Application Note 276

Automated screening for trace-level explosives in water and fabrics using HiSorb™ probes and Centri® extraction and enrichment technology

Automated screening for explosives from both solid and liquid samples from our surroundings would be beneficial for defence, forensic analysis and environmental monitoring applications. Here, we demonstrate a protocol that couples robust high-capacity sorptive extraction probes (HiSorb) with gas chromatography–mass spectrometry (GC–MS) to screen for six explosives on fabrics and in water. Both immersive and headspace extraction procedures can be fully automated using HiSorb probes and using them for screening proved to be a versatile and sensitive approach. Excellent signal-to-noise ratios were achieved from as little as 5 ng of each compound.

Introduction

The determination of explosive compounds in solids and liquids is important for forensic and defence monitoring applications such as identification of unexploded residues following a blast, forensic examination of clothing from a suspect or analysis of materials at a crime scene where illicit manufacture or storage is suspected. Furthermore, explosive compounds may find their way into the environment *via* use in warfare or domestic terrorism, as waste from illicit manufacture or inadvertently as part of legitimate activities. Many explosives cause ecological harm,[1] and where contamination of waterways is likely, monitoring should be carried out.

Many relevant sample matrices are highly complex, complicating the determination of explosives at low levels. Currently, liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are commonly used in explosives detection;[2,3] however, these techniques are predominantly manual and time-consuming and involve extensive use of expensive and potentially hazardous solvents. Solid-phase microextraction (SPME) is an alternative technique,[4,5] but fragile SPME fibers are usually restricted to headspace sampling and limited for trace-level applications by the low phase loading (typically 0.5–1 µL).

Moreover, the highly labile nature of explosives always presents a challenge for GC–MS analysis with some compounds tending to decompose before reaching the detector, especially if excessive temperatures are used or if there is any activity in the system. Any alternative extraction and enrichment technology must therefore take this into account. Markes' Centri system configured with HiSorb probes is one such technology.

Background to Centri®

Markes International's Centri system for GC–MS is the first sample extraction and enrichment platform to offer high-sensitivity unattended sampling and preconcentration of VOCs and SVOCs in solid, liquid and gaseous samples.

Centri allows full automation of sampling using HiSorb™ high-capacity sorptive extraction, headspace(–trap), SPME(–trap), and tube-based thermal desorption. Leading robotics and analyte-trapping technologies are used to improve sample throughput and maximise sensitivity for a range of applications – including profiling of foods, beverages and fragranced products, environmental monitoring, clinical investigations and forensic analysis.

In addition, Centri allows samples from any injection mode to be split and re-collected onto clean sorbent tubes, avoiding the need to repeat lengthy sample extraction procedures and improving security for valuable samples, amongst many other benefits.

For more on Centri, visit www.markes.com.

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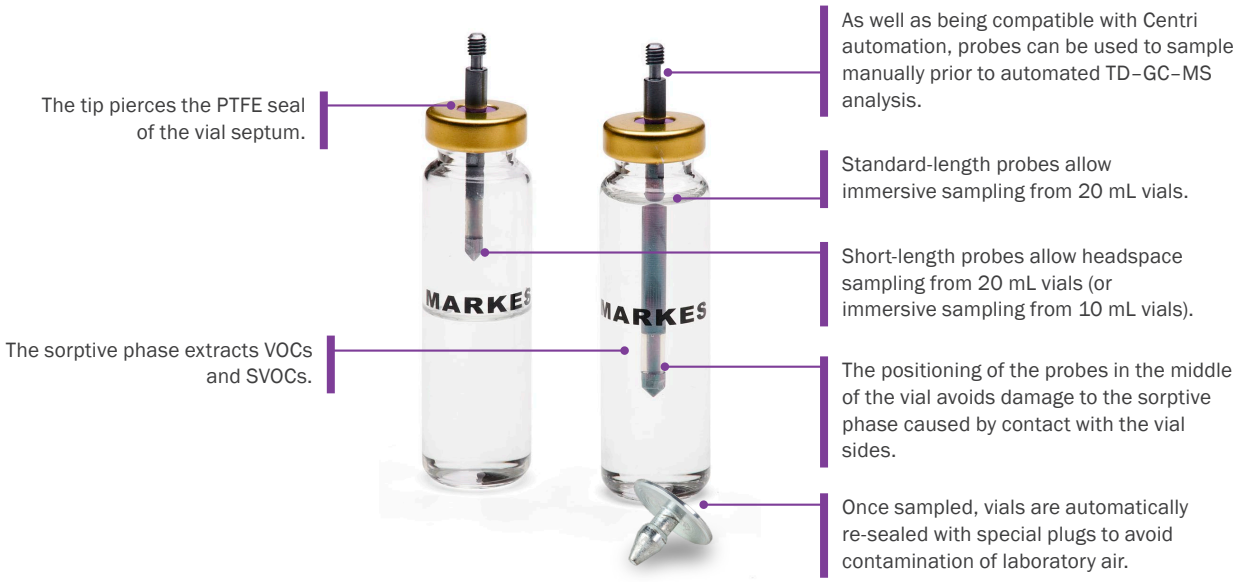


