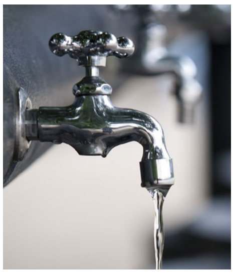
MARKES
international

Centri
Application

Water analysis by
headspace–trap
Released: February 2019

THE QUEEN'S AWARDS
FOR ENTERPRISE:
INTERNATIONAL TRADE
2015



Application Note 256

Analysis of volatile organic pollutants in water using headspace–trap GC–MS: Maximising performance for ppt-level VOCs

This study demonstrates the analysis of a broad range of trace-level volatile organic compounds in drinking water using the headspace–trap sampling mode of the Centri automated multi-mode sampling and concentration system. Analysis of a 72-component standard mix using GC–MS with selected ion monitoring (SIM) acquisition provided mean detection limits as low as 2 ppt, with excellent mean linearities (R^2 0.999), recoveries (97.8%) and repeatabilities (4.7% RSD) – performance that is comfortably lower than required by all major regulations. In addition, tap water was analysed and found to contain a range of VOCs at low-to-medium levels (2–200 ppt), in addition to ppb-level chlorinated compounds.

Introduction

Chemical contamination of rivers, reservoirs and ground water used as sources of drinking water originates from intentional and accidental discharges from industry, agriculture and urban pollution. This contamination requires extensive treatment, but such processes can also result in the formation of contaminants – such as the trihalomethanes that are formed by the reaction of the common oxidant chlorine with organic matter. Such contamination is naturally of concern, and acceptable levels for the volatile organic compound (VOC) content of drinking water are specified by a variety of regulatory bodies, including the European EEA, US EPA, Chinese EPA and WHO.

Headspace analysis is a well-established and robust method for the determination of VOCs in water, but in certain aspects it offers limited flexibility. In particular, the injection of larger headspace sample volumes to improve sensitivity can cause undesirable chromatographic effects such as broad or split peaks, and options such as multiple injections are usually not possible. There are also limited options for water management, meaning that analyses can suffer from reduced analyte response and repeatability, as well as negative impacts on column and detector lifetime.

In this study we demonstrate how the use of a backflushed, cryogen-free focusing trap packed with multiple sorbent beds, in conjunction with GC–MS, can overcome such issues for the headspace analysis of residual VOCs in drinking water. In particular, we show how SIM acquisition allows quantitation of target analytes at low-ppt levels, while avoiding issues relating to interference from water.

Experimental

Samples:

Calibration standards:

A set of calibration standards at seven levels from 50 ppt (50 ng/L) to 20 ppb (20 µg/L) was prepared by volumetric dilution of a 2000 ppm stock solution using HPLC-grade methanol. The mix contained 72 components, including one internal standard (fluorobenzene) and two surrogate standards (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. The methanol solutions were spiked into 10 mL of HPLC-grade water contained in a standard 20 mL crimped-top vial prior to headspace–trap GC–MS analysis.

Calibration curves and performance results were calculated based on the on-column concentration as detected by the MS system.

Drinking water:

10 mL of tap water from Markes International's Technical Centre (Llantrisant, South Wales, UK) was added to a 20 mL headspace vial containing 2.5 g (25% w/v) of sodium sulfate. The sample was spiked with 2.0 ppb (2.0 µg/L) of the internal standard and capped as described above.

Sampling and preconcentration:

Instrument:	Centri® (Markes International)

Headspace–trap:

Headspace sample:	1 mL
Incubation:	80°C (10 min)

Injection: 200°C (2 min)

Preconcentration:

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

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: 180°C
Ion source: 300°C
Mass range: m/z 35–300
Solvent delay: 0 min
SIM groups: Multiple
Tune type: E-tune

Results and discussion

Table 1 lists the performance for all the compounds, and indicates very good quantitative results down to low ppt values. These results are discussed in more detail in Section 1 (chromatography), Section 2 (target species) and Section 3 (internal standard and surrogate standards). Section 4 presents data on a real tap-water sample.

