METHANOLIC EXTRACTION OF SOILS BY AUTOMATED SELECTED ION FLOW TUBE MASS SPECTROMETRY (SIFT-MS)

APPLICATION NOTE AS-244

Authors

Mark Perkins

Element Lab Solutions
Unit 4, Wellbrook Court, Girton Road,
Cambridge, CB3 0NA

+44 (0)1223 279210
enquiries.cambridge-ls@element.com

Abstract

Soil can become contaminated with benzene, toluene, xylenes and ethylbenzene (BTEX) from a number of source and may pose health and ecological risks. Automated SIFT-MS is a powerful technique for the analysis of volatiles from a range of different matrices, and benefits from significant throughput gains, versus more conventional chromatographic techniques. Methanolic extraction followed by GC-MS analysis is a common method for determination of BTEX in soil and this Application Note demonstrates that GC-MS methods, even those with more complex sample preparation requirements, can readily be converted to automated SIFT-MS methods, with all the throughput gains and ease of analysis that this brings. Working through a standard validation procedure, we demonstrate that robust and reliable routine analytical methods can be developed and validated, using automated SIFT-MS. Additionally, the data gives confidence to results obtained during real-time analysis, where validation of methods can be more challenging.

INTRODUCTION

Methanolic extraction of soils is a widely used preparation technique for the analysis of BTEX contamination. The two most commonly used sample introduction techniques are closed-system purge and trap and static headspace. Single quadrupole GC-MS is the main chromatographic and detection method, and all of the current methods have drawbacks:

- Low throughput – significant extraction times and long analytical runs
- High maintenance burden – purge and trap is notoriously troublesome when dealing with high matrix samples such as soil
- Poor reproducibility – extraction of volatile organic chemicals from any matrix is tricky to perform in a reproducible manner

Element Lab Solutions Application Note AS151 has shown how this methodology can be automated using the GERSTEL MPS sampler. Additionally, a number of Application Notes (AS191, AS209 and AS212) have shown it is possible to combine the power of direct analysis using Selected Ion Flow Tube Mass Spectrometry with GERSTEL automation (automated SIFT-MS) to greatly simplify headspace analysis, improving method performance, reducing the need for extensive maintenance and improving throughput. Whilst the sample preparation time will not be improved by using SIFT-MS, the analysis time will be reduced threefold when compared to the GC-MS method presented in AS151.

Traditional SIFT-MS analysis often involves relatively simple, and manual, sample introduction. This Application Note demonstrates that it is possible to, not only validate common analytical methods for use with automated SIFT-MS, but also apply automated SIFT-MS to more complicated sample preparation techniques.

Use of methanol as extraction solvent

Due to the high sensitivity of SIFT-MS to all volatile organic compounds, and a dynamic range of sub-parts-per-billion (<ppbV) to around 100 parts-per-million (ppmV), analysis in the presence of high levels of solvent, as described in the method below (figure 3) should not be achievable, as all available reagent ions would be consumed by the high levels of solvent in the headspace. However, as can be seen in Table 1, the reaction of methanol with NO^+ is slow, approximately two orders of magnitude slower than would usually be expected. Consequently, if the analytes of interest are analysed using only NO^+ derived product ions then it is possible to carry out the analysis in the presence of high levels of methanol in the headspace.

Figure 1 shows the relative levels for a 1 ppm standard containing 250 µL of methanol (~10 ppmV for benzene, toluene and xylene compared to ~1500 ppmV for methanol). Figure 3 shows the NO^+ counts for this injection , clearly demonstrating no significant consumption of reagent ions, despite the higher levels of methanol in the headspace.

