplying the measured concentration by the ratio of inlet flow to injection speed, the actual concentration in the headspace can be calculated. (Note: there are some additional factors related to syringe temperature that need to be taken into account and these are discussed in Appendix A).

The details of test and sampling conditions will be described within the results section for each application discussed below.

Results

The results discussed within this section show some initial data for a range of applications that can be applied to automated SIFT-MS analysis. They cover repeatability, static headspace analysis, multiple headspace extraction analysis, method development applications and aqueous solution analysis. The accompanying SIFT-MS concentration plots for the reported data are shown in Appendix B.

AMBIENT TEMPERATURE STATIC HEADSPACE - REPEATABILITY

One of the major benefits of automated SIFT-MS analysis is the speed of analysis. As there is no requirement for chromatographic separation, as soon as the sample is introduced to the instrument, measurement can take place. Clearly, the rate limiting step is the speed of the autosampler and the minimum measurement time needed for reproducible results to be generated. The data shown below shows repeat injections from a gas phase sample held in a Tedlar bag at ambient temperature. The sample was produced by eating a fruit-flavoured boiled sweet and inflating a 1L Tedlar bag by mouth. Two flavour compounds; butyl acetate and limonene and two breath compounds; acetone and isoprene were analysed for. Additionally, toluene vapour was spiked into the bag, at a higher concentration to demonstrate range.

Analysis Conditions
Bag attached to Tedlar bag tray at room temperature.
Syringe temperature = 150°C (temperature factor = 1.42)
Sample volume = 2.0 mL
Pull-speed 200 µL/s, viscosity delay = 5s
Injection Speed = 200 µL/s (injection time = 10s)
Inlet flow = 26 mL/min (dilution factor = 2.2)
Inlet temperature = 150°C

Table 1 shows the results obtained for 50 repeat injections from the Tedlar bag. The concentrations shown are the average of the central ten data points across the injection peak (see figs 19a-d, App. B). Figures 4a and 4b show a graphically representation of this data, where the error bars represent +/- three standard deviations of the ten measured data points. It can be seen that the instrument shows very good repeatability across a range of concentrations, with RSDs between 0.7 and 5.6%. It should be noted that these measurements are made without reference to an internal standard.

Figure 5 shows the GERSTEL Maestro software schedule for this analysis and shows that the total analysis time is less than 36 minutes, equivalent to 42 seconds per measurement. Another benefit of SIFT-MS is that adding additional compounds to the method would not increase the analysis time.

Injection No.	Acetone	Butyl acetate	Isoprene	Limonene	Toluene
1	0.370	0.021	0.046	0.178	5.994
2	0.361	0.021	0.046	0.179	5.972
3	0.356	0.020	0.045	0.180	6.002
4	0.370	0.021	0.046	0.180	5.968
5	0.367	0.022	0.045	0.180	5.955
6	0.380	0.018	0.045	0.180	5.996
7	0.378	0.021	0.045	0.189	6.048
8	0.366	0.022	0.048	0.183	6.024
9	0.377	0.022	0.044	0.184	6.027
10	0.370	0.022	0.047	0.189	6.018
11	0.385	0.022	0.046	0.187	6.068
12	0.375	0.020	0.047	0.183	6.076
13	0.385	0.022	0.046	0.182	6.076
14	0.382	0.021	0.047	0.186	6.079
15	0.382	0.022	0.046	0.183	6.061
16	0.381	0.021	0.049	0.190	6.057
17	0.377	0.021	0.046	0.184	6.027
18	0.378	0.020	0.049	0.176	6.044
19	0.370	0.022	0.048	0.181	6.091
20	0.378	0.020	0.045	0.187	6.086
21	0.366	0.019	0.047	0.177	6.042
22	0.365	0.023	0.046	0.186	6.093
23	0.364	0.021	0.047	0.184	6.086
24	0.366	0.023	0.044	0.186	6.084
25	0.371	0.021	0.046	0.182	6.074
26	0.367	0.022	0.047	0.184	6.079
27	0.371	0.021	0.046	0.186	6.051
28	0.370	0.020	0.049	0.187	6.105
29	0.371	0.020	0.047	0.183	6.049
30	0.374	0.021	0.047	0.179	6.033
31	0.357	0.020	0.048	0.184	6.036
32	0.358	0.022	0.046	0.183	6.017
33	0.367	0.019	0.047	0.182	6.005
34	0.369	0.020	0.043	0.180	6.018
35	0.353	0.020	0.046	0.185	6.016
36	0.364	0.020	0.047	0.184	6.022
37	0.363	0.023	0.046	0.177	6.002
38	0.362	0.020	0.048	0.182	6.004
39	0.361	0.020	0.047	0.182	6.015
40	0.363	0.021	0.047	0.179	6.046
41	0.361	0.019	0.045	0.177	6.026
42	0.356	0.020	0.045	0.184	6.003
43	0.364	0.023	0.044	0.184	5.992
44	0.367	0.021	0.046	0.177	5.972
45	0.353	0.021	0.045	0.181	5.965
46	0.359	0.020	0.045	0.186	5.967
47	0.359	0.022	0.047	0.178	5.984
48	0.367	0.021	0.047	0.178	5.989
49	0.362	0.021	0.046	0.178	5.968
50	0.363	0.020	0.047	0.179	5.968
Mean	0.368	0.021	0.046	0.182	6.028
Std. Dev.	0.008	0.001	0.001	0.004	0.041
%RSD	2.3	5.6	2.8	1.9	0.7

Table 1 – Measured concentrations in ppmv for contents of Tedlar bag.
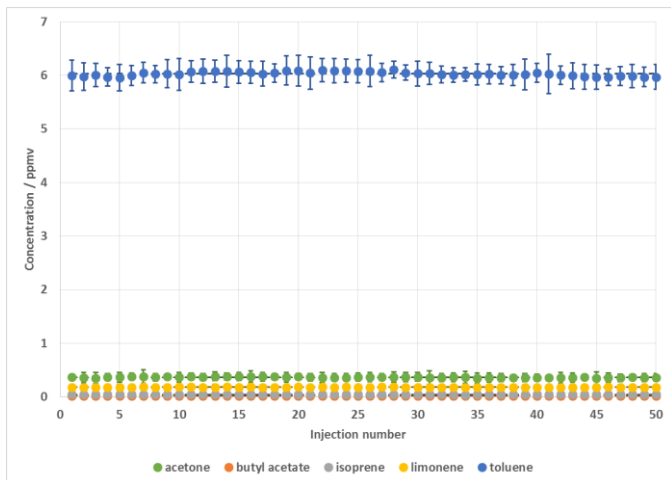
Figure 4a – Measured concentrations in Tedlar bag, with the error bars showing the variability of each individual measurement.
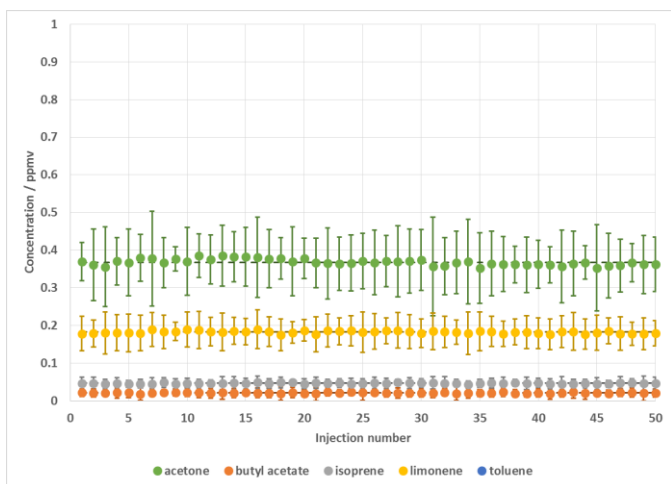

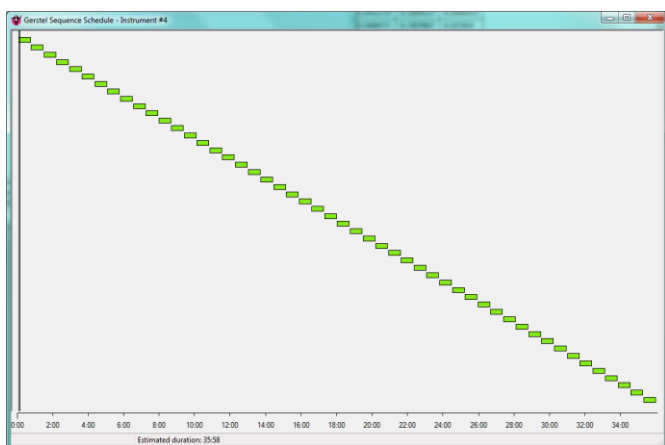*Figure 4b – Data presented in figure 4a, with the higher concentration toluene data removed.*

Figure 5 – GERSTEL Maestro software sequence schedule for the 50 injections detailed above (less than 36 minutes in total).

