Application Note No. 093

Petrol Range Organics In Soils, Sludges And Wastewaters by Headspace GC-MS

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Introduction

Most PRO methods quantify the petrol range organics by indiscriminately integrating the area between two points, this area being calibrated against a petrol or other suitable standard. There are numerous possible sources of error with such a method not the least of which is the reporting of peaks and areas that are not actually petrol based. For this reason it was felt that there was a need to produce results that reported what was being asked for i.e. Petrol content.

Several petrol samples were obtained and analysed by Headspace GC-MS to evaluate the major components, these were determined to be mostly aromatic in nature in fresh product. It was also likely that degraded petrol was to be found and to this end the aliphatic fraction of petrol would also be analysed for, in addition to these compounds a series of oxygenates or additives would be included.

The aim was to provide a sound overall indication as to the level of contamination from a petrol source, this method was deemed to provide such data. The compounds selected are shown below. The chromatographic analysis of these compounds was carried out by Headspace GC-MS. This would allow the rapid turnaround of samples while still being able to resolve the compounds of interest from any other peaks that eluted along with the sample. It also provided the possibility of identification for non-targeted peaks.

The finalized method was tested by spiking all of the target compounds into water, topsoil and sandy soil, the quantification was against a series of calibration standards containing the target compounds and using toluene-d^8 as both an internal and a surrogate standard.

Instrumentation

- Focus Robotic Sample Processor with Headspace option
- Agilent 6890 GC with 5973MSD Agilent Chemstation
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Analysis Method

Water samples:

- Add 2 mL sample to a 20ml headspace vial
- Add toluene-d^8 internal standard
- Crimp on a magnetic cap and place in sample tray

Soil samples:

- Place 2 g of sample in a 20 ml headspace vial
- Add 2mL methanol
- Add 2mL matrix modifying solution
- Add toluene-d^8 internal standard
- Crimp on a magnetic cap and place in sample tray

The Focus autosampler places the vials into a heated agitator and shakes it for a preset period of time. A set volume of the headspace is then injected into the GC inlet. The GC is runtime is only 4 minutes with the 5973 detector in full scan mode. The data analysis is then automatically carried out by the Chemstation software.

Results

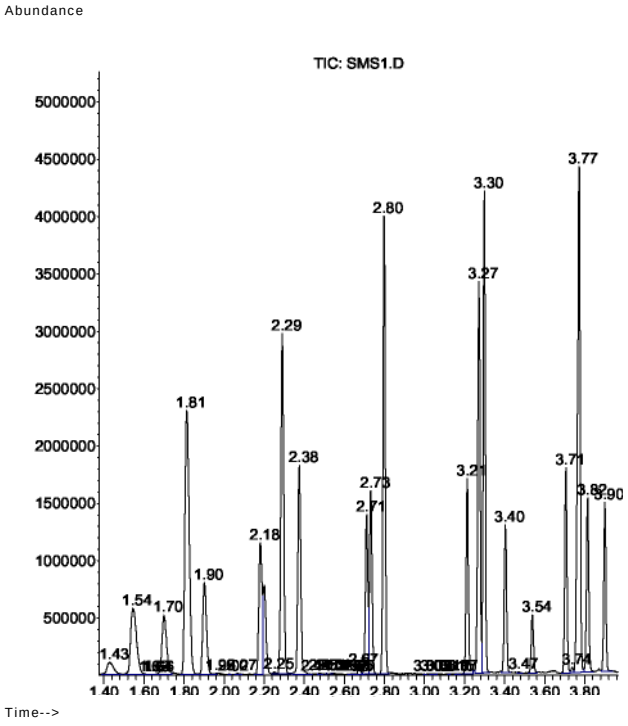

Figure 1: *Typical chromatogram of a medium soil spike at 2.5 ppm: (1.70 min) Methyl tert-Butyl Ether; (1.81 min) Hexane & Isopropyl Ether; (1.90 min) Ethyl tert-Butyl Ether; (2.18 min) Benzene; (2.20 min) tert-Amyl Methyl Ether; (2.29 min) Heptane; (2.73 min) Toluene; (2.80 min) Octane; (3.21 min) Ethylbenzene; (3.27 min) m,p -Xylene; (3.30 min) Nonane; (3.40 min) o -Xylene; (3.70 min) 1-ethyl, 3-methyl Benzene; (3.76 min) 1,3,5-Trimethylbenzene; (3.77 min) Decane; (3.82 min) 1-ethyl, 2-methyl Benzene; (3.90 min) 1,2,4-Trimethylbenzene.*