Table 1: *SIFT-MS reaction chemistry for methanol.*

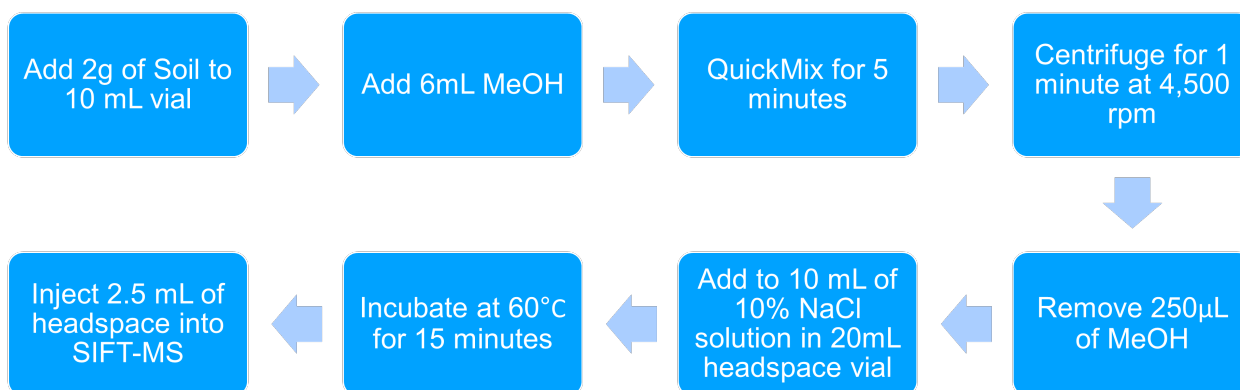| Reagent Ion	Reaction Rate (k)	Product Ion	m/z
H_3O^+	2.7×10^{-9}	CH_5O^+	33
NO^+	1.0×10^{-11}	$CH_3OH.NO^+$	62
O_2^+	1.0×10^{-9}	CH_3O^+	31
		CH_4O^+	32
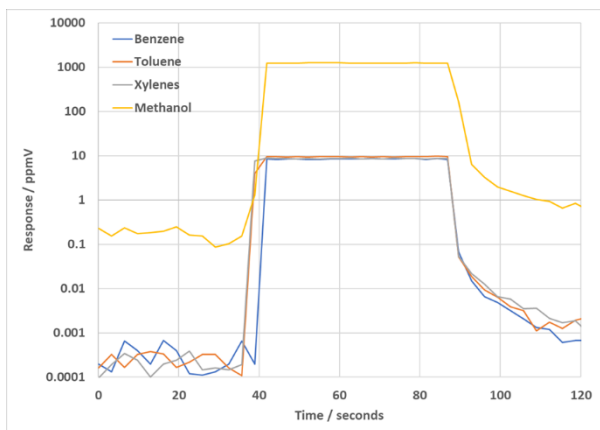
Figure 1: *1 ppm standard of BTEX, containing 250 μL of methanol (note log scale for response).*
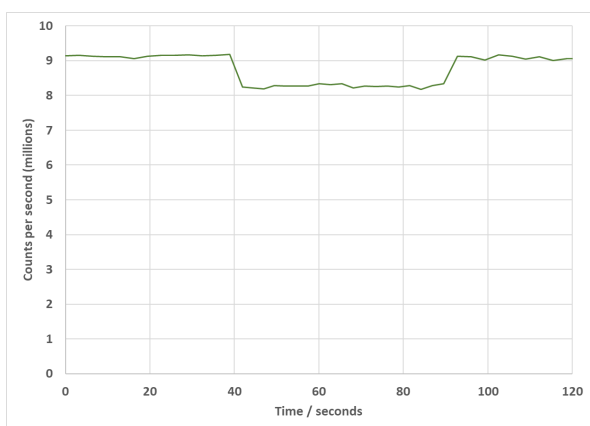
Figure 2: *NO⁺ reagent ion counts for the injection shown in figure 1.*

By limiting the reagent ion chemistry to NO⁺ , it is not possible to speciate the xylenes from ethylbenzene as previous described in App Note (AS211), as the O_2^+ reagent ion is required. For this reason, the xylenes and ethylbenzene will be reported as total C2-benzenes in this Note.

EXPERIMENTAL

Instrumentation

SIFT-MS: Syft Technologies Dual Polarity Voice200*ultra* with GERSTEL Robotic Pro autosampler.

GESRTEL MPS modules: QuickMix, CF200 centrifuge.

METHOD

An outline of the methanolic extraction method is shown in figure 3 and can also be found in Application note AS151.

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

SIFT-MS Analysis

A stock standard solution was prepared by adding 30 μL each of benzene, toluene and m-xylene to 15 mL of methanol. The stock solution was stored at 2 - 8°C. All subsequent calibration and spiking solution used in this Note were derived, by dilution, from this stock solution. Preparation of all samples used for the validation will be described in the requisite results sections below.

