

Automated analysis of VOCs and SVOCs in soils: Versatile options for extending analyte range and sensitivity

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Introduction

Soils are fundamental to a wide range of ecosystem functions, and monitoring soil health is essential to ensure that these functions can be maintained. Unfortunately, robust indicators of soil health that could be widely adopted across the agricultural sector have remained elusive.

However, a promising avenue of research is the analysis of volatile and semi-volatile organic compounds (VOCs and SVOCs) released from soil. These compounds are produced by microbes, fungi, animals and plants, and many of them are essential for inter-species signalling in a way that is now beginning to be understood. As a result, obtaining an overview of the volatile profile of soil has promise as a diagnostic tool to determine soil health.

In this poster, we describe analytical technologies that open up opportunities for the analysis of VOCs and SVOCs in soil. As well as describing options for improving sensitivity and analyte range for *ex-situ* and *in-situ* sampling, we point out how modern instrumentation is reducing the burden on the analyst by automating previously labour-intensive operations.



Automated sampling and analysis of soils

Analysis of VOCs and SVOCs in soil previously required labour-intensive sample preparation, often using hazardous solvents or operationally difficult purge-and-trap methods. Modern techniques such as solid-phase microextraction (SPME) and static headspace offer greatly improved ease-of-use, but still suffer from relatively low sensitivity.

A new sample preconcentration platform from Markes International addresses this issue. Centri[®] automates a range of sample preparation techniques (Figures 1 and 2), while optimising chromatographic performance by use of a sorbent-packed focusing trap. This trap preconcentrates analytes into a small volume, with subsequent ultra-fast desorption/injection into the GC column providing improved detection limits, increased selectivity and a wide dynamic range. The whole system operates without using cryogen, for greater convenience and lower running costs.



Figure 1: The Centri[®] multi-mode preconcentration platform.

HS & HS-trap

Versatile sampling from solids and liquids contained in regular headspace vials.



HiSorb high-capacity sorptive extraction

Convenient probes for immersive or HS sampling of liquids & solids.



SPME & SPME-trap

Fast and sensitive sample extraction, with a range of selective fiber types.



Thermal desorption

The ideal option for analysis of trace VOCs and SVOCs.



Figure 2: Sampling modes available on Centri[®].

Ex-situ sampling: Improving the sensitivity of SPME

Methodology

SPME is a popular technique for *ex-situ* VOC sampling of soils, because it is fast, easily automated, and does not require solvents. Although detection limits can be as low as ppt-level in some cases, the small volume of sorptive phase on SPME fibers remains a limitation for trace-level analysis.

In **SPME-trap**, this limitation is removed by incorporating a trapping stage to preconcentrate the analytes and so improve sensitivity. In a variation of this technique known as **SPME-trap with enrichment**, a single sample is extracted multiple times onto the *same* trap, before desorption into the GC (Figure 3). This process repeatedly depletes the headspace of the sample, and so eliminates phase competition effects often seen in SPME analysis.

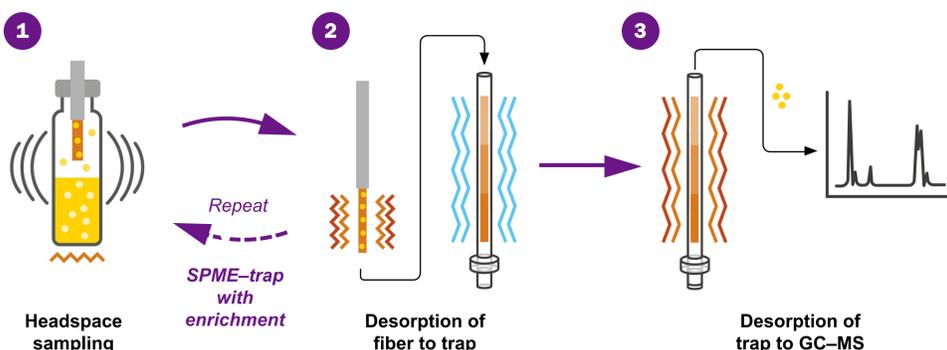


Figure 3: Workflow for SPME-trap, with and without enrichment. In the latter procedure, a single sample is acquired onto the same trap multiple times, before desorption to the GC-MS (step 3).

Soil analysis

To compare the performance of the two methods, a soil sample from Llantrisant, UK, was analysed using SPME-trap and SPME-trap with two rounds of enrichment (Figure 4). A multi-phase SPME (DVB/CAR/PDMS) fiber was used, and compound identification was performed by comparison of mass spectra against the NIST 2017 library (version 2.3, match factor >750).

VOCs from a large variety of compound classes (including carboxylic acids, alcohols, terpenes, amines, esters and alkenes) were identified, and many of these showed increased responses when using enrichment. In addition, a total of 138 compounds were identified using SPME-trap with enrichment – 54 more than for regular SPME-trap (84 compounds).