Background to Centri®

Markes International's Centri system for GC–MS is the first 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, 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.

No.	Compound	Primary quant ion (m/z)	t_R (min)	R^2 (7 points, 10–4000 ppt)	RRF RSD (%) (7 points)[a]	MDL (ppt)[b]	PQL (ppt)[c]	Recovery (%)[d]	RSD (%)[d]
1	Dichlorodifluoromethane	85	1.34	>0.999	11.08	1.0	5.9	81.1	8.8
2	Chloromethane	50	1.54	0.997	9.65	1.9	11.5	115.7	4.0
3	Vinyl chloride	62	1.65	>0.999	5.48	1.3	7.6	114.2	2.2
4	Bromomethane	94	2.04	0.997	16.59	1.5	8.9	112.7	0.9
5	Chloroethane	64	2.10	>0.999	13.07	1.5	9.2	104.2	3.6
6	Trichlorofluoromethane	101	2.39	0.999	6.30	1.1	6.9	114.1	2.6
7	Diethyl ether	59	2.75	>0.999	12.22	0.9	5.4	105.2	7.0
8	1,1-Dichloroethene	96	3.04	>0.999	8.58	1.8	10.9	109.5	7.5
9	Iodomethane	142	3.22	0.998	17.94	1.5	8.9	85.3	4.7
10	Carbon disulfide	76	3.30	>0.999	12.78	2.1	12.6	89.2	5.0
11	Allyl chloride	41	3.52	0.996	13.45	2.4	14.4	108.8	4.0
12[e]	Dichloromethane	84	3.69	–	–	–	–	–	–
13	*trans*-1,2-Dichloroethene	61	4.08	>0.999	14.55	1.0	6.3	89.2	3.4
14	1,1-Dichloroethane	63	4.58	0.999	7.87	2.0	12.2	112.6	1.1
15	*cis*-1,2-Dichloroethene	61	5.30	0.999	13.34	2.1	12.5	112.6	5.9
16	2,2-Dichloropropane	77	5.32	0.998	13.17	1.8	11.0	111.5	3.8
17	Methyl acrylate	55	5.50	0.999	16.83	1.1	6.7	81.0	3.8
18	Tetrahydrofuran	42	5.54	>0.999	18.54	3.4	20.4	90.4	7.5
19	Bromochloromethane	49	5.66	>0.999	15.77	0.6	3.3	113.8	8.2

Table 1: Performance data for headspace–trap analysis of the 72-component standard in water. * = Internal standard. † = Surrogate standards. [a] Using fluorobenzene as the internal standard, with n = 4. [b] Calculated using data for the standard mix at 10 ppt on-column. [c] Set at 6× the MDL. [d] Calculated using data for the standard mix at 100 ppt on-column, with n = 10. [e] Dichloromethane is ubiquitous and values cannot be reported because of laboratory contamination. *(Continued on next page)*

