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SPECIATION OF DICHLOROMETHANE AND CHLOROFORM USING NEGATIVE ION SIFT-MS

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INTRODUCTION

Organochlorine compounds, despite greatly reduced industrial use, continue to be significant contaminants in air, soil and water. In previous Application Notes (AS191, AS209 and AS212) it has been shown that by combining the power of direct analysis using Selected Ion Flow Tube Mass Spectrometry and GERSTEL automation (automated SIFT-MS), headspace analysis of volatile compounds in water can be greatly simplified. Additionally, with analysis time allowing for at least 15 samples per hour to be run, significant gains in sample throughput can be achieved. Particularly when compared to traditional purge and trap methods.

Whilst automated SIFT-MS can be used to analyse broad suites of organochlorine compounds simultaneously, one limitation is the difficulty in speciating chloroform from dichloromethane using positive ion SIFT-MS. A similar issue is also seen with the speciation of ethylbenzene from the xylenes. However, it has been shown that using a calibration approach and the differential branching ratios for the O_2^+ reactions for ethylbenzene and the xylenes, it is possible to separate these compounds in real-time (Application Note AS211). This is found not to be possible with chloroform and dichloromethane, due to identical product ions being formed for both compounds, requiring different methodology to separate them.

This application note demonstrates the use of negative ion SIFT-MS, making use of Syft Technologies' Dual Polarity Voice200*ultra*, to fully speciate chloroform and dichloromethane and shows some preliminary data for linearity and repeatability from aqueous mixtures of these two compounds.

INSTRUMENTATION

SIFT-MS: Syft Technologies Dual Polarity Voice200*ultra* with GERSTEL MPS Robotic Pro autosampler. Inlet temperature = 150°C, inlet flow = 25 mL/min, make-up gas = zero-grade air, headspace syringe temperature = 150°C.

Figure 1: Syft Technologies Voice200*ultra* SIFT-MS with GERSTEL MPS Robotic autosampler.

METHOD

Details of the SIFT-MS technique can be found in Application Note AS191

Full Scan Analysis

1 mL of solvent was placed into a 20 mL headspace vial and allowed to reach equilibrium at room temperature. Using the GERSTEL MPS Robotic, 0.5 mL of headspace vapour was then removed and added to a pre-flushed 20 mL headspace vial, to achieve a suitable concentration. 2.5 mL of vapour from this second vial was then injected into the SIFT-MS at 50 µL/sec, with the instrument running in either positive full scan mode, or negative wet full scan mode.

Selected Ion Monitoring Analysis

A 2000 ppm (v/v) stock solution of chloroform and dichloromethane was prepared by pipetting 40 µL of each solvent into 20 mL of DMSO. Two working standards, at 100 ppm (v/v) and 10 ppm (v/v), were prepared by pipetting 500 µL and 50 µL, respectively, of the stock solution into 10 mL of water. All subsequent samples were prepared by serial dilution of the working standards in 10 mL of water.

The samples for the linearity and repeatability were analysed by headspace analysis using the automated SIFT-MS. The samples were heated, with agitation, at 60°C for 15 minutes followed by injection of 2.5 mL of headspace into the SIFT-MS at 50 µL/sec. Analysis was carried out in Selected Ion Monitoring (SIM) mode using either O_2^+ reaction products for the positive ion analysis or OH^- reaction products for the negative ion analysis. It should be noted that accurate reaction rate constants were not generated for the OH^- reaction and an assumed reaction rate, k, of 2 x 10^{-9} was used for both analytes. Providing calibration curves are generated prior to any further unknown sample analysis, this will not affect the accuracy or precision of the method.

RESULTS

Mass Spectra Results

Figures 2 and 3 show the mass spectra for the reaction of chloroform and dichloromethane with both positive O_2^+ and negative OH^- reagent ions.

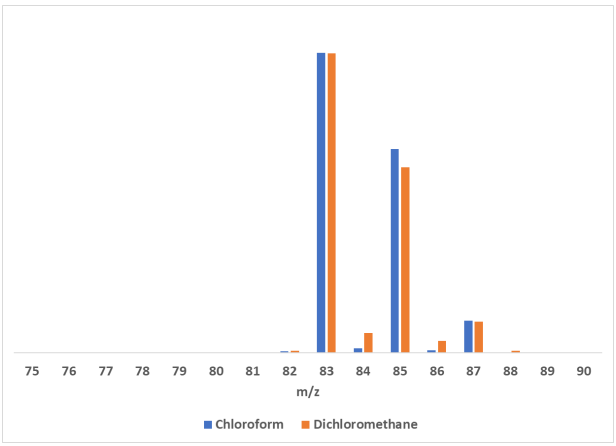

Figure 2: Mass spectra of chloroform and dichloromethane using the O_2^+ reagent ion.

