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Application News

No. AD-0073

HS-20 & GCMS-QP2010Ultra

Quantitative Determination of Volatile Organic Compounds in Drinking Water by EPA Method with Headspace Trap GC-MS

❑ Introduction

Volatile Organic Compounds (VOCs) refer to a group of easily vapourised organic compounds. Under atmospheric pressure, these compounds boil below 250°C. Studies have shown that prolonged exposure to the VOCs could increase the risk of various health problems, such as cancer. VOCs are commonly present in gasoline, dry cleaning solvents and degreasing agents. Due to improper storage, disposal or spillage of chemicals, these hazardous chemicals could contaminate the drinking water. In order to protect human health and the environment, the U.S. Environmental Protection Agency (EPA) has developed a standard method, namely EPA 524.3 to identify and quantify the purgeable organic compounds in finished drinking water by using purge-and-trap with GC-MS.

Headspace with trap mode could serve as an alternative option in analysing the purgeable VOCs. During incubation, VOCs from water samples are effectively partitioned into the headspace. Shimadzu HS-20 headspace sampler is ideal for extraction and concentration of VOCs from water samples. This application news reports a robust analysis method of VOCs complying with the EPA 524.3 criteria based on dynamic headspace coupled with gas chromatography-mass spectrometry. The combination of HS-20 headspace sampler and GCMS-QP2010 Ultra provides an alternative method of choice to extract purgeable organic compounds from drinking water followed by analysis of GC-MS.

❑ Experimental

Instrument and Analytical Conditions

The HS-20 Trap sampler utilizes the headspace technology. A water sample containing VOCs is sealed tightly inside a headspace vial. Under specified conditions of temperature, agitation and time, the VOCs in water sample achieve equilibrium between water phase and the gaseous phase. HS-20 Trap was used as an alternative sample preparation technique for the purge-and-trap. The trap mode HS-20 extracts analytes from the water sample and concentrates on a sorbent trap prior to desorbing to GC-MS. The analytical parameters of both headspace and GC-MS are presented in Table 1.

Table 1: GC-MS and Headspace sampler conditions

HS-20	
Mode	Trap
Oven Temp.	60°C
Trap Cooling Temp.	5°C
Trap Equilib Temp.	25°C
Trap Desorb Temp.	250°C
Equilibrating Time	30 min
GC	
Column	Rtx-VMS 60mx0.25mmx1.4µm
Carrier Gas	He
Flow Control Mode	Linear Velocity
Linear Velocity	31.3 mL/min
Purge Flow	3 mL/min
Split Ratio	10
Column Oven Temp	45°C(4.5min), 12°C/min →100°C(0min), 25°C/min → 240°C (5.32min)
MS	
Ion Source Temp.	200°C
Interface Temp.	200°C
Ionization Mode	Electron impact (EI)
Ionization Voltage	70 eV
Solvent cut Time	1.5 min
Acquisition Mode	SCAN
m/z	35 - 300

Preparation of Tuning Standard

Based on the EPA 524.3, the mass and abundance scales of the mass spectrometer was calibrated in order to meet the ion ratio specification for 4-bromofluorobenzene (BFB). Prior to the analysis, the mass spectrometer was tuned according to the instrument default condition. Approximately 10mL of 0.4 µg/mL BFB was prepared and filled into headspace vials. The BFB solution was introduced into the system by dynamic HS and analysed by GC-MS using the same sample analysis condition (Table 1).

Preparation of Primary Dilution Standard

Primary dilution standard was the most important as it will be used to prepare the calibration standards and standard for fortification. A series of primary dilution standards, concentration ranged from 2µg/mL to 160µg/mL were

prepared in 2mL microreaction vials with Mininert caps. The EPA 524.3 analytes, internal standards and surrogate standards were commercially available in 2000µg/mL ampules. 20µL of internal standard/surrogate standard mixture was spiked into each primary dilution standard. VOCs standard stock solution was added accordingly as 2, 4, 8, 20, 40, 80 and 160. Finally, methanol was added into the microreaction vials to obtain 2mL of final volume.

