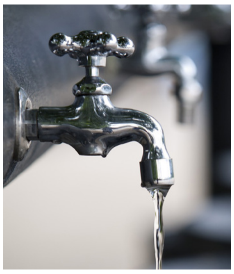


Application Note 253

Quantitative determination of volatile organic pollutants in water using headspace–trap GC–MS

This study shows that headspace samples acquired on the new Centri automated multi-mode sampling and concentration system for gas chromatography–mass spectrometry (GC–MS) can be used to quantify a wide range of volatile organic pollutants in water. Analysis of an 83-component standard based on the list in US EPA Method 524.2 showed chromatographic performance within the requirements of the method, as indicated by the mean values for linearity (R^2 0.9990), reproducibility (6.9% RSD) and analyte recovery (90%), and a mean detection limit of 0.11 ppb.

Introduction

Pollution of water can be the result of contamination from numerous sources, including agriculture, petrochemical extraction and processing, major industry, and waste-water processing plants. Many of these pollutants are volatile organic compounds (VOCs), ranging in volatility from halomethanes to petrochemical-derived aromatics.

To identify and quantify these chemicals in water samples, US EPA Method 524.2[1] is commonly applied. This uses purge-and-trap technology, but in those cases where strict adherence to the EPA protocol is not required, the use of headspace in conjunction with sorbent-based trapping ('headspace–trap') is a similarly robust sampling method. Headspace–trap also offers several practical advantages compared to purge-and-trap, namely compatibility with the use of disposable vials, and avoidance of problems associated with foaming and aerosol formation.

Headspace–trap is one of the various injection modes automated by the Centri® sample preparation system from Markes International. In this study we examine the use of Centri with GC–MS to quantitatively detect VOCs in an 83-component set of Method 524.2 compounds in the headspace above a water sample. We show how the use of the focusing trap operating at sub-ambient temperatures, in conjunction with appropriate sorbent packing, provides excellent chromatographic performance and sensitivity while avoiding issues relating to interference from water. We also demonstrate the performance of Markes' sample re-collection technology for facilitating repeat analysis of samples.

Background to Centri®

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

Centri allows full automation of sampling using HiSorb™ high-capacity sorptive extraction, headspace, SPME, 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.

Experimental

Samples:

Calibration standard:
The VOC calibration standard used contained 80 target compounds stipulated in Method 524.2, along with one internal standard (fluorobenzene) and two surrogates (4-bromofluorobenzene and 1,2-dichlorobenzene-d_4). The volatility of the compounds in the standard mix ranged from dichlorodifluoromethane (b.p. –29.8°C) to 1,2,3-trichlorobenzene and naphthalene (b.p. 218°C), and included six compounds that are gases at ambient temperature.

Using methanol, the standards were volumetrically diluted from high-ppb stock solutions, in order to generate a seven-point calibration curve from 1–200 ppb (1–200 µg/L). The methanol solutions were spiked into 10 mL of HPLC-grade water contained in a standard 20 mL vial, prior to headspace–trap GC–MS analysis.

Real water sample:
10 mL of tap water from Markes International's Technical Centre (Llantrisant, South Wales, UK) was added to a 20 mL headspace vial containing 4 g of sodium chloride. The sample was spiked with 25 ppb (25 µg/L) of the internal standard and the two surrogates, and capped as described above.

Instrument parameters:

Headspace–trap:

Instrument:	Centri® (Markes International)
Headspace sample:	1 mL
Incubation:	80°C (10 min)
Injection:	200°C (2 min)
Focusing trap:	'TO-15/TO-17 Air toxics' (part no. U-T15ATA-2S).
Purge flow:	50 mL/min for 1 min
Trap low:	20°C
Trap high:	280°C (0.5 min)
Split ratio:	5 : 1 (12.5 : 1 for the re-collection study)[2]
Re-collection:	'Universal' stainless steel sorbent tube (part no. C3-AAXX-5266)

GC:

Column type:	MEGA®-624, 30 m × 250 µm × 1.4 µm
Column flow:	2 mL/min (constant flow)
Purge flow:	3 mL/min
Oven program:	35°C (3 min), then 10°C/min to 100°C, then 30°C/min to 220°C (1 min)

Quadrupole MS:

Transfer line:	200°C
Ion source:	200°C
Mass range:	≤2.5 min: m/z 45–300; >2.5 min: m/z 35–300
Mode:	Scan

Results and discussion

1. Water management

Minimising the water content from headspace samples prior to GC separation is important to ensure good chromatography and avoid loss of sensitivity in the mass spectrometer. In this study, issues with water were minimised by:

- Careful selection of sorbents used to pack the focusing trap. The wide boiling range of the Method 524.2 mixture meant that it was necessary to find a compromise between hydrophobicity and the ability to retaing analytes across the entire volatility range, and the multi-bed 'TO-15/TO-17 Air toxics' trap was found to be ideal for the purpose, combined with the trap low of 20°C.
- Operating the focusing trap at the relatively high temperature of 20°C helped to avoid trapping excessive amounts of water.
- Use of a trap purge (50 mL/min for 1 min) prior to trap desorption further reduced the amount of water transferred to the GC column.