AMBIENT TEMPERATURE STATIC HEADSPACE – ALDEHYDE ANALYSIS

A class of analytes that are well-suited to SIFT-MS analysis are small, polar molecules – particularly the small aldehydes. These can be analysed directly, without derivatization or preconcentration. To demonstrate the benefits that a lack of derivatization and rapid analysis times can bring, two 1L Tedlar bags were spiked with 10 µL of an aqueous solution of $C_1 – C_6$ n-aldehydes and formaldehyde solution respectively. They were left to equilibrate for 30 minutes and then sampled in quick succession via the Tedlar bag tray.

Analysis Conditions
Bags attached to Tedlar bag tray at room temperature.
Syringe temperature = 150°C (temperature factor = 1.42)
Sample volume = 2.5 mL
Pull-speed 500 µL/s, viscosity delay = 0s
Injection Speed = 200 µL/s (injection time = 12.5s)
Inlet flow = 26 mL/min (dilution factor = 2.2)
Inlet temperature = 150°C

Figure 6 shows analysis of the samples taking place every 30 seconds, with sample 1 showing all the n-aldehydes and sample 2 just formaldehyde as expected. Analytes collected in Tedlar bags have a limited time before diffusion to, and through, the walls of the bag can adversely affect the results obtained, so the ability to analyse samples quickly and easily is of clear benefit.
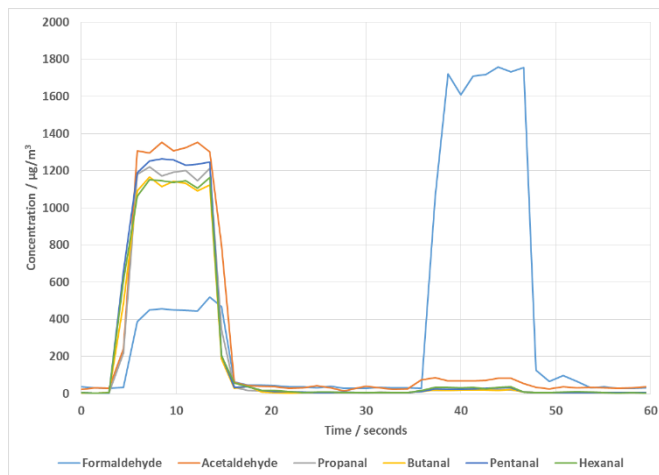

Figure 6 – Measurement of two 1L Tedlar bags for aldehydes.

AMBIENT TEMPERATURE STATIC HEADSPACE – RESIDUAL MONOMER ANALYSIS

Polymeric materials can contain residual monomers, and other compounds from their processing, that may be released whilst in use. This is of particular importance for applications such as pharmaceutical packaging, vehicle interior air quality (VIAQ) and food contact. For this reason, rapid measurement of residual monomer content, both during processing and in the final product, as part of a Quality by Design (QbD) approach to manufacture, is highly desirable.

Analysis Conditions
20mL headspace vials at room temperature
Syringe temperature = 150°C (temperature factor = 1.42)
Sample volume = 2.5 mL
Pull-speed 200 µL/s, viscosity delay = 0s
Injection Speed = 100 µL/s (injection time = 25s)
Inlet flow = 26 mL/min (dilution factor = 4.3)
Inlet temperature = 150°C

Figure 7 shows the residual monomer content from 1g samples of freezer-milled polymer that has been allowed to equilibrate at room temperature in 20 mL sealed headspace vials. The monomers styrene, from polystyrene, formaldehyde from polyoxymethylene and acetaldehyde from polyethylene terephthalate were all measured in the same SIFT-MS method, across several orders of magnitude.
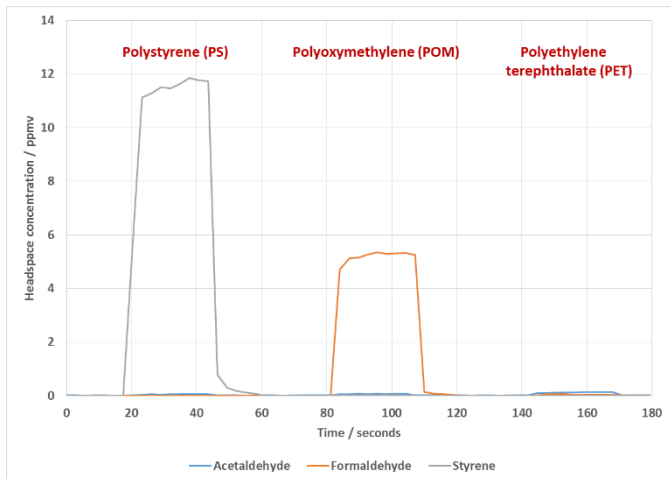

Figure 7 – Static headspace measurement of residual monomers from three polymer samples (polystyrene, polyoxymethylene and polyethylene terephthalate).

STATIC HEADSPACE – RESIDUAL MONOMER ANALYSIS (FORMALDEHYDE)

Whilst static headspace analysis at room temperature is often carried out, it is more common to incubate the sample at elevated temperatures, as this facilitates the release of VOCs from the bulk and also allows for less volatile compounds to enter the headspace.

Analysis Conditions
20mL headspace vials at 80°C for 15 mins
Syringe temperature = 150°C (temperature factor = 1.20)
Sample volume = 2.5 mL
Pull-speed 200 µL/s, viscosity delay = 5s
Injection Speed = 100 µL/s (injection time = 25s)
Inlet flow = 26 mL/min (dilution factor = 4.3)
Inlet temperature = 150°C
Syringe flush time = 2 mins

Table 2 shows the results from heating various amounts of polyoxymethylene at 60°C for 15 minutes, prior to analysis of the released formaldehyde. It can be seen that, as the mass of polymer analysed increases, the measured headspace concentration of formaldehyde also increase, in a linear manner, as expected. Figure 8 shows the linearity plot for this data over the range 0 – 150 mg of polymer and demonstrates that headspace analysis carried out using automated SIFT-MS is an acceptable method for this type of analysis.

Figure 9 shows the GERSTEL Maestro sequence schedule for the above analysis. Due to the short instrument run time for these measurements (60 seconds per analysis), the six available incubator positions and the PrepAhead functionality with the GERSTEL MPS system, it can be seen that highly efficient sequences can be generated. In this instance, the 11 analyses were carried out in 67 minutes, including the 15 minute incubation time. Additionally, lengthening the incubation time would not lead to significantly longer sequences, as the sample overlap would still be optimal. Also, as before, adding additional analytes to the method would not increase the analysis time.