Preparation of Final Calibration Standard

Ascorbic acid and maleic acid with a final concentration of 0.625g/L and 5g/L respectively in reagent water was first prepared. Seven 100mL volumetric flasks were prepared, labelled with respective concentration level and filled with 95mL of reagent water. Subsequently, 25µL of each primary dilution standard was spiked into the respective volumetric flask. Reagent water was filled to reach the gauge line of volumetric flasks. After the analytes and reagent water were mixed homogeneously, 10mL of the sample was taken into headspace vials. Immediately, the headspace vials were crimped tightly to minimize loss of VOCs.

Preparation of Field Samples

Tap water was used as the field sample. In preparing field samples, water was collected directly from the tap and dechlorinated with ascorbic acid at pH 2.00. 0.625g of ascorbic acid and 5g of maleic acid were added into a 1L volumetric flask. 400mL of tap water was added to volumetric flask to dissolve the solid preservatives. After that, tap water was then used to fill the volumetric flask to the gauge line.

❑ Results and Discussion

Initial Mass Spectrometry Tune

The MS was tuned based on the default parameter. BFB was analysed under the same analytical condition. The system performance was evaluated based on a single spectrum at the apex of the BFB peak with subtraction of the background. Shimadzu GCMSsolution QA/QC function is able to check the BFB tuning results with respect to the EPA 524 method. Figure 1 shows the result of the BFB evaluation using the QA/QC function. All BFB mass spectrum criteria must be achieved before carrying out further analysis. If the MS tune results does not meet the required mass intensity criteria, the MS should be retuned by changing the tuning conditions and repeated with BFB analysis.

Chromatogram

This revised EPA 524.3 has included some new emerging contaminants, gasoline additives and potential breakdown of MtBE which gives a total of 76 target analytes, 3 internal standards and 3 surrogate standards. Most of the compounds have distinctive mass fragmentation. By matching the retention time, target ions and reference ions, all compounds could be identified. All the target compounds were well separated based on the respective mass chromatogram (MC), except m-xylene and p-xylene. Due to the same elution time and mass fragmentation, these two compounds were integrated together. Figure 2 showed the standard Total Ion Chromatogram (TIC) of all the compounds, including targets, internal standards and surrogate standards.