Instrumental Parameters

Incubation - 15 minutes at 60°C
Headspace injection – 2.5 mL at 50 μL/sec
Syringe temperature - 150°C
Inlet flow – 25 mL/min

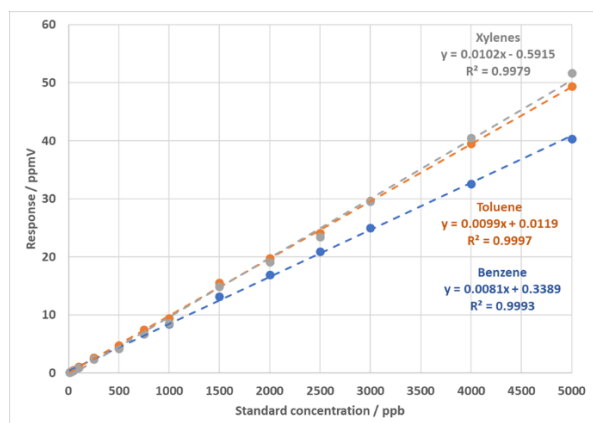**Figure 3:** *Outline of Methanolic Extraction method.*

RESULTS

Linearity

Analytical standards were prepared, using the GERSTEL MPS, by adding suitable volumes of stock solution to 10 mL of 10% NaCl solution. Methanol was added to ensure the total volume of solvent was consistent at 250 µL per standard. Linearity of response was investigated from 10 – 5000 ppb in the aqueous standards. These were then analysed by SIFT-MS. The results can be seen in Table 2 and Figure 4.

Table 2: *Linearity data*

Solution conc. / ppb	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
10	0.107	0.117	0.104
25	0.223	0.248	0.220
50	0.471	0.517	0.454
100	0.947	1.056	0.938
250	2.368	2.656	2.411
500	4.308	4.736	4.191
750	6.698	7.436	6.681
1000	8.438	9.446	8.561
1500	13.198	15.494	14.871
2000	16.898	19.796	19.071
2500	20.898	24.096	23.471
3000	24.998	29.596	29.571
4000	32.598	39.496	40.471
5000	40.298	49.396	51.671
R^2	0.9993	0.9997	0.9979

Figure 4: *Linearity plot for data presented in Table 2.*

From the data presented in Table 2, R^2 for all analytes is at least 0.998, indicating that the method is linear over the analytical range of 10 – 5000 ppb for the analytical standards.

System Precision

System precision was assessed by analysing six replicate standards at 500, 1500 and 3000 ppb. The standards were prepared using the GERSTEL MPS, by adding suitable volumes of stock solution to 10 mL of 10% NaCl solution. Methanol was added to ensure the total volume of solvent was consistent at 250 µL per standard. Tables 3a – c show the results obtained for each standard concentration and figure 5 assesses the linearity of the mean of the results.

Table 3a: *System precision (500 ppb standard)*

Replicate (500 ppb standard)	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
1	4.61	5.31	5.03
2	4.71	5.34	5.00
3	4.53	5.12	4.72
4	4.58	5.17	4.80
5	4.60	5.16	4.70
6	4.63	5.22	4.79
Mean	4.61	5.22	4.84
Std. Dev.	0.054	0.080	0.129
%RSD	1.2	1.5	2.7

Table 3b: *System Precision (1500 ppb standard)*

Replicate (500 ppb standard)	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
1	13.80	16.00	15.40
2	12.80	14.60	13.40
3	13.80	15.80	15.20
4	13.90	15.90	15.20
5	12.90	14.70	13.80
6	12.90	15.40	15.50
Mean	13.35	15.40	14.75
Std. Dev.	0.486	0.563	0.828
%RSD	3.6	3.7	5.6

Table 3c: *System Precision (3000 ppb standard)*

Replicate (500 ppb standard)	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
1	24.80	29.60	29.50
2	25.90	31.20	31.90
3	25.10	30.20	30.10
4	26.00	30.50	30.70
5	24.40	28.40	27.40
6	25.40	30.10	30.10
Mean	25.27	30.00	29.95
Std. Dev.	0.571	0.862	1.361
%RSD	2.3	2.9	4.5
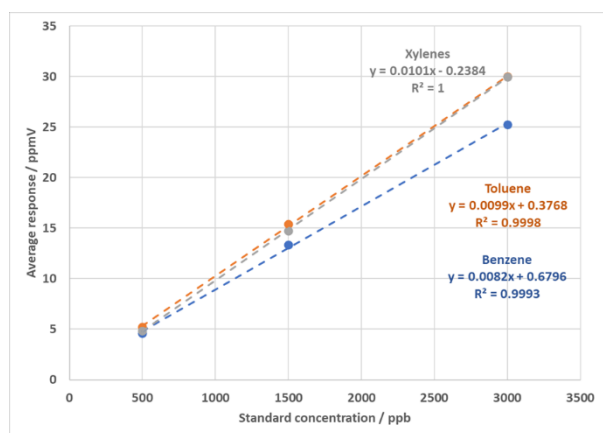
Figure 5: *Linearity of system precision data*