Weight of Sample / mg	Average Measured Concentration (ppmv)	Standard Deviation
0	0.013	0.012
15	0.62	0.006
30	1.38	0.016
45	2.11	0.016
60	2.74	0.016
75	3.39	0.029
90	3.94	0.021
105	4.71	0.037
120	5.27	0.032
135	5.76	0.048
150	6.48	0.023
Slope (m)	0.043	
Intercept (c)	0.0857	
R²	0.9985	

Table 2 – Results from the analysis of residual formaldehyde in polyoxymethylene polymer samples across a range of sample weights.
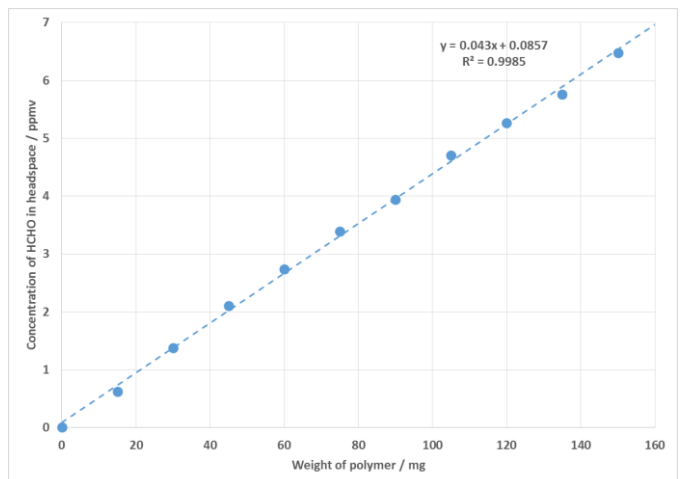

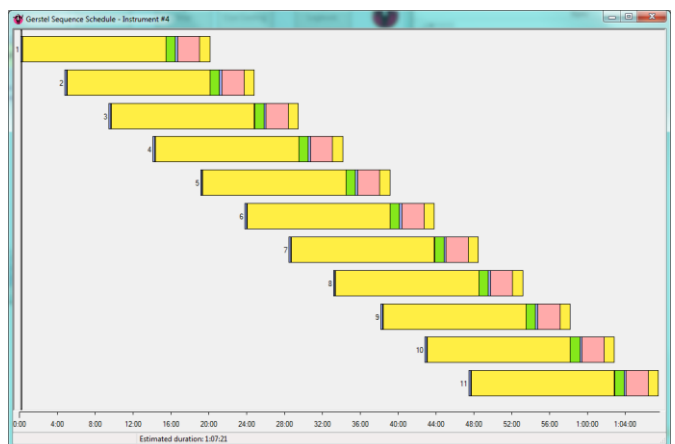*Figure 8 – Linearity plot for data presented in Table 2.*

Figure 9 – GERSTEL Maestro sequence schedule for data presented in Table 2.

MULTIPLE HEADSPACE EXTRACTION ANALYSIS

Static headspace analysis is a highly useful tool for the analysis of VOCs in a wide variety of matrices, however the limitation is that what is being measured is the concentration of VOCs that are in the headspace above the matrix. Without a good knowledge of partitioning of the analytes from the sample (for example, Henry's Law coefficients), it gives no information about what remains within the matrix. For liquid matrices it is possible to quantify against a calibration set, however, this is not possible when analyzing solid samples. Knowing the <u>total</u> VOC content of a sample may be critical for quality control purposes. One approach is to use multiple headspace extraction analysis (MHE). The basic methodology is illustrated below.

Matrix independent measurement of <u>total</u> VOC in a solid sample

...or fit to an exponential and extrapolate
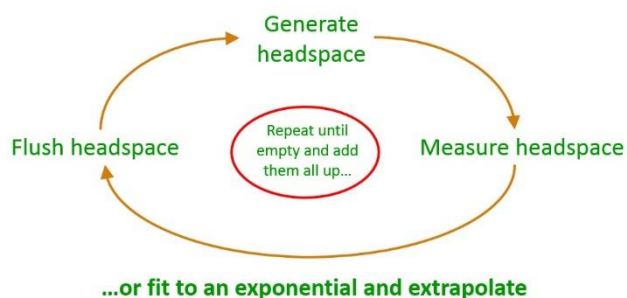
A headspace is generated above the sample, which is measured and then flushed, at room temperature, for several minutes with clean background gas matrix. A new headspace is then generated, which will be lower than before, as some of the VOCs have been removed from the matrix. This is then measured, flushed and the process repeated. In well behaved systems, the reduction in concentration will follow an exponential decay, from which the total VOC content can be extrapolated. (For more information and theory, see the Agilent application note "Multiple Headspace Extraction-Capillary Gas Chromatography for Quantitative Determination of Volatiles in Solid Matrices" published in May 1996). For good analytical precision, the number of measurement cycles should be between 4 and 10 – analyte and matrix dependent. Obviously, as multiple measurements are needed for each sample, the analysis times can be long using traditional GC methods. It should be possible, using the fast analysis times available to SIFT-MS, to optimise MHE measurements.

An example MHE analysis using automated SIFT-MS is shown in Table 3 and figures 10a and 10b. The sample was a freezer-milled polybutylene terephthalate (PBT) polymer. PBT can release residual tetrahydrofuran (THF), which was measured in this analysis. The analysis conditions are shown below, and 10 measurement cycles were carried out, primarily to demonstrate the good exponential curve fit that can be obtained with this method. By using the slope of the ln(concentration) plot (figure 10b) and applying to the standard MHE equation – [Point 1] / (1 – exp(slope) – it was possible to calculate the total THF concentration, in this case 9.3 ppmV, which can be converted to mass using the molar volume of THF at 80°C. Again, it is worth pointing out that multiple compounds can be analysed simultaneously with no increase in runtime.

Analysis Conditions
20mL headspace vials at 80°C for 15 mins
Syringe temperature = 150°C (temperature factor = 1.20)
Sample volume = 2.5 mL
Pull-speed 200 µL/s, viscosity delay = 0s
Injection Speed = 400 µL/s (injection time = 6.25s)
Inlet flow = 26 mL/min (dilution factor = 1.1)
Inlet temperature = 150°C
Vial purge time = 2 mins

Injection	Average Measured Concentration (ppmv)	Standard Deviation	ln(concentration)
1	2.923	0.069	1.072
2	1.962	0.051	0.674
3	1.302	0.027	0.264
4	0.918	0.024	-0.086
5	0.618	0.018	-0.481
6	0.437	0.014	-0.828
7	0.335	0.010	-1.093
8	0.249	0.013	-1.390
9	0.172	0.012	-1.760
10	0.123	0.003	-2.096
Slope (m)	-0.3466		
Intercept (c)	1.3341		
R^2	0.9972		

Table 3 – Headspace concentration data for a multiple headspace extraction (MHE) measurement of residual tetrahydrofuran (THF) above polybutylene terephthalate (PBT). Note, linearity statistic refer to the ln(concentration) plot (figure 10b).
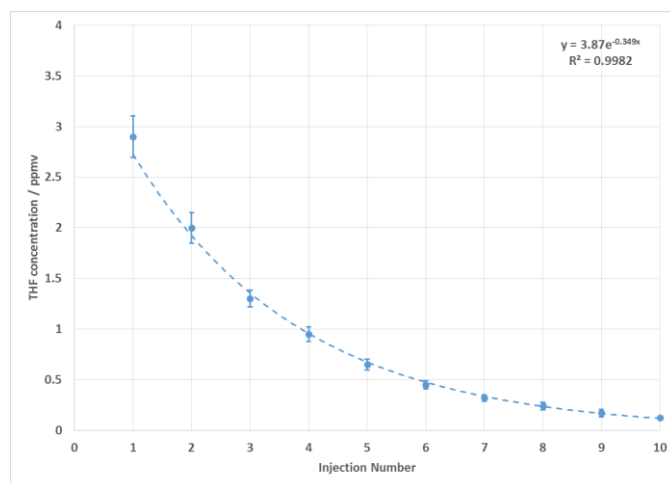

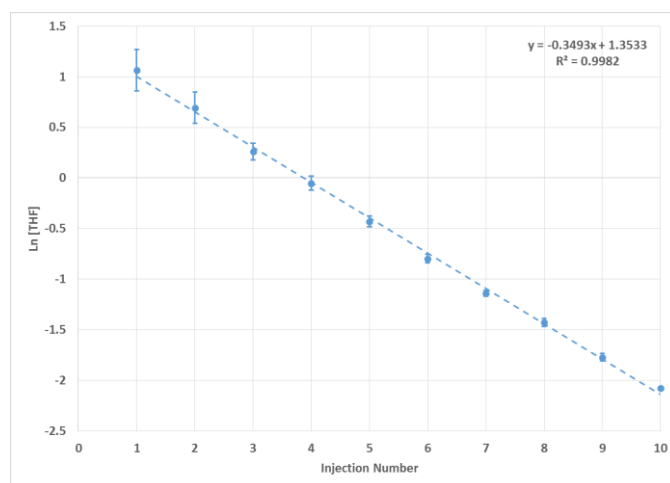*Figure 10a – Exponential curve fit for data presented in Table 3.*

Figure 10b – ln(concentration) linearity plot for data presented in Table 3. The slope of this data is used in the MHE calculation.