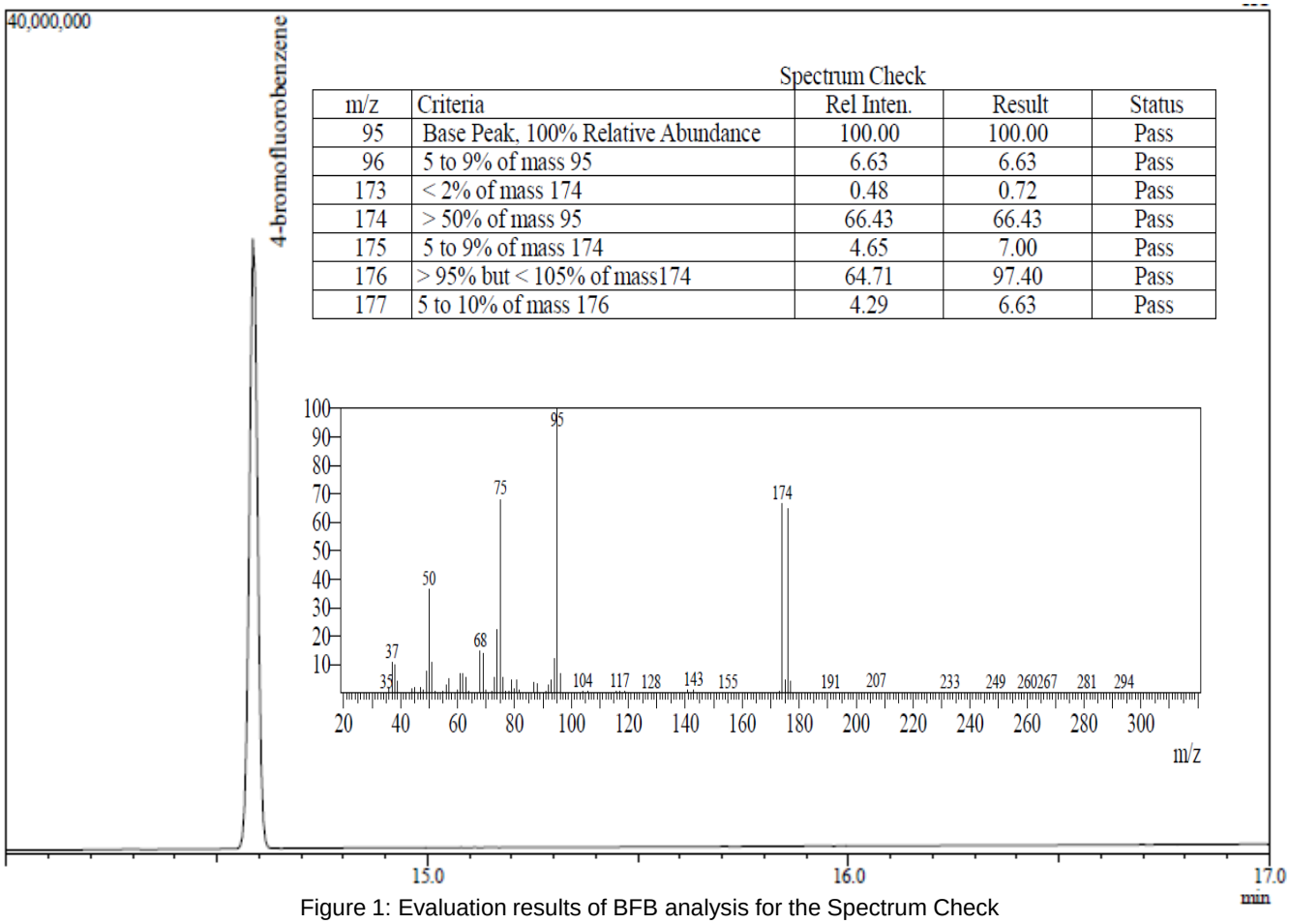

Figure 1: Evaluation results of BFB analysis for the Spectrum Check

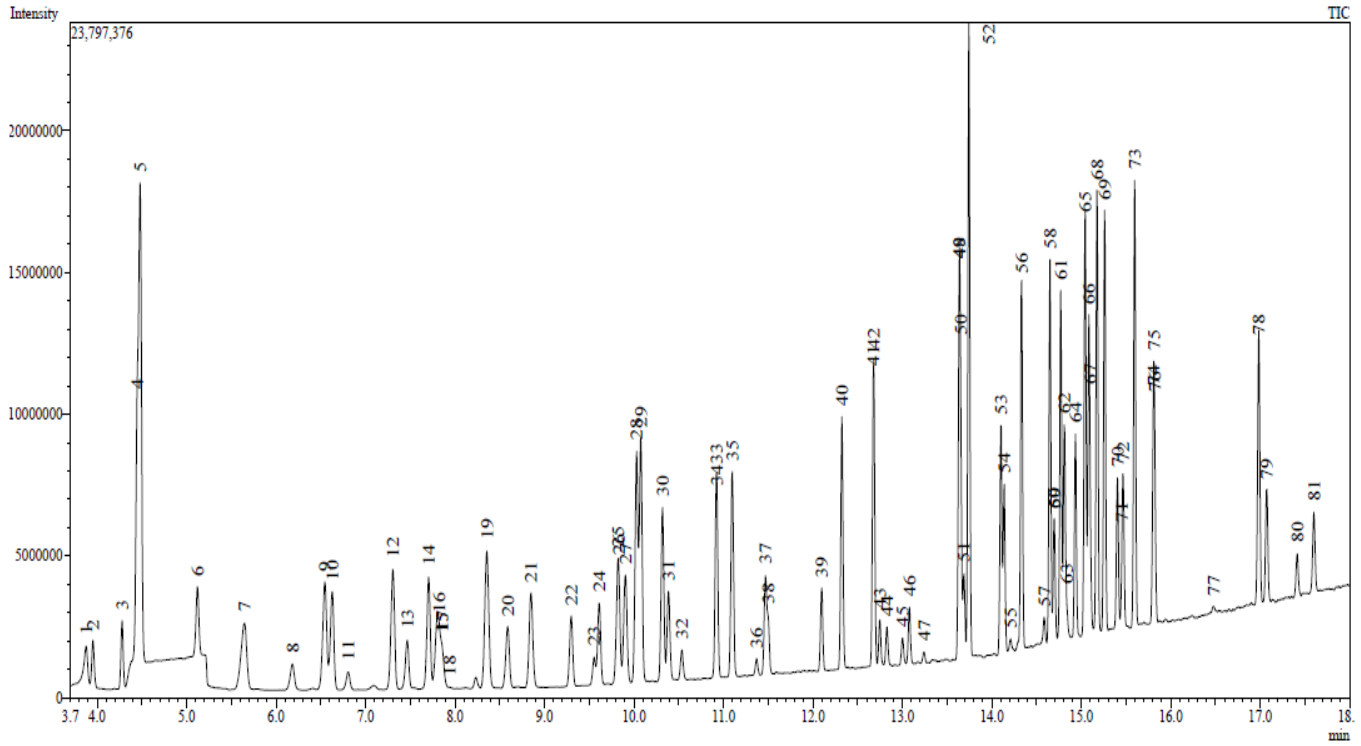

Figure 2: TIC chromatogram of VOCs based on EPA method 524.3 and analysis at 20 µg/L

Calibration

All the target analytes were calibrated by using internal standard technique. Seven calibration standards, ranging from 0.5µg/L to 40µg/L were prepared and analysed. Each calibration point is treated as an unknown. Concentration of the calibration point is calculated based on the calibration curve. According to the EPA 524.3, either linear or quadratic regression is permitted as long as the initial calibration point is within ±50% of its true value and all other points are within ±30% of their true values. An example of Benzene quadratic calibration curve is illustrated in Figure 3. Correlation coefficient for all the compounds were more than 0.995. Some of the compounds gave R^2-value as high as 1.000. Recovery of each calibration point and correlation regression are tabulated in Table 2.

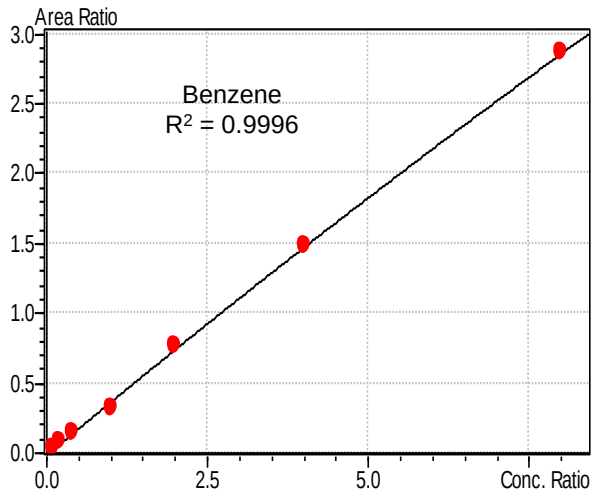

Figure 3: Calibration curve of Benzene from 0.5µg/L to 40µg/L

Detection Limit

Method detection limit is a statistical method used to determine reported value that is greater than zero with 99% confidence level. The MDL of each analyte was calculated based on the equation below.

$$\mathrm{MDL} = \mathrm{s} \times \mathrm{t}_{(\mathrm{n}-1,1-\alpha=0.99)}$$