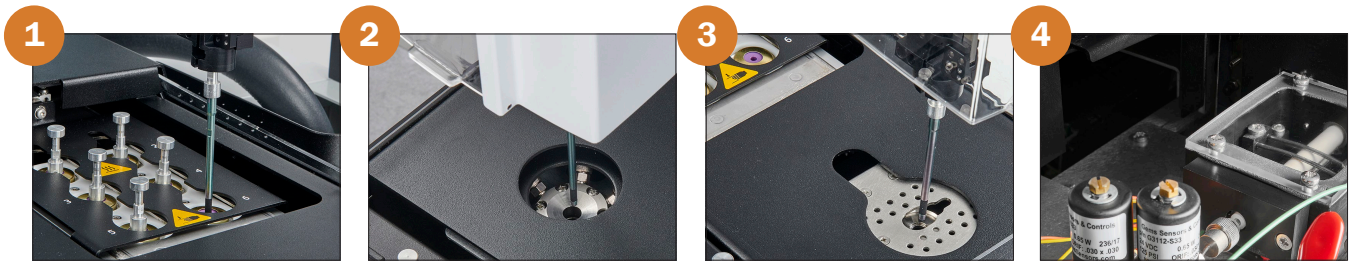
Figure 1: Headspace (left) and Immersive (right) sampling with HiSorb probes.

HiSorb sampling probes comprise >60 µL of sorptive phase mounted on a sturdy, inert-coated metal rod. Centri fully automates HiSorb sampling and desorption as follows: First, the probe is inserted into sealed, temperature-controlled sample vials. Shorter probes are used to sample headspace vapours, while longer probes allow sorptive probes to be fully immersed in the sample so that analytes partition directly from the liquid into the sorptive phase (Figure 1).

Several probes can be sampling at the same time, allowing sample preparation to be overlapped, thus optimising throughput. Once each probe has completed its selected sampling period, it is withdrawn from the sample vial and automatically rinsed and dried. It is then thermally desorbed using heat and a flow of inert carrier gas, transferring the extracted analytes into Centri's electrically-cooled focusing trap, which retains and enriches the compounds of interest. Any residual water is selectively purged from the focusing trap at this stage. At the end of this process, the trap heats rapidly (user selected rate up to 100°C/s) in a reverse flow of carrier gas so that analytes are released and injected into the GC capillary column in a narrow, concentrated band of vapour. This triggers the start of the GC–MS run. Steps in this automated Centri sequence are illustrated in Figure 2.

Although conceptually similar to SPME, HiSorb probes offer many advantages such as:

- Robustness – Can be used for reliable immersive as well as headspace sampling (immersive sampling is better suited to compounds with a low partition co-efficient like explosives).
- Greater sampling capacity – HiSorb probes typically have ~100 times more sorptive phase than a SPME fiber.
- Faster throughput *via* sample overlap on Centri – See Figures 2 and 3.



Probe insertion and analyte extraction: The robot inserts the probe into the vial, and the assembly is incubated/agitated to ensure analyte equilibration.

