Thermal desorption–GC–MS for environmental contaminant analysis

These application notes demonstrate how thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) supports the trace-level analysis of contaminants across solid, liquid and gaseous matrices. This collection includes:

- **Microplastics in salt samples** – direct TD enables quantitation of characteristic polymer markers from microgram residues.
- **PAHs in water** – high-capacity sorptive extraction with TD–GC–MS provides ppt-level sensitivity and excellent reproducibility.
- **Volatile fluorinated compounds from PFAS destruction** – TD preconcentration allows sub-ppt detection in accordance with US EPA OTM-50.

Key technical strengths of TD–GC–MS

- Direct, solvent-free preconcentration
- High sensitivity and quantitative repeatability
- Applicability to diverse environmental matrices
- Rapid, cryogen-free operation

Together these studies illustrate how TD–GC–MS offers a versatile and reproducible platform for environmental monitoring and regulatory compliance, enabling confident characterisation of complex pollutant mixtures.

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Released: March 2022
Updated November 2022

Application Note 161

Addressing multiple challenges of microplastics analysis using versatile TD–GC–MS – Evaluation of salt samples

Summary

Volatile organic compounds (VOCs) from polymer standards were analysed to establish marker compounds for microplastics analysis using direct thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS). The marker compounds enabled quantitation of multiple types of microplastics in a variety of salt samples. Sample introduction into the GC–MS was automated using the TD100-xr™ thermal desorber, which increases the throughput of large sample volumes.

Introduction

Over the last 100 years, plastics have transformed our way of life, but there has been no major push to study the long-term effects of plastic on the environment and on human health until recently. A group of plastics called microplastics – polymer fragments 1 µm to 5 mm in size – can enter the human body from our food and water, and even from the air we breathe. As a result, scientists are focusing on investigating microplastics.

Various analytical techniques are used for the investigation of microplastics. These range from TD/extraction to pyrolysis and spectroscopic identification. These complementary techniques can identify and quantify the plastics present, enabling the composition of samples to be characterised. In addition, TD enables polymeric additives or contaminants that may have become trapped either within or on the surface of the microplastic to be identified.

Here, salt samples, including rock salt and sea salt, were analysed so that comparisons could be made between them. Sea salt is expected to be contaminated with microplastics whereas mined rock salt should be less so. An interesting aspect of sea salt analysis is that testing samples from different geographic locations should allow the distribution of different polymeric pollution sources and types to be mapped out.

Direct TD combined with analysis by GC–MS was applied to the quantitative analysis of microplastic residues in salt samples. Selection and validation of the specific marker compounds for different polymers is described.

Direct thermal desorption – an introduction

In this study, samples extracted onto filters or weighed into empty sample tubes were subjected to a two-stage thermal extraction and concentration process (Figure 1). In the first stage, samples are heated to break down the microplastics, which releases their characteristic marker compounds and generates a distinctive chromatographic profile or 'fingerprint' for each type of microplastic. (Note that most common polymers degrade from 300°C upwards.[1]) Alternatively, lower desorption temperatures can be used for selectively extracting and characterising any VOC contaminants adsorbed on the surface of microplastic residues. In either case, the volatile and semi-volatile organic compounds released during sample desorption are swept out of the tube in a flow of inert (carrier) gas and focused on a small, electrically-cooled sorbent trap. When the period of sample desorption is complete (typically 10–15 minutes), the focusing trap is rapidly heated, at rates up to 100°C/sec, in a reverse flow of carrier gas to inject the compounds into the GC capillary column as a sharp, focused band of vapour. Reversing the flow of carrier gas during GC injection is important because it allows the trap to be packed with two or more sorbents thus extending the volatility range of analytes that can be analysed simultaneously. The thermal mass of the trap and the rate of heating are also critical in order to deliver narrow peaks to the head of the GC column thus optimising sensitivity and chromatographic resolution.

The transfer of analytes from the sample tube to the focusing trap and the subsequent injection of focused analytes from the trap into the GC column can be carried out as either split or splitless. Large combined split ratios, for example 100:1 on the way into the trap (by using a minimum flow of 2 mL/min to the focusing trap) and then the same 100:1 split ratio during trap desorption enables the analysis of larger, more representative microplastic samples when required without overloading the analytical system. In the example given, the overall split ratio would be 10,000:1.

Note that all Markes' TD systems, manual and automated, offer quantitative re-collection of both split flows, allowing repeat analysis for data confirmation. Split re-collection is also used to simplify method validation as recommended in standard methods. Please see Application Note 024[2] and

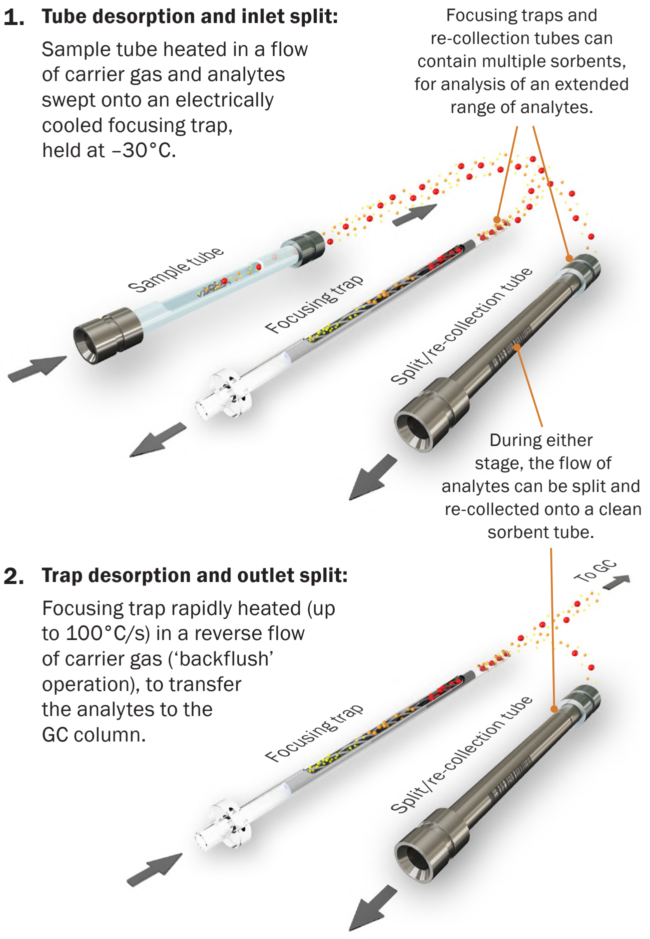

Figure 1: Two-stage thermal desorption process.

Instant Insight 006[3] for more information on this important functionality.

Direct TD offers a number of advantages compared to other GC sample introduction methods. These include:

- **Automation (automated sample introduction):** a TD100-xr has capacity for automation of up to 100 samples or up to 199 samples on an ULTRA-xr Pro™.
- **Representativeness:** TD accommodates a range of sample sizes, allowing meaningful results to be obtained from relatively inhomogeneous samples.
- **Versatility:** TD allows both composition analysis and characterisation of surface contaminants.
- **Sensitivity:** TD enables analysis of trace-level compounds such as contaminants adsorbed to the surface. (The profile for adsorbed VOCs can indicate the source of a sample, the length of time it has been in the environment and/or the type of environment it has been exposed to.)
- **Productivity:** Direct desorption of subsequent samples can begin while GC analysis of the previous sample is ongoing.
- **Enhanced analytical quality control:** in compliance with best laboratory practice, Markes' automated TD systems allow a gas-phase internal standard to be added to the sampling end of the focusing trap just before the start of sample desorption.

Specifically regarding microplastics, direct desorption enables sample sizes from low microgram to mg levels to be analysed at a variety of temperatures and split flows for different purposes of microplastic analysis. In this application note, salt samples were analysed.

Sample preparation and analysis

A small aliquot of each salt was weighed onto a quartz microfibre filter, which was then placed inside glass filtration equipment (Figure 2). Microplastic-free Milli-Q™ water was used to dissolve the salt, and the solution passed through the filter to leave the residue for analysis on the surface. The filter was then washed with solvents to remove sample matrix (see Application Note 150 for details[4]).

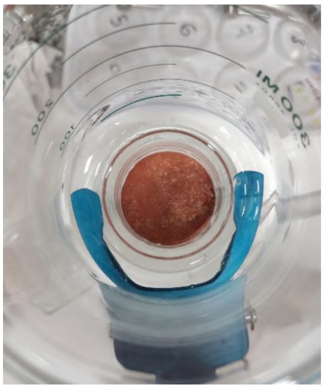

Figure 2: Salt sample dissolved onto filter paper in glass filtration equipment.

For other types of samples, the exact protocol required for extraction of microplastic residues will vary depending on the matrix under study and so this part of the sample preparation process can be modified depending on the type of sample under investigation.

The filter papers were then dried and large sections, typically ¼, or the entire filter papers transferred to empty TD tubes and either sealed with long term caps ready for storage, or fitted with DiffLok™ caps (Figure 3) for processing by automated TD–GC–MS. After the analytical sequence, the filters were removed from the tubes for disposal so that the tubes could be re-used. Analysis was carried out using the 100-tube TD100-xr thermal desorber (Figure 4) coupled to a GC–MS.

TD:

Instrument:	TD100-xr (Markes International)
Tubes:	Empty stainless-steel tubes (C0-AXXX-0000)
Flow path:	200°C
Pre-purge:	1 min at 20 mL/min
Tube desorption:	320°C (12 min)
Trap flow:	20 mL/min
Split flow:	60 mL/min
Trap purge:	1.0 min at 50 mL/min
Focusing trap:	'Air toxics' (part no. U-T15ATA-2S)

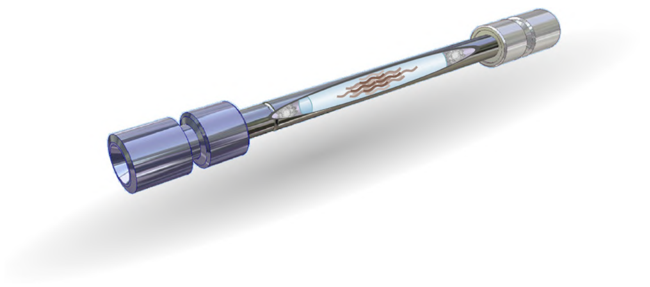

Figure 3: Schematic of a sample tube containing a sample for direct desorption capped with DiffLok™ caps. The caps allow gas to flow when pressure is applied and prevent contaminant ingress and analyte loss before and after automated TD–GC–MS analysis.

Figure 4: Markes' TD100-xr automated thermal desorber (100-tube capacity).

Focusing trap low:	-15°C
Focusing trap high:	300°C (3 min)
Trap heat rate:	MAX
Outlet split:	30 mL/min

GC:

Column:	DB-624™ 30 m × 0.25 mm × 1.4 µm
Carrier gas:	Helium, constant flow
Column flow:	1.2 mL/min
Oven:	40°C (2 min), 10°C/min to 60°C, 30°C/min to 250°C (10 min)

MS:

Source:	230°C
Transfer line:	230°C
Quadrupole:	150°C
Scan range:	m/z 34–350

Samples

Step 1: Marker compounds and calibration

When the TD–GC–MS methodology was finalised, the polymer standards were directly desorbed and analysed to check the specificity and validity of the marker compounds for the following four polymers:

- Polyethylene terephthalate (PET)
- Polyvinyl chloride (PVC)
- Nylon-6
- Polystyrene (PS)

The polymers were chosen because they are abundant in surface water samples,[5] so are also expected to be found in salt.