Seven replicated control samples were prepared at 0.1µg/L. The Shimadzu GCMSsolution QA/QC function will automatically generate the calculation of MDL. As shown in Table 2, target analytes MDL is lower than the first calibration point, except *t*-butyl alcohol which commonly gives poor MS response.

Precision and Accuracy

In the demonstration of system stability, seven replicate samples in reagent water were prepared at 5µg/L which is the midrange of the initial calibration curve. Percentage of relative standard deviation (RSD) was calculated based on the equation below to determine the system precision.

$$\%\mathrm{RSD} = \frac{\text{Standard deviation of Measured Concentrations}}{\text{Average Concentration}} \times 100\%$$

System accuracy is calculated based on the percentage of recovery using the same seven replicate samples.

$$\%\mathrm{Recovery} = \frac{\text{Average Measured Concentration}}{\text{Fortified Concentration}} \times 100\%$$

These seven replicate samples concentration must not deviate more than 20% from the true concentration with %RSD less than 20%. All analytes %RSD and %Recovery are found to be within the allowable limit. Chromatogram of chlorodifluoromethane from seven replicate samples were overlaid in *Figure 4*. 90% of this highly volatile analyte were recovered with deviation of 2.9%.

Table 2: Summary of the response of all the target analytes which showed the correlation coefficient, detection limit and recovery at each calibration level ranged from 0.5 to 40 µg/L. Internal Standards and Surrogate Standards were omitted for the ease of data comparison.