2. BFB tune

Method 524.2 stipulates that mass spectrometric tuning must be carried out using no more than 25 ng of 4-bromofluorobenzene (BFB) at 70 eV. The ion ratios must fall into defined ranges in order for a 'Pass' status to achieved and analysis to proceed; if not then the mass spectrometer must be re-tuned.

In this case a 25 ppb sample was analysed using the HS–trap conditions described in the Experimental section, and Table 1 shows that all ion ratios pass the criteria.

Ion (m/z)	BFB criterion	Result (%)	Pass/Fail
50	15–40% of m/z 95	19.78	Pass
75	30–80% of m/z 95	48.94	Pass
95	Base peak, 100%	100	Pass
96	5–9% of m/z 95	7.00	Pass
173	<2% of m/z 174	1.80	Pass
174	>50% of m/z 174	101.53	Pass
175	5–9% of m/z 174	7.55	Pass
176	95–101% of m/z 174	95.68	Pass
177	5–9% of m/z 176	8.09	Pass

Table 1: Results obtained against the BFB tuning criteria.

3. Chromatography

Figure 1 shows the profile of the 20 ppb standard, and Table 2 lists the performance results for all 83 compounds. These results are discussed in more detail in Section 4 (target species), Section 5 (internal standard and surrogates) and Section 6 (sample re-collection).

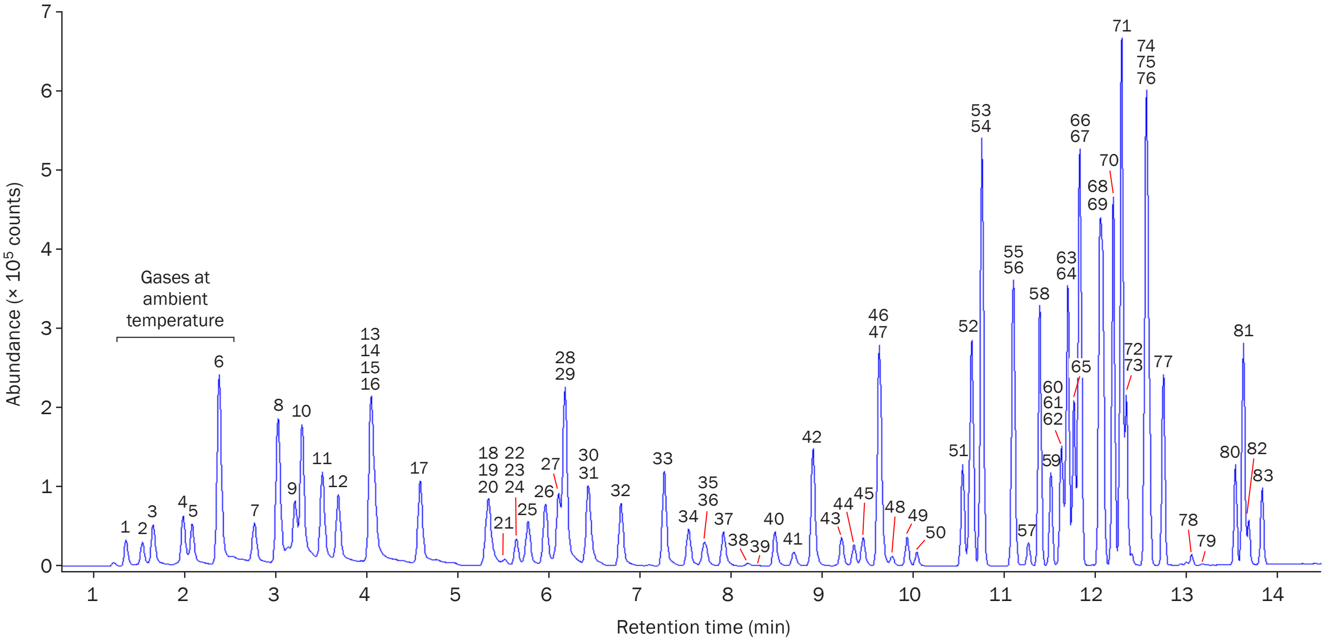


Figure 1: Headspace–trap analysis (TIC) of the 20 ppb, 83-component standard in water.