Analytical Precision

Three samples of soil were used to determine analytical precision – labelled Loamy Sand, Silt Loam and BTEX in Soil. Extractions were carried out as described above.

Tables 4a – c show the results for each soil type.

RSDs for all analytes are less than 3% for all samples analysed, as seen in Table 3, indicating good analytical precision for all soil types.

Table 4a: *Analytical precision (Loamy Sand)*

Replicate (Loamy Sand)	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
1	0.55	8.99	10.50
2	0.53	8.72	10.20
3	0.54	8.70	10.30
4	0.53	8.65	10.30
5	0.54	8.73	10.30
6	0.52	8.51	10.10
Mean	0.54	8.72	10.28
Std. Dev.	0.010	0.143	0.121
%RSD	1.8	1.6	1.2

Table 4b: *Analytical Precision (Silt Loam)*

Replicate (Silt Loam)	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
1	0.42	0.25	0.80
2	0.40	0.24	0.78
3	0.40	0.24	0.79
4	0.40	0.24	0.77
5	0.40	0.24	0.77
6	0.41	0.24	0.79
Mean	0.40	0.24	0.78
Std. Dev.	0.007	0.005	0.012
%RSD	1.7	2.0	1.6

Table 4c: *Analytical precision (BTEX in Soil)*

Replicate (BTEX in Soil)	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
1	0.38	0.53	1.32
2	0.35	0.51	1.25
3	0.37	0.52	1.29
4	0.35	0.50	1.24
5	0.36	0.51	1.28
6	0.35	0.50	1.26
Mean	0.36	0.51	1.27
Std. Dev.	0.010	0.005	0.012
%RSD	2.7	0.9	1.0

Extraction Parameters

Whilst the extraction conditions are detailed in App Note AS151, following the determination of analytical precision , a series of tests were carried out to determine whether these were optimum.

Extraction Efficiency

The efficiency of the QuickMix extraction was assessed by extracting 2g of soil, decanting the methanol, re-extracting the sample with clean methanol, followed by analysis of both extracts. Table 5 shows the amount of BTEX remaining in the second extract, as a percentage of the first extract.

Table 5: *Percentage of BTEX remaining in samples after first extraction*

Soil Type	Benzene / %	Toluene / %	C2-benzenes / %
Loamy Sand	2.5	0.9	0.9
Silt Loam	0.7	1.3	2.9
BTEX in Soil	1.3	0.8	2.2

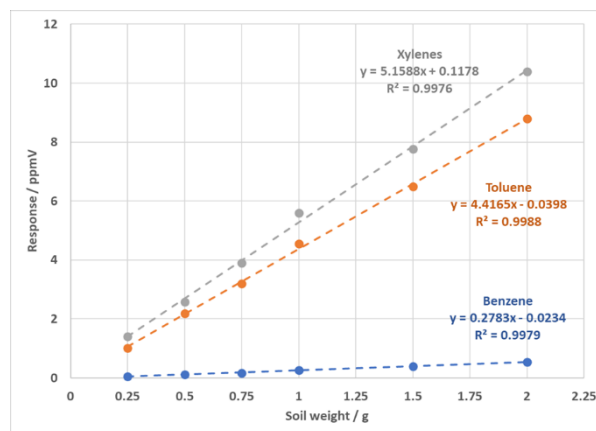*Sample Weight*

The method, as detailed in figure 1, used 2g of soil for the extractions. For samples with very high levels of BTEX, it is possible that the final extract concentration may be beyond the upper linear limit of the SIFT-MS. For this reason, a series of extractions were carried out using