The polymers were sourced in pellet form (Sigma Aldrich) and ground into powder using a ceramic ball mill. The powders were weighed onto 0.3-µm quartz microfibre 47-mm filter papers (QF1-047 CHM Lab) using a metal spatula and microbalance before the filters were placed inside empty stainless-steel tubes. The tubes were then capped with DiffLok™ caps ready for analysis.

Step 2: Salt samples

20g of each salt sample were weighed and placed on a quartz microfibre filter. Each sample was dissolved using Milli-Q ultra-pure water and then washed in multiple stages with solvents, including hydrogen peroxide, acetone and methanol, with water washes in between. This procedure was optimised to break down external contamination from the salt, before the filters were dried in an oven for 30 minutes at 100°C.

The dried filters were folded and placed inside empty stainless-steel TD tubes, which were then capped before analysis (Figure 5). Sample preparation takes less than an hour, can be applied to multiple filters at the same time and is used for a wide range of sample types with optimised solvent choices.

Salt samples from five different sources were analysed:

- Laboratory-grade sodium chloride
- Table salt (brand A)
- Table salt (brand B)
- Himalayan rock salt
- Celtic Sea salt

Results and discussion

Step 1: Confirming the marker compounds for polymer identification and quantitation

Each of the four powdered polymer standards thermally degraded during analysis to form characteristic compounds that were significant and specific enough to be used as markers to identify and quantify the presence of the four plastics (Figure 5). The thermal degradation processes are well-known in each case.[6,7]

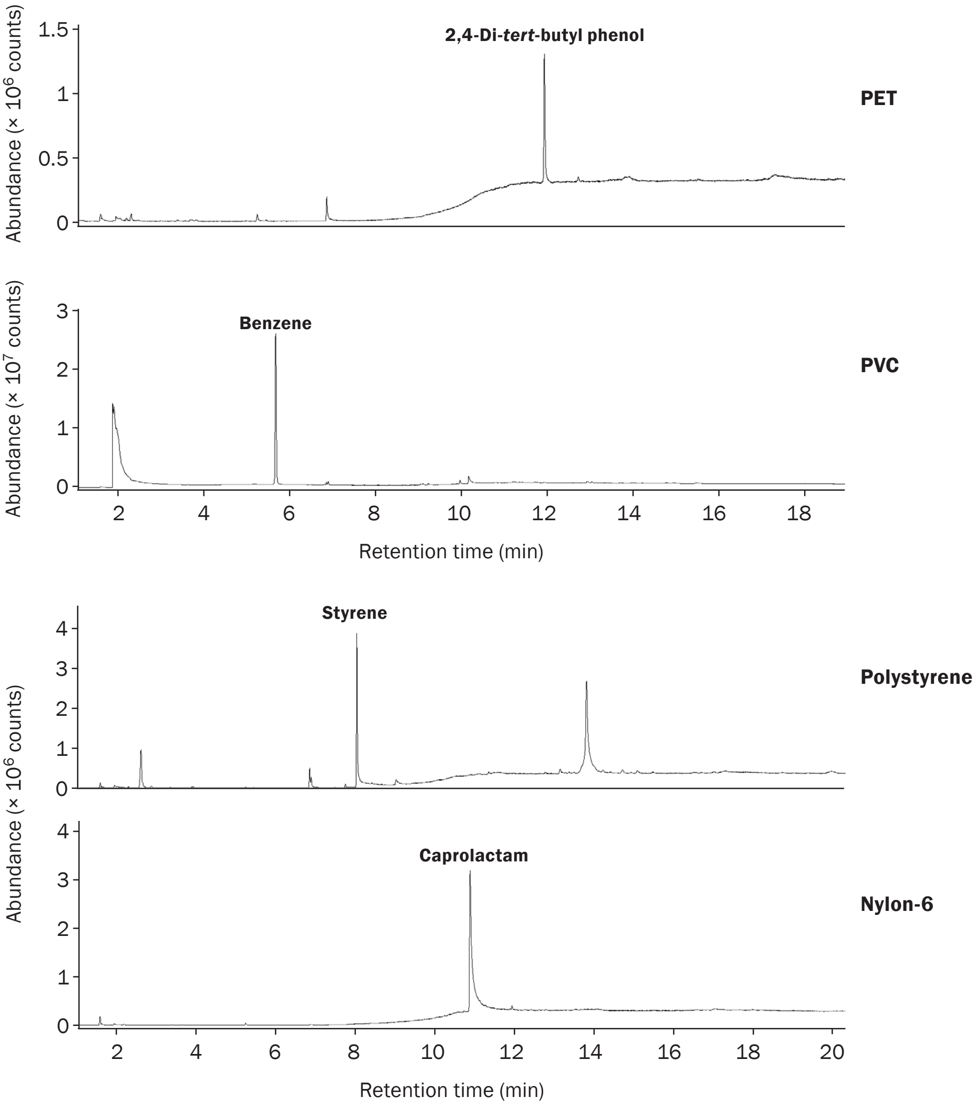

Figure 5: Identification of marker compounds for the four polymer standards displayed.

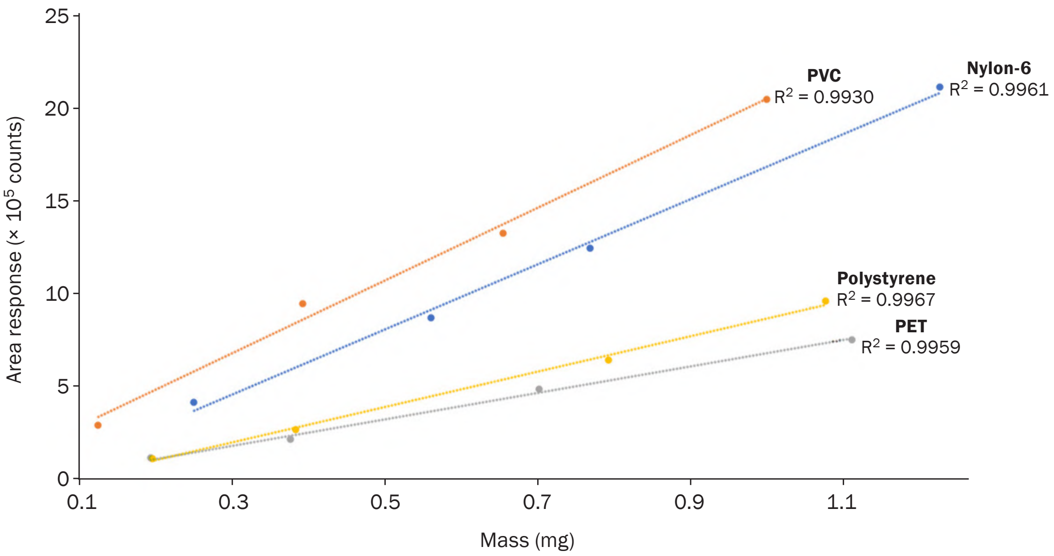

Figure 6: Linearity plots of polymers (0.1 to 1.2 mg) using quantitative marker compounds.

Polymer	Marker compound	Retention time	Linearity	Degradation process
Nylon-6	Caprolactam	10.9	0.9961	Depolymerisation of caprolactam
PET	2,4-DTBP	11.9	0.9959	PET glass transition[8]
Polystyrene	Styrene	8.05	0.9967	Depolymerisation of styrene
PVC	Benzene	5.67	0.9930	Dehydro-chlorination process of PVC

Table 1: Retention time and linearity for each polymer's marker compound and the degradation process.

The value of each marker compound for quantifying the mass of each plastic present was then evaluated by varying the mass of plastic desorbed and checking the linearity of the marker compound response. The results obtained for each polymer marker under these method conditions are illustrated in Figure 6 and presented in Table 1.

Step 2: Applying the method to characterise microplastics present in the salt samples

Five different salt samples and associated blanks were analysed using the method described for comparison.

The resulting chromatograms for three samples – the Celtic Sea salt, Himalayan rock salt and brand A table salt – are shown in Figure 7. The Celtic Sea salt has a busy profile with many peaks at high concentrations. This is due to the increasing amount of pollution in oceans, particularly in areas such as the Celtic Sea, which is close to the English Channel – one of the world's busiest shipping lanes.

The Himalayan rock salt displays a cleaner profile, with fewer peaks at lower concentrations relative to the Celtic Sea salt. Despite being deposited ~150 million years ago, this salt still exhibits some traces of microplastic contamination. During excavation, production, packaging and transport, the Himalayan rock salt is exposed to today's environment and therefore the contamination of microplastics, hence the presence of different polymers within this sample. It is important to point out that mixtures of different marker compounds were observed in most samples analysed. These were easily identified using the method described even within these complex matrixes.

Of all the samples, branded table salt A exhibited the fewest peaks at the lowest concentrations, suggesting that the process of reversed osmosis used in the production of this table salt removes most of the microplastic contamination from the four targeted polymers.

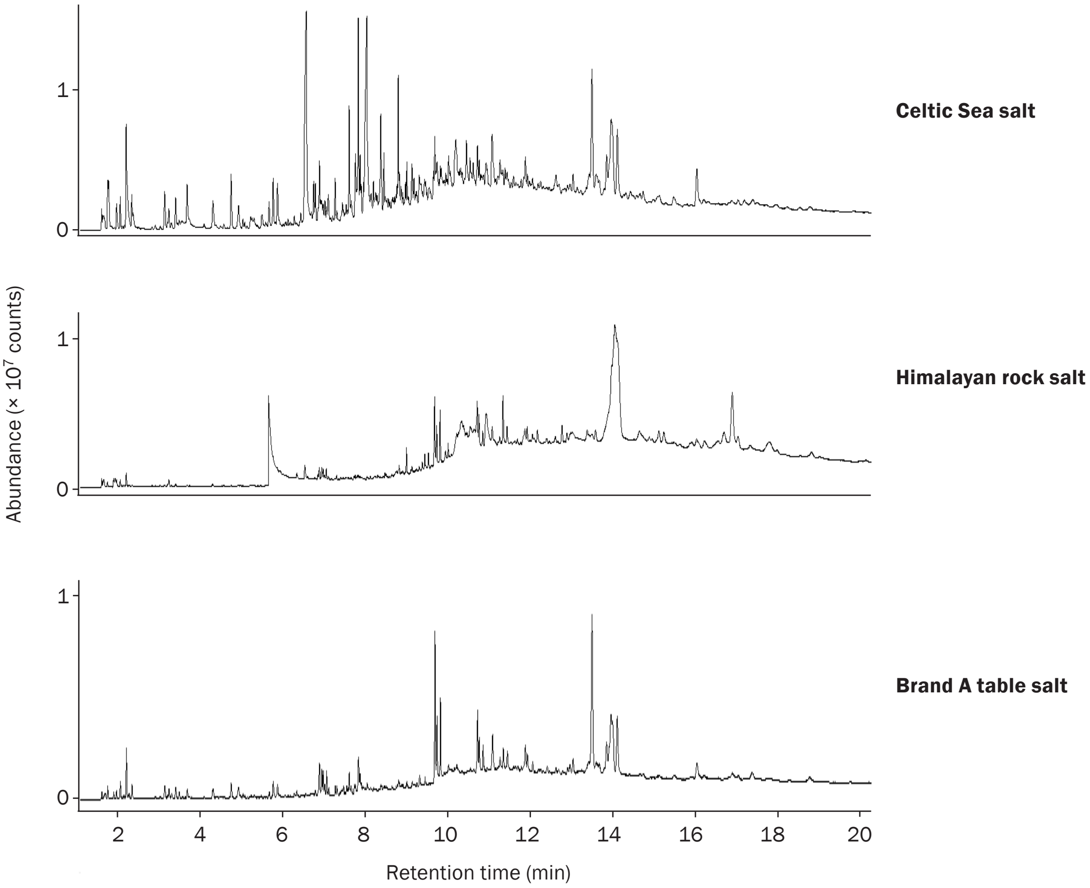

Figure 7: Total ion chromatograms for Celtic Sea salt (top), Himalayan rock salt (middle) and brand A table salt (bottom).

