

Mass Spectrometry & Spectroscopy

Extension of residual solvents analysis by SIFT-MS to non-aqueous solutions

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Automated selected ion flow tube mass spectrometry (SIFT-MS), by avoiding the need for chromatographic separation of analytes, significantly increases sample throughput for headspace sample analysis. However, the technique is susceptible to saturation by non-aqueous solvents matrices, leading to erroneous results [1], and water has traditionally been used as the universal solvent for headspace analysis. By selecting solvents with suitable physiochemical properties this limitation can be avoided and this article describes the evaluation of six solvents via linearity and repeatability measurements on 14 commonly used residual solvents.

The SIFT-MS technique

SIFT-MS (Figure 1) uses soft chemical ionisation (CI) to generate mass-selected reagent ions [2] that can rapidly quantify volatile organic compounds (VOCs) down to part-per-trillion concentrations (by volume, pptV). Up to eight reagent ions (H_3O^+ , NO^+ , O_2^+ , O , OH , O_2^- , NO_2^- and NO_3^-) are obtained from a microwave discharge in air [3]. These 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 enables direct, real-time analysis of samples to be achieved at trace and ultra-trace levels without pre-concentration. Rapid switching between reagent ions provides high selectivity because the multiple reaction mechanisms give independent measurements of each analyte [4]. The multiple reagent ions frequently remove uncertainty from isobaric overlaps in mixtures containing multiple analytes.

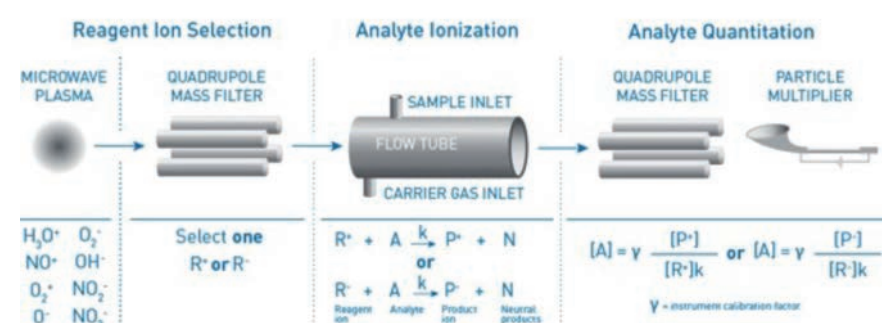


Figure 1: Schematic diagram of the SIFT-MS technique, which utilises soft chemical-ionisation for direct analysis of samples.

Syft Technologies' TracerTM SIFT-MS instrument was coupled with a multipurpose autosampler (MPS Robotic Pro, Gerstel) controlled using Gerstel's Maestro software. Analysis of samples was carried by transferring 2.5 mL of headspace from an incubated vial, via a heated syringe, followed by injection into the SIFT-MS instrument at $50 \mu L s^{-1}$. High-purity nitrogen was used as a make-up gas as a balance for the required instrument sample flow. It should be noted that, unlike conventional GC-based headspace analysis, sample is transferred to the instrument over 50 seconds as slow introduction of sample is required to obtain suitable signal responses. A typical injection plot is shown in Figure 2.

Experimental

Table 1 summarises the six solvents used in this study. A characteristic of all solvents, with the exception of methanol, is their high boiling point and low Log K_{ow} . This ensures that, at suitable concentrations in water, the partitioning into the headspace is minimal, thus ensuring that the analyser response is not saturated. Despite its low boiling point, methanol can be used due to its very slow reactions with the NO^+ reagent ion, however, this does limit methods to those that only use NO^+ as the reagent ion.

Table 1: Solvents evaluated in this study.

Solvent	Boiling Point / °C	Log K_{ow}	Product ions from solvent		
			H_3O^+	NO^+	O_2^+
Dimethylacetamide (DMAC)	265	-0.77	88	87, 117	43, 87
Dimethylformamide (DMF)	153	-1.10	29, 74	72, 73, 103	43, 73
Dimethyl sulfoxide (DMSO)	189	-1.98	79	78, 108	79
1,3-Dimethyl-2-imidazolidinone (DMI)	225	-0.3	115	114	113, 114
Methanol (MeOH)	65	-0.77	33	62	31, 32
Triacetin	259	0.25	45, 59, 159	159, 248	103, 115, 116, 145

Table 2 shows the 14 analytes used to assess the non-aqueous solvents mixtures and these cover a range of chemical classes and polarities. As there was significant variability in headspace partitioning, five different concentration ranges were used. For the sake of clarity 'level' is used throughout and Table 2 correlates 'level' with actual solution concentration for each group of solvents and Figure 2 shows a typical headspace injection.