Probe washing: The probe is removed from the vial and a wash/dry station removes residual sample matrix.

Probe desorption: The probe is thermally desorbed and vapours transferred to the focusing trap.

Analysis: The trap is thermally desorbed at up to 100°C/s to inject the sample into the GC–MS as a narrow band.

Figure 2: The main steps of HiSorb sampling using Centri.

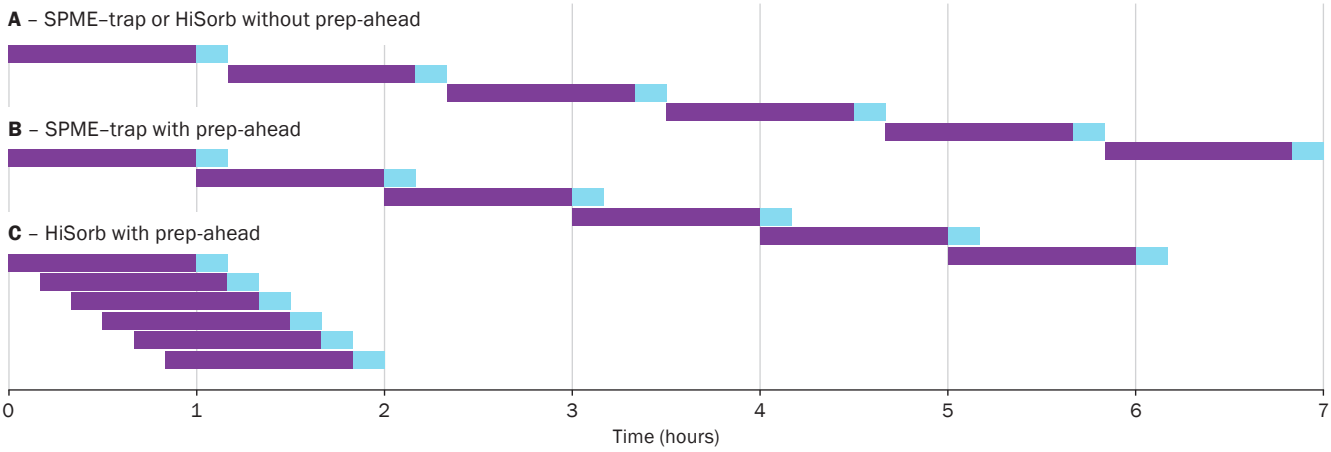


Figure 3: Comparison of overall sequence times for three operational modes on Centri, for a set of six samples with a typical 60-minute incubation time (■) and a 10-minute GC run-time (■).

Note that while Centri offers full automation of all steps illustrated in Figure 2, HiSorb samples can also be desorbed successfully using a conventional thermal desorber such as Markes' fully automated TD100-xr™ or single-tube UNITY-xr™ system (Figure 4).

In this study, HiSorb probes and Centri were evaluated for the determination of six explosive compounds in fabric and water matrices.

Figure 4: (Top left) Fully automated TD100-xr™. (Top right) Single-tube UNITY-xr™. (Bottom) Manual insertion of a HiSorb probe into an empty inert-coated stainless steel tube.

Experimental

Target explosives

Target explosives together with their boiling points and quantifier ions are shown in Table 1.

Compound	Abbreviation	1° ion (m/z)	Boiling point (°C)
Nitrobenzene	NB	77	211
Triacetone triperoxide	TATP	43	317
1,3-Dinitrobenzene	DNB	168	297
2,4-Dinitrotoluene	DNT	165	285
Trinitrotoluene	TNT	210	240
Trinitrobenzene	TNB	213	315

Table 1: Target analytes with associated abbreviations and quantifier ions.

Standard mixes

NB, DNB, DNT, TNT and TNB were acquired as a mixture with the concentration of each analyte at 1000 ng/µL in acetonitrile. TATP was acquired separately at the 100 ng/µL level in acetonitrile.