No.	Compound	Quant ion (m/z)	t_R (min)	R^2 (1–200 ppb, n = 4)	RRF RSD (%) (1–200 ppb, n = 4)	MDL (ppb)	Recovery (%) (5 ppb, n = 11)	Response RSD (%) (5 ppb, n = 11)	Re-collection response RSD (%) (n = 6)
1	Dichlorodifluoromethane	85	1.36	0.9998	6.95	0.24	112.9	6.4	0.43
2	Chloromethane	50	1.55	1.0000	7.97	0.27	113.2	7.6	8.25
3	Vinyl chloride	62	1.66	0.9977	3.96	0.25	83.1	6.8	4.18
4	Bromomethane	94	1.98	0.9987	7.26	0.05	110.6	7.6	7.22
5	Chloroethane	64	2.08	0.9991	14.17	0.26	104.7	8.0	39.1
6	Trichlorofluoromethane	101	2.39	0.9995	11.58	0.12	115.0	8.0	1.01
7	Diethyl ether	74	2.76	0.9983	12.60	0.27	77.4	9.6	2.01
8	1,1-Dichloroethene	96	3.02	0.9995	10.46	0.18	76.8	8.5	0.46
9	Iodomethane	142	3.22	0.9988	14.94	0.03	84.3	8.5	1.36
10	Carbon disulfide	76	3.29	0.9998	5.59	0.05	85.1	7.0	1.37
11	Allyl chloride	76	3.53	0.9994	16.86	0.003	92.8	10.0	1.16
12	Dichloromethane	84	3.79	0.9985	12.53	0.05	102.4	5.2	0.84
13	*trans*-1,2-Dichloroethene	96	4.04	0.9991	7.65	0.12	96.3	9.6	3.52
14	Methyl *tert*-butyl ether	73	4.07	0.9996	13.86	0.07	79.6	6.0	0.76
15	Acetone	43	4.11	1.0000	16.10	0.15	85.4	6.7	1.94
16	Acrylonitrile	53	4.13	0.9993	10.59	0.13	101.0	6.6	5.30
17	1,1-Dichloroethane	63	4.57	0.9996	10.88	0.14	80.2	5.7	1.40
18	2,2-Dichloropropane	77	5.33	0.9979	16.65	0.15	87.7	12.7	1.16
19	*cis*-1,2-Dichloroethene	96	5.34	0.9995	4.66	0.05	83.2	9.8	3.31
20	Butan-2-one	43	5.42	0.9999	4.69	0.12	109.3	7.1	2.70
21	Methyl acrylate	55	5.54	0.9992	7.26	0.15	85.8	7.4	1.97
22	Methacrylonitrile	67	5.66	0.9997	7.91	0.08[a]	114.6	7.0	1.80
23	Bromochloromethane	130	5.66	0.9988	9.43	0.14	87.1	8.7	2.77
24	Tetrahydrofuran	42	5.71	0.9994	13.84	0.08	81.8	9.3	2.12
25	Chloroform	83	5.77	0.9998	8.84	0.12	79.8	7.1	2.06
26	1,1,1-Trichloroethane	97	5.98	0.9994	7.20	0.19	90.3	6.9	0.92
27	1-Chlorobutane	56	6.13	0.9992	9.80	0.10	94.2	8.0	1.84
28	1,1-Dichloropropene	75	6.18	0.9995	11.88	0.13	100.2	8.2	1.53
29	Tetrachloromethane	117	6.18	1.0000	9.97	0.06	71.8	7.7	1.02
30	Benzene	78	6.45	0.9981	12.95	0.09	83.6	7.4	1.89

Table 2: Performance data for the headspace–trap analysis of the 83-component standard in water. * = Internal standard. † = Surrogates. [a] Value calculated using the 1 ppb data. [b] Value calculated using n = 3. [c] Value calculated using the 25 ppb data with n = 22. This value is not included in the mean at the bottom of the column. [d] Value calculated using the 2 ppb data. *(Continued on next page)*