Table 6: *Extraction of variable sample weights*

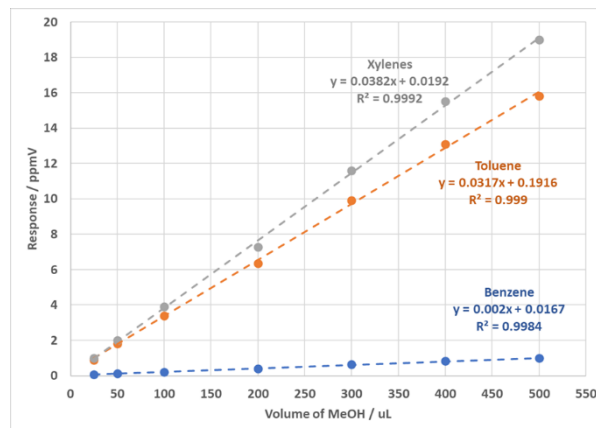| Weight of Soil / g	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
0.25	0.05	1.02	1.41
0.50	0.12	2.19	2.58
0.75	0.17	3.20	3.90
1.00	0.26	4.56	5.60
1.50	0.39	6.49	7.77
2.00	0.54	8.80	10.40
R^2	0.998	0.999	0.998

Loamy Sand, with sample weights between 0.25 and 2g. Table 6 shows the data obtained, whilst figure 6 shows the linearity plot across this weight range for each of the analytes.

Figure 6: *Linearity of Sample Weight analysis*

Methanol Aliquot Volume

The final headspace analysis step of the method requires an aliquot of methanol to be added to 10% NaCl solution prior to incubation and analysis and the method states that the volume of extract should be 250 µL. However, as discussed in the previous section, it may be necessary to vary the sensitivity of the method to fit within the linear range of the SIFT-MS. Sample weight adjustment is one approach, but varying the aliquot volume will also allow for modification of the analytic range. For this reason, variable aliquot volumes (25 – 500 µL), for extraction of Loamy Sand, were analysed. The data is shown in Table 7, with the linearity plot shown in Figure 7.

Figure 7: *Linearity of Aliquot Volume analysis*

Table 7: *Variable aliquots volumes*

Volume of aliquot / μL	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
25	0.06	0.89	1.00
50	0.12	1.81	2.00
100	0.21	3.40	3.90
200	0.41	6.36	7.27
300	0.63	9.92	11.60
400	0.82	13.10	15.50
500	0.98	15.80	19.00
R^2	0.998	0.999	0.999

It is clear from the data presented that whilst 2g of soil and a 250 μL aliquot are effective parameters to work with, other volumes and weights can be used, if the limits of the analytical range determine this.

Accuracy and Recovery

Accuracy and recovery were assessed on both Silt Loam and BTEX in Soil by spiking soil, prior to extraction, with known amounts of stock standard and following the (optimised) extraction and analysis method.

Accuracy

Accuracy was determined by analysing triplicate samples of soil, spiked with 250, 500 and 750 μL of a 1 ppm stock BTEX standard, together with unspiked soil, followed by analysis of the samples. Tables 8a and b show the results for Silt Loam, whilst Tables 9a and b show the results for BTEX in Soil. Both sets of data are graphically shown in figures 8 and 9.

Silt Loam

Table 8a: *Accuracy data for Silt Loam*

Replicate + spike volume	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
1	0.431	0.260	0.836
2	0.426	0.258	0.824
3	0.424	0.259	0.834
1 + 250 μL	0.545	0.440	0.987
2 + 250 μL	0.570	0.448	0.993
3 + 250 μL	0.581	0.457	1.010
1 + 500 μL	0.680	0.622	1.120
2 + 500 μL	0.683	0.632	1.130
3 + 500 μL	0.684	0.619	1.110
1 + 750 μL	0.893	0.853	1.360
2 + 750 μL	0.880	0.845	1.350
3 + 750 μL	0.873	0.832	1.340