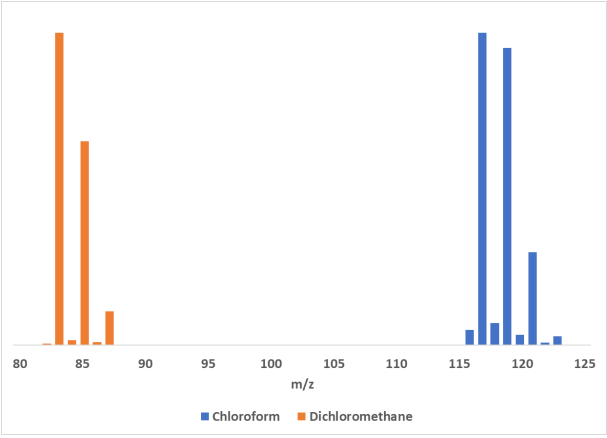

Figure 3: Mass spectra of chloroform and dichloromethane using the OH^- reagent ion.

From the spectra above it is clear why positive ions are unable to separate a mixture of chloroform and dichloromethane, as both compounds generate the same product ions after reaction with O_2^+. Figure 4 below shows the results of varying the ratio of chloroform to dichloromethane from 0:100 to 100:0 chloroform:dichloromethane followed by analysis using O_2^+. Instead of seeing two curves with opposing slopes, as the compound ratios vary, the result is simply the sum of both compounds, with the slope arising from the different reaction rates of the two compounds.

The mass spectrum obtained using OH^- as the reagent ion, shows a clear mass difference between the two compounds, based on the additional chlorine in chloroform. Consequently, analysis of mixtures of chloroform and dichloromethane can be separated, as demonstrated in figure 5 below, as distinct from the results seen in figure 4.

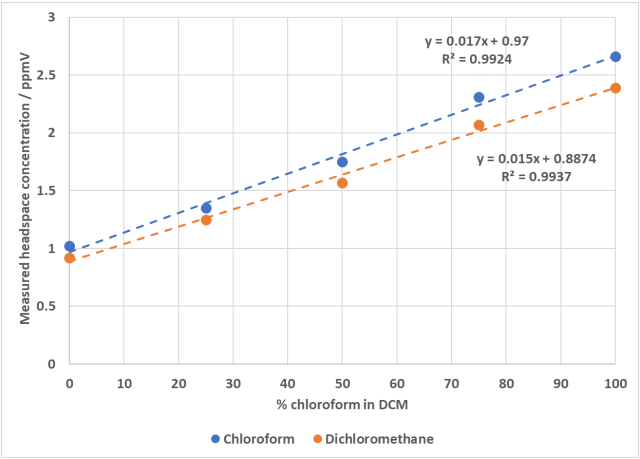

Figure 4: Results from measuring aqueous mixtures of chloroform and dichloromethane at differing concentration ratios, analysed using the O_2^+ reagent ion.

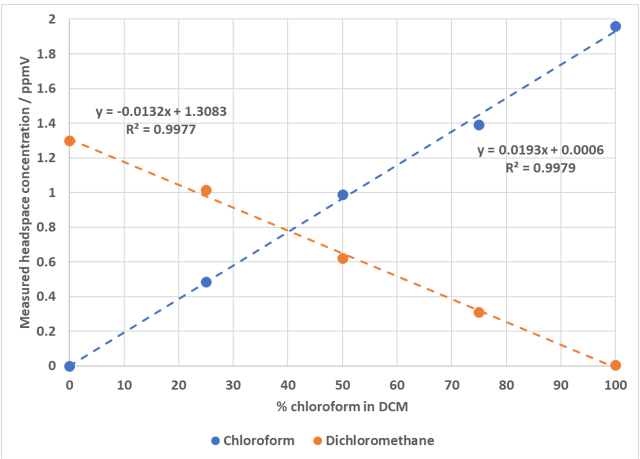

Figure 5: Results from measuring aqueous mixtures of chloroform and dichloromethane at differing concentration ratios, analysed using the OH^- reagent ion.

Linearity

To assess the linearity of measurement using the OH^- reagent ion, a series of standards were prepared, containing both chloroform and dichloromethane in water, from 2 ppb to 2000 ppb (v/v). Analysis was carried out using both the 117 and 119 Da product ions for chloroform and the 83 and 85 Da product ions for dichloromethane. Table 1 and figures 6 and 7 shows the data obtained.