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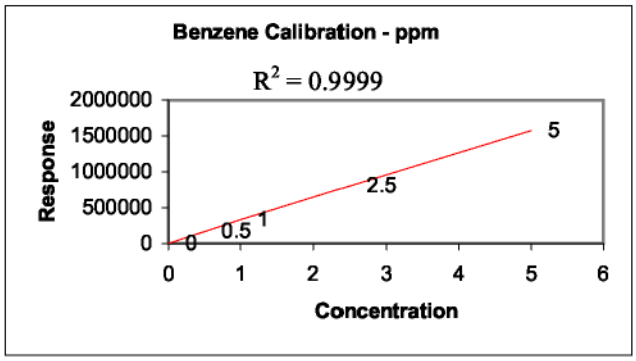

Figure 2: Calibration line of Benzene

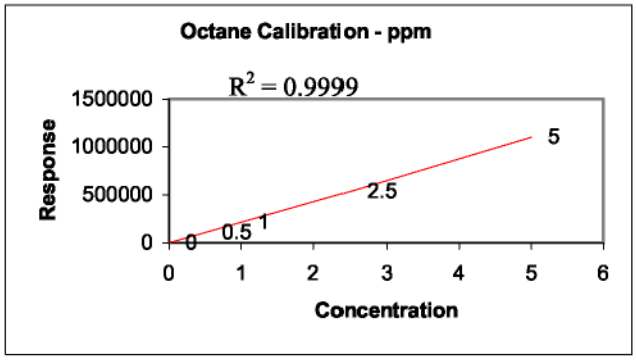

Figure 3: Calibration of Octane

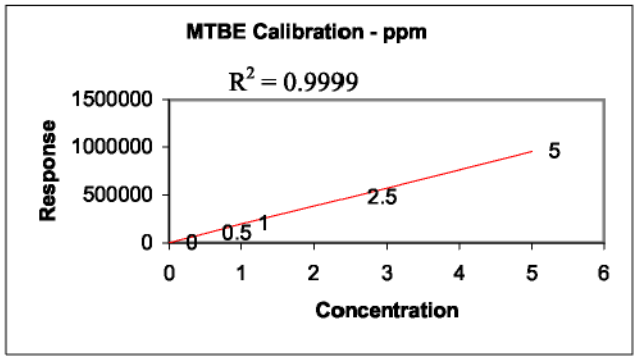

Figure 4: Calibration of MTBE

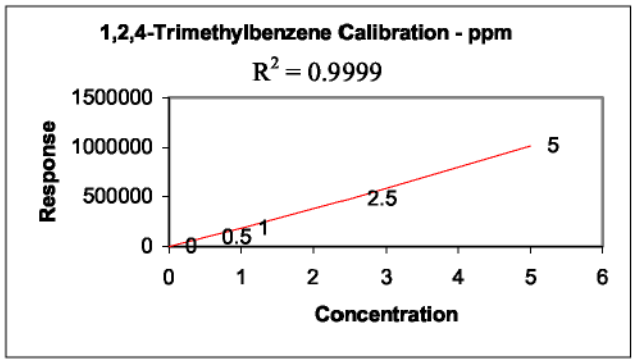

Figure 5: Calibration of 1,2,4-Trimethylbenzene

Table 1: Soil Performance Data - 2 matrices: sandy soil and topsoil at 3 spiking levels (results in ppm)