No.	**Compound**	**Primary quant ion (m/z)**	**t_R (min)**	**R^2 (7 points, 10–4000 ppt)**	**RRF RSD (%) (7 points)[a]**	**MDL (ppt)[b]**	**PQL (ppt)[c]**	**Recovery (%)[d]**	**RSD (%)[d]**
20	Chloroform	83	5.77	>0.999	15.74	1.9	11.4	89.0	4.1
21	1,1,1-Trichloroethane	97	5.97	>0.999	11.51	2.4	14.3	113.9	1.2
22	1-Chlorobutane	56	6.11	0.999	13.98	0.8	5.0	85.4	2.3
23	1,1-Dichloropropene	75	6.19	0.998	15.50	2.0	11.8	83.4	4.7
24	Carbon tetrachloride	117	6.22	>0.999	9.87	1.7	10.4	113.0	3.6
25	Benzene	78	6.43	>0.999	11.74	1.9	11.6	98.8	0.6
26	1,2-Dichloroethane	62	6.48	0.998	11.54	2.5	15.1	117.1	6.0
27*	Fluorobenzene	96	6.79	>0.999	–	0.4	2.5	103.0	7.0
28	Trichloroethene	95	7.25	0.999	14.28	1.3	7.7	109.6	10.1
29	1,2-Dichloropropane	63	7.53	>0.999	14.32	1.0	6.1	99.5	3.6
30	Dibromomethane	174	7.70	>0.999	14.54	1.6	9.6	107.1	4.6
31	Methyl methacrylate	69	7.73	0.996	16.81	2.4	14.2	93.5	2.2
32	Bromodichloromethane	83	7.91	>0.999	8.27	2.5	14.7	100.7	3.6
33	2-Nitropropane	43	8.22	0.999	10.76	4.7	28.2	109.3	5.4
34	*cis*-1,3-Dichloropropene	75	8.50	0.999	13.08	0.9	5.5	115.9	7.3
35	Toluene	91	8.92	0.998	18.98	2.6	15.5	87.4	5.2
36	*trans*-1,3-Dichloropropene	75	9.22	0.999	14.21	3.4	20.4	81.7	9.0
37	Ethyl methacrylate	69	9.35	0.998	16.24	0.6	3.3	84.9	3.1
38	1,1,2-Trichloroethane	97	9.44	0.999	11.85	2.7	16.4	108.5	3.9
39	Tetrachloroethene	166	9.61	>0.999	10.38	2.4	14.3	100.4	6.1
40	1,3-Dichloropropane	76	9.67	>0.999	13.85	0.6	3.3	98.9	5.0
41	Chlorodibromomethane	129	9.94	0.999	11.79	2.6	15.3	106.0	7.4
42	1,2-Dibromoethane	107	10.04	>0.999	13.21	2.4	14.6	101.8	1.0
43	Chlorobenzene	112	10.55	0.999	17.91	1.7	10.0	82.7	7.2
44	Ethylbenzene	91	10.65	0.995	16.59	0.6	3.3	92.1	6.1
45	*m*- + *p*-Xylene	91	10.76	0.999	14.99	0.3	2.0	84.1	4.0