No.	Compound	Quant ion (m/z)	t_R (min)	R^2 (1–200 ppb, n = 4)	RRF RSD (%) (1–200 ppb, n = 4)	MDL (ppb)	Recovery (%) (5 ppb, n = 11)	Response RSD (%) (5 ppb, n = 11)	Re-collection response RSD (%) (n = 6)
31	1,2-Dichloroethane	62	6.48	0.9998	7.03	0.13	75.9	8.2	2.24
32*	Fluorobenzene	96	6.79	0.9994[b]	–	2.18	88.3[c]	3.9[c]	–
33	Trichloroethene	95	7.28	0.9998	5.59	0.24	99.0	7.7	1.90
34	1,2-Dichloropropane	63	7.55	0.9998	8.59	0.22	92.2	7.9	2.47
35	Dibromomethane	93	7.73	0.9975	9.77	0.23	85.8	10.1	1.13
36	Methyl methacrylate	41	7.74	0.9987	6.00	0.35	85.9	5.9	1.58
37	Bromodichloromethane	83	7.93	0.9996	6.26	0.20	86.7	7.1	1.46
38	2-Nitropropane	43	8.22	0.9970	4.93	0.15[a]	93.1	15.9	10.0
39	Chloroacetonitrile	75	8.34	0.9979	11.81	0.13	79.5	8.6	1.76
40	*cis*-1,3-Dichloropropene	75	8.50	0.9995	6.17	0.28	83.2	6.9	1.53
41	2-Methylbutan-2-one	43	8.72	0.9989	7.56	0.05	82.0	6.2	1.66
42	Toluene	91	8.92	0.9998	15.19	0.08	89.7	7.0	1.70
43	*trans*-1,3-Dichloropropene	75	9.23	0.9997	7.48	0.09	79.8	7.7	1.38
44	Ethyl methacrylate	69	9.37	0.9993	12.24	0.21	80.3	6.8	1.43
45	1,1,2-Trichloroethane	97	9.47	0.9998	8.90	0.40	91.1	5.6	2.31
46	Tetrachloroethene	164	9.65	0.9998	13.88	0.06	89.5	5.8	1.65
47	1,3-Dichloropropane	76	9.68	1.0000	11.39	0.03	113.8	3.5	1.31
48	Hexan-2-one	43	9.80	1.0000	12.19	0.18	85.6	7.9	2.38
49	Chlorodibromomethane	129	9.95	0.9985	9.76	0.14	94.4	6.3	1.68
50	1,2-Dibromoethane	107	10.05	0.9992	10.98	0.09	90.6	10.2	3.21
51	Chlorobenzene	112	10.55	0.9998	7.88	0.04	86.7	6.0	1.51
52	Ethylbenzene	91	10.66	0.9993	14.95	0.05	91.8	3.7	1.54
53,54	*m*- + *p*-Xylene	91	10.77	0.9964	18.00	0.02	88.9	6.3	1.77
55	*o*-Xylene	91	11.11	0.9990	15.17	0.03	104.8	3.4	1.33
56	Styrene	104	11.12	0.9997	14.09	0.02	79.5	3.8	1.33
57	Bromoform	173	11.28	0.9997	15.76	0.06	88.7	6.8	3.64
58	Isopropylbenzene	105	11.40	0.9982	8.20	0.002	86.6	6.0	1.09
59†	4-Bromofluorobenzene	95	11.52	0.9954[b]	–	3.50	108.8[c]	7.2[c]	–
60	Bromobenzene	156	11.63	0.9997	17.86	0.09	83.9	4.7	2.63
61	1,1,2,2-Tetrachloroethane	83	11.64	0.9931	16.89	0.10	92.9	5.1	3.86
62	1,2,3-Trichloropropane	75	11.66	0.9995	12.84	0.09	90.7	10.7	2.59
63	*trans*-1,4-Dichlorobut-2-ene	75	11.68	0.9995	12.84	0.08	82.7	10.4	3.20
64	n-Propylbenzene	91	11.71	0.9991	9.28	0.02	86.2	4.9	1.76
65	2-Chlorotoluene	91	11.77	0.9992	19.67	0.01	85.8	4.0	1.59
66	1,3,5-Trimethylbenzene	105	11.83	0.9984	14.51	0.02	83.7	5.8	1.93
67	4-Chlorotoluene	91	11.85	0.9962	22.13	0.02	88.7	4.1	2.08
68	Tetra-n-butylbenzene	119	12.06	0.9997	19.71	0.02	81.8	4.5	1.37
69	1,2,4-Trimethylbenzene	105	12.09	0.9995	7.09	0.03	83.1	3.6	7.69
70	*sec*-Butylbenzene	105	12.21	0.9991	9.84	0.01	80.7	5.3	1.75
71	*p*-Isopropyltoluene	119	12.30	0.9997	9.47	0.02	110.2	3.8	1.21
72	1,3-Dichlorobenzene	146	12.35	0.9997	7.53	0.03	90.5	4.0	1.37
73	1,4-Dichlorobenzene	146	12.35	0.9994	19.90	0.04	88.6	6.7	2.42
74	n-Butylbenzene	91	12.56	0.9969	17.64	0.09	84.1	7.6	1.89
75†	1,2-Dichlorobenzene-d_4	150	12.58	0.9951[b]	–	1.34	91.1[c]	6.6[c]	–
76	1,2-Dichlorobenzene	146	12.59	0.9990	15.34	0.11	106.8	6.6	2.32
77	Hexachloroethane	117	12.76	0.9973	17.09	0.05	98.7	7.0	2.23
78	1,2-Dibromo-3-chloropropane	75	13.07	0.9996	8.66	0.04	87.4	6.6	1.46
79	Nitrobenzene	77	13.19	0.9995	3.78	0.27[d]	108.6	7.4	5.12
80	1,2,4-Trichlorobenzene	180	13.54	0.9997	19.05	0.18	80.6	4.1	3.47
81	Hexachlorobutadiene	225	13.63	0.9997	14.80	0.04	86.8	3.5	2.15
82	Naphthalene	128	13.69	0.9992	13.02	0.13	83.7	5.5	2.59
83	1,2,3-Trichlorobenzene	180	13.84	0.9998	4.24	0.13	87.2	6.0	1.30
	Mean			**0.9990**	**11.29**	**0.11**	**90.2**	**6.9**	**2.75**