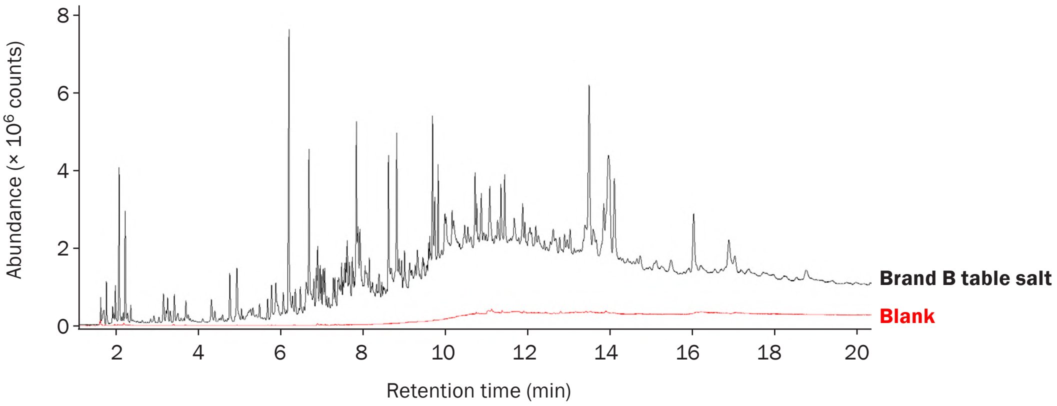

Figure 8: The chromatogram for the table salt sample (black) was compared with a laboratory-grade NaCl sample blank (red), demonstrating that the analytical system and sample preparation process are free from microplastics as well as other forms of contamination.

Further, a table salt chromatogram was compared with that of a blank run with laboratory-grade NaCl (Figure 8). Note that the same filter as that used for sample preparation was used for the blank run. The filter underwent the same extraction and preparation processes (water, solvent, drying, *etc.*). No significant artefacts from sample preparation or analysis can be seen in the chromatogram for the blank run.

Blanks are a vital part of method development; in this study, system blanks, filter blanks and microplastic-free water blanks showed that the workflow was free from contamination that could lead to false positive results, as shown in Table 2. In addition, the simple sample preparation steps and direct analysis of the filter reduced the possibility of contamination from additional sources.

Two spiked samples were also analysed for confirmation of the identified markers. These comprised laboratory-grade NaCl spiked with (a) 0.3 mg of nylon-6 or (b) a mixture of unknown quantities of PET, PVC and polystyrene. The results led to the correct identification of the polymers present in the mixture and quantified the spiked nylon-6 salt sample, confirming the robustness of the method.

Salt type	PET mg/g	PVC mg/g	Polystyrene mg/g	Nylon-6 mg/g
NaCl internal blank	0.000	0.000	0.000	0.000
QC 1 (NaCl spiked with 0.3 mg of Nylon-6)	0.000	0.000	0.000	0.330
QC 2 (NaCl with polymer mix)	0.0236	0.194	0.184	0.000
Himalayan rock salt	0.00775	0.000165	0.0207	0.000
Celtic Sea salt	0.0159	0.00102	0.00463	0.000
Table salt (brand A)	0.00257	0.000265	0.00298	0.000
Table salt (brand B)	0.00173	0.00012	0.00152	0.000

Table 2: Results for various salt samples showing quantified values of each polymer per 20g sample size.

The quantities of each polymer found in the 20-g salt samples, blanks and spiked NaCl samples are shown in Table 2.

Conclusions

TD–GC–MS was proven to be an excellent technique for identifying, characterising and quantifying microplastics from various salt samples. Marker compounds for quantitative analysis were identified for four polymers and linear calibration curves determined in each case. Microplastics were detected and identified in all the real-world salt samples analysed, which highlights the ubiquitous nature of microplastic contamination.

Future research in this area will focus on related aspects – for example exploring the wealth of additional forensic information hidden within the samples, such as surface-adsorbed VOCs. Here, TD–GC–MS will be used to apply lower desorption temperatures and split ratios, and to accommodate larger sample masses to facilitate trace analysis.

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3. Instant Insight 006: How can I use re-collection to simplify method validation and development?

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Acknowledgements

This application note was developed in collaboration with Eurofins IPROMA (Madrid, Spain) and the data reproduced here were kindly provided by Antonio Rosado Sanz and Nuria Font Cardona.

Markes International gratefully acknowledges Dr David Megson and David Jones at Manchester Metropolitan University, UK, for their expert advice on the selection of marker compounds and mechanisms of production during thermal analysis

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Centri
Application
Water by HiSorb
Released: August 2025

Application Note 291

A straightforward method for the analysis of PAHs in water by high-capacity sorptive extraction and TD–GC–MS

Regulatory limits on the levels of polycyclic aromatic hydrocarbons (PAHs) in water demand highly sensitive and rapid analytical methods. In this application note, we describe the use of HiSorb high-capacity sorptive extraction probes, in combination with Centri 90 preconcentration trapping technology, to detect PAHs at low-ppt concentrations in various water samples, with excellent reproducibility and quantitative analysis up to 300 ppt. The method is fully automated, with parallel processing of samples to ensure high throughput, and with hydrogen carrier gas chosen in this case to keep GC run times as short as possible.

Introduction

PAHs are semi-volatile organic compounds (SVOCs) with toxic, genotoxic and carcinogenic properties[1] that are emitted into the atmosphere by human activities such as fossil fuel combustion and vehicle emissions, as well as by natural events such as forest fires or volcanic eruptions. Once in the air they enter waterways via deposition and rainfall runoff and then persist there. Waterborne PAHs therefore pose a long-term environmental hazard, as well as a risk to human health should they enter drinking water supplies.[2] As such, levels of PAHs in both environmental and drinking waters are monitored and regulated across the globe. For example, the EU directive 2020/2184 stipulates a maximum of 100 ng/L for the sum of several PAHs in drinking water, and 10 ng/L for the particularly carcinogenic PAH benzo[*a*]pyrene.[3]

There is therefore a need for analytical methods that are sensitive enough to detect PAHs in water at these low concentrations and also rapid enough to handle large numbers of samples efficiently. Small sample volumes are also beneficial, as this reduces the costs associated with sample transport and storage. Liquid/liquid extraction (LLE) coupled with gas chromatography–mass spectrometry (GC–MS) is commonly used to analyse PAHs, but this methodology involves a multi-step, manual sample preparation stage, reducing throughput and increasing the risk of operator error. It also generates large volumes of solvent waste that are costly to dispose of and that may cause environmental harm.[4]

Here, a straightforward, fully automated method for PAH analysis using HiSorb high-capacity sorptive extraction probes (Figure 1) is described. Due to their robust design, HiSorb probes are well-suited for direct immersion into the water matrix, allowing for efficient transfer even of large, high-boiling PAHs to the sorptive phase. Subsequent heating of the probes then releases analytes, and in this case the probes were thermally desorbed in a Centri 90 unit (Figure 2), with analytes swept onto an electrically-cooled focusing trap packed with a sorbent combination specially suited for SVOCs like PAHs. Subsequent rapid heating of the trap (up to 100°C/s) in a reverse flow of carrier gas ensures analytes are transferred to the GC column in a narrow band of vapour, producing sharp peaks that improve limits of detection (LODs) and quantitation (LOQs).

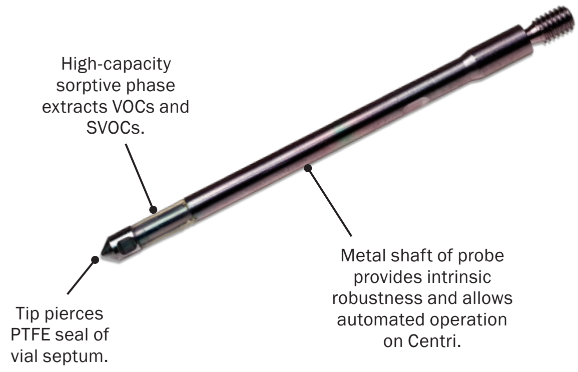

Figure 1: HiSorb probe.

Coupling HiSorb with Centri allows the workflow to be fully automated, with no user intervention required from the moment samples are loaded onto the sample tray (Figure 3). Compatibility with hydrogen carrier gas ensures short GC

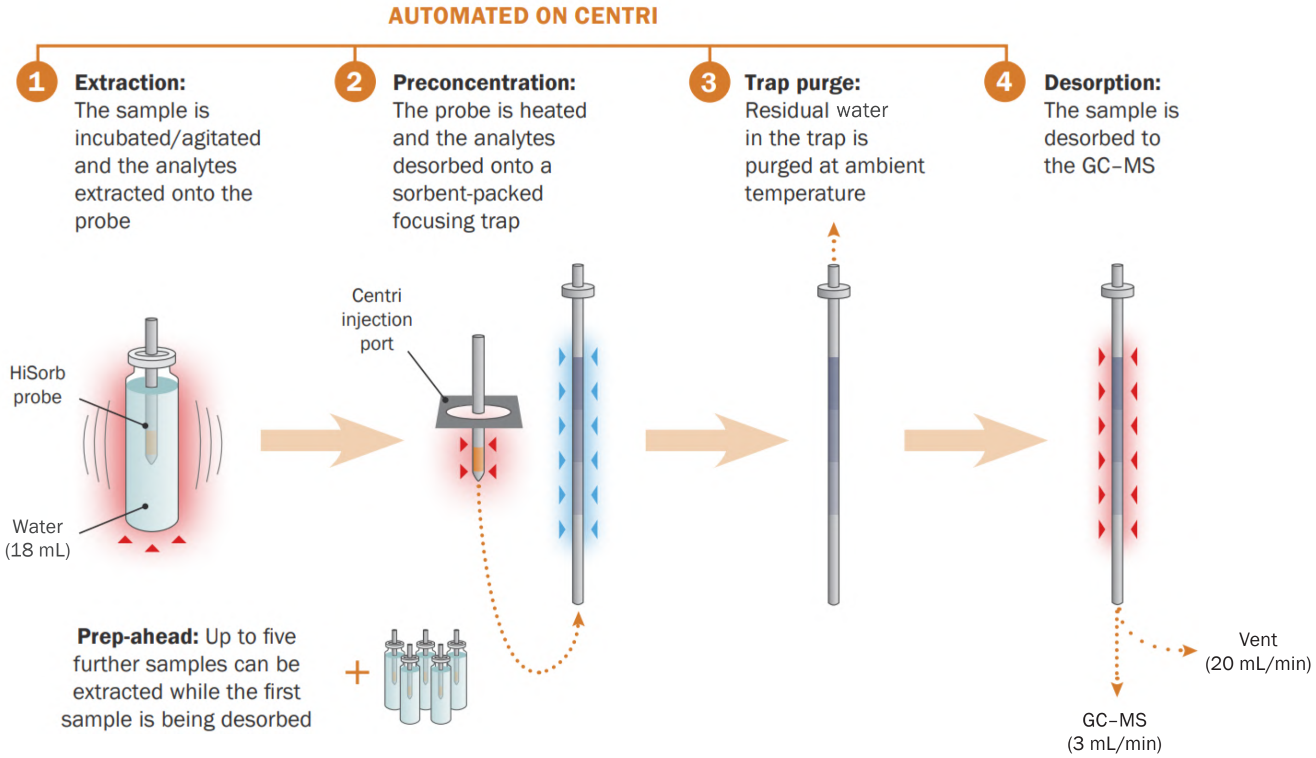

Figure 2: Workflow for PAH analysis on Centri.