46	*o*-Xylene	91	11.10	0.999	19.04	1.6	9.3	84.8	9.4
47	Styrene	104	11.13	0.994	18.81	1.8	10.6	103.3	2.0
48	Bromoform	173	11.27	>0.999	12.43	4.4	26.3	94.6	8.0
49	Isopropylbenzene	105	11.40	0.999	15.65	2.2	13.2	101.9	6.3
50†	4-Bromofluorobenzene	95	11.50	>0.999	18.54	2.1	12.5	100.4	6.5
51	Bromobenzene	77	11.63	0.999	16.65	2.1	12.3	115.9	5.2
52	1,1,2,2-Tetrachloroethane	83	11.64	0.999	16.77	1.0	6.0	107.3	3.5
53	1,2,3-Trichloropropane	75	11.65	>0.999	16.77	2.3	14.0	93.2	5.6
54	*trans*-1,4-Dichlorobut-2-ene	75	11.68	>0.999	9.66	3.9	23.3	108.9	2.8
55	n-Propylbenzene	91	11.70	0.995	4.38	1.7	10.0	81.2	1.8
56	2-Chlorotoluene	91	11.77	0.996	4.26	1.6	9.3	91.5	4.9
57	1,3,5-Trimethylbenzene	105	11.83	0.999	7.21	0.7	4.4	85.0	3.3
58	4-Chlorotoluene	91	11.85	0.999	16.42	2.5	14.8	90.7	2.8
59	Tetra-n-butylbenzene	119	12.06	0.999	3.13	1.8	11.0	76.1	2.1
60	1,2,4-Trimethylbenzene	105	12.09	0.992	7.18	2.4	14.5	83.2	2.6
61	*sec*-Butylbenzene	105	12.20	>0.999	16.13	1.9	11.2	79.7	1.2
62	*p*-Isopropyltoluene	119	12.29	0.993	18.86	1.5	9.2	84.5	1.3
63	1,4-Dichlorobenzene	146	12.35	0.999	17.86	1.5	9.2	85.7	2.7
64	n-Butylbenzene	91	12.55	0.995	15.52	1.8	10.8	82.8	8.7
65†	1,2-Dichlorobenzene-d_4	150	12.58	>0.999	18.12	3.6	21.3	99.7	8.0
66	1,2-Dichlorobenzene	146	12.59	0.988	15.12	10.7	64.4	115.1	10.0
67	Hexachloroethane	117	12.75	>0.999	12.72	1.9	11.3	107.7	5.7
68	1,2-Dibromo-3-chloropropane	157	13.07	0.999	16.71	2.7	16.3	81.2	5.3
69	1,2,4-Trichlorobenzene	180	13.54	>0.999	12.57	3.0	18.2	85.4	1.8
70	Hexachlorobutadiene	225	13.62	0.998	14.48	3.0	18.0	112.6	3.1
71	Naphthalene	128	13.67	0.999	17.34	1.3	7.6	79.4	2.9
72	1,2,3-Trichlorobenzene	180	13.84	0.999	10.83	3.5	21.0	95.6	6.0
Mean				**0.999**	**13.46**	**1.9**	**11.4**	**97.8**	**4.7**