Table 2: Performance data for the headspace–trap analysis of the 83-component standard in water. * = Internal standard. † = Surrogates. [a] Value calculated using the 1 ppb data. [b] Value calculated using n = 3. [c] Value calculated using the 25 ppb data with n = 22. This value is not included in the mean at the bottom of the column. [d] Value calculated using the 2 ppb data. *(Continued from previous page)*

4. Performance for target compounds

Linearity

Table 2 shows that excellent linearity was obtained for all target compounds, with R^2 values for the seven-point calibrations from 1–200 ppb exceeding 0.999 for 60 compounds, and with the lowest value being 0.9931 for 1,1,2,2-tetrachloroethane (#61). The linearity was also calculated as the relative standard deviation (RSD) of the relative response factor (RRF) for each analyte against the internal standard, with mean values being 11%. This is well below the Method 524.2 requirement of 20%.

Calibration curves are shown in Figure 2 for the six most volatile compounds in the standard mix (all of which are gases under ambient conditions), based on four replicates per level. The R^2 values indicate very good linearity for these challenging compounds. Figure 3 shows the extracted ion chromatogram for dichlorodifluoromethane (#1, the most volatile compound in the mix), at the 1 ppb level. The highly symmetrical peak indicates that the molecular sieve sorbent in the focusing trap efficiently retains and releases this compound quantitatively, even at 20°C.

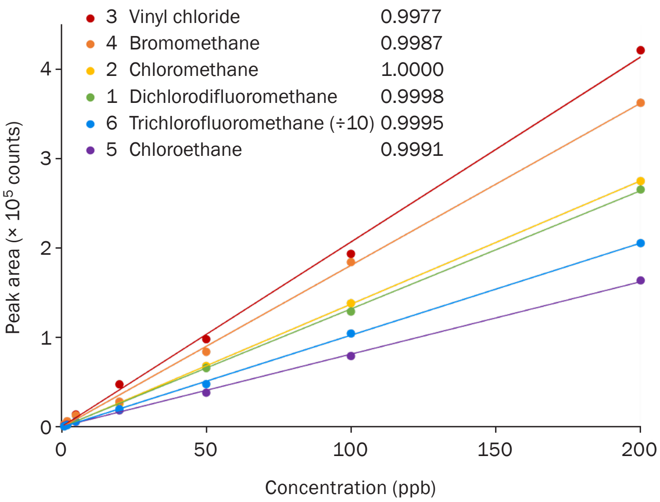


Figure 2: Seven-point calibration curves and R^2 values for the six most volatile compounds in the standard mix.

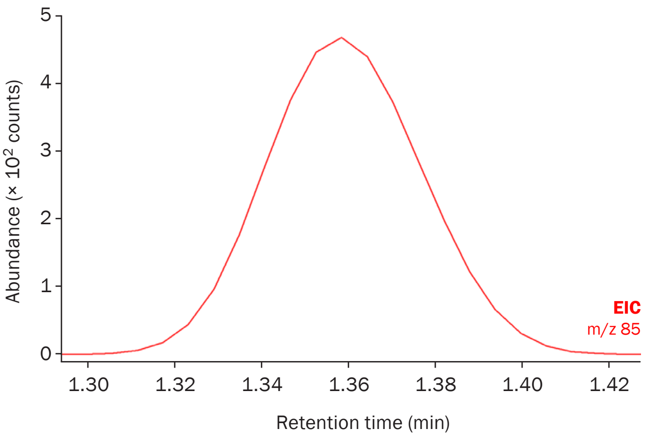


Figure 3: The highly symmetrical profile for dichlorodifluoromethane (#1).

Recovery and reproducibility

Method 524.2 requires that the recovery of each analyte in the standard falls between 80% and 120%. Our data shows a mean recovery of 90.2%, with an RSD of 6.94%, based on seven replicate standards at 5 ppb. This is well within the requirements of the method, and indicates a high degree of system stability.

Detection limits

Method detection limits (MDLs) for each target compound were calculated based on data from 11 replicate injections of a 0.5 ppb calibration standard, with the resulting concentrations being multiplied by 2.764 (the Student's t-value for 99% confidence for 11 values). The mean MDL was 0.11 ppb, with an RSD of 8%, and with values ranging from 0.002 ppb for isopropylbenzene (#58) to 0.40 ppb for 1,1,2-trichloroethane (#45).

These results are based on a conventional headspace sample volume of 1 mL, but it is worth noting that because of the use of the focusing trap, MDLs could be substantially lowered by use of a higher sample volume (*e.g.* 5 mL). The focusing trap also allows true splitless analysis and analysis of multiple headspace injections, which could also improve sensitivity.