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 3: HiSorb automation on Centri 90. To see HiSorb automation in motion, please see ref. 5.

cycle times, while sample overlap, in which multiple samples are extracted simultaneously, minimises GC downtime. Therefore, the HiSorb–Centri method is straightforward, requiring very little sample preparation, generates no solvent waste, and is rapid enough to be readily applied to large sample batches.

In this report, the method is shown to be linear, reproducible and highly sensitive, with LODs well below regulatory requirements. Use of the method on both drinking water and environmental waters demonstrates applicability to a wide range of real-life water matrices.

Experimental

Preparation of laboratory standards

Laboratory standards for method development and validation were prepared by combining a mix of 18 PAHs (Table 1) with HPLC-grade water in industry-standard 20 mL headspace vials for a final concentration of 1–300 ng/L per PAH. An internal standard (IS) mix containing three deuterated PAHs (Table 1, italic text) was also added to achieve a final concentration of 100 ng/L each. Blanks comprised only HPLC-grade water and IS. In all cases, final volumes were 18 mL. After addition of all components, vials were crimp-capped and added to the Centri sample tray.

No.	Compound	Internal standard no.	B.p. (°C)	RT in helium (min)	RT in hydrogen (min)	Quant ion	Qualifier ion
1	Naphthalene	5	218	9.29	6.34	128	64
2	2-Methylnaphthalene	5	242	10.20	6.96	142	115
3	1-Methylnaphthalene	5	242	10.33	7.04	142	115
4	Acenaphthylene	5	280	11.32	7.70	152	76
IS1	Acenaphthene-D$_{10}$	–	279	11.50	7.83	164	80
5	Acenaphthene	5	279	11.54	7.85	153	76
6	Fluorene	8	295	12.15	8.27	166	82
IS2	Phenanthrene-D$_{10}$	–	340	13.27	9.02	188	94
7	Phenanthrene	8	340	13.29	9.03	178	76
8	Anthracene	8	340	13.34	9.07	178	89
9	Fluoranthene	8	375	14.73	10.00	202	101
10	Pyrene	14	404	14.99	10.17	202	101
11	Benz[*a*]anthracene	14	438	16.44	11.15	228	114
IS3	Chrysene-D$_{12}$	–	448	16.46	11.16	240	120
12	Chrysene	14	448	16.50	11.18	228	114
13	Benzo[*b*]fluoranthene	14	481	17.68	11.97	252	126
14	Benzo[*k*]fluoranthene	14	480	17.70	11.99	252	126
15	Benzo[*a*]pyrene	14	495	18.00	12.20	252	126
16	Indeno[1,2,3-*cd*]pyrene	14	536	19.30	13.09	276	138
17	Dibenzo[*a*,*h*]anthracene	14	524	19.33	13.12	278	139
18	Benzo[*ghi*]perylene	14	550	19.64	13.33	276	138

Table 1: Target compounds. IS = Internal standard. RT = Retention time.

Preparation of water samples

The four water samples (Table 2) were all collected from South Wales, UK. Sample water and the IS mix were combined in 20 mL headspace vials to a final volume of 18 mL.

Sample extraction

Platform:	Centri 90
HiSorb probe:	PDMS, standard length (part number H1-DXAAC-06)
Sample equilibration:	1 min at 65°C, 500 rpm
Sample extraction:	2 h at 65°C, 500 rpm

Thermal desorption

Probe desorption:	20 min at 300°C, 100 mL/min
Flow path:	250°C
Focusing trap:	'PAH/SVOC' (part number U-T19PAH-2S)
Trap low:	–25°C
Trap purge:	1 min at 25°C, 50 mL/min
Trap desorption:	Max heating rate to 380°C, 10 min (helium) or 7 min (hydrogen)
Split flow:	20 mL/min (7.6:1 split ratio)

GC–MS

GC inlet:	300°C
Column:	5-MS, 30 m × 0.25 mm, 0.25 µm
Carrier gas:	Helium or hydrogen
Oven programme:	Helium: 50°C (5 min), 20°C/min to 310°C (5 min) Hydrogen: 50°C (3.5 min), 30°C/min to 310°C (3.5 min)
Column flow:	3 mL/min
MS transfer line:	300°C
Detection:	Selected ion mass (SIM) mode using quant and qualifier ions (see Table 1).

Sample	Description	Appearance
A	Drinking water from an indoor tap	Colourless, no particulates
B	As for sample A, after passing through a kitchen water purifier	Colourless, no particulates
C	Lake water from an industrial area	Faintly yellow, a few small particulates
D	Lake water from a semi-rural area	Faintly yellow, a few small particulates

Table 2: Water samples studied.

Results and discussion

Method development

The high boiling point of some PAHs (Table 1) could lead to poor desorption efficiency from the trap or probe, as well as condensation within the analytical flow path, leading to carryover and poor recovery. Method parameters were therefore selected to minimise these issues, drawing on previous work analysing PAHs in air.[6,7] The Centri flow path was heated to 250°C to prevent analyte condensation, and various probe desorption times and temperatures were tried, in order to identify parameters that did not cause significant carryover. Cooling the trap to sub-zero temperatures during probe desorption helped focus PAHs at the front of the trap, ensuring efficient transfer during subsequent trap desorption. Consequently, carryover on the trap, injector (to account for the full flow path) and probe were all found to be minimal (Table 3).

Compound	Carryover (%)		
	Trap	Injector	Probe
Naphthalene	3.24	1.54	1.79
2-Methylnaphthalene	0.79	0.50	0.90
1-Methylnaphthalene	0.45	0.25	0.82
Acenaphthylene	0.06	0.21	0.31
Acenaphthene	0.13	0.15	0.34
Fluorene	0.50	0.58	0.66
Phenanthrene	0.41	1.01	1.31
Anthracene	0.34	0.27	0.32
Fluoranthene	0.20	0.56	0.86
Pyrene	0.19	0.59	0.95
Benz[*a*]anthracene	0.18	0.49	0.65
Chrysene	0.27	0.56	0.85
Benzo[*b*]fluoranthene	0.19	1.34	1.41
Benzo[*k*]fluoranthene	0.23	1.28	1.56
Benzo[*a*]pyrene	0.34	0.74	1.25
Indeno[1,2,3-*cd*]pyrene	0.34	1.24	3.15
Dibenzo[*a*,*h*]anthracene	0.51	1.52	3.20
Benzo[*ghi*]perylene	0.45	1.26	4.13
Mean	**0.49**	**0.78**	**1.36**

Table 3: Carryover determined as peak area from a trap, injector or probe blank as a percentage of the peak area from a 300 ng/L laboratory standard.

Chromatography

Centri 90 is independently certified as safe for use with hydrogen as the GC carrier gas. Hydrogen is less costly to acquire than helium, can be produced via a generator (avoiding the inconvenience and potential downtime associated with changing cylinders), and allows for shorter GC run times without sacrificing analyte resolution, potentially enhancing sample throughput.[8]

Chromatographic performance with helium and hydrogen carrier gas was therefore compared, with adjustments made to the GC programme to ensure faster elution of compounds with the latter (see Experimental). Trap desorption time was also reduced to take advantage of more efficient desorption in hydrogen.[8] The result was that elution of all target analytes was achieved within 13.5 min with hydrogen, compared with 21 min with helium (Figure 4) – a reduction of approximately 35%.

PAH chromatography is characterised by critical pairs – compounds that elute very close together and have the same quant ion (Table 1), making them potentially difficult to distinguish.[9] Here, all compounds were chromatographically resolved, with both helium and hydrogen carrier gas providing clear separation of peak apices even for the closest-eluting critical pair, benzo[*b*]fluoranthene and benzo[*k*]fluoranthene (Figure 5), so that accurate integration could be achieved. Therefore, hydrogen carrier gas allowed GC run times to be reduced without sacrificing analyte separation.

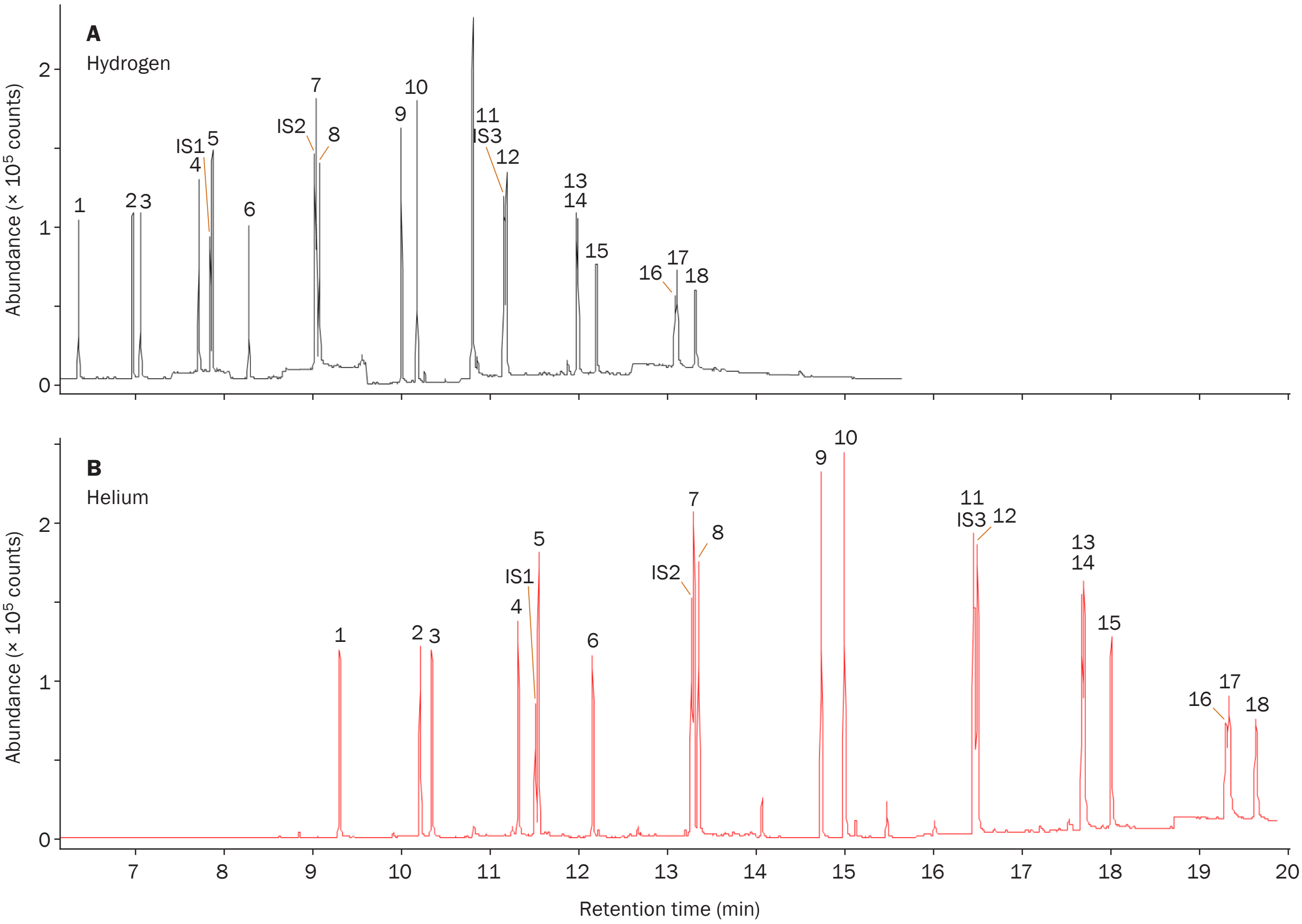

Figure 4: HiSorb analysis of PAHs (Table 1) at 100 ng/L using (**A**) hydrogen or (**B**) helium as the GC carrier gas. Peak identities are listed in Table 1.