Table 1 *(Continued from previous page)*

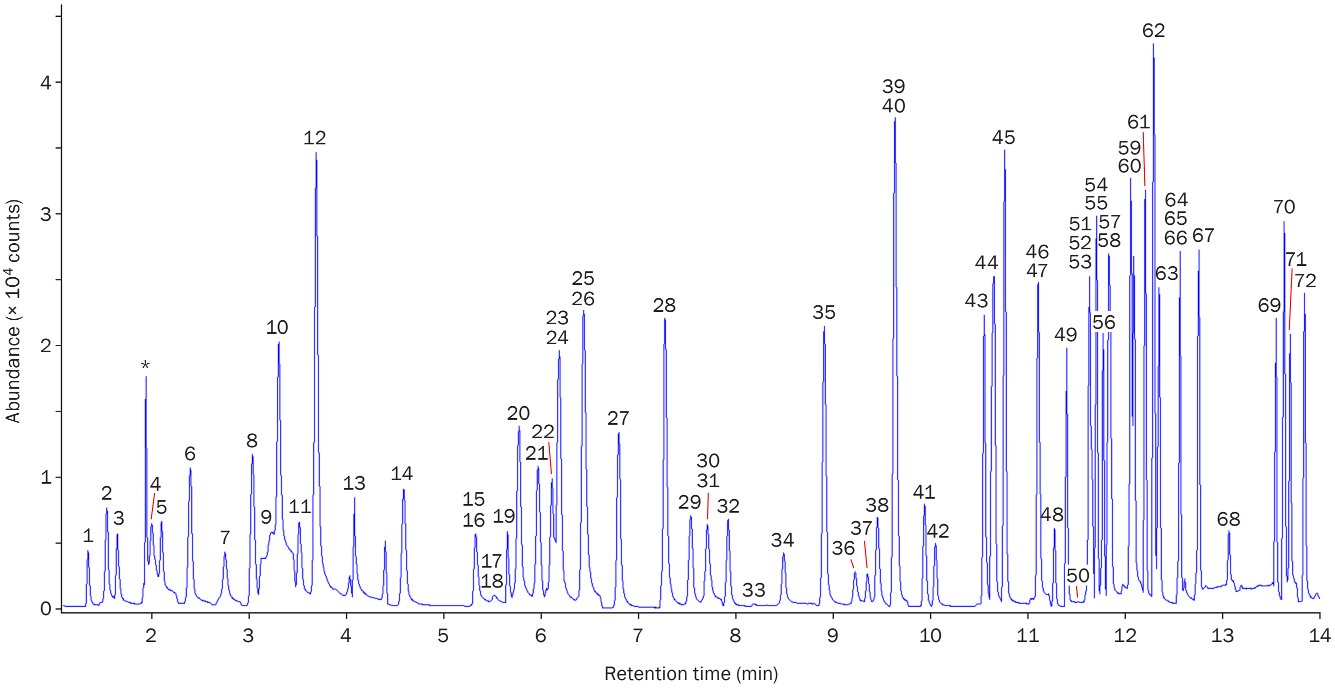


Figure 1: Headspace–trap SIM analysis of the standard mix at 100 ppt on-column. * Contamination from unknown compound.

1. Chromatography

Figure 1 shows the overlaid SIM responses for all VOC compounds of the standard mix at 100 ppt on-column.

For accurate quantitation of the early-eluting gaseous compounds at these low concentrations, peak shape is important. Figure 2 shows the SIM responses for the first three peaks in the standard mix at 20 ppt on-column. These are difficult compounds to analyse at low-ppt concentrations, but in this study the peak shape is highly symmetrical.

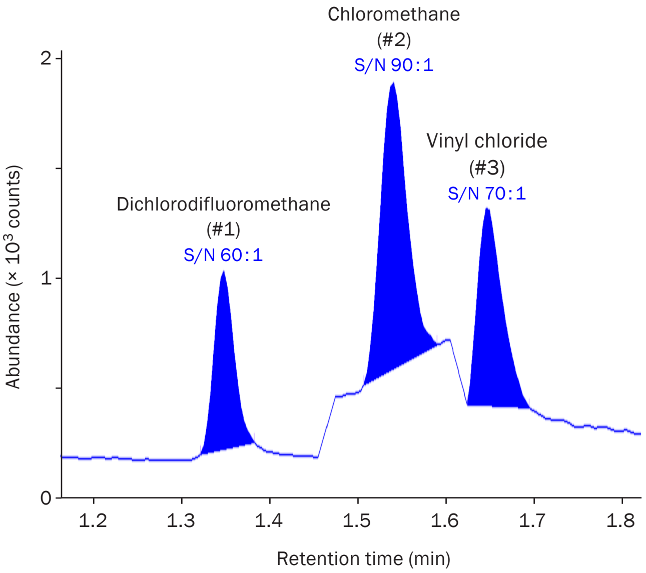


Figure 2: Headspace–trap SIM analysis of the three most volatile components in the standard mix, at 20 ppt on-column.

2. Performance for target compounds

Linearity

Table 1 shows that excellent linearity was obtained for all target compounds, with a mean R^2 value for the seven-point calibrations from 10–4000 ppt being 0.999, and with the lowest value being 0.988 for 1,2-dichlorobenzene (#66). The linearity was also calculated as the relative standard deviation (RSD) of the relative response factor (RRF) for each analyte against the internal standard, using four replicate injections per level across the calibration range, and these values are also shown in Table 1. These results indicate that very high confidence in quantitation is possible down to low-ppt levels.

The use of R^2 as a measure of how well a set of data fits a calibration curve is well-established. However, there is a growing desire within certain organisations and regulatory bodies to use a separate metric, the relative standard error (RSE).[1] The key difference is that, whereas R^2 tends to under-represent deviations at low concentrations, RSE is equally sensitive to deviations across the concentration range. Acceptable values for RSE are method-dependent or based on RSD values, but in general, values below 20% are indicative of a good fit.

Figure 3 shows the R^2 and RSE values for the six most volatile compounds in the standard mix (all of which are gases under ambient conditions). RSE values range from 4.2% (chloromethane, #2) to 18.5% (chloroethane, #5), confirming a good curve fit across the concentration range.