Table 2: Generic 'level' used and the relationship to actual solution concentration.

'Level'	Solution Concentration / ppm				
	Benzene Toluene Trichloroethylene (TCE)	Chloroform Isooctane Propanal	Tetrahydrofuran (THF) Butanone (MEK)	Acetone Acetonitrile 2-Propanol (IPA) Nitromethane	1-Butanol Methanol
20	0.01	0.04	0.4	1	2
50	0.025	0.1	1	2.5	5
100	0.05	0.2	2	5	10
200	0.1	0.4	4	10	20
250	0.125	0.5	5	12.5	25
300	0.15	0.6	6	15	30
400	0.2	0.8	8	20	40
500	0.25	1	10	25	50

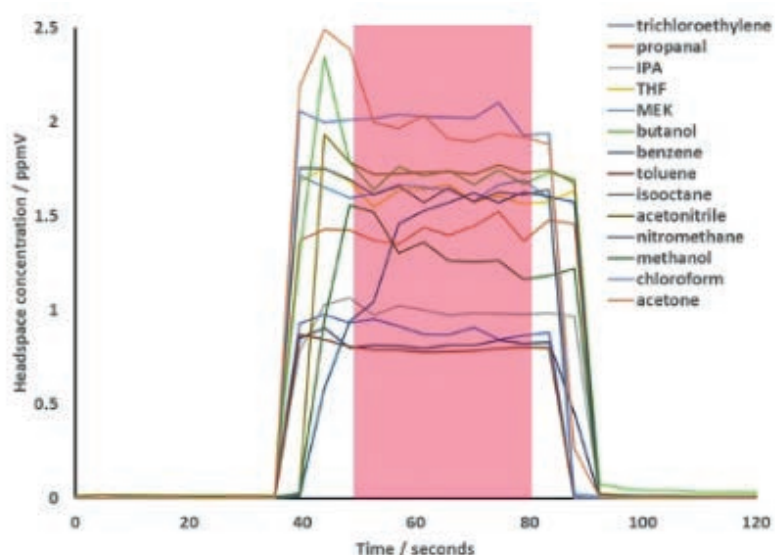


Figure 2: Example headspace injection of 'level' 250 from water. The shaded section shows the region of the injection over which concentration measurements were averaged.

Initial evaluation to 10% solvent in water

The first step in evaluating the compatibility of non-aqueous solvents with SIFT-MS is to determine the dilution level in water that can be tolerated without significant effects on signal responses. For this, level 250 standards were prepared in water-solvent mixtures up to 10% solvent concentration. Figure 3 shows the effects on the response to toluene and butanol only (for clarity), although all analytes were evaluated. The response is shown relative to signal response in 100% water. Other than for methanol, the more non-polar analytes are more adversely affected as the solvent concentration increases. Also, there is a marked decrease in response above 6% triacetin and this is due to it being immiscible in water above 6.1% and selectively removing non-polar compounds from the aqueous fraction. The increasing response for butanol with DMF is due to an interference product ion from the DMF artificially inflating the apparent butanol signal.

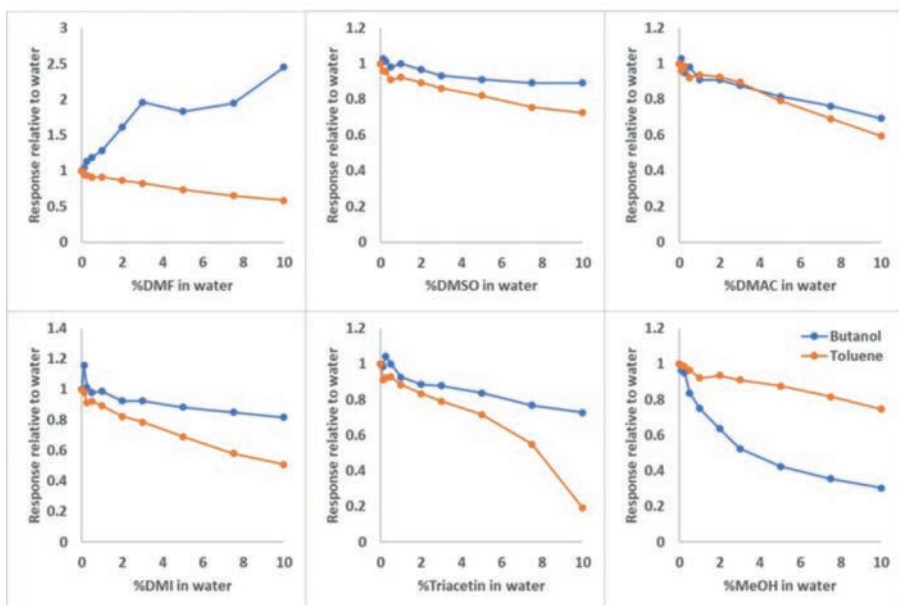


Figure 3: Toluene and butanol signal responses to increasing solvent levels in water, from 0 to 10%.

