

## Automated Approach for Determination of BTEX in Soil

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### Introduction

Significant levels of benzene, toluene and the xylenes (BTEX) can be found in soil due to pollution. Petrol spills and leaking underground storage tanks can be some of the common causes. Different extraction approaches have been tried in the past such as vapour partitioning. However, methanolic extractions have been shown to be far more robust to extract and recover VOCs from soil [1].

This application note takes the methodology one stage further to automate the majority of the analysis. A soil sample (3g) is weighed out into a 10 ml vial and made up in methanol. Using the Dual-Head MultiPurpose Sampler (MPS), the samples are vigorously mixed and centrifuged. An aliquot is taken and diluted in a salt solution for headspace analysis. Figure 2 shows the set up for this analysis.



Figure 1 – GERSTEL Dual Head, mVortex and Centrifuge with Agilent GC-MS (5977) at Anatune

### Instrumentation

Dual Head GERSTEL MPS 2 with Headspace option/Agitator  
GERSTEL mVortex vortex mixer  
Anatune CF200 Centrifuge  
Maestro software integrated  
Agilent 7890 GC with a 5977 single quadrupole mass spectrometer

### Method

A set of garden soil samples were prepared in methanol and spiked with Benzene, Toluene, Ethylbenzene, Ortho, Meta and Para-xylene standards at six different concentrations between 66ppb to 1.7ppm relative to the soil weight taken. A further low-level spike was prepared at 3ppb. A deuterated Toluene and Benzene mixture was used as internal standard. A blank soil sample was also prepared.

Using the Dual Head MPS, mVortex and CF200, each sample was vigorously mixed at 3000rpm for a short period of time, then centrifuged at 4500rpm.

An aliquot of the clear supernatant was taken and added to a saturated salt solution in a 20ml vial. The second MPS head with a heated 2.5ml syringe was then used to carry out conventional headspace analysis.

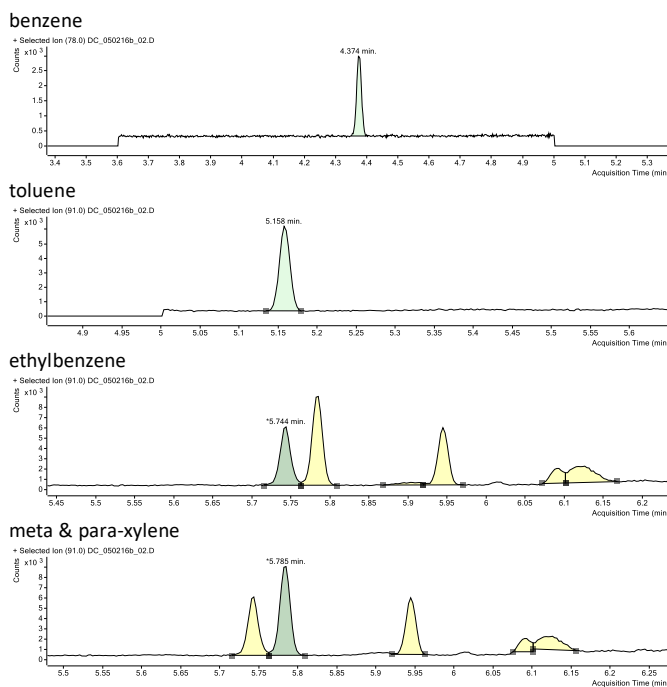
### Results

Figure 2 shows typical soil samples before and after centrifugation.



Figure 2 – Soil samples before and after centrifugation

Figure 3 shows SIM chromatograms for each analyte at 3ppb in garden soil.



## ortho-xylene

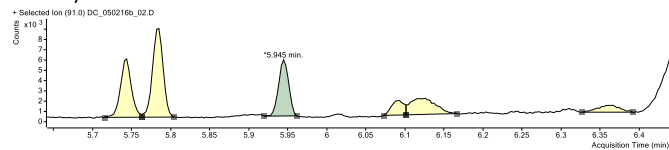
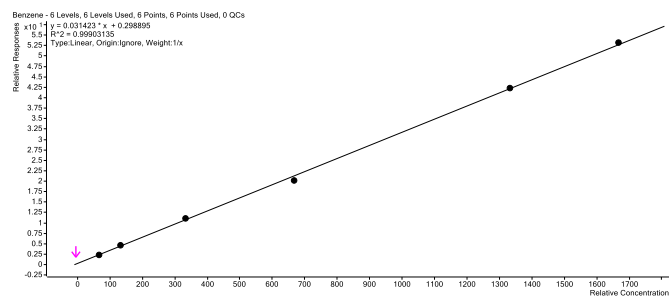


Figure 3 – Low level BTEX spike at 3ppb in soil

Figure 4 shows six-point calibration of Benzene from 66ppb to 1.7ppm



Good linearity was also observed for Ethylbenzene, Toluene, and the Xylenes. Table 1 shows correlation coefficients for BTEX mixture.