ID	Compound	Correlative Regression (R^2)	Recovery at each calibration level (%)							Method Detection Limit (MDL, µg/L)
			0.5 µg/L	1 µg/L	2 µg/L	5 µg/L	10 µg/L	20 µg/L	40 µg/L	
1	Dichlorodifluoromethane	0.9988	148	131	119	73	101	102	100	0.100
2	Chlorodifluoromethane	0.9999	118	104	107	92	101	100	100	0.163
3	Chloromethane	0.9996	132	114	104	95	94	103	100	0.113
4	Vinyl Chloride	0.9995	144	121	105	87	97	103	100	0.092
5	1,3-Butadiene	0.9991	150	123	111	77	102	102	100	0.181
6	Bromomethane	0.9999	134	97	103	96	99	101	100	0.179
7	Trichlorofluoromethane	0.9993	134	127	108	80	100	102	100	0.100
8	Diethyl ether	0.9998	114	118	95	91	104	100	100	0.039
9	1,1-Dichloroethene	0.9995	118	123	106	82	106	100	100	0.024
10	Carbon Disulfide	0.9996	112	115	107	85	105	100	100	0.065
11	Methyl Iodide	0.9998	124	114	102	88	103	100	100	0.047
12	Allyl Chloride	0.9996	134	113	98	86	106	99	100	0.028
13	Methylene Chloride	0.9998	110	110	95	93	105	99	100	0.241
14	trans-1,2-Dichloroethene	0.9996	108	108	102	88	107	99	100	0.055
15	Methyl Acetate	0.9993	142	124	110	81	101	102	100	0.285
16	Methyl-t-Butyl Ether (MtBE)	0.9999	92	101	102	97	103	99	100	0.033
17	t-Butyl Alcohol (TBA)	0.9998	114	75	87	110	102	99	100	0.881
18	Diisopropyl Ether (DIPE)	0.9999	114	99	104	95	102	100	100	0.026
19	1,1- dichloroethane	0.9998	118	105	103	89	105	99	100	0.071
20	t-Butyl Ethyl Ether (ETBE)	0.9998	100	96	101	94	106	98	100	0.026
21	cis-1,2-dichloroethene	0.9997	88	97	99	95	107	98	100	0.060
22	Bromochloromethane	1.0000	94	92	102	99	103	99	100	0.037
23	Chloroform	0.9997	86	91	97	98	107	98	100	0.387
24	Carbon Tetrachloride	0.9997	132	114	112	85	99	102	100	0.035
25	Tetrahydrofuran	0.9978	108	97	66	95	119	94	100	0.121
26	1,1,1-Trichloroethene	0.9998	130	110	108	89	100	101	100	0.019
27	1,1-Dichloropropene	0.9996	118	117	102	85	106	99	100	0.039
28	1-Chlorobutane	0.9997	110	108	107	87	105	99	100	0.033
29	Benzene	0.9998	130	117	98	89	103	100	100	0.023
30	t-Amyl Methyl Ether (TAME)	0.9999	122	96	106	94	101	100	100	0.038
31	1,2-Dichloroethane	0.9998	86	90	98	100	105	98	100	0.041
32	Trichloroethene	0.9999	98	105	104	92	104	99	100	0.048
33	t-Amyl Ethyl Ether (TAEE)	0.9998	104	98	102	92	106	99	100	0.021
34	Dibromomethane	0.9999	98	100	103	94	104	99	100	0.021
35	1,2-Dichloropropane	0.9998	114	123	103	89	100	101	100	0.035
36	Bromodichloromethane	0.9998	102	102	100	93	105	99	100	0.060
37	cis-1,3-Dichloropropene	0.9997	92	90	101	96	107	98	100	0.035
38	Toluene	0.9996	104	106	106	88	106	99	100	0.063
39	trans-1,3-Dichloropropene	0.9995	80	104	105	90	108	98	100	0.048
40	Tetrachloroethene	0.9995	118	110	110	84	105	100	100	0.047
41	Ethyl Methacrylate	0.9995	94	107	100	90	108	98	100	0.043
42	1,1,2-Trichloropropane	0.9997	100	95	98	96	107	98	100	0.270
43	Dibromochloromethane	0.9998	64	104	108	95	105	99	100	0.054
44	1,3-Dichloropropane	0.9995	100	100	98	92	109	98	100	0.070
45	1,2-Dibromoethane	0.9992	136	94	107	84	108	98	100	0.054
46	Ethylbenzene	0.9998	120	103	105	90	103	100	100	0.173
47	Chlorobenzene	0.9996	108	102	106	88	106	99	100	0.062
48	1,1,1,2-Tetrachloroethane	0.9999	128	97	106	94	100	101	100	0.077
49	m-Xylene, p-Xylene	0.9992	150	115	101	87	99	103	86	0.249
50	o-Xylene	0.9999	94	96	104	96	104	99	100	0.110
51	Styrene	0.9997	112	103	102	91	105	99	100	0.084
52	Bromoform	0.9993	66	71	108	99	109	96	100	0.101
53	Isopropylbenzene	0.9995	138	114	110	85	100	102	100	0.043
54	n-propylbenzene	0.9989	150	133	105	82	97	104	99	0.039
55	1,1,2,2-Tetrachloroethane	0.9999	106	96	102	96	103	99	100	0.196
56	Bromobenzene	0.9995	96	110	98	88	109	98	100	0.182
57	1,3,5-Trimethylbenzene	0.9997	142	119	102	85	102	101	100	0.033
58	2-Chlorotoluene	0.9998	124	104	100	90	105	99	100	0.024
59	1,2,3-Trichloropropane	0.9995	128	76	93	114	93	101	100	0.303
60	4-Chlorotoluene	0.9998	118	111	100	89	104	99	100	0.062
61	t-Butylbenzene	0.9998	110	112	99	89	106	99	100	0.030
62	1,2,4-Trimethylbenzene	0.9998	138	120	105	86	100	101	100	0.058
63	Pentachloroethane	0.9998	114	103	113	88	103	100	100	0.067
64	sec-Butylbenzene	0.9988	148	133	109	80	98	104	99	0.032
65	4-Isopropyltoluene	0.9995	150	127	104	83	100	102	100	0.061