Table 3 shows the data generated for repeatability and linearity for all analytes at 5% solvent concentration.

Table 3: Summary of linearity and repeatability for all 14 analytes at 5% solvent concentration. (* excludes butanol due to interferences, ** excludes benzene due to interferences, *** excludes TCE due to low sensitivity with NO⁺ reagent ion).

Matrix	R ²	Repeatability		
		"Level" 50	"Level" 250	"Level" 500
Water	0.998 - 0.999	1.2 - 2.6%	2.1 - 6.9%	0.9 - 2.7%
5% DMF*	0.994 - 0.999	1.5 - 6.5%	0.7 - 7.0%	0.6 - 4.6%
5% DMI	0.996 - 0.999	1.3 - 8.0%	0.8% - 4.8%	1.4 - 4.8%
5% DMSO**	0.998 - 0.999	0.8 - 7.0%	1.1 - 4.4%	0.7 - 3.8%
5% DMAC	0.990 - 0.998	2.1 - 7.6%	1.3 - 6.3%	1.2 - 4.5%
5% MeOH***	0.999 - 1.000	1.2 - 5.6%	1.6 - 2.8%	0.7 - 4.1%
Triacetin	0.996 - 0.999	1.3 - 9.6%	0.9 - 5.1%	0.6 - 5.4%

Extending the solvent range

Following the initial evaluation, three solvents were selected to assess whether higher proportions of solvent were usable. Based on their physicochemical properties, DMSO, DMAC and DMI were assessed up to 100% solvent as matrix. Figure 4 shows the responses to five analytes added at generic level 250 (see Table 2), although all analytes were evaluated [5]. It is quite clear the partitioning of non-polar compounds is particularly diminished as the solvent proportion increases. Additionally, for DMI, partitioning of methanol is significantly enhanced.

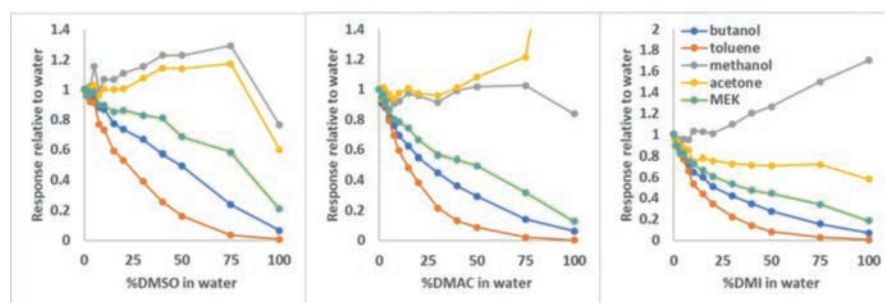


Figure 4: Response of a range of analytes as solvent proportion in the matrix is increased to 100%.

Summary/Conclusion

The data presented demonstrates that by selecting suitable solvents, it is possible to expand the range of matrix solvents beyond just water, and for 5% solvent in water, the sensitivity of the analysis remains essentially the same as for wholly aqueous systems. There are limitations, including a reduction in sensitivity for non-polar analytes as the proportion of solvent increases, and the presence of interfering ions from the solvent itself which can limit the range of analytes for particular solvents choices. Table 4 summarises the solvent limits, and limitations that apply to each solvent evaluated. However, with suitable method development it is now possible to extend automated SIFT-MS headspace analysis to non-aqueous solvent systems.

Table 4: Summary of solvent limits and analytical limitations for the solvents evaluated in this study.

	Solvent Limit	Comments
DMAC	≤50%	Impacts analysis of acetone.
DMF	≤10%	Impacts analysis of butanol, butylamines etc.
DMSO	≤25%	Impacts analysis of benzene and isooctane.
DMI	≤100%	Watch for impurities in solvent, including adsorption from air. Impacts analysis of isooctane.
MeOH	≤10%	Analysis limited to NO ⁺ reagent ion products.
Triacetin	≤6%	Limited by miscibility of water.

References

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