		Rsd		Rsd		Rsd	LOD
Mean (%)			Mean (%)		Mean (%)		*
Benzene	1.00	5.63	2.51	4.59	3.98	3.61	0.03
Toluene	1.01	2.79	2.49	2.36	4.03	2.29	0.03
Ethylbenzene	0.99	4.82	2.50	3.83	4.09	4.12	0.00
m,p-Xylene	1.95	5.00	5.06	3.29	8.18	3.93	0.02
o-Xylene	1.00	5.53	2.51	4.40	4.10	4.61	0.02
1-ethyl, 3-methyl Benzene	1.00	7.41	2.54	4.45	4.13	5.79	0.02
1,3,5-Trimethylbenzene	0.96	7.75	2.54	4.08	4.10	5.36	0.02
1-ethyl, 2-methyl Benzene	1.00	6.31	2.52	4.02	4.07	5.94	0.02
1,2,4-Trimethylbenzene	0.98	7.53	2.52	4.13	4.10	6.10	0.03
Hexane	1.03	8.15	2.41	9.38	3.78	6.40	0.20
Heptane	0.96	10.19	2.49	12.67	3.83	7.42	0.09
Octane	0.94	8.55	2.49	11.77	3.87	6.61	0.00
Nonane	0.94	7.88	2.49	10.73	3.88	5.77	0.00
Decane	0.92	9.67	2.47	10.23	3.89	5.47	0.03
tert-Amyl Methyl Ether	1.01	4.32	2.55	3.27	4.12	2.76	0.02
Methyl tert-Butyl Ether	1.01	5.46	2.53	4.39	4.02	3.09	0.00
Ethyl tert-Butyl Ether	1.01	5.63	2.53	4.25	4.02	3.01	0.04
Isopropyl Ether	0.99	5.43	2.53	4.75	3.99	3.09	0.00

* LOD determined from blank data

Table 2: Waters Performance Data - 2 levels (results in ppm)

	Mean	Rsd (%)	Mean	Rsd (%)	LOD*
Benzene	1.00	2.52	2.50	1.72	0.00
Toluene	1.00	2.80	2.50	1.79	0.00
Ethylbenzene	0.93	2.74	2.50	1.66	0.00
m,p-Xylene	1.95	2.78	5.02	1.90	0.00
o-Xylene	0.97	2.66	2.51	2.04	0.00
1-ethyl, 3-methyl Benzene	0.94	4.80	2.51	2.73	0.00
1,3,5-Trimethylbenzene	0.97	3.73	2.51	2.33	0.00
1-ethyl, 2-methyl Benzene	0.98	2.87	2.50	2.09	0.00
1,2,4-Trimethylbenzene	0.95	3.17	2.50	2.17	0.00
Hexane	1.01	2.81	2.50	1.76	0.03
Heptane	0.98	2.85	2.50	1.76	0.01
Octane	0.98	2.35	2.50	1.78	0.00
Nonane	0.99	2.62	2.50	1.99	0.00
Decane	0.98	3.70	2.49	2.49	0.00
tert-Amyl Methyl Ether	0.96	2.55	2.50	1.68	0.00
Methyl tert-Butyl Ether	0.96	2.51	2.49	1.66	0.00
Ethyl tert-Butyl Ether	0.97	2.44	2.49	1.79	0.00
Isopropyl Ether	0.99	2.62	2.51	1.61	0.00

* LOD determined from blank data

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The Focus, when set up for headspace analysis, is capable of analyzing up to 96 20ml vials without being reloaded. There is also no transfer line with the Focus and hence an eradication of flow related problems. This enables the fast and very reproducible headspace injection of samples into the GC. The run time of 4 minutes provided excellent separation, see Fig 1.

Conclusions

The Focus Autosampler configured together with a 6890GC and 5973MSD has provided an excellent system from which to produce PRO results. The method clearly demonstrates a high level of performance of the part of both the instruments and the method. There are clearly advantages to the laboratory and client alike as the data will be more accurate and reach a lower detection limit than results produced by traditional methods. The ease of analysis and preparation as well as the speed of the chromatography provide a fast and far superior alternative to the traditional PRO methods. As a headspace sampler the Focus has proved extremely reliable, it is, and will undoubtedly be in the future, the headspace sampler of choice.

This method is UKAS accredited for both soils and waters.

Appendix: Conditions

Focus Parameters:

Syringe size:	2.5 mL-HS
Injection volume:	400 µL
Incubation temperature:	80°C
Incubation time:	3.5 mins
Syringe temperature:	100 °C
Agitator speed:	750 rpm
Fill speed:	1000 µL/s
Fill strokes:	0
Pull-up delay:	200 ms
Injection speed:	1000 µL/s
Pre-inject delay:	500 ms
Post-inject delay:	500 ms
Flush time:	2 mins

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