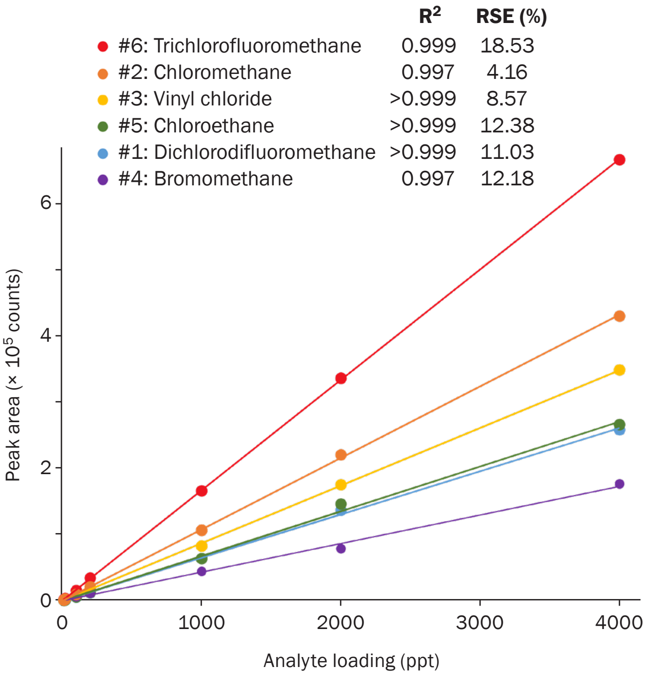


Figure 3: Seven-point calibration curves showing R^2 and RSE values for the six most volatile compounds in the standard mix.

Recovery and repeatability

Recoveries were calculated based on 10 replicate injections of the standard mix at 100 ppt on-column, using raw peak area values (Table 1). The mean recovery was 98%, with a mean RSD of 4.6%, and with RSDs less than 10% for the most volatile compounds. This indicates very high stability in overall system performance.

Detection limits

Method detection limits (MDLs) were calculated using injections of the standard mix at 10 ppt on-column (Table 1 and Figure 4). The mean MDL was 1.9 ppt, with values ranging from 0.6 ppt (for bromochloromethane, #19) to 10.7 ppt (1,2-dichlorobenzene, #66).

Also shown in Table 1 are the practical quantitation limits (PQLs). The PQL is the minimum measurable concentration of an analyte for which there can be a high degree of confidence that the analyte is present at or above that concentration. The PQL is typically set at 6× to 10× the MDL, and in this study we used 6× MDL. This gave a mean PQL of 11.4 ppt, with the most volatile compounds all having values <20 ppt.

Table 2 compares the limit levels for several key VOCs specified by several agencies for water quality (including the relatively stringent EEA Directive 98/83/EC[2]) with the PQL values obtained in this study. This shows that the current work provides detection levels significantly lower than required by all major regulations.