Three standards were prepared in methanol:

- 1 ng/µL
- 10 ng/µL
- 100 ng/µL (containing all compounds except TATP as this was the level of the standard acquired so no further dilution was required).

Extraction and enrichment parameters

Instrument:	Centri (Markes International)
Flow path:	150°C
Probe:	PDMS, standard or short length, inert-coated (part nos. H1-AXAAC and H1-AXABC)
Trap:	'Chemical weapons' (part no. U-T10CW-2S)
Sample incubation:	65°C for 20 min, 250 rpm

Post-incubation:	Automated washing and drying of probe (immersive sampling only)
Probe desorption:	180°C for 6 min, then 210°C for 4 min
Trap temperature:	-10°C
Trap dry purge:	1 min at 50 mL/min
Trap desorption:	32°C/s to 190°C (3 min)
Split flow:	18 mL/min (7:1 split)

GC–MS parameters

Inlet:	230°C
Column:	MEGA®-5MS, 15 m x 0.25 mm i.d. x 0.25 µm film thickness
Column flow:	3 mL/min
Oven ramp:	60°C (5 min), 15°C/min to 220°C (10 min)
MS transfer line:	230°C
MS source:	250°C
Quad:	180°C
Scan range:	35–300 m/z

Sample matrices

Cotton:	3 cm^2 square of fabric cut from a 100% cotton t-shirt (white)
Poly mix:	3 cm^2 square of fabric cut from 70% polyester, 30% viscose trousers (black)
Water:	HPLC-grade water – 19 mL for immersive and 10 mL for headspace sampling

Sample preparation

Samples were placed in 20 mL glass vials. 5 µL of a 1, 10 or 100 ng/µL liquid standard was injected onto the sample matrix such that 5, 50 or 500 ng masses of each target analyte were introduced, then the vial was sealed using crimp-caps. Another aspect of Centri's inherent flexibility is that it offers the option of integrated automatic thermal desorption (TD). The constraints of this project prohibited further work at this stage, but the automated TD module would also allow fabric samples to be rolled up in empty inert sample tubes and directly extracted into the focusing trap using low-temperature TD. We hope to investigate this option for explosive residues on different fabric types in the future.

Results and discussion

Method development

HiSorb parameters were optimised by spiking 20 and 200 ng levels of target analytes in 20 µL methanol in empty vials.

Screening of water

Initially, water headspace samples were collected by suspending short-length HiSorb probes above 10 ml volumes of water. As expected, the results obtained using this approach were poor, with only two of the target compounds recovered because of the low partition co-efficient of most explosives. Subsequently, immersive sampling of 19 mL volumes of water was trialled where the sorptive phase was completely immersed in the liquid sample, allowing direct contact during extraction.

Figure 5 shows the extracted ion chromatograms (EICs) obtained by immersive sampling of explosives at the masses indicated. Robust responses were achieved for all target explosives, with NB, DNB, DNT and TNT all readily detected at 5 ng and TATP and TNB at 50 and 500 ng levels, respectively. The excellent signal-to-noise (S:N) ratios indicate a potential sub-nanogram limit for some compounds and even the higher levels remain relevant to a scenario of acute contamination, such as in the aftermath of a blast or following disposal of illicit material into a water body.