STATIC HEADSPACE – METHOD DEVELOPMENT

Optimisation of all headspace parameters is an important part of developing robust analytical methods, but can be time consuming, due to the length of the incubation period the sample needs prior to analysis and the time taken for traditional chromatographic methods to run. In fact, the incubation time itself can be critical, but often this is not fully considered, again, due to time constraints. The fast analysis time with SIFT-MS and the ability to overlap analyses using the Maestro PrepAhead function allows for multiple incubation times to be assessed in minimal time periods.

Table 4 shows the increase in headspace concentration of styrene from a polystyrene sample as the incubation time is increased from 4 to 13 minutes, with figure 11 clearly showing the styrene levels plateauing around 12 minutes, suggesting an optimum incubation time has been reached.

Analysis Conditions
20mL headspace vials at 80°C for 4 - 13 mins
Syringe temperature = 150°C (temperature factor = 1.20)
Sample volume = 2.5 mL
Pull-speed 200 µL/s, viscosity delay = 0s
Injection Speed = 100 µL/s (injection time = 25s)
Inlet flow = 26 mL/min (dilution factor = 4.3)
Inlet temperature = 150°C

Incubation Time / minutes	Average Measured Concentration (ppmv)	Standard Deviation
4	5.27	0.012
5	5.64	0.006
6	6.26	0.016
7	6.49	0.016
8	6.83	0.016
9	7.03	0.029
10	7.05	0.021
11	7.45	0.037
12	7.59	0.032
13	7.39	0.048

Table 4 – Increasing headspace concentrations of styrene from polystyrene as the incubation time is increased.
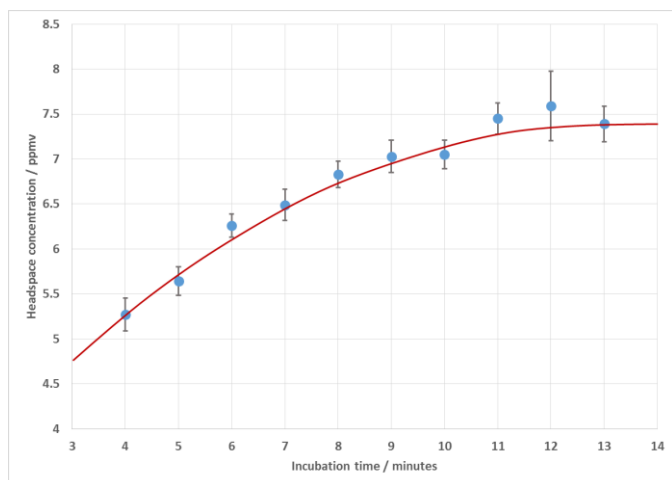

Figure 11 – Plot of data presented in Table 4, clearly showing a plateau being reached at around 12 minutes of incubation.

Figure 12 shows the Maestro sequence schedule for the data presented in Table 4 and shows that the short SIFT-MS runtimes and Maestro PrepAhead function allows for significant time savings to be made. The total runtime for all 10 analyses is just over 25 minutes, which compares favorably with the total equivalent GC-MS method runtime of 4½ hours.
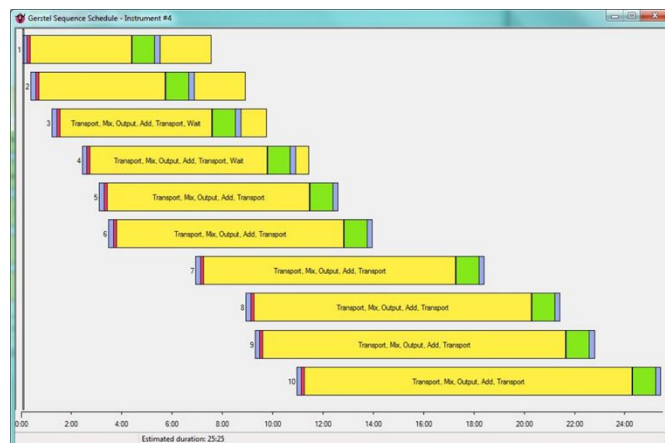

Figure 12 – Sequence schedule for data in Table 4.

AQUEOUS SOLUTION ANALYSIS - BTEX

The measurement of low level environmental VOCs in water is an important application of static headspace. The use of automated SIFT-MS allows for a wide range of compound types to be rapidly detected, directly from the water matrix, with no sample clean up or water handling issues that can affect GC-MS methods.

Table 5 shows the results from an initial linearity study of the BTEX compounds (benzene, toluene, xyelenes & ethylbenzene) and chloroform, from 0.1 nL/mL to 20 nL/mL. Linearity data was calculated for both the full range of the method, as well as the low level subset from 0.1 – 2.5 nL/mL. Good R^2 values were obtained for both ranges, as well as good agreement for the slope and intercept of both ranges, demonstrating that the low level linearity is not skewed by the weight of the higher concentration points. Figures 13a and 13b show plots of the data presented in Table 5, with the error bars representing 3 standard deviations of the repeated measurements made during a single 50 second sample injection. It should be noted that the lower and upper limit of this analysis could be extended by at least one order of magnitude in each direction.

Figure 14 shows the Maestro sequence schedule for the data presented in Table 5, and again shows how the PrepAhead functions and the rapid measurement time available to SIFT-MS can yield significant throughput gains when compared to equivalent GC-MS methods.

Analysis Conditions
20mL headspace vials at 60°C for 15 mins
Syringe temperature = 150°C (temperature factor = 1.27)
Sample volume = 2.5 mL
Pull-speed 200 µL/s, viscosity delay = 5s
Injection Speed = 50 µL/s (injection time = 50s)
Inlet flow = 26 mL/min (dilution factor = 8.7)
Inlet temperature = 150°C
Syringe flush time = 2 mins

Technical note no. AS191

Aqueous concentration nL/mL	Measured headspace concentration (ppmv)			
	Benzene	Toluene	Xylenes	Chloroform
0.1	0.024	0.019	0.018	0.019
0.25	0.062	0.037	0.042	0.053
0.5	0.119	0.065	0.079	0.097
1	0.222	0.128	0.154	0.178
2.5	0.627	0.326	0.415	0.461
5	1.279	0.679	0.877	0.952
7.5	1.889	0.995	1.279	1.369
10	2.509	1.345	1.699	1.899
20	4.879	2.565	3.379	3.679
Entire Range (0.1 – 20 nL/mL)				
Slope (m)	0.2454	0.1846	0.1694	0.1291
Intercept (c)	0.0123	0.0064	0.0004	0.0123
R^2	0.9996	0.9999	0.9997	0.9993
Reduced Range (0.1 – 2.5 nL/mL)				
Slope (m)	0.2506	0.1822	0.1654	0.1285
Intercept (c)	0.0072	0.0029	0.0023	0.0032
R^2	0.9974	0.9988	0.9992	0.9995