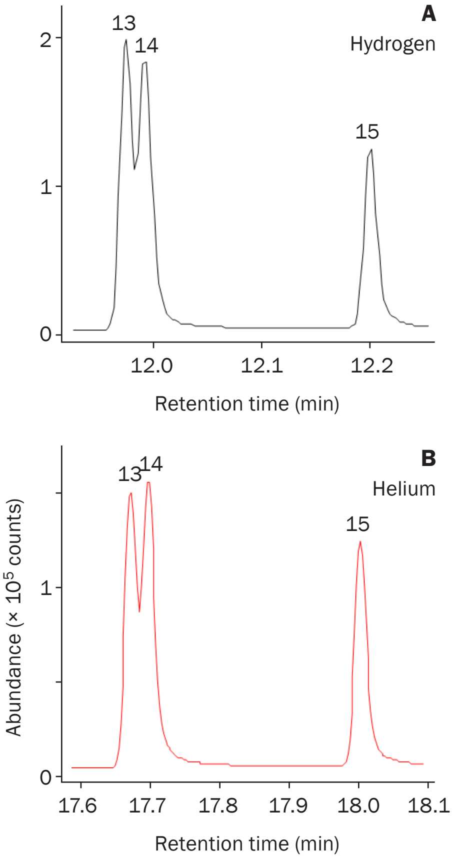

Figure 5: Benzo[*b*]fluoranthene (peak 13), benzo[*k*]fluoranthene (peak 14) and benzo[*a*]pyrene (peak 15), analysed with (**A**) hydrogen and (**B**) helium as the GC carrier gas, showing apex separation of peaks 13 and 14, the closest-eluting critical pair.

Method validation

Subsequent method validation work used hydrogen carrier gas. IS-corrected peak areas for the 18 target compounds (Table 1) were used for all metrics. Linearity was assessed from 1 to 300 ng/L over an 8-point calibration, with correlation coefficients (r^2) being above 0.998 for all compounds, with a mean of 0.9996 (Table 4). Reproducibility was taken as the relative standard deviation (RSD) of 10 replicates at 50 ng/L, with RSD below 10% for all compounds (Table 4). This compares favourably with other sorptive extraction methods from water, which often struggle to achieve RSDs below 10% for late-eluting PAHs.[10,11]

Sensitivity was determined from 12 replicates at 5 ng/L. The standard deviation of these replicates was compared to a calibration curve to determine an equivalent concentration in ng/L, and this value was multiplied by 3 to give the LOD and by 10 to give the LOQ. LOQs for all compounds were below 6 ng/L, indicating excellent sensitivity (Table 4). Crucially, the LOQ for benzo[*a*]pyrene (2.66 ng/L) was well below the 10 ng/L maximum permitted in drinking water by EU directive 2020/2184,[3] making the HiSorb method suitable for regulatory compliance testing.

Compound	r2	RSD (%)	LOD (ng/L)	LOQ (ng/L)
Naphthalene	0.9999	3.92	1.38	4.60
2-Methylnaphthalene	0.9999	4.65	1.43	4.75
1-Methylnaphthalene	0.9999	3.32	1.04	3.46
Acenaphthylene	0.9995	3.77	0.77	2.56
Acenaphthene	0.9998	2.76	0.68	2.28
Fluorene	0.9999	4.14	0.97	3.23
Phenanthrene	1.0000	0.62	1.32	4.39
Anthracene	1.0000	1.74	0.76	2.54
Fluoranthene	0.9998	2.88	0.64	2.12
Pyrene	0.9998	2.80	0.61	2.04
Benz[*a*]anthracene	1.0000	1.73	0.49	1.64
Chrysene	1.0000	2.05	0.70	2.34
Benzo[*b*]fluoranthene	0.9994	5.28	0.61	2.02
Benzo[*k*]fluoranthene	0.9996	5.24	0.90	3.01
Benzo[*a*]pyrene	0.9997	4.93	0.80	2.66
Indeno[1,2,3-*cd*]pyrene	0.9985	7.90	1.66	5.52
Dibenzo[*a*,*h*]anthracene	0.9988	8.28	0.96	3.20
Benzo[*ghi*]perylene	0.9987	9.17	1.65	5.50
Mean	**0.9996**	**4.18**	**0.97**	**3.21**

Table 4: Performance metrics for HiSorb extraction of PAHs from water.

Water samples

The four water samples listed in Table 2 were analysed (Figures 6 and 7), with concentrations being determined by comparing IS-corrected peak areas to a calibration curve. Target PAHs were considered present at known concentration if their calculated concentrations exceeded the LOQ, and were considered present at trace levels if their calculated concentrations were lower than the LOQ but higher than the LOD.

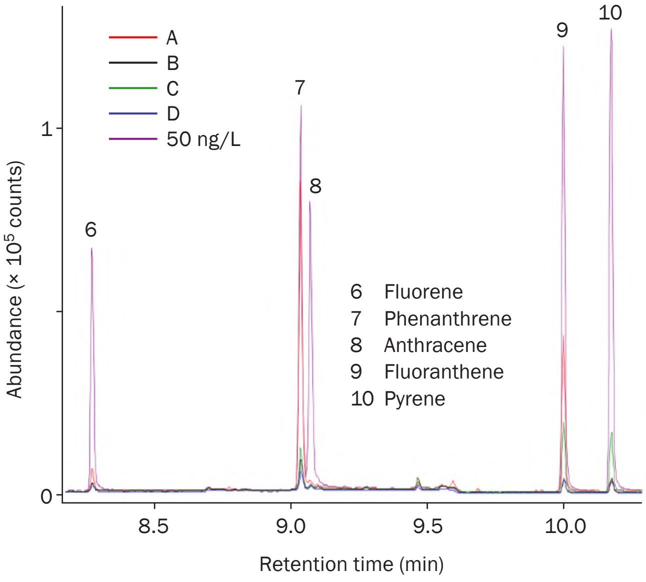

Figure 6: HiSorb extraction results for the four water samples (A to D) and HPLC-grade water with PAHs added to 50 ng/L.

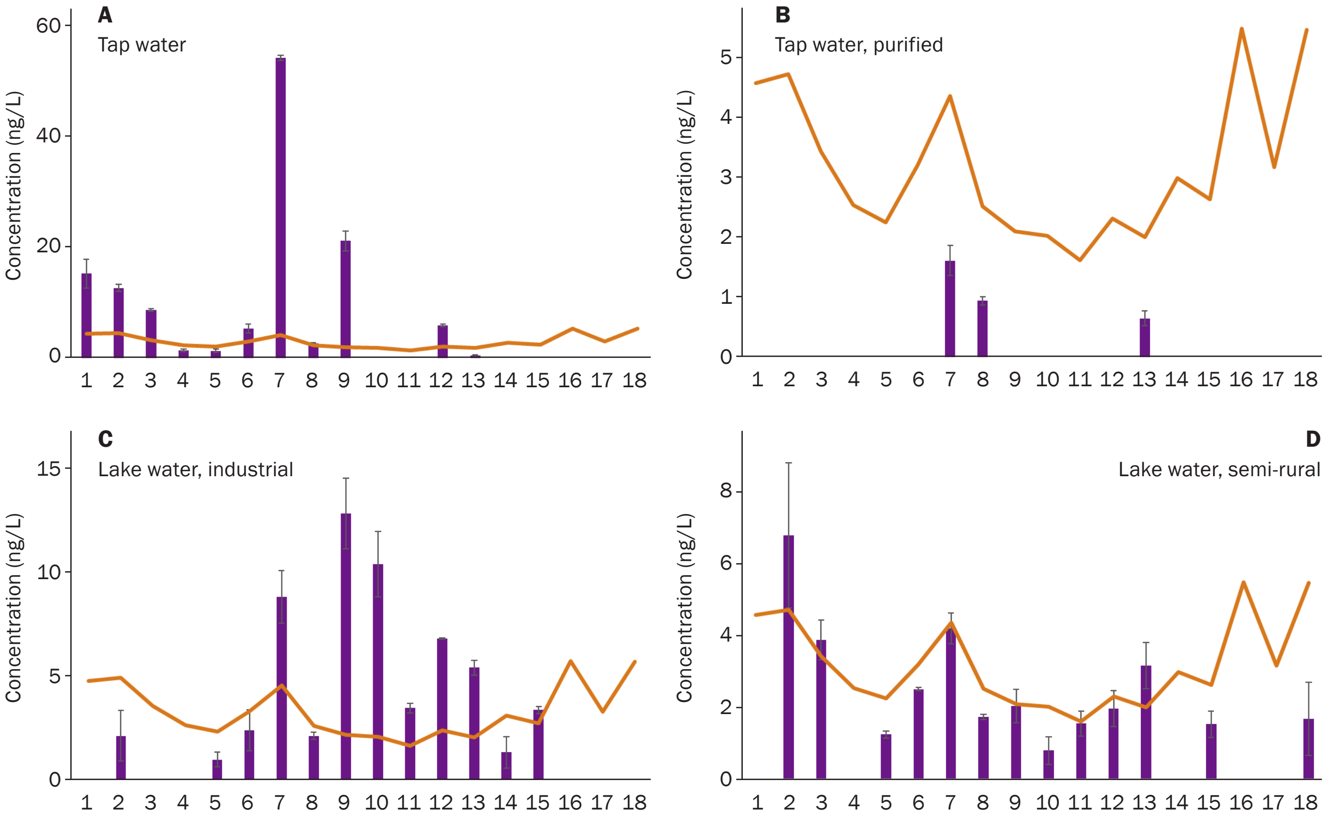

Figure 7: PAH levels in four water samples. Orange lines indicate the LOQ for each compound. Compounds detected below the LOQ cannot be formally quantified and are said to be present at trace levels. Error bars are standard deviations (n = 3). Compound identities are given in Table 1.

The tap water (sample A) showed surprisingly high levels of phenanthrene (54 ng/L) and fluoranthene (21 ng/L), with several other PAHs also surpassing the LOQ. However, none of the compounds regulated by the EU were present above trace levels, indicating this water remained safe to drink by the standards of the EU directive. High levels of phenanthrene could potentially interfere with quantitation of its critical pair partner, anthracene, but the chromatographic separation achieved between these two compounds allowed them to be easily distinguished into two clear peaks (Figure 6). Therefore, while phenanthrene levels were high in tap water, anthracene levels were confidently determined to be below quantifiable levels. When water from the same tap was passed through a kitchen water purifier, only trace amounts of PAHs remained (Figure 7). The manufacturer describes the purifier as containing a UV lamp and “multi-stage carbon filtration”, and it’s likely that this carbon filter is responsible for removing PAHs from the tap water.

Comparison of the two lake water samples (samples C and D) showed that, while both contained several PAHs at detectable levels, only two compounds exceeded the LOQ in sample D, while seven did in sample C (Figure 7). Sample C was collected from a lake abutting an industrial estate, and it’s possible that PAH run-off from local industrial activities may contribute to PAH contamination. In contrast, sample D was collected from a lake in a semi-rural area with minimal industrial activity in the immediate surroundings.