Table 1: Linearity data for aqueous standards of chloroform and dichloromethane from 2 – 2000 ppb (v/v).

Solution concentration / ppb	Measured headspace concentration / ppmV			
	Chloroform (119)	Chloroform (117)	DCM (85)	DCM (83)
2	0.004	0.009	0.031	0.034
10	0.006	0.020	0.045	0.047
50	0.078	0.086	0.065	0.068
100	0.165	0.172	0.116	0.124
250	0.430	0.414	0.285	0.297
500	0.842	0.809	0.541	0.551
750	1.357	1.254	0.854	0.865
1000	1.657	1.564	1.044	1.055
2000	3.417	3.154	2.144	2.155
R^2	0.9991	0.9995	0.9992	0.9991

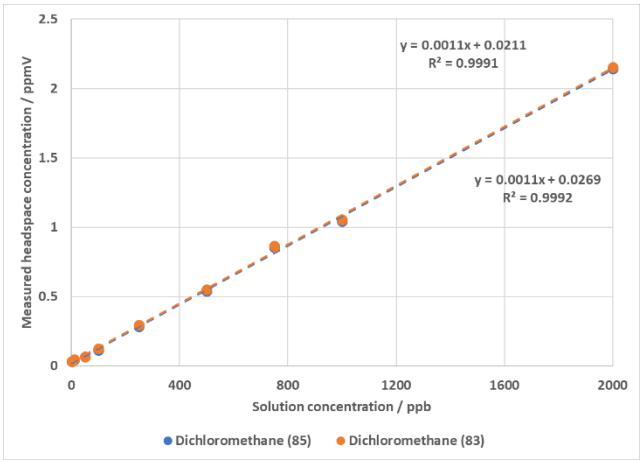

Figure 6: Linearity data for dichloromethane from aqueous standards of chloroform and dichloromethane from 2 – 2000 ppb (v/v).

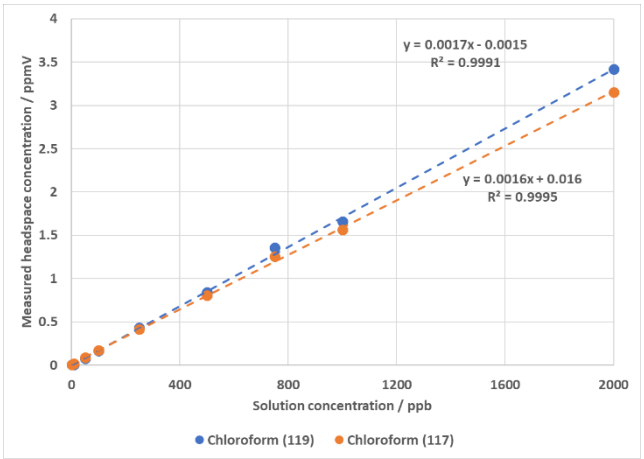

Figure 7: Linearity data for chloroform from aqueous standards of chloroform and dichloromethane from 2 – 2000 ppb (v/v).

The data above shows very good linearity across the range investigated, with R^2 for all product ions greater than 0.999. There was very good agreement between the two product ions for dichloromethane, however, for chloroform there was a slight divergence between its two product ions. This is probably due to a small rounding error in the branching ratios for these two product ions and is not significant, particularly if calibration standards are run prior to analysis.

Repeatability

To assess the repeatability of measurement using the OH^- reagent ion, six replicate standards were prepared, containing both chloroform and dichloromethane in water, at 200 ppb (v/v). As before, analysis was carried out using both the 117 and 119 Da product ions for chloroform and the 83 and 85 Da product ions for dichloromethane. Table 2 and figure 8 show the data obtained.

Table 2: Repeatability data for six replicate aqueous standards of chloroform and dichloromethane at 200 ppb (v/v).

200 ppb standard	Measured headspace concentration / ppmV			
	Chloroform (119)	Chloroform (117)	DCM (85)	DCM (83)
Replicate 1	0.381	0.379	0.255	0.253
Replicate 2	0.331	0.331	0.227	0.230
Replicate 3	0.400	0.393	0.267	0.275
Replicate 4	0.363	0.365	0.243	0.248
Replicate 5	0.338	0.346	0.233	0.236
Replicate 6	0.364	0.362	0.254	0.264
Mean	0.363	0.363	0.246	0.251
Standard Dev.	0.024	0.020	0.014	0.015
%RSD	6.5	5.6	5.6	6.1