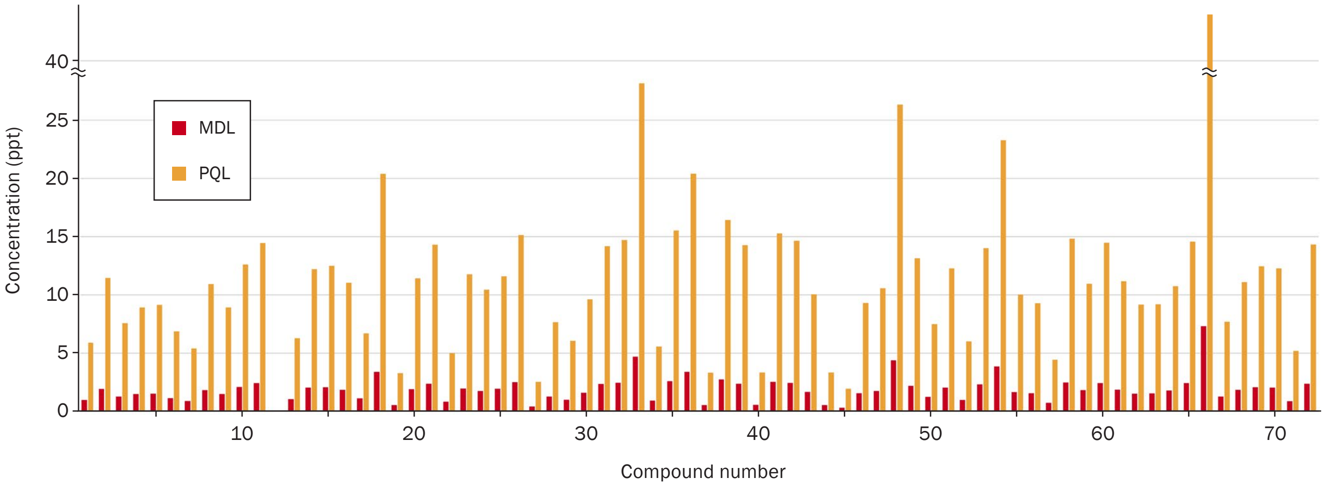


Figure 4: MDL and PQL values for the 72 components in the standard mix.

No.	Compound	Limit level (ppb)					PQL in this study (ppb)
		US EPA	Chinese EPA	European EA	Canadian DWQG	WHO	
3	Vinyl chloride	2	5	0.5	2	0.3	0.011
25	Benzene	5	10	1	5	10	0.017
28	Trichloroethene	10	10	10	10	20	0.011
44	Ethylbenzene	700	300	–	140	300	0.005
45–46	Xylenes	10,000	500	–	90	500	0.003–0.014

Table 2: Water-quality specifications for key compounds.

3. Performance for internal standard and surrogate standards

The stabilities, repeatabilities and recoveries of the internal standard and the two surrogate standards were determined by running 12 replicate injections at 20 ppt on-column, and plotting the raw peak area against run number. This provides a practical way of assessing the stability of the system, making it straightforward to identify when re-calibration is required.

Mean recoveries (and RSDs) for fluorobenzene (#27), 4-bromofluorobenzene (#50) and 1,2-dichlorobenzene-d_4 (#65) were 103.0% (RSD 7.0%), 100.4% (RSD 6.5%) and 99.7% (RSD 8.0%), respectively. Figures 5 and 6 show the results graphically and indicate high levels of recovery and stability at this low concentration (20 ppt).

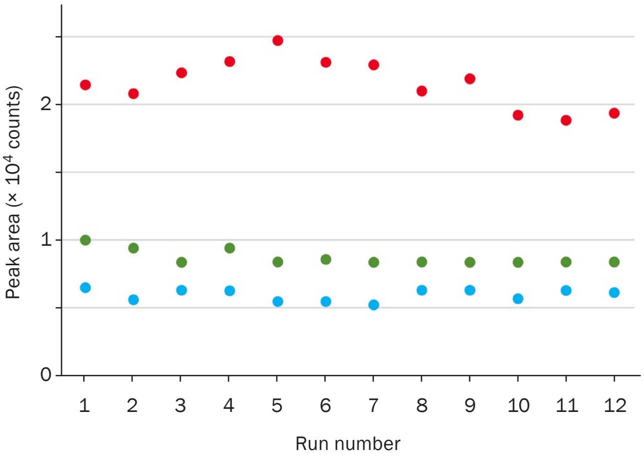


Figure 5: Peak area recoveries over 12 replicate analyses at 20 ppt for fluorobenzene (●), bromofluorobenzene (●) and 1,2-dichlorobenzene-d_4 (●).