Table 5 – Linearity data for headspace analysis of benzene, toluene, xylenes & ethylbenzene and chloroform in water.
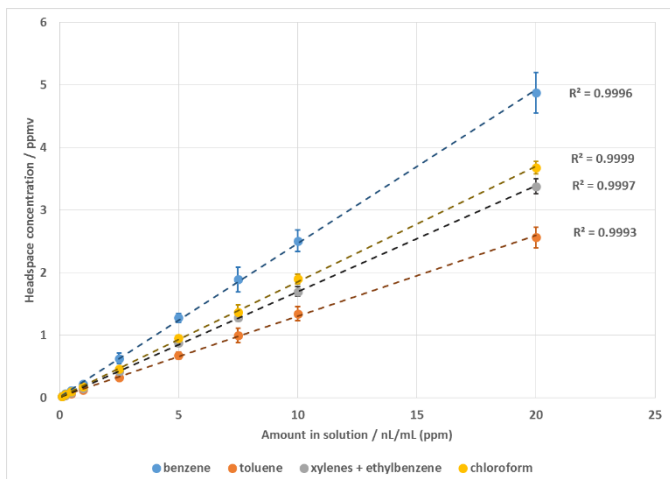
Figure 13a – Full range linearity plot for data presented in Table 5.
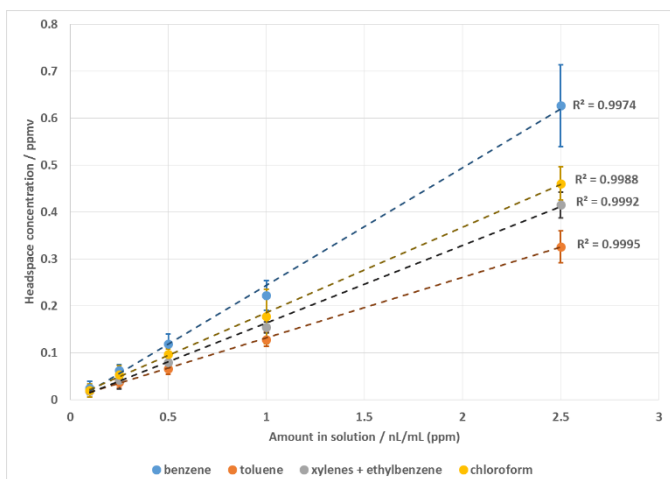
Figure 13b – Low level linearity plot for data in Table 5.
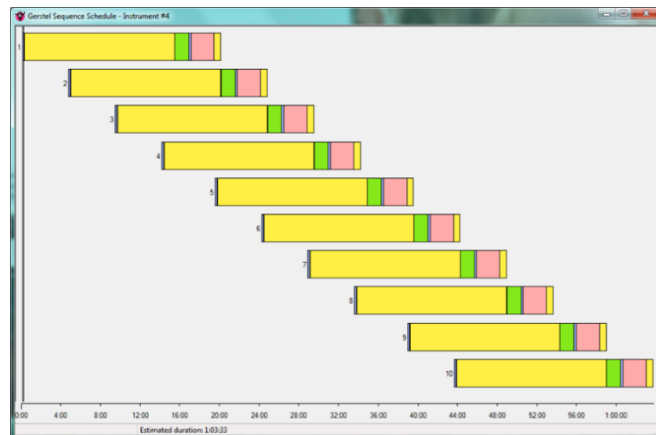
Figure 14 –Maestro sequence schedule for data in Table 5.

AQUEOUS SOLUTION ANALYSIS - ALCOHOLS

In addition to the analysis of the relatively straightforward non-polar compounds, as demonstrated above, automated SIFT-MS also allows for the analysis of aqueous solutions of polar compounds such as alcohols and aldehydes.

Table 6 shows the results from the analysis of aqueous solutions of ethanol and pentanol, incubated at both 40°C and 60°C and demonstrates very good linearity across the range. Whilst the preliminary investigation used a linear range from 20 to 100 nL/mL, the upper and lower limits of this analysis could be extended by at least two orders of magnitude.

Figure 15 shows a plot of the data presented in Table 5, with the error bars corresponding to 3 standard deviations of the repeated measurements made during a single 50 second sample injection.

Analysis Conditions
20mL headspace vials at 40°C and 60°C for 15 mins
Syringe temperature = 150°C (temperature factor = 1.35 and 1.27)
Sample volume = 2.5 mL
Pull-speed 200 µL/s, viscosity delay = 5s
Injection Speed = 50 µL/s (injection time = 50s)
Inlet flow = 26 mL/min (dilution factor = 8.7)
Inlet temperature = 150°C
Syringe flush time = 2 mins

Aqueous concentration nL/mL	Measured headspace concentration (ppmv)			
	Ethanol 40°C	Ethanol 60°C	Pentanol 40°C	Pentanol 60°C
20	0.290	0.786	0.433	1.252
40	0.591	1.526	0.800	2.301
60	0.877	2.334	1.193	3.488
80	1.180	2.977	1.623	4.894
100	1.470	3.926	2.025	6.342
Slope (m)	0.0147	0.0387	0.0200	0.0639
Intercept (c)	0.0032	0.0098	0.0125	0.1763
R^2	0.9999	0.9971	0.9993	0.9954

Table 6 – Linearity data for headspace analysis aqueous solutions of ethanol and pentanol.
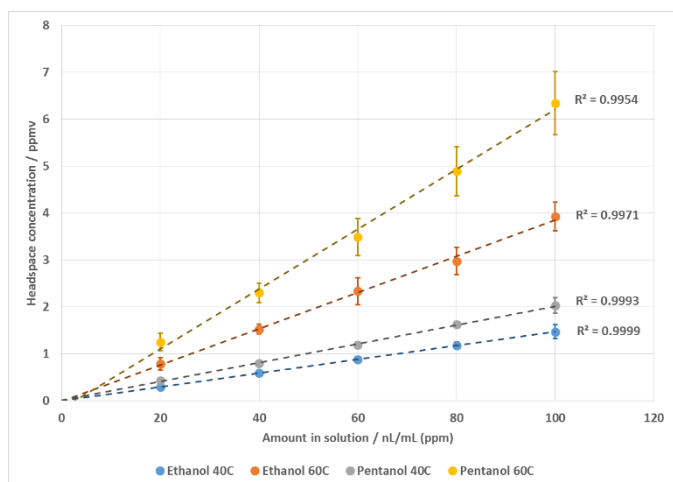
Figure 15 – Linearity plot for data presented in Table 6.

The measured headspace concentration for pentanol is approximately 40% higher than for the equivalent ethanol solutions. This is representative of the relative partition coefficients of the two compounds, with ethanol being more polar and thus preferentially remaining in the aqueous phase. It is worth noting that HS-SIFT-MS may offer a simplified approach to the generation of Henry's Law coefficients.

Discussion

The above data shows that by coupling a GERSTEL MultiPurpose Sampler (MPS) to Syft Technolgies' SIFT-MS, it is possible to produce highly efficient and sensitive analytical methods that effectively combine the fast measurement that SIFT-MS offers with automated sample preparation and handling. The reproducibility of the measurements is excellent with a broad range of analyses available, from rapid residual monomer analysis to the measurement of environmentally important compounds directly from water.

Appendix A

SYRINGE TEMPERATURE EFFECTS

In syringe-based headspace techniques, the temperature of the sampling syringe is often held at a higher temperature than the sample incubation temperature. This minimises condesation of volatiles in the syringe and reduces sample carryover. For headspace GC measurements, sample concentrations are calculated with refernce to a calibration curve, generated under the same conditions as the sample. SIFT-MS is inherently quantitative and gives absloute concentration measurments of the headspace. Consequently, the measured headsapce concentration will be affected by the temperature difference between the sample and the sampling syringe. This is due to increased expansion of the volatiles in the hotter sampling syringe, when compared to the headsapce vial and these differences can be shown to be directly proportion to absolute temperature.

If we consider that the gas phase analytes behave as ideal gases then the ideal gas equation can be applied to relate temperature, pressure and volume, *ie*. PV = nRT

If the sampling syringe was a sealed system of constant volume, then as the temperature of the sampled volatiles, relative to the incubated vial, increased on sampling, then the pressure would also increase. However, the syringe is an open system, where excess pressure can be vented through the needle, consequently, the pressure and volume within the syringe remain constant, regardless of the temperature. If PV remains constant (R is also a constant), then as T increases, n (the number of moles of analyte) has to decrease to balance the equation. This shows itself as decreasing measured concentration as the temperature difference between the sampling syringe and the incubated vial increases and varies as the ratio of the absolute temperature (in Kelvin) of the two heated zones. Therefore, measured concentrations need to be scaled by this ratio to corrected for the difference – the "temperature factor" in the above analysis conditions sections. This will apply to all analytes that do not deviate significantly from ideal behaviour.

The following data demonstrates this for both formaldehyde and toluene. Concentrations of both analytes were prepared in separate 1L Tedlar bags and sampled, at room temperature (23°C), using syringes at 50, 100 and 150°C.

Table 7 shows the data obtained from 5 repeat measurements at each temperture for the formaldehyde sample. The headspace injections are shown in figure 16, where the darker blue traces correspond to the syringe at 150°C and the lighter blue traces at 100°C and 50°C respectively.