Table 8b: *Accuracy data for Silt Loam*

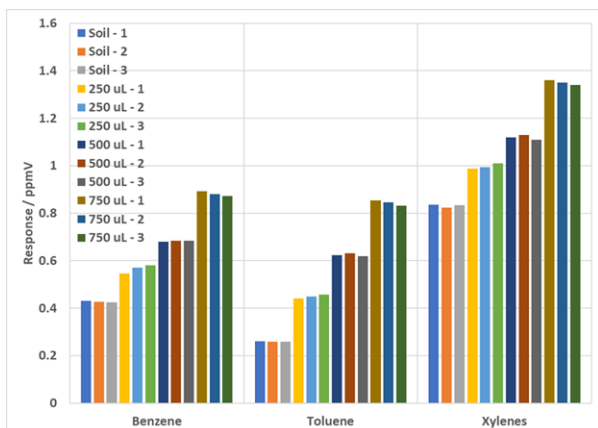|	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
	Unspiked Silt Loam		
Mean	0.427	0.259	0.831
Std. Dev.	0.0029	0.0008	0.0052
%RSD	0.7	0.3	0.6
	250 μL spike		
Mean	0.565	0.448	0.997
Std. Dev.	0.0151	0.0069	0.097
%RSD	2.7	1.5	1.0
	500 μL spike		
Mean	0.682	0.624	1.120
Std. Dev.	0.0017	0.0056	0.0082
%RSD	0.2	0.9	0.7
	750 μL spike		
Mean	0.882	0.843	1.350
Std. Dev.	0.0083	0.0087	0.0082
%RSD	0.9	1.0	0.6

Figure 8: *Accuracy data for Silt Loam*

BTEX in Soil

Table 9a: *Accuracy data for BTEX in Soil*

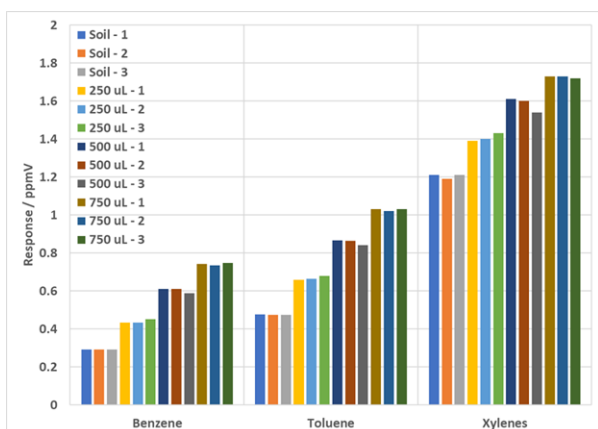| Replicate + spike volume	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
1	0.293	0.477	1.21
2	0.291	0.475	1.19
3	0.293	0.473	1.21
1 + 250 µL	0.434	0.66	1.39
2 + 250 µL	0.433	0.663	1.4
3 + 250 µL	0.451	0.678	1.43
1 + 500 µL	0.612	0.867	1.61
2 + 500 µL	0.611	0.865	1.6
3 + 500 µL	0.589	0.842	1.54
1 + 750 µL	0.743	1.03	1.73
2 + 750 µL	0.734	1.02	1.73
3 + 750 µL	0.747	1.03	1.72

Figure 9: *Accuracy data for BTEX in Soil*

Table 9b: *Accuracy data for BTEX in Soil*

	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
Unspiked BTEX in Soil			
Mean	0.292	0.475	1.203
Std. Dev.	0.0009	0.0016	0.0094
%RSD	0.3	0.3	0.8
250 µL spike			
Mean	0.439	0.667	1.407
Std. Dev.	0.0083	0.0079	0.0170
%RSD	1.9	1.2	1.2
500 µL spike			
Mean	0.604	0.858	1.583
Std. Dev.	0.0106	0.0113	0.0309
%RSD	1.8	1.3	2.0
750 µL spike			
Mean	0.741	1.027	1.727
Std. Dev.	0.0054	0.0047	0.0047
%RSD	0.7	0.5	0.3

Recovery

In order to determine the recovery, a set of calibration standards was prepared and analysed, prior to the above data set being generated. Three replicates prior to analysis, and one replicate post analysis were determined and the calibration data can be seen in Table 10.

Table 10: *Calibration data for recovery calculations*

Calibration standards	Benzene / ppmV	Toluene / ppmV	C2-benzenes / ppmV
Blank	0.0236	0.0157	0.0319
Cal 1	8.23	9.79	9.67
Cal 2	8.39	10.00	9.89
Cal 3	8.29	9.86	9.82
xcheck	8.02	9.43	9.29
Mean	8.30	9.88	9.79
Std. Dev.	0.066	0.087	0.092
%RSD	0.8	0.9	0.9
%xcheck	96.6	95.4	94.9

From this, the recovery for each spike level can be calculated and the results can be seen in Tables 11 and 12, for Silt Loam and BTEX in soil respectively. The data is shown graphically in figures 10 and 11.

The data presented for the accuracy and recovery exercise, together with the previously presented data demonstrates that the method is suitable for the analysis of BTEX in soil following methanolic extraction and quantitation using automated SIFT-MS.