5. Performance for internal standard and surrogates

Linearity

Figure 4 shows the linearity for the internal standard and the two surrogates in the range 1–200 ppb, using three replicates at each level. All R^2 values are greater than 0.99.

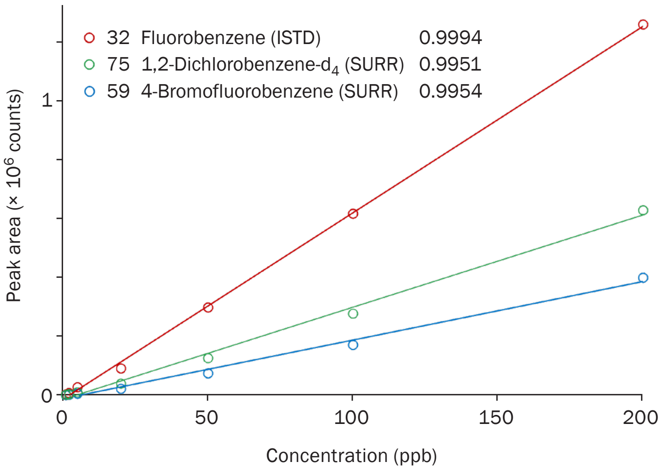


Figure 4: Seven-point calibration curves and R^2 values for the internal standard and the two surrogates used in the standard mix.

Recovery and reproducibility

Table 2 shows that the recoveries for the internal standard and the two surrogates (from 22 consecutive analyses of the 25 ppb standard) fall within the 80–120% range, with RSDs below 10%. Figure 5 illustrates this graphically, allowing assessment of variation in system performance and identification of timescales for re-calibration.

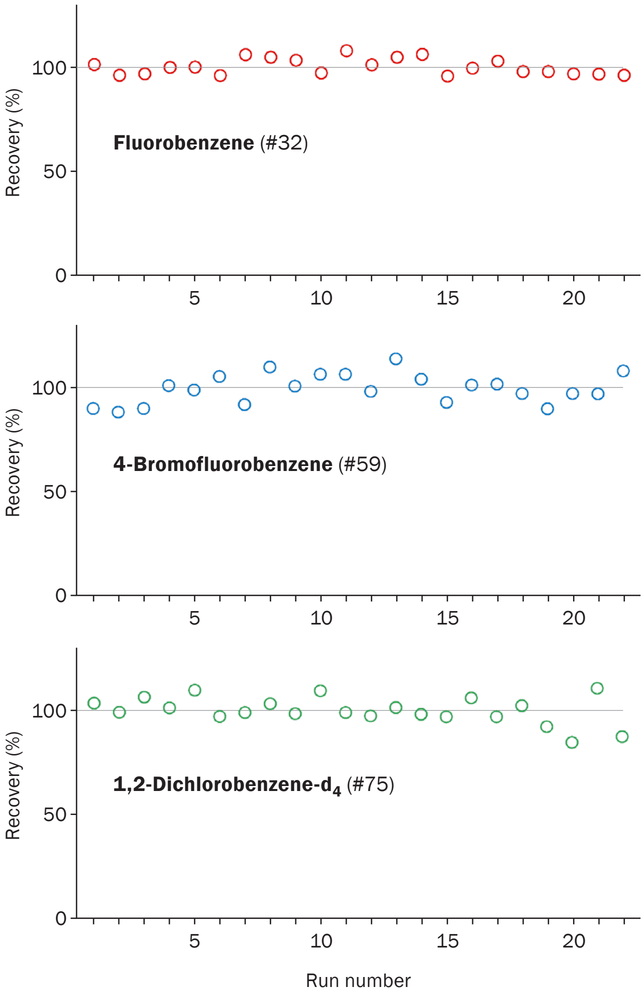


Figure 5: Recoveries for the internal standard and two surrogates across 22 consecutive runs.

6. Sample re-collection

Re-collection is a procedure in which a user-defined portion of the sample desorbed from the focusing trap is passed into a clean TD tube, rather than being lost through the split line. Re-collection overcomes the drawbacks of procedures relying on a single injection, and the TD-50 module on Centri allows the procedure to be automated for all sampling modes (including headspace–trap, which is one of the unique features of Centri).

With regard to analysis of volatiles in water, re-collection is not a requirement of Method 524.2, but from a practical perspective it has a number of advantages, namely:

- **Improved method development:** The re-collected sample can be analysed again (multiple times if needed), to optimise analytical conditions without having to prepare new samples.
- **Sample archiving:** Valuable samples collected on the re-collection tubes can be stored and re-analysed on the same platform, or indeed another system (for example, with a different GC or detector setup).
- **Method validation:** Re-collection makes it easy to identify any sorbent or system biases.