Injection no.	Measured Headspace Concentration / ppmv		
	50°C	100°C	150°C
1	0.1158	0.0991	0.0834
2	0.1153	0.0984	0.0836
3	0.1145	0.0985	0.0830
4	0.1154	0.0984	0.0833
5	0.1139	0.0977	0.0833
Mean	0.1150	0.0984	0.0833
Standard Dev.	0.0007	0.0004	0.0002
%RSD	0.6	0.5	0.2

Table 7 – Measured headspace concentration of formaldehyde from a 1L Tedlar bag at varying syringe temperatures.
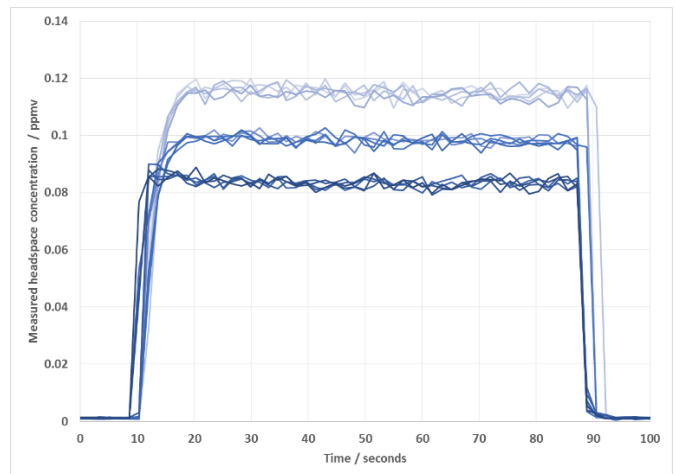

Figure 16 – Plot of the data presented in Table 7. Dark blue = 150°C, mid blue = 100°C and light blue = 50°C.

Table 8 and figure 17 show the equivalent data for the toluene sample. Dark green corresponds to the syringe at 150°C and the lighter colours to 100°C and 50°C respectively.

Injection no.	Measured Headspace Concentration / ppmv		
	50°C	100°C	150°C
1	2.9451	2.5474	2.1757
2	2.9539	2.5389	2.1732
3	2.9450	2.5317	2.1793
4	2.9485	2.5357	2.1828
5	2.9377	2.5218	2.1896
Mean	2.9460	2.5351	2.1801
Standard Dev.	0.0053	0.0084	0.0057
%RSD	0.2	0.3	0.3

Table 8– Measured headspace concentration of toluene from a 1L Tedlar bag at varying syringe temperatures.
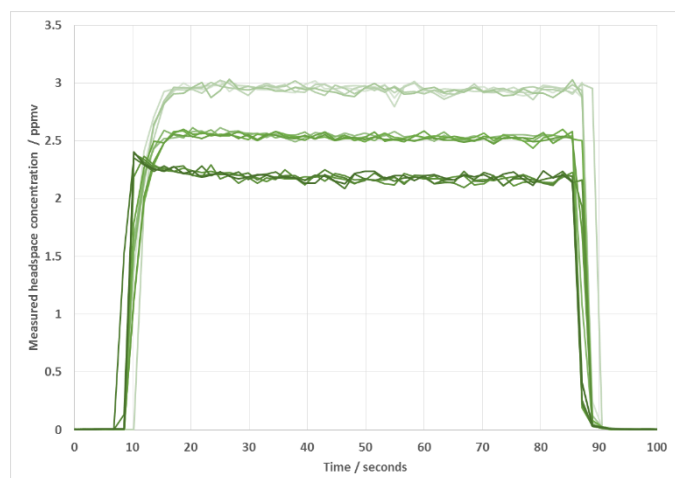

Figure 17 – Plot of the data presented in Table 7. Dark green = 150°C, mid green = 100°C and light green = 50°C.

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Figures 18a and 18b and Table 9 show the above data after adjustment for the syringe temperature effects as detailed above, *ie*. multiplication of the 50°C data by (323/296), the 100°C data by (373/296) and the 150°C data by (423/296). It can clearly be seen that this "normalization" corrects for the differences in measured concentration, with good repeatability across all 15 injections for each sample.

It is worth pointing out that at the maximum allowable syringe temperature of 150°C, if this temperature effect is not allowed for, then measurements made at room temperature will under report concentrations by nearly 45%.

Injection no. (Syringe Temp.)	Temperature Adjusted Headspace Concentration	
	Formaldhyde / ppmv	Toluene / ppmv
1 (50°C)	0.1255	3.1925
2 (50°C)	0.1250	3.2020
3 (50°C)	0.1242	3.1923
4 (50°C)	0.1251	3.1962
5 (50°C)	0.1234	3.1845
1 (100°C)	0.1241	3.1893
2 (100°C)	0.1232	3.1787
3 (100°C)	0.1234	3.1697
4 (100°C)	0.1232	3.1747
5 (100°C)	0.1224	3.1573
1 (150°C)	0.1183	3.0874
2 (150°C)	0.1186	3.0838
3 (150°C)	0.1178	3.0924
4 (150°C)	0.1182	3.0975
5 (150°C)	0.1183	3.1071
Mean	0.1220	3.1537
Standard Dev.	0.0028	0.0440
%RSD	2.3	1.4

Table 9 – Temperature adjusted headspace concentration for data in Tables 7 and 8.

Figure 18a – Temperature adjusted headspace concentrations for formaldehyde measurements in figure 16.
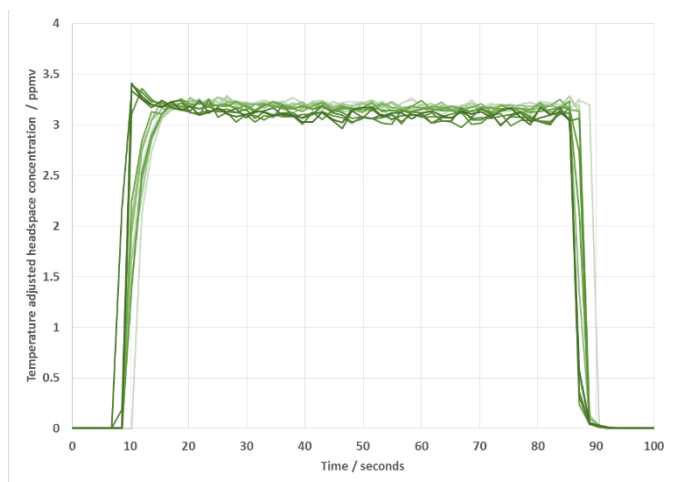
Figure 18b – Temperature adjusted headspace concentrations for toluene measurements in figure 17.

Appendix B

This appendix contains various plots of the data used for the main body of this application note.

AMBIENT TEMPERATURE STATIC HEADSPACE - REPEATABILITY
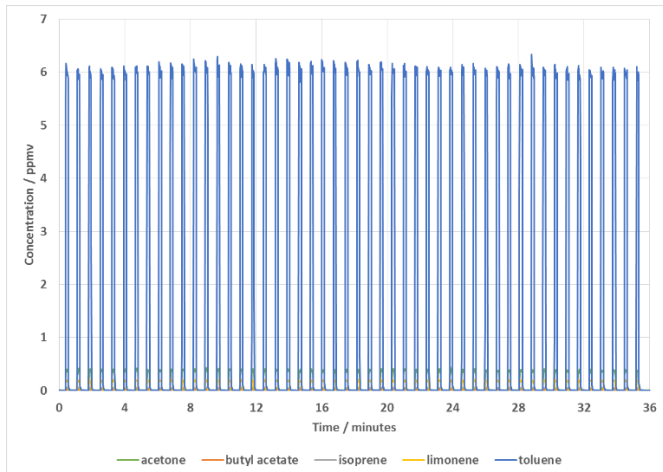
Figure 19a – 50 repeat injections from a 1L Tedlar bag containing toluene, acetone, butyl acetate, isoprene and limonene.
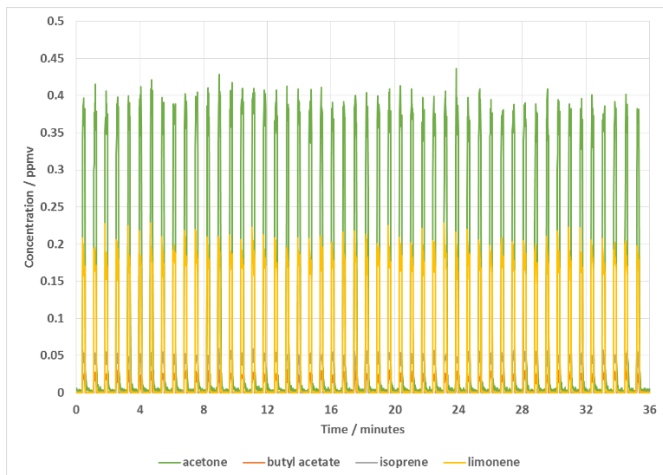