Analyte	SIM Ion	Correlation Coefficient (r2)	Fit
Benzene	78	0.9990	Linear
Toluene	91	0.9989	Linear
Ethylbenzene	91	0.9984	Linear
Meta & Para-Xylene	91	0.9984	Linear
Ortho-Xylene	91	0.9984	Linear

Table 1 – Correlation coefficients from a 6 point calibration of BTEX in soil

Five different soil samples were then prepared and BTEX standard was spiked at 333ppb. Table 2 shows the precision achieved for Benzene.

Amount Spiked ppb	Amount Observed ppb Benzene	Recovery %
333.335 Spike Solution 1	339	102
333.335 Spike Solution 2	330	99
333.335 Spike Solution 3	350	105
333.335 Spike Solution 4	275	82
333.335 Spike Solution 5	349	105
Mean	329	98.5
SD	31.2	
% Relative Standard Deviation	9.5	

Table 2 – Precision achieved for 5 different BTEX spikes at 333ppb in garden soil

Table 3 shows amount observed for Toluene, Ethylbenzene, Meta and Para-Xylene, and Ortho-Xylene for the 333.335ppb spike.

Solvent	Amount Observed (mean) ppb	% RSD	Recovery % Mean
Toluene	331	9.6	99
Ethylbenzene	332	10.2	100
Meta and Para-Xylene	662	10.2	99
Ortho-Xylene	328	9.6	98

Table 3 – Average amount observed for Toluene, Ethylbenzene, Meta and Para-Xylene and Ortho-Xylene

## Prep Ahead Functionality

The automated sample preparation time for this method is approximately 15 minutes. Without the Prep Ahead Functionality set, running 14 samples would take over 7.5 hours as illustrated by Figure 5.

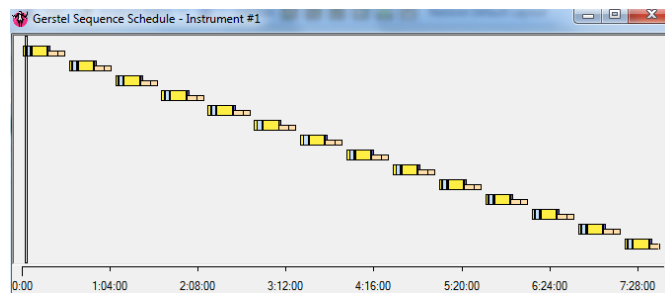


Figure 5 – Without Prep Ahead (time sample analysis in hours)

However, if the Prep Ahead feature is selected, the sample preparation can be carried out within the GC run and this can save a significant amount of time. Figure 6 illustrates how long a run of 14 samples would take with Prep Ahead.

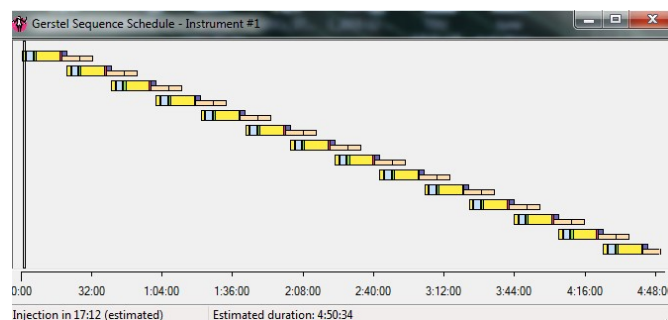


Figure 6 – With Prep Ahead (time sample analysis in hours)

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## Discussion

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This application note sets the scene for what is now possible for soil methanolic extractions. Recent advances in automation including the *mVorex* mixer and Anatune's CF200 have meant that this is now possible. Further work will be carried out in different matrices such as clay and sand. Please call Anatune if you need any further information.

We would like to thank John Quick at ALS Coventry for his help with this work.

[1] Hewitt, A.D Comparison of Sample Preparation Methods for the Analysis of Volatiles Organic Compounds in Soil Samples: Solvent Extraction vs Vapour Partitioning; Environ. Sci Technol. 1998, 32 143-149.