Though sample C contained more PAHs than sample D, neither sample approached the levels of phenanthrene or fluoranthene in the tap water (sample A). This suggests that the PAHs in the tap water did not come from local natural waterways but rather were introduced at some point during the water treatment process.

Conclusion

This application note describes a highly-sensitive and solvent-free method for the analysis of PAHs in water using HiSorb high-capacity sorptive extraction probes with GC–MS. Simple sample preparation and full automation on the Centri platform contributed to high throughput, while hydrogen carrier gas enabled shorter GC runs without sacrificing chromatographic separation, even enabling good separation of critical pairs to be achieved.

Some PAHs can be challenging to analyse due to their low volatility, but our validation data shows excellent reproducibility and linearity metrics and no significant carryover, even for the least volatile compounds. Limits of quantitation were below 6 ng/L (6 ppt) for all of 18 target PAHs, with the LOQ for the particularly carcinogenic compound benzo[*a*]pyrene being well below regulatory requirements.

This work has explored the use of immersive HiSorb for the analysis of PAHs in various water samples; however, there is scope for the method to be applied to other aqueous matrices, such as beverages. For example, alcoholic beverages aged in wood-fired barrels often acquire PAH contamination from the wood.[12] Immersive HiSorb, automated on Centri, could provide a sensitive, high-throughput method for the quantitation of PAHs in such drinks.

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Released: April 2025

Application Note 177

Monitoring volatile gases released during PFAS destruction in accordance with US EPA OTM-50

Summary

This application note demonstrates how the UNITY–CIA *Advantage*-xr combined with Kori-xr water management is a robust, cryogen-free TD–GC–MS solution for monitoring 30 volatile fluorinated compounds (VFCs) in stationary sources, in accordance with the canister-based method OTM-50. Compliance with OTM-50's rigorous quality control requirements is demonstrated, along with detection limits as low as 11 ppt for ultra-volatiles like CF_4, assisted by streamlined workflows for efficient monitoring of PFAS destruction and environmental safety.

Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a group of fluorinated chemicals that can harm human health and the environment, and are known as 'forever chemicals' because they do not break down easily. Governments worldwide are increasing regulations requiring the removal of PFAS from the environment, and disposing of PFAS-containing products is an important and evolving conversation.

Remediating PFAS typically involves separation/removal of PFAS from the environment, media or other contaminants, and then destroying it. PFAS destruction technologies are required to break down compounds into smaller components (hydrogen fluoride, carbon dioxide and water), in a process known as 'mineralisation'. These compounds are then captured or neutralised.

The range of remediation treatments is evolving (Figure 1),[1,2] but there is still a lack of understanding of the efficiency of the degradation, and thus the need to carefully monitor the process and outcomes. If the degradation does not happen under the correct conditions, products of incomplete destruction (PIDs) are created, which are typically volatile fluorinated compounds (VFCs), which have their own damaging effect upon human health and the environment.

Environmental agencies, including the US EPA, are stepping up their regulations around PFAS and PFAS destruction. To support this, monitoring methods are being developed, such as Other Test Method 50 (OTM-50),[3] which can be used to monitor PFAS destruction to ensure efficient mineralisation. In this application note, we discuss how to comply with OTM-50, and how the UNITY–CIA *Advantage*-xr combined with Kori-xr overcomes many of the method's more challenging aspects.

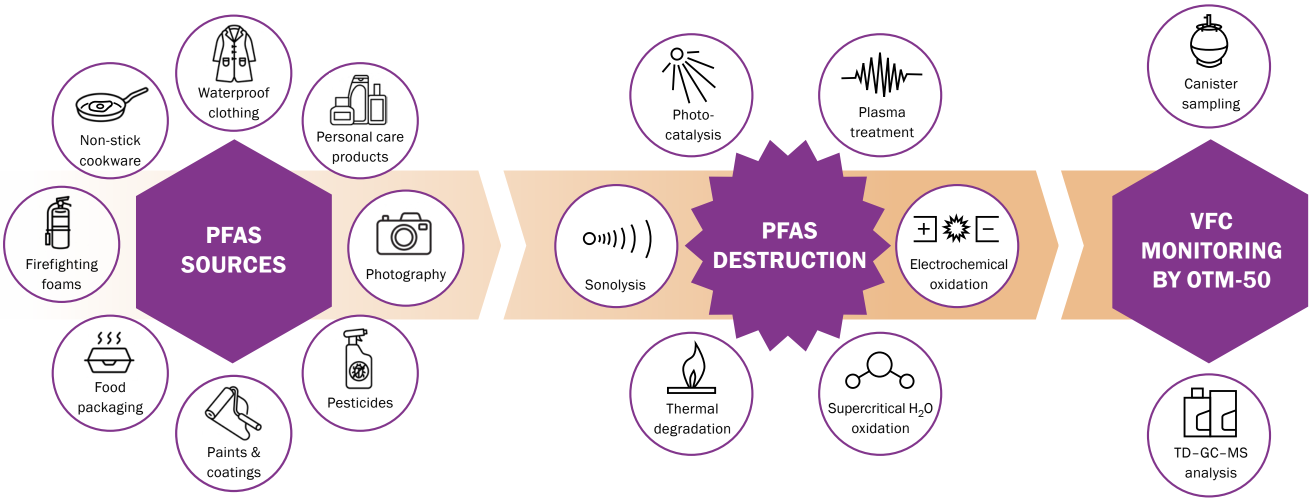


Figure 1: PFAS sources, destruction and analysis methods.

Background to OTM-50

Overall scope

OTM-50 is a performance-based method for collecting and quantitatively analysing VFCs originating from industrial products and incomplete destruction. Canisters (6 L volume) are used to collect gas samples from industrial stationary sources, and can be combined with a sample train to manage humidity, acid gases and sample temperature.

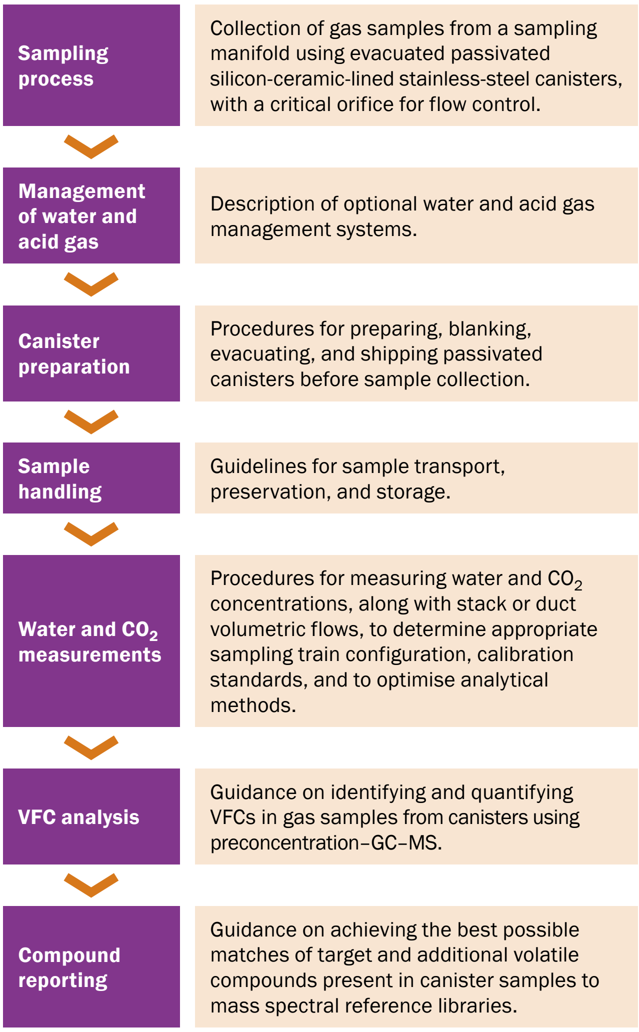
The 30 target VFC compounds (Table 1) are expected to be present in concentrations from ~1000 µg/m³ (300 ppbv) down to the method detection limit (MDL), which is in the range of 11–30 ppt. Additional VFCs can be analysed after verification and validation. The method uses preconcentration with gas chromatography–mass spectrometry (GC–MS) for the analysis, and recommends users have experience with US EPA Method TO-15(A) and ASTM D5466.

No.	Full name	Short name	Formula	CAS No.
1	Tetrafluoromethane	CFC-14	CF_4	75-73-0
2	Hexafluoroethane	CFC-116	C_2F_6	76-16-4
3	Chlorotrifluoromethane	CFC-13	$CClF_3$	75-72-9
4	Trifluoromethane	HFC-23	CHF_3	75-46-7
5	Octafluoropropane	CFC-218	C_3F_8	76-19-7
6	Difluoromethane	HFC-32	CH_2F_2	75-10-5
7	1,1,1-Trifluoroethane	HCFC-143a	$C_2H_3F_3$	420-46-2
8	Octafluorocyclobutane	FC-C318	C_4F_8	115-25-3
9	Perfluorobutane	R610	C_4F_{10}	355-25-9
10	Dodecafluoropentane	–	C_5F_{12}	678-26-2
11	Tetrafluoroethylene	TFE	C_2F_4	116-14-3
12	Fluoromethane	HFC-41	CH_3F	593-53-3
13	Pentafluoroethane	HFC-125	CHF_5	354-33-6
14	Hexafluoropropylene	R1216	C_3F_6	116-15-4
15	Hexafluoropropylene oxide	HFPO	C_3F_6O	428-59-1
16	Tetradecafluorohexane	FC-72	C_6F_{14}	355-42-0
17	1H-Perfluoropentane	–	C_5HF_{11}	375-61-1
18	Hexadecafluoroheptane	–	C_7F_{16}	335-57-9
19	Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether	Fluoroether E-1	$C_5HF_{11}O$	3330-15-2
20	1H-Perfluorohexane	–	C_6HF_{13}	355-37-3
21	1H-Perfluoroheptane	–	C_7HF_{15}	375-83-7
22	2H-Perfluoro-5-methyl-3,6-dioxanonane	Fluoroether E-2	$C_8HF_{17}O_2$	3330-14-1
23	1H-Perfluorooctane	–	C_8HF_{17}	335-65-9
24	Octadecafluorooctane	PF5080	C_8F_{18}	307-34-6
25	1H-Nonafluorobutane	–	C_4HF_9	375-17-7
26	1H-Heptafluoropropane	R-227ca	C_3HF_7	2252-84-8
27	1,1,1,2-Tetrafluoroethane	HCFC-134a	$C_2H_2F_4$	811-97-2
28	Chlorodifluoromethane	HCFC-22	$CHFCl_2$	75-45-6
29	Octafluorocyclopentene	FC-C1418	$C_5H_2F_8$	559-40-0
30	Trichloromonofluoromethane	CFC-11	$CFCl_3$	75-69-4

Table 1: The 30 target VFCs cited in OTM-50. The numbers refer to the labels in Figure 5.

Workflow

The OTM-50 workflow comprises the steps shown in Figure 2 (the focus of this work is on the VFC analysis step).



Sampling process – Collection of gas samples from a sampling manifold using evacuated passivated silicon-ceramic-lined stainless-steel canisters, with a critical orifice for flow control.

Management of water and acid gas – Description of optional water and acid gas management systems.

Canister preparation – Procedures for preparing, blanking, evacuating, and shipping passivated canisters before sample collection.

Sample handling – Guidelines for sample transport, preservation, and storage.

Water and CO_2 measurements – Procedures for measuring water and CO_2 concentrations, along with stack or duct volumetric flows, to determine appropriate sampling train configuration, calibration standards, and to optimise analytical methods.