Figure 19b – Expanded view of figure 19a (with the toluene trace removed).
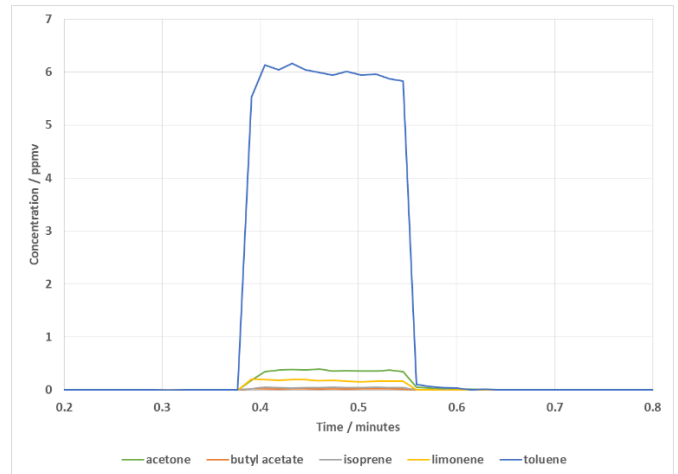

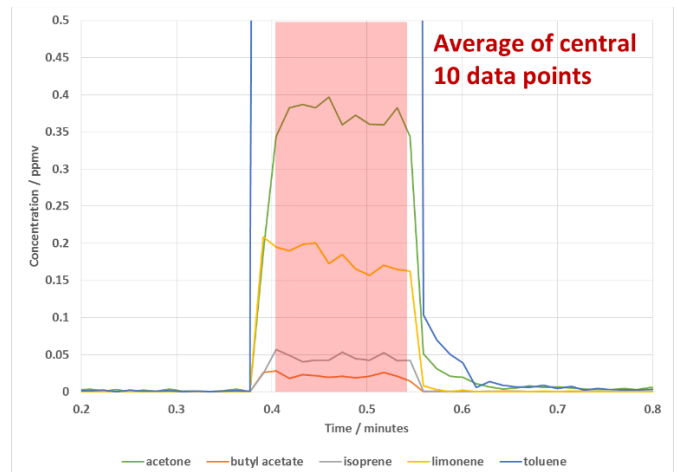*Figure 19c – Example of one injection cycle for data presented in figure 19a.*

Figure 19d – Example of the central data points from which the average concentration is taken for the repeatability study.

STATIC HEADSPACE – RESIDUAL MONOMER ANALYSIS (FORMALDEHYDE)
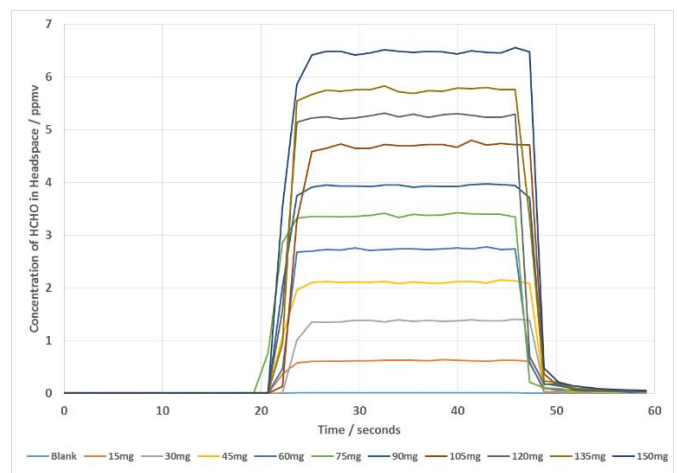
Figure 20 – Measured headsapce formaldehyde concentration from polyoxymethylene for a range of sample weights from 0 – 150 mg.

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MULTIPLE HEADSPACE EXTRACTION ANALYSIS
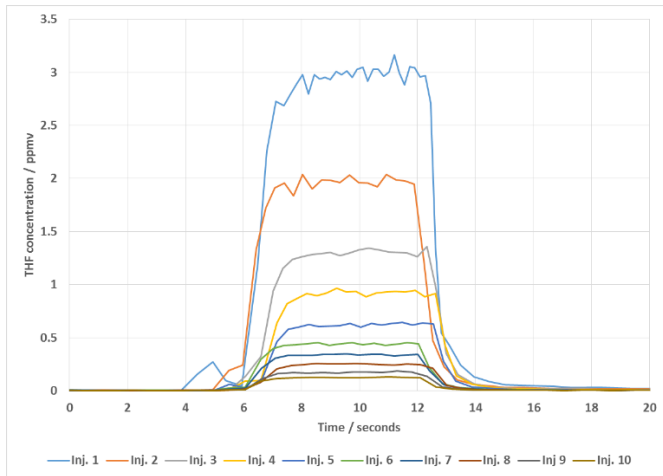
Figure 21 – Measured headsapce tetrahydrofuran (THF) concentration from polybutylene terephthalate (PBT) for 10 multiple headspace extraction (MHE) cycles.

STATIC HEADSPACE – METHOD DEVELOPMENT
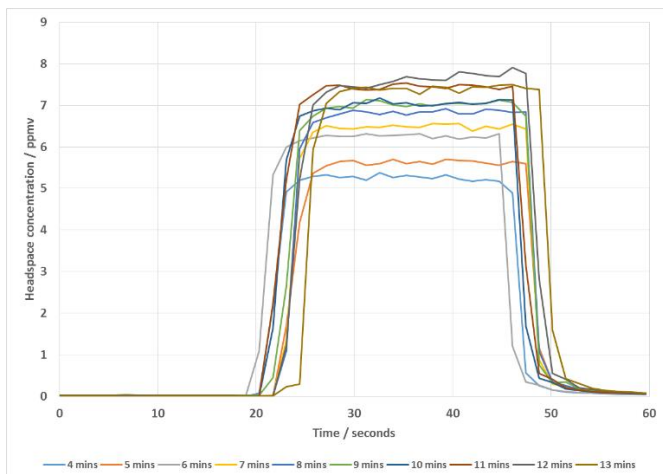
Figure 22 – Measured headspace styrene concentration from polystyrene samples incubated from 4 – 13 minutes.
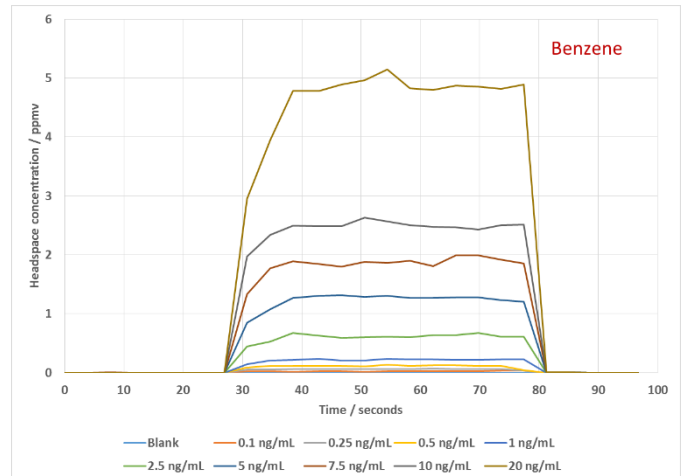
AQUEOUS SOLUTION ANALYSIS - BTEX