**Table 11:** *Recovery data for Silt Loam*

Silt Loam	Benzene		Toluene		C-2 benzenes	
Spike Amount /ppb	Amount / ppb	%recovery	Amount / ppb	%recovery	Amount / ppb	%recovery
16.6 rep 1	14.2	85.3	18.3	109.9	15.9	95.4
16.6 rep 2	17.2	103.3	19.1	114.	16.5	99.0
16.6 rep 3	18.5	111.3	20.0	119.2	18.2	109.5
33.3 rep 1	30.5	91.4	36.7	110.2	29.5	88.4
33.3 rep 2	30.8	92.5	37.7	113.2	30.5	91.5
33.3 rep 3	31.0	92.9	36.4	109.3	28.5	85.4
50.0 rep 1	56.1	112.2	60.1	119.2	54.0	108.0
50.0 rep 2	54.6	109.1	59.3	118.6	53.0	105.9
50.0 rep 3	53.7	107.4	58.0	116.0	51.9	103.9

Table 12: *Recovery data for BTEX in Soil*

BTEX in Soil	Benzene		Toluene		C-2 benzenes	
Spike Amount /ppb	Amount / ppb	%recovery	Amount / ppb	%recovery	Amount / ppb	%recovery
16.6 rep 1	17.1	102.4	18.7	112.3	19.1	114.4
16.6 rep 2	16.9	101.6	19.0	114.1	20.1	119.5
16.6 rep 3	19.1	114.7	20.5	123.2	23.1	138.9
33.3 rep 1	38.5	115.5	39.7	119.0	41.5	124.6
33.3 rep 2	38.4	115.1	39.5	118.4	40.5	119.5
33.3 rep 3	35.7	107.2	37.1	111.4	34.4	103.1
50.0 rep 1	54.3	108.6	56.2	112.3	53.8	107.6
50.0 rep 2	53.2	106.4	55.1	110.3	53.8	107.6
50.0 rep 3	54.8	109.5	56.2	112.3	52.8	105.5
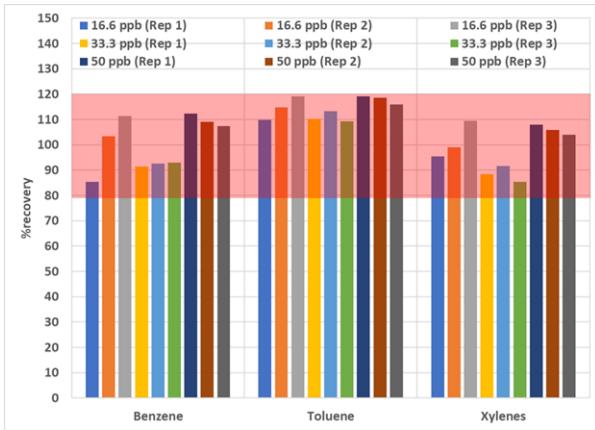
Figure 10: *Recovery data for Silt Loam*
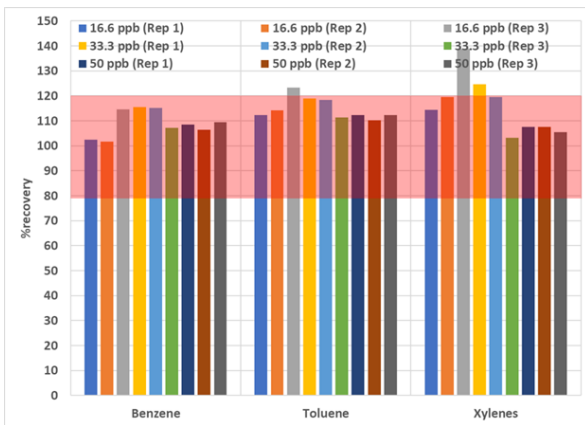
Figure 11: *Recovery data for BTEX in Soil*

CONCLUSION

Previous Application Notes have demonstrated how the GERSTEL MPS robotic system can be coupled to a SIFT-MS for the automated analysis of headspace samples. By using the wide variety of additional modules available – in this instance the QuickMix and the CF200 centrifuge – more complex analyses can be undertaken. This application note shows how previously automated methanolic extractions of soils can be applied to automated SIFT-MS, utilising both the flexibility of the GERSTEL MPS and the higher throughput available with SIFT-MS.