VFC analysis – Guidance on identifying and quantifying VFCs in gas samples from canisters using preconcentration–GC–MS.

Compound reporting – Guidance on achieving the best possible matches of target and additional volatile compounds present in canister samples to mass spectral reference libraries.

Figure 2: Information on optional management systems to avoid interference from moisture and corrosive gases during sampling or analysis

Sample collection

The volatility of the target VFCs means that sample collection must be carried out using canisters. Condensable water and acid gases (which can be present in the matrix) must be removed prior to sampling into the canister. The sample train shown in Figure 3 is an example of one design that can be used to remove these interferents.

The sample conditioning required to remove the acid gases and condensable water means that while canisters could capture both polar and non-polar PFAS, only the non-polar species will be quantitated using this method, as the polar species will remain in the liquid water.

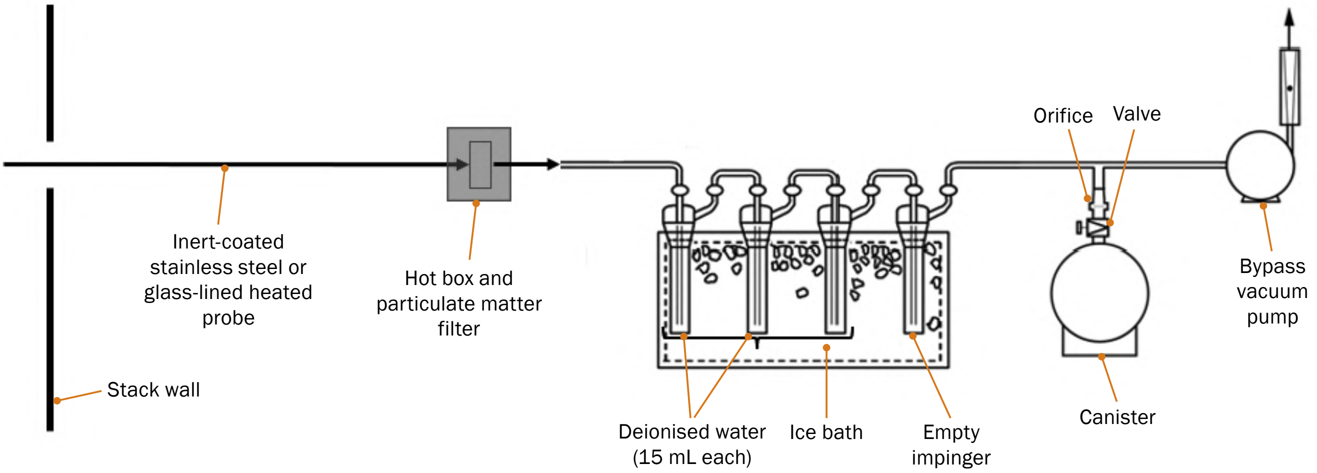


Figure 3: To take the sample, the heated probe is inserted through the stack wall and a pump draws the sample through the train. Particulate matter is removed by a filter, acid gases are removed in the three impingers of deionised water, and condensable water collects in the empty, cooled impinger. Finally, the sample is taken into the silicon-ceramic-lined canister. Diagram derived from OTM-50 document.[3]

Figure 4: The UNITY–CIA *Advantage*-xr system used for analysis of VFCs by OTM-50.

Analytical equipment

The analytical system used for this application was Markes' cryogen-free UNITY–CIA *Advantage*-xr canister preconcentrator system with water removal using Kori-xr, shown in Figure 4.

The CIA *Advantage*-xr HL model has 14 sample channels for canisters (or bags) as standard, with an option to add a further 13 channels. Samples are taken using a mass flow controller (MFC) or a 0.5 mL sample loop for small volumes. When analysing stationary source samples it is not uncommon for the sample concentration to be unknown. Small volumes taken using the loop can be used for sample screening when concentrations are unknown or expected to be higher than the calibration range.

All CIA *Advantage*-xr models include the ability to introduce a gas-phase internal standard as a fixed volume, either using the mass flow controllers (MFCs) or through a 1 mL loop. When using mass spectrometry for detection (as required by OTM-50), instrument drift can introduce extra work for analysts through the requirement to recalibrate frequently. Internal standards added to every run save time, because drift can be quantitated; the CIA *Advantage*-xr offers further flexibility by allowing laboratories to choose the internal standard gas introduction method and therefore cylinder concentration.

Before entering the thermal desorber, samples pass through the Kori-xr, which efficiently removes humidity from the air stream to give a dew point of –30°C. During this process, sampling of compounds to the focusing trap continues unaffected. The focusing trap within UNITY-xr is narrow-bore (2 mm), and electrically cooled to as low as –30°C. The trap is filled with multiple sorbents in order of increasing strength. For the OTM-50 application the 'Ozone-depleting substances' focusing trap was designed to enable retention of ultra-volatile species and ensure optimal CO_2 purging prior to injection to the GC. Once the analytes are trapped, the flow of gas is reversed, and the trap is heated rapidly (up to 100°C/s), to 'backflush' the analytes onto the GC column.

In principle, the analysis of VFCs by OTM-50 is similar to that used for 'air toxics' by US EPA Method TO-15(A). The key differences between the two methods are the sorbents used in the focusing trap, the column choice, and the sample matrix. If desired, analysts could run both methods on this hardware with the necessary consumable changes.

Experimental

Standards:
Standards for testing were as follows:

- **Standard A** contained CF_4 at 10 ppm in N_2.
- **Standard B** contained the following nine species at a concentration of 75 ppm in N_2:
  - Chlorotrifluoromethane (CFC-13)
  - Difluoromethane
  - Dodecafluoropentane
  - Hexafluoroethane
  - Octafluoropropane
  - Octafluorocyclobutane (FC-C318)
  - Perfluorobutane
  - 1,1,1-Trifluoroethane (HCFC-143a)
  - Trifluoromethane.
- **Standard C** contained all 30 components in the OTM-50 list. Note: At the time data was collected there was no

commercially available gas standard but this mixture was donated by the US EPA, and was used to ensure the method was capable of analysing all compounds of interest. At the time of writing (March 2025), a 29-component OTM-50 mixture is available for purchase.

Canister sampling:

Instrument:	CIA *Advantage*-xr (Markes International)
Sample volume:	Method-dependent

Water removal:

Instrument:	Kori-xr (Markes International)
Trap temperatures:	–30°C / +300°C

Thermal desorption:

Instrument:	UNITY-xr (Markes International)
Flow path:	100°C
Sample purge:	50 mL/min, 2 min
Sample flow:	25 mL/min
Post-sampling line purge:	5 min at 50 mL/min (with Kori-xr)
Trap purge:	Method-dependent
Cold trap:	'Ozone-depleting substances' (U-T25ODS-2S)
Trap low:	–30°C
Trap desorb:	280°C, 7 min
Split (ratio):	5 mL/min (6:1)

GC:

GC column:	Gas Pro 60 m × 320 µm
Constant flow:	1 mL/min
Oven:	Method-dependent

Quadrupole MS:

Transfer line:	250°C
Scan type:	SIM (details in Table 2)

Results

Due to the volatility of CF_4, two analytical methods were developed to analyse the entire OTM-50 list: a method specifically for CF_4, and a method for all other compounds. These two methods are run from the same canister, on the same instrument, and within the same sequence, with no changes required to hardware.

1. Chromatography

As demonstrated by the total ion chromatograms (TICs) in Figures 5 and 6, excellent peak shape was achieved across the volatility range, even in the presence of 33% relative humidity (RH) and CO_2. This indicates efficient release from the cryogen-free focusing trap and rapid injection into the GC column by the UNITY-xr, greatly facilitating quantitation. The standard also contained other fluorinated species, demonstrating the suitability of the instrument for measuring non-targets, which is a secondary requirement of OTM-50.

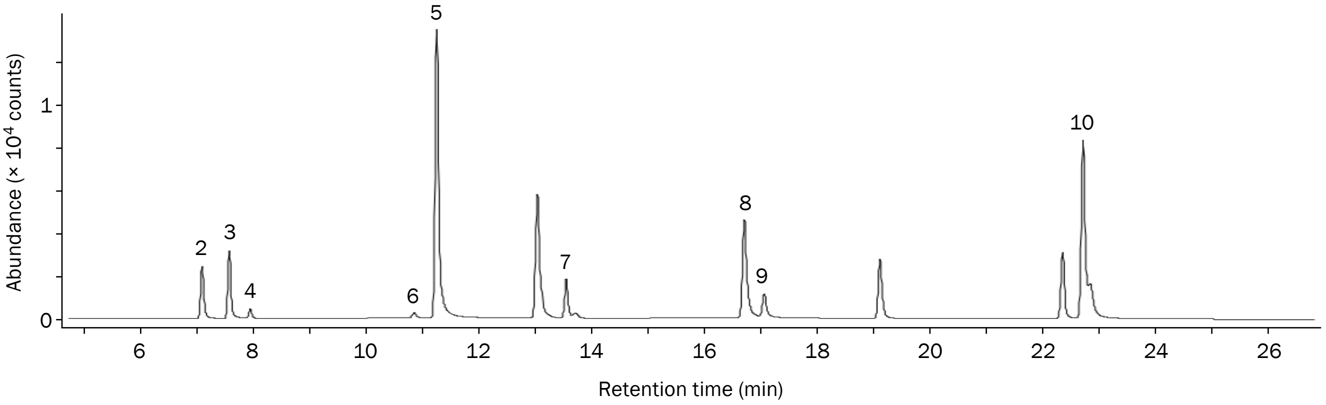


Figure 5: TIC for 200 mL of Standard B (10 ppbv, 33% RH, zero-air). Peak identities are provided in Table 1.

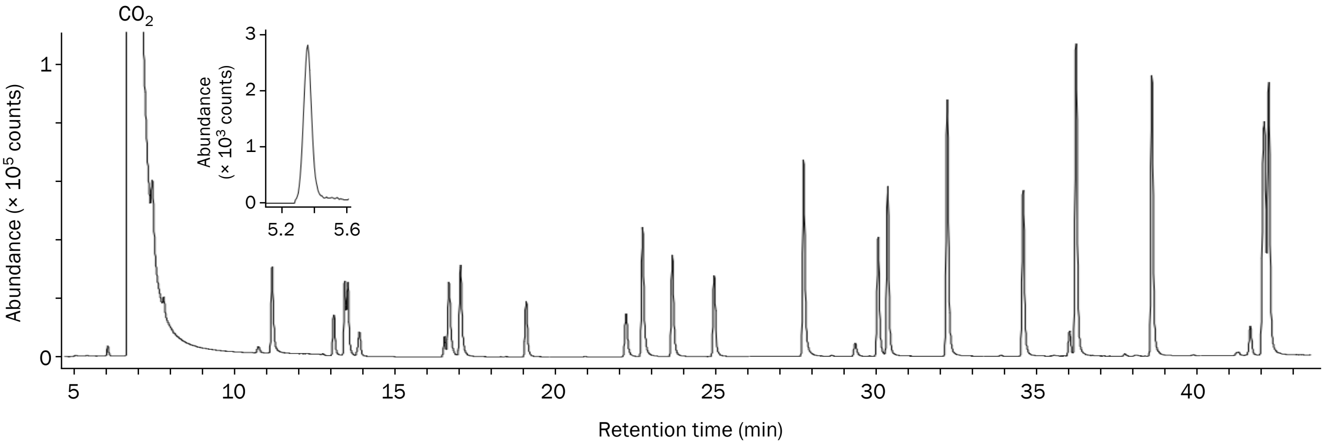


Figure 6: TIC for 200 mL of Standard C (10 ppbv, 33% RH, air containing 4% CO_2). Inset: Peak shape for 20 mL of CF_4.