To demonstrate this re-collection capability in the current study, the headspace from six vials containing the standard mixture at 50 ppb was analysed using the conditions described earlier (except with a 12.5 : 1 split ratio). However, this time the split portion from each analysis was automatically re-collected on a multi-bed sorbent tube in the TD-50 module of Centri.

An example of one pair of runs is shown in Figure 6, showing that the re-collected profile is almost identical to the original, and indicating the absence of any bias within the analytical system. The mean recovery was 92%, with RSDs (n = 6) being just 2.75%. However, four VVOCs (#2–#5: chloromethane, vinyl chloride, bromomethane, chloroethane) co-elute with the residual water and methanol solvent, and consequently performed less well than the majority. If these compounds were of particular interest, this issue could be alleviated by reducing the methanol concentration, and/or modifying the TD–GC conditions to separate them from the co-eluting matrix.

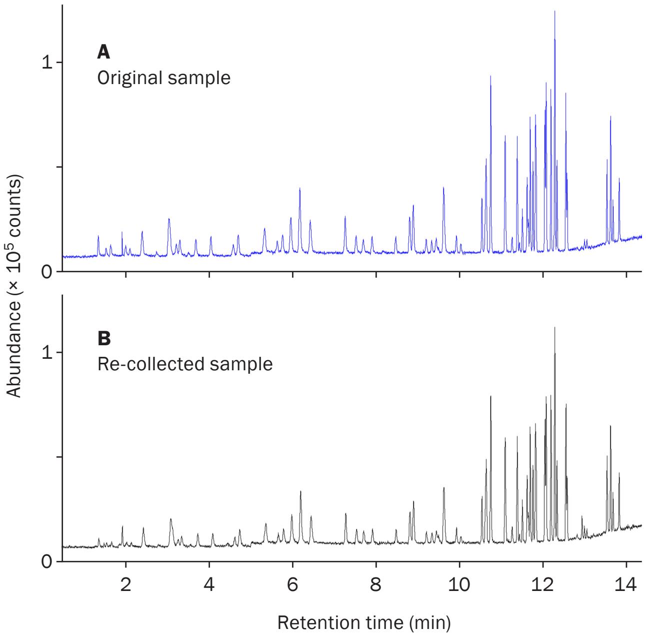
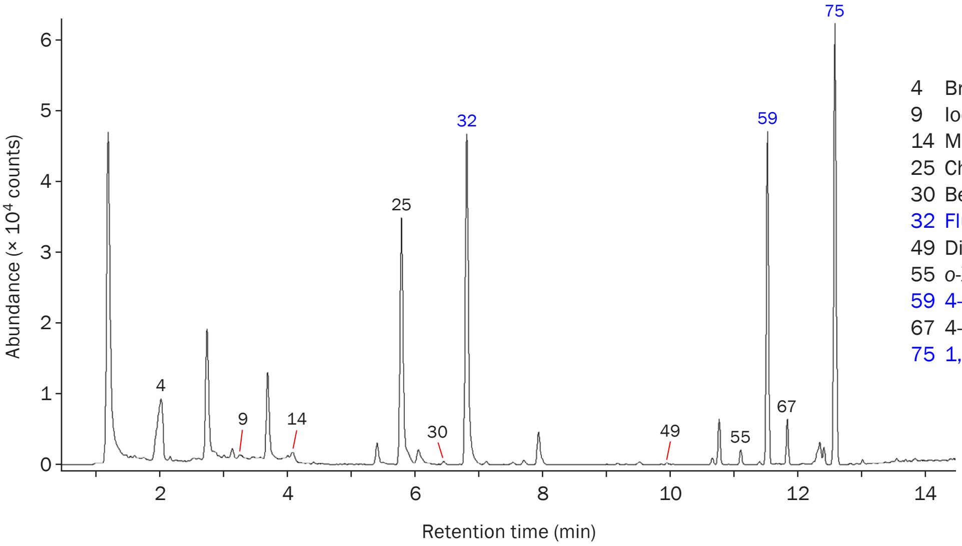


Figure 6: Headspace–trap analysis (TIC) of the 50 ppb, 83-component standard in water: (**A**) Original sample; (**B**) Sample re-collected using the TD-50 module of Centri.

6. Real water sample

Figure 7 shows the headspace–trap analysis of 10 mL of tap water, containing 25 ppb of the internal standard and the two surrogates. Quantitation indicated the presence of chloroform at 25 ppb, and a number of other volatile contaminants at levels in the range 0.3–2 ppb.

Although the TIC profiles for some of the compounds in Figure 7 are non-symmetrical, Figure 8 shows that the EIC profiles are all symmetrical, allowing reliable peak integration and quantitiation to be carried out.