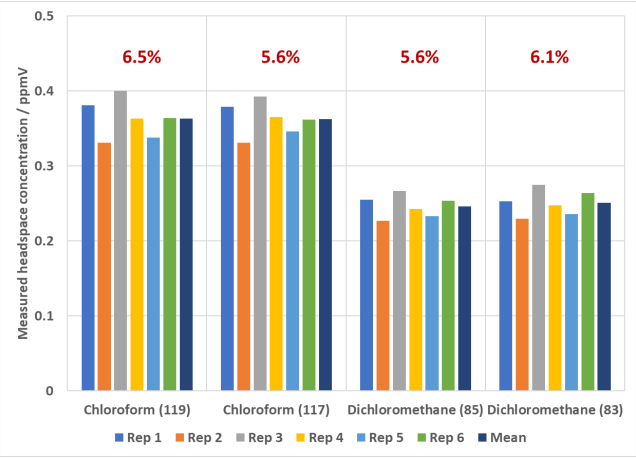

Figure 8: Repeatability data for six replicate aqueous standards of chloroform and dichloromethane at 200 ppb (v/v).

From the data presented for the repeatability study, it can be seen that there is good precision for all product ions, with RSDs of less than 7%. It should be noted that the six replicate standards were prepared manually and the efficient partitioning of both chloroform and dichloromethane into the headspace from water may lead to some variable losses prior to the samples are capped. It is likely that by using the automated preparation functions of the MPS Robotic, prior to incubation, these RSDs could be lowered further.

DISCUSSION

This study demonstrates that by using negative ion SIFT-MS, specifically the OH^- reagent ion, it is possible to speciate mixtures of chloroform and dichloromethane. The method shows good linearity across at least three orders of magnitude and the precision of the method is good, with RSDs of less than 7% for all measurements. Coupled with the fast analysis times that automated SIFT-MS can achieve, this method shows significant promise in the analysis of chlorinated VOCs.

REFERENCES

AS191 – Automated Selected Ion Flow Tube Mass Spectrometry (SIFT-MS)
AS209 – Rapid Analysis of BTEX in Water Using Automated SIFT-MS
AS211 – Realtime Speciation of Ethylbenzene for the Xylenes Using SIFT-MS
AS212 – Rapid Analysis of Organochlorine Compounds in Water Using Automated SIFT-MS

APPENDIX A

Analytical data for results presented in the above Application Note.

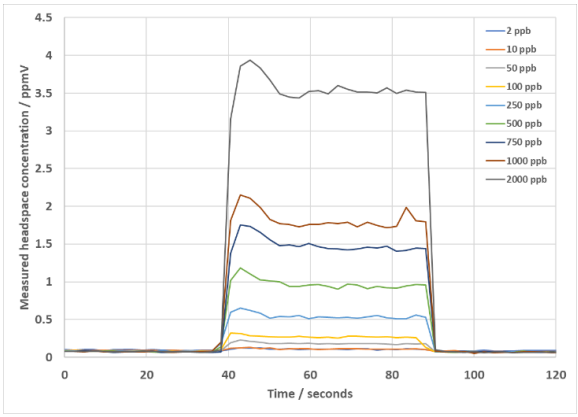

Figure 9: Linearity data for chloroform (119 Da)

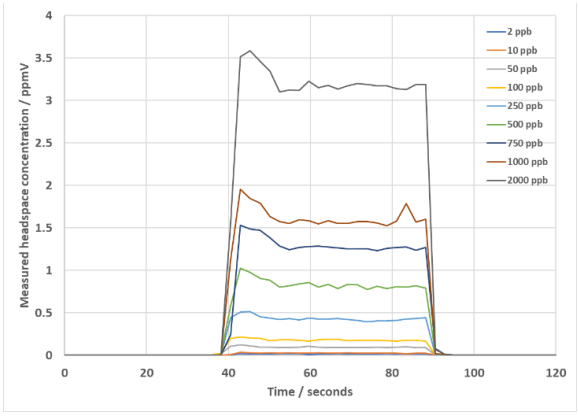

Figure 10: Linearity data for chloroform (117 Da)

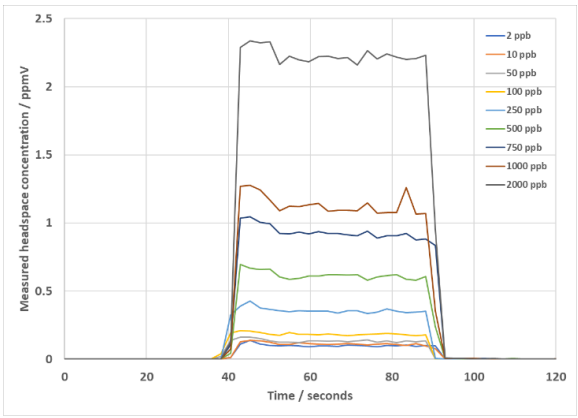

Figure 11: Linearity data for dichloromethane (85 Da)