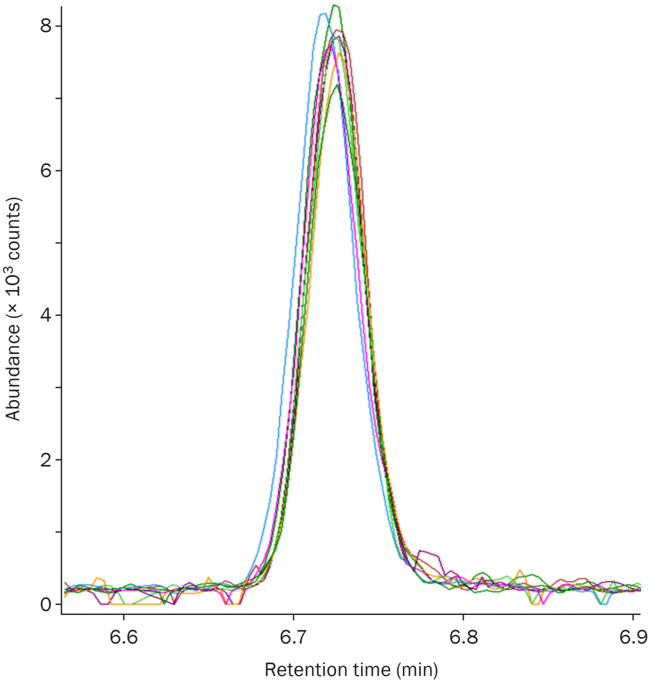


Figure 6: Stability of SIM profiles for the internal standard fluorobenzene over 12 replicate analyses at 20 ppt.

4. Real water sample

A tap water sample, spiked with the internal standard mix at 2 ppb on-column, was analysed for residual VOCs, and the concentrations are shown in Figure 7. In addition to three chlorinated VOCs present at low ppb levels, a number of ppt-level VOCs were found, of which benzene, ethylbenzene and the xylenes are regulated, and were present well below stipulated levels.

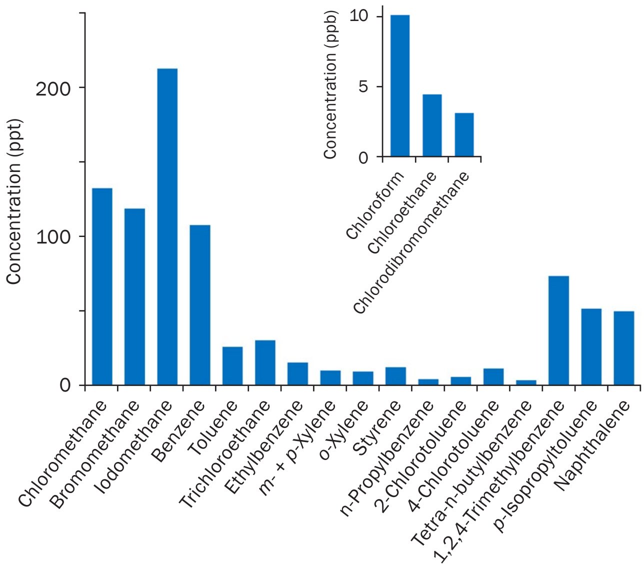


Figure 7: Concentrations of VOCs present in tap water, determined using headspace–trap analysis.

Conclusions

This study has shown that static headspace sampling combined with preconcentration on the multi-mode Centri platform, in conjunction with GC–MS in SIM mode, allows the detection of low-ppt VOCs in water. Limits of detection are significantly below limit levels specified in a variety of regulations, and the system stability, precision and accuracy are all excellent, which allows quantitative analysis across a broad concentration range.

The use of a backflushed, cryogen-free focusing trap packed with multiple sorbent beds provides excellent retention and release of analytes, ranging from the very volatile permanent gases through to the higher-boiling compounds. The availability of a trap also allows re-collection of split samples for repeat analysis, with key benefits in this case being streamlined method validation and detection using different methods.

To further enhance sensitivity, Centri could be operated in splitless injection mode, and set to allow multiple samples from the same vial to be preconcentrated onto the same focusing trap, prior to desorption. These two approaches will be the subject of future work.

References

1. Two documents are available that assist the calculation of RSE: (a) Calculating RSE, NELAC Institute, 2017, http://nelac-institute.org/docs/comm/emmec/Calculating RSE.pdf; (b) Basic RSE calculator, NELAC Institute, 2017, http://nelac-institute.org/docs/comm/emmec/Basic RSE calculatorv4.xlsx.
2. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, European Commission, 1998, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A31998L0083.