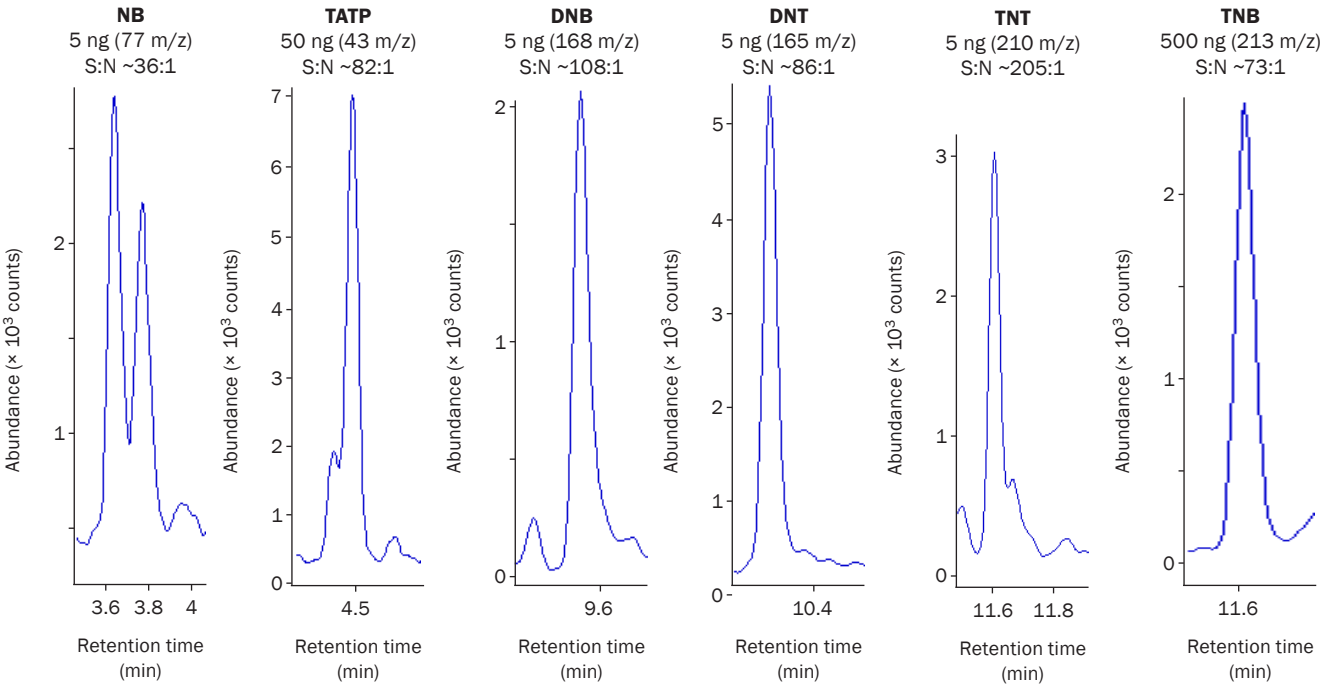


Figure 5: EICs (ions as shown) obtained following immersion of a HiSorb probe in a 19 mL water sample enriched with explosives at the masses indicated.

Material	Mass (ng)	Signal-to-noise ratio					
		NB	TATP	DNB	TNB	TNT	TNB
Cotton	5	28:1		13:1	14:1		
	50		217:1				
	500					63:1	30:1
Poly mix	5	39:1	98:1				
	50			49:1	50:1	12:1	
	500						34:1

Table 2: S:N ratios produced for the lowest measured levels of explosive compounds introduced to the fabric samples.

Textiles

The confident determination of explosive residue on a suspect's clothing, or on fabrics found at a suspected illicit manufacturing location, is valuable in both defence and forensics scenarios. Screening for explosives on clothing may also be important when estimating personal exposure, for example as a check on safety precautions at a legitimate manufacturing facility. Fabrics represent complex matrices likely to emit a wide range of organic vapours both from the material itself and from products the fabric may have been in contact with (for example, laundry detergent). Hence, a screening procedure must be highly sensitive and selective to pick out low-level explosives among other, potentially much more abundant, compounds.

Here, we tested two commonly used fabrics: 100% cotton and a blend of 70% polyester, 30% viscose ('poly mix'). In Table 2, the S:N ratio produced for each compound at the minimum detected mass is displayed. In most cases, high S:N ratios indicate potential limits of detection well below the masses tested.

Conclusions

This study demonstrates the development of a fully automated screening protocol for the detection of trace-level explosive compounds in relevant example matrices – two common fabrics and water. While sensitivity varied among compounds and among matrices, most target analytes were detected at the lower spiking level of just 5 ng and signal-to-noise ratios often indicated limits of detection well below this value. Of note, we were able to detect TATP, an explosive of particular significance due to its recent use in terrorist activities, at 50 ng or less in all matrix types. High sensitivity and method reliability are demonstrated for this challenging application.

References

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Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.