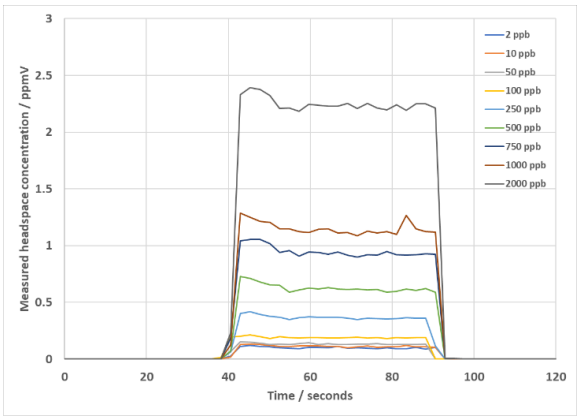

Figure 12: Linearity data for dichloromethane (83 Da)

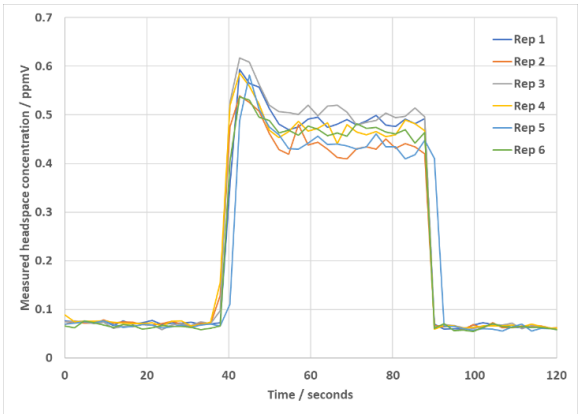

Figure 13: Repeatability data for chloroform (119 Da)

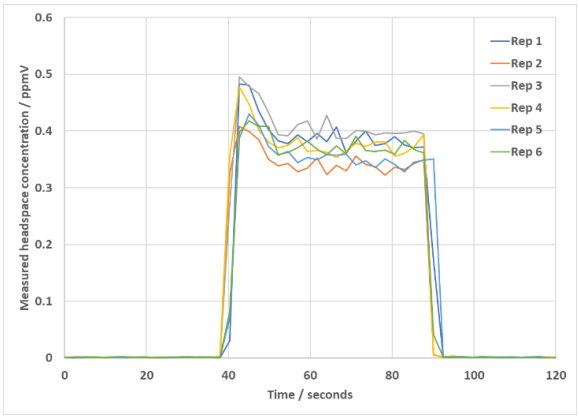

Figure 14: Repeatability data for chloroform (117 Da)

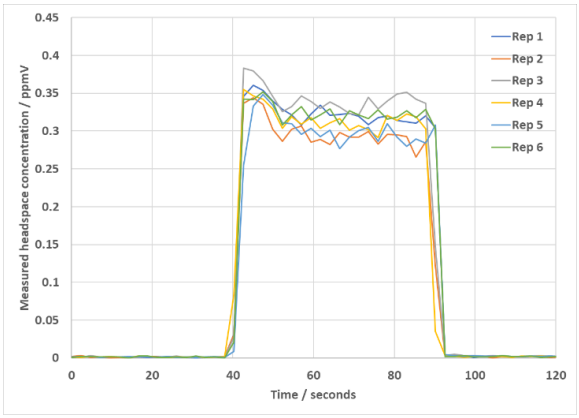

Figure 15: Repeatability data for dichloromethane (85 Da)

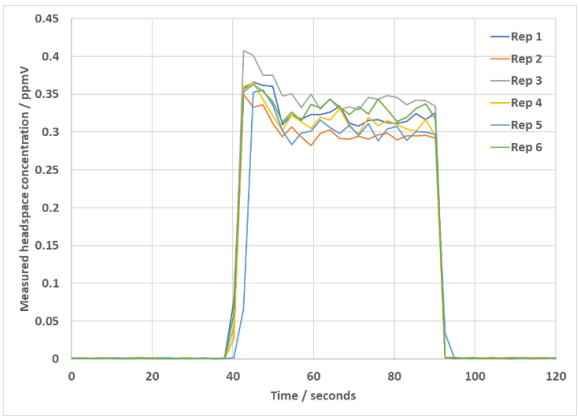

Figure 16: Repeatability data for dichloromethane (83 Da)