4	Bromomethane	0.39 ppb
9	Iodomethane	0.94 ppb
14	Methyl *tert*-butyl ether	1.01 ppb
25	Chloroform	25.6 ppb
30	Benzene	0.90 ppb
32	Fluorobenzene (ISTD)	25.0 ppb
49	Dibromochloromethane	0.52 ppb
55	*o*-Xylene	1.71 ppb
59	4-Bromofluorobenzene (SURR)	25.0 ppb
67	4-Chlorotoluene	0.31 ppb
75	1,2-Dichlorobenzene-d$_4$ (SURR)	25.0 ppb

Figure 7: Headspace–trap analysis (TIC) of tap water containing the internal standard and the two surrogates.

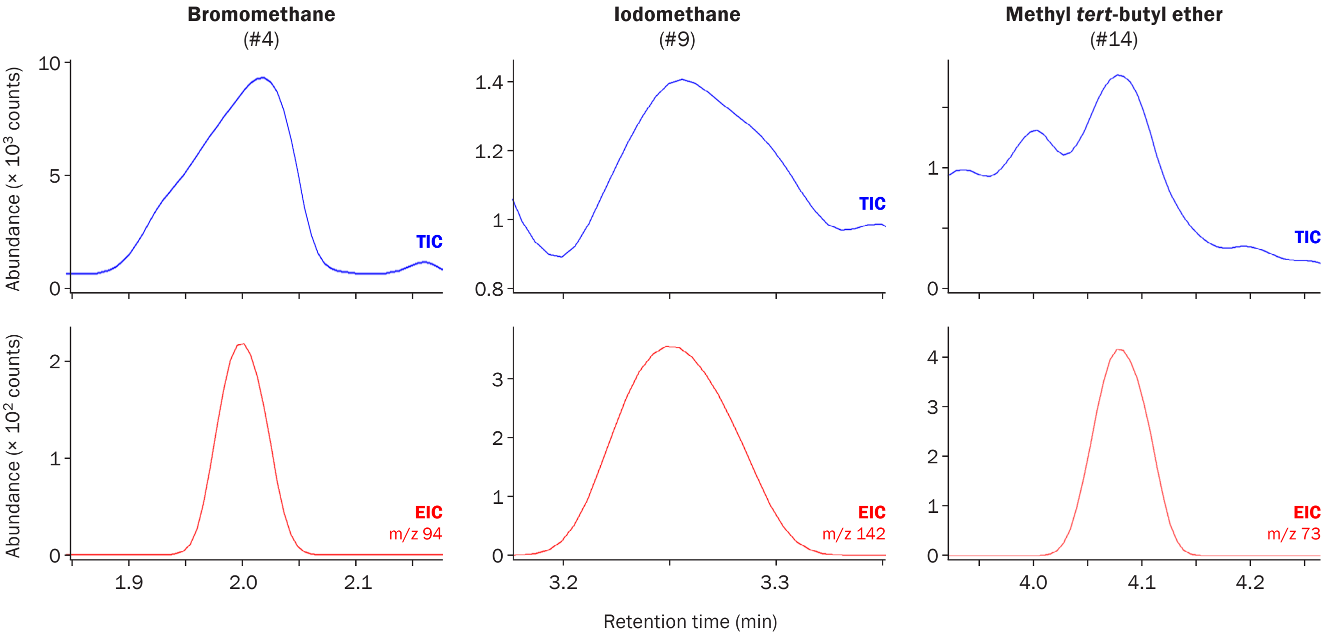


Figure 8: Expansions of Figure 7 for three compounds showing non-symmetrical peaks in the TIC (top, blue), and the corresponding symmetrical EIC profiles (bottom, red).

Conclusions

This study has demonstrated that the multi-mode Centri platform, in conjunction with GC–MS, allows the identification and quantitation of a wide range of volatile organic compounds in water, using the headspace–trap technique. The method met all the requirements of US EPA Method 524.2 (including for MS tuning), with a mean linearity of 0.9990, a mean reproducibility of 6.9% RSD, and a mean recovery of 90%.

Despite the use of a relatively low split ratio for this study, the performance of the focusing trap resulted in excellent peak shape across the analyte range and a high level of sensitivity, with a mean MDL of 0.11 ppb. In addition, there is scope to improve this further, by using (a) a headspace sample volume of 5 mL rather than the conventional 1 mL, (b) true splitless injection, and (c) multiple headspace injections onto the same focusing trap.

The value of Markes' sample splitting and re-collection technology for repeat analysis has also been demonstrated, indicating a high degree of reproducibility between successive runs of the same re-collected sample, and the absence of bias in the analytical system.

References and notes

1. Method 524.2: Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry, US Environmental Protection Agency, 1992, www.epa.gov/homeland-security-research/epa-method-5242-measurement-purgeable-organic-compounds-water-capillary.
2. This low ratio is a consequence of the relatively low column, septum purge and split flows, and results in a relatively high proportion of the sample being sent to the GC. However, this does not adversely affect the peak shape of the early-eluting compounds, because of the use of the focusing trap.