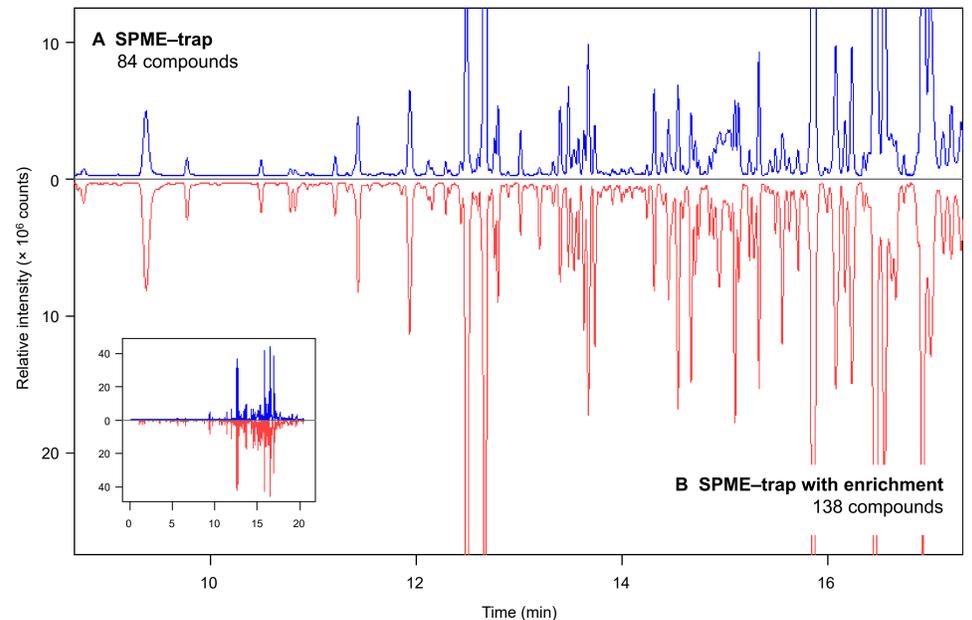


Figure 4: Zoom-in of the analysis of soil headspace using (A) SPME-trap (1 hour extraction), and (B) SPME-trap with enrichment (1 hour + 20 min + 20 min extraction). The inset shows the complete TIC profile.

In-situ sampling: Versatile sorbent-tube options

Methodology

For *in-situ* analysis of trace-level VOCs and SVOCs from a wide range of soil environments, sorbent-packed thermal desorption tubes are a versatile choice. Two tube-based methods are used:

- **Pumped sampling** allows collection of large sample volumes in a short time-frame. Wide analyte ranges can be accommodated by the use of multi-bed tubes.
- **Passive sampling** is a cost-effective option when samplers need to be deployed over a wide area (e.g. for pollution mapping), for sampling over periods of days to weeks.

In both cases, Markes' VOC-Mole[™] soil-gas sampler (Figure 5) can be used, followed by analysis on Centri in accordance with standard methods.

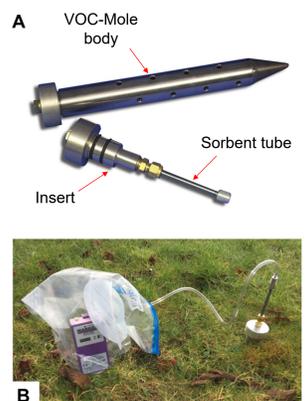


Figure 5: (A) VOC-Mole components. (B) VOC-Mole being used with an ACTI-VOC[™] low-flow pump for field sampling.

Soil analysis

To compare pumped and passive sampling of soil, petroleum-spiked soil was analysed using both methods (Figure 6). Very similar results are obtained across the whole analyte range, allowing the analyst to choose the best option according to factors such as timescale and budget.

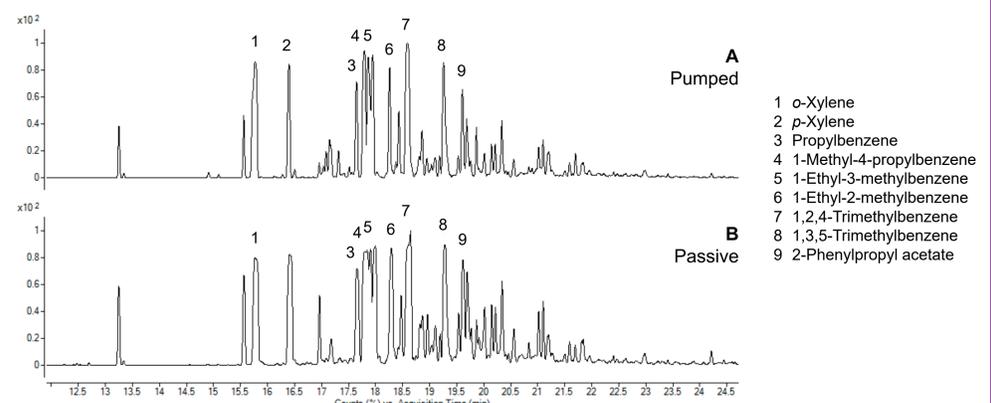


Figure 6: Analysis of petrol-spiked soil by (A) 1-hour pumped sampling and (B) 7-day passive sampling onto sorbent tubes.

Conclusions

- Soil analysis using modern analytical instrumentation from Markes avoids labour-intensive procedures such as solvent extraction, and the inconvenience and expense of cryogenic cooling.
- The sorbent-packed focusing trap on Centri offers improved peak shape and enhanced sensitivity for a variety of sampling modes and a broad range of VOCs and SVOCs.
- SPME-trap with enrichment offers extended sensitivity and more comprehensive VOC profiles.
- Pumped and passive sampling onto TD tubes provide versatile, high-performing options for *in-situ* sampling of soil gas.