Figure 23a – Measured headspace benzene concentrations for a range of aqueous sloutions of BTEX compounds.
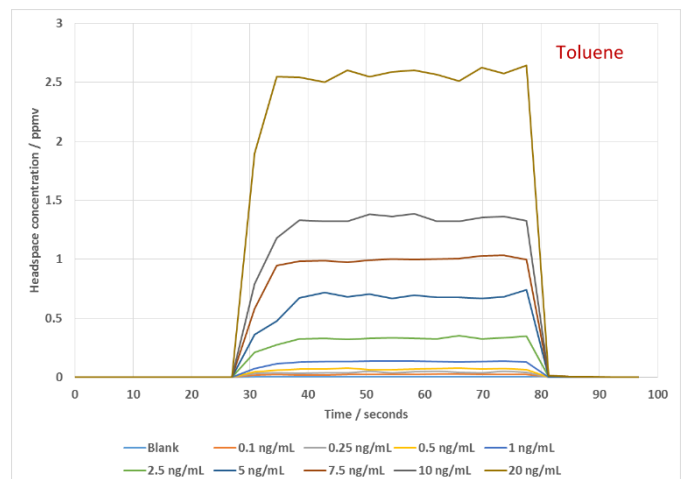
Figure 23b – Measured headspace toluene concentrations for a range of aqueous sloutions of BTEX compounds.
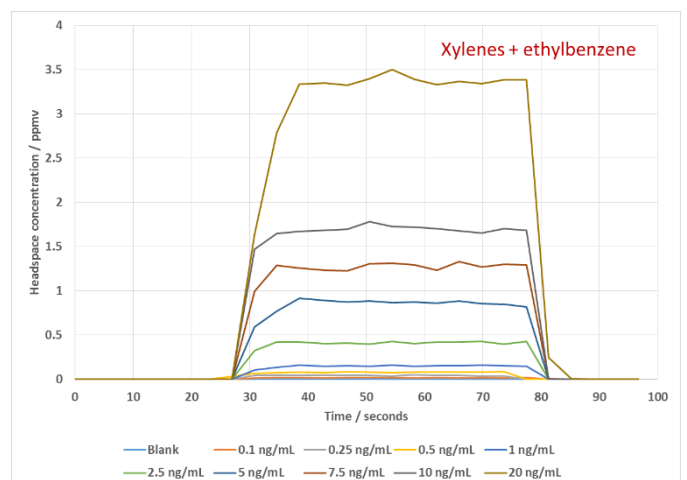
Figure 23c – Measured headspace xylenes + ethylbenzene concentrations for a range of aqueous sloutions of BTEX compounds.
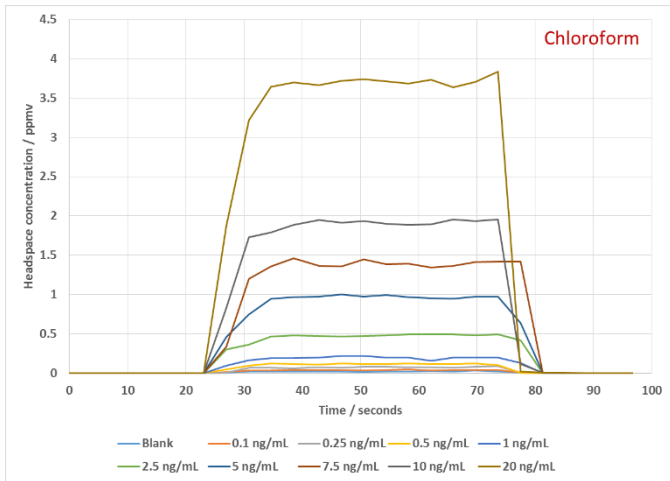
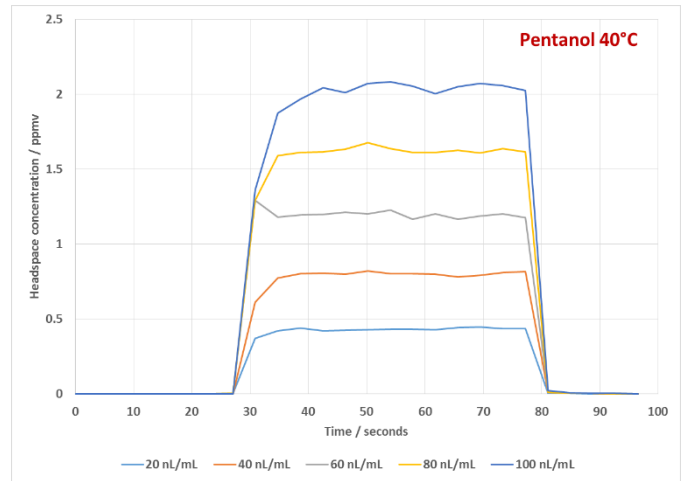*Figure 23d – Measured headspace chloroform concentrations for a range of aqueous sloutions of BTEX compounds.*
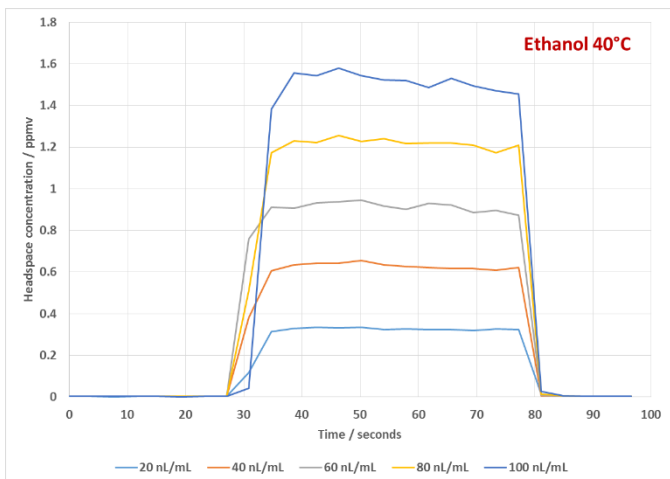
AQUEOUS SOLUTION ANALYSIS - ALCOHOLS

Figure 24a – Measured headspace ethanol concentrations for a range of aqueous sloutions of ethanol and pentanol at 40°C.
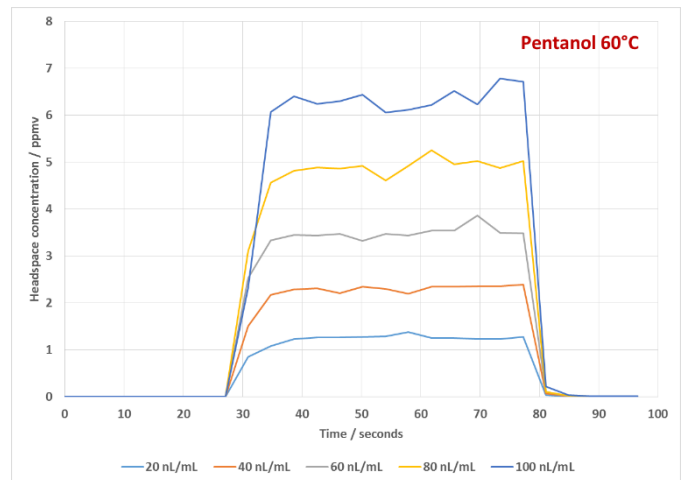

Figure 24b – Measured headspace ethanol concentrations for a range of aqueous sloutions of ethanol and pentanol at 60°C.

Figure 24c – Measured headspace pentanol concentrations for a range of aqueous sloutions of ethanol and pentanol at 40°C.

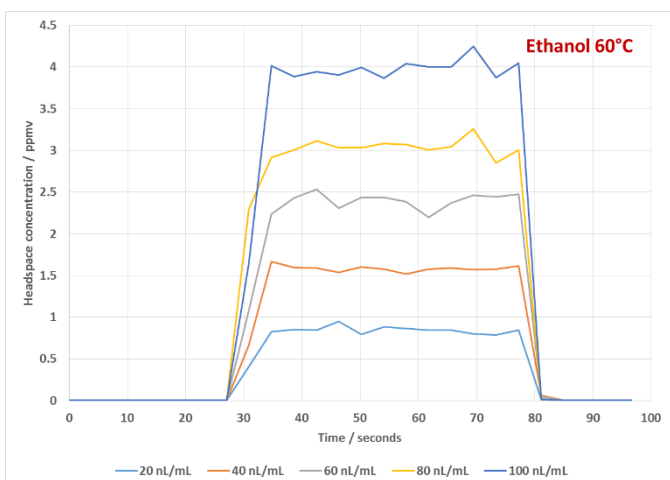*Figure 24d – Measured headspace pentanol concentrations for a range of aqueous sloutions of ethanol and pentanol at 60°C.*