2. QC requirements

Section 9.2 of OTM-50 lists the quality control requirements for this method; this is also summarised in Table OTM-50-4 within the document. These requirements outline the performance criteria the instrument must meet prior to running samples. The UNITY–CIA *Advantage*-Kori-xr system was tested to these requirements for the compounds available.

3. Instrument calibration

An instrument calibration should include the analysis of a minimum of five calibration levels. Each calibration level must be calculated to be within ±20% of its true value or, if using average relative response factor (RRF) calibration, the average RRF must be less than or equal to 20% of the relative standard deviation (RSD). The calibrations were generated using individual canisters as recommended by OTM-50. Figures 7 and 8 show the calibrations for tetrafluoromethane (CF_4) and the other components at 33% RH.

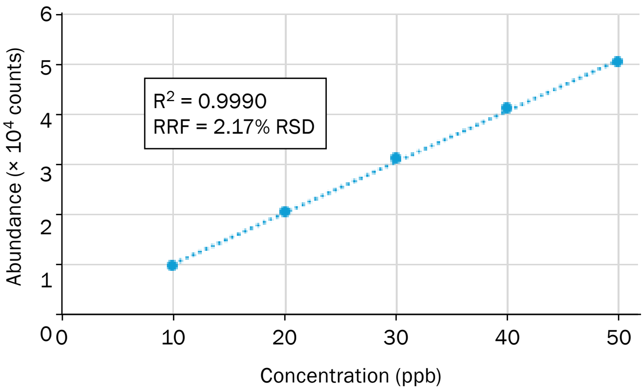


Figure 7: Calibration for CF_4 performed by taking 20 mL from five individual canisters from 10–50 ppb.

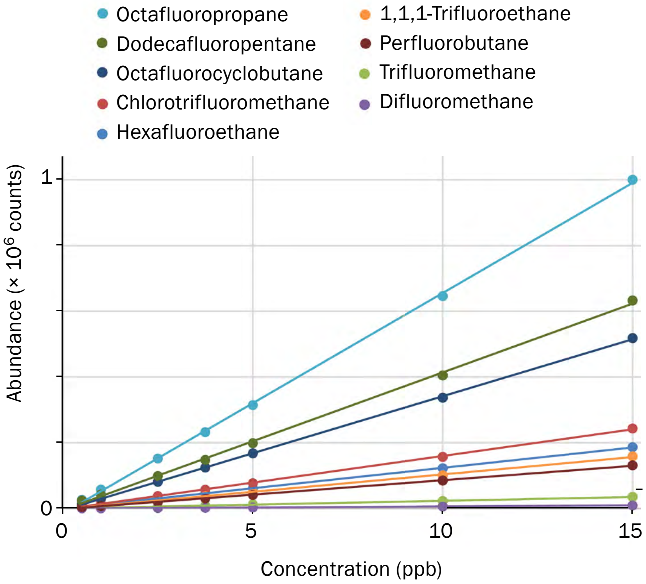


Figure 8: Calibration for nine OTM-50 compounds performed by taking 200 mL from seven individual canisters from 0.5–15 ppb.

4. Method detection limit

The method detection limits (MDLs) for this study were calculated by comparing n = 10 method blanks with n = 10 standards at a 'challenge level' according to US EPA guidance.[4] The average MDL for all species in Standard B was 10 ppt, and the MDL for Standard A (CF_4) was 30 ppt – well within the OTM-50 method requirements. MDLs calculated for individual compounds can be found in Table 2.

5. Laboratory blank

The laboratory blank is tested using a canister filled with humidified (50% RH) diluent gas – in this case, air. OTM-50 states that the the laboratory blank should be less than three times the MDL or less than 50% of the project-required reporting limit, whichever is higher for the analytes in the sample. The laboratory blank should be tested after the highest calibration standard and at the beginning of the analytical sequence.

A laboratory blank was run after the highest calibration points for the two methods (15 ppb and 50 ppb). The average reported value for the laboratory blank was 0.09% (23 ppt) – significantly below the reporting limit and less than three times the MDL (12 ppt × 3 = 36 ppt).

6. Precision

The RSD of seven replicates should be less than 25%. A mid-point standard was run 10 times and showed an average RSD of 0.54% for all target species in Standard B, and 2.17% RSD for Standard A (CF_4). These values are significantly below the OTM-50 requirement, and show the very high stability of the analytical system (Figure 9).

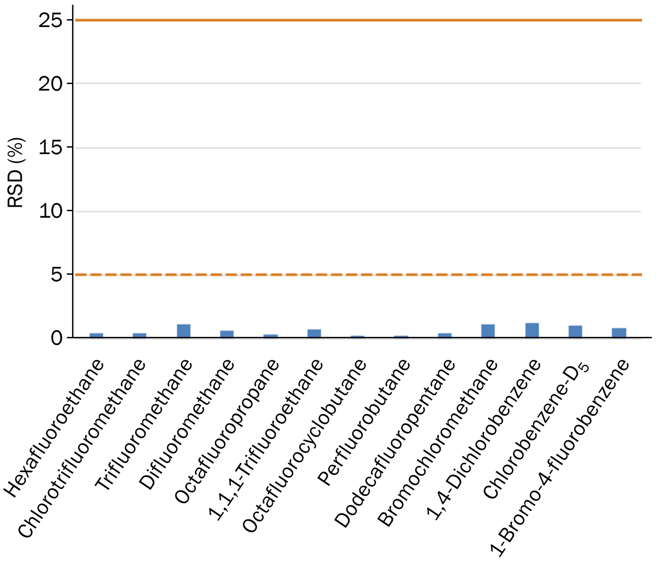


Figure 9: Repeatability for all compounds in Standard B from a 5 ppb standard at 33% RH. A typical performance spec for many TD-based methods would be 5%, whereas OTM-50 requires 25%. The UNITY–CIA *Advantage*-xr system outperforms both these criteria.

Compound	Quant ion (m/z)	R^2	RRF (%)	Precision (n = 10) (%)	MDL (n = 10) (ppt)	Lab blank
Tetrafluoromethane	69	0.9990	2.17	2.03	30	ND
Hexafluoroethane	69	0.9999	1.86	0.48	6	0.10%
Chlorotrifluoromethane	69	0.9977	2.52	0.44	8	0.15%
Trifluoromethane	69	0.9977	5.12	1.13	10	0.05%
Difluoromethane	69	0.9993	3.11	0.64	11	0.05%
Octafluoropropane	51	0.9996	7.64	0.38	14	0.21%
1,1,1-Trifluoroethane	69	0.9988	5.33	0.76	13	0.21%
Octafluorocyclobutane	100	0.9998	7.14	0.26	11	0.14%
Perfluorobutane	119	0.9995	4.00	0.29	9	0.07%
Dodecafluoropentane	69	0.9989	7.65	0.43	9	ND
Average	**–**	**0.9990**	**4.65**	**0.60**	**12**	**0.09%**

Table 2: Performance for all compounds available to test.

7. Bias

High concentrations of CO_2, between 1% and 12%, are expected to be present in samples and must be managed by analysts, because if CO_2 reaches the GC column it has the potential to overload the detector and supress key components of interest such as C_2F_6. This effect leads to significant bias in the analysis.

The CO_2 is managed at two points: in the sample prior to connecting to the instrument, and within the analytical method. Prior to connecting the sample to the system it should be diluted three-fold, ensuring that even samples with 12% CO_2 do not introduce more than 4% CO_2 into the system. Once the sample has been diluted, the analytical method should be set up to purge as much CO_2 as possible to vent prior to sample injection. If the method is not optimised correctly, it can lead to bias in the analysis.

In order to monitor this bias, a CO_2 bias check should be performed (Figure 10). This is undertaken by comparing two standards made up with 4% CO_2 in the matrix to the equivalent level on the calibration curve; the concentrations should be at the top and bottom points of the curve.

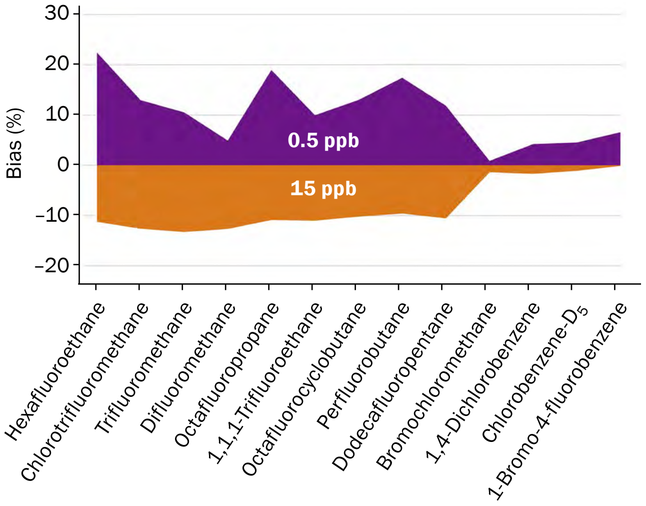


Figure 10: CO_2 bias checks for the compounds in the OTM-50 method for which the CO_2 can be purged from the trap. The bias should be no more than ±30%, so all compounds pass. Bias was also assessed for the internal standard (a TO-14 internal mix). Due to the inability to purge more during the CF_4 method, it did not pass the bias check, but can still be reported.

8. Assessing breakthrough volumes

Both tetrafluoromethane (CF_4) and trifluoromethane (CHF_3) were identified in OTM-50 as compounds that may have breakthrough volumes lower than 200 mL. Although this was true for CF_4 when the breakthrough volume was tested using the analytical method developed for running all other OTM-50 species, CHF_3 showed no sign of breakthrough at sample volumes over 1 L (Figure 11).

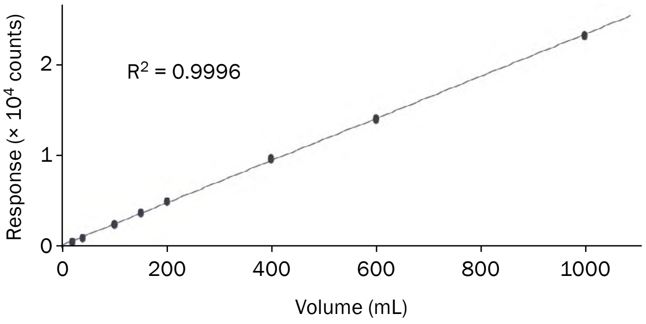


Figure 11: Linearity of response for trifluoromethane up to 1 L, showing no breakthrough up to this volume.

Conclusions

In this application note, we have shown that Markes' UNITY–CIA *Advantage*–Kori-xr system is able to meet the challenges of OTM-50 for monitoring VFCs resulting from PFAS destruction. By using two analytical runs, the ultra-volatile CF_4 and the other 29 compounds listed in OTM-50 can be analysed without the need to change the hardware or consumables.

As dilution is likely to always be part of the laboratory sample preparation SOP due to the CO_2 concentration, other interferents such as water will also be diluted. Due to the low sample volume, the system is able to manage CO_2 without bias for all compounds except for CF_4, which is likely to be biased at the 15% CO_2 level. However, if desired, a matrix-matched calibration can be performed. A humidity level of 33% RH post-dilution poses no issues for the system, and 100% RH has been assessed in other studies of similar compounds.

Acknowledgements

We are grateful to Ariel Wallace, Stephen Jackson and the team at US EPA for their advice.

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