ID	Compound	Correlative Regression (R^2)	Recovery at each calibration level (%)							Method Detection Limit (MDL, µg/L)
			0.5 µg/L	1 µg/L	2 µg/L	5 µg/L	10 µg/L	20 µg/L	40 µg/L	
66	1,3-Dichlorobenzene	0.9999	108	109	101	93	103	100	100	0.147
67	1,4-Dichlorobenzene	0.9998	112	104	94	94	105	99	100	0.059
68	n-Butylbenzene	0.9994	150	125	103	84	99	102	100	0.034
69	Hexachloroethane	0.9997	106	123	95	87	107	99	100	0.107
70	1,2-Dichlorobenzene	1.0000	84	102	103	97	103	99	100	0.065
71	1,2-Dibromo-3-chlropropane	0.9982	112	95	100	78	118	96	100	0.379
72	Hexachlorobutadiene	0.9998	124	116	102	86	105	100	100	0.081
73	1,2,4-Trichlorobenzene	0.9997	138	106	93	89	107	99	100	0.169
74	Naphthalene	0.9998	108	105	97	92	106	99	100	0.122
75	1,2,3-Trichlorobenzene	0.9992	86	106	89	93	112	97	100	0.136

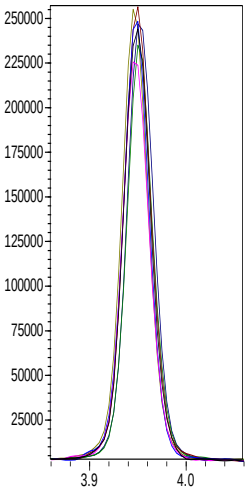

Figure 4: Recovery of Chlorodifluoromethane which is the most volatile compounds of the analysis gave 90% recovery with RSD of only 2.9%.

Quality Control

The system stability and accuracy of existing calibration were monitored through the Continuing Calibration Checks (CCC). CCC is a calibration standard which contains the method analytes, internal standards and surrogate analytes. CCC was analysed at the beginning of each Analysis Batch, after every tenth field sample and at the end of each Analysis Batch. Each CCC contained 5µg/L of method analytes, internal standards and surrogate analytes. Each analyte was calculated to be within 3.5µg/L and 6.5µg/L, which is equivalent to ±30% of true concentration. Throughout the analysis, all the target analytes in CCC detected were within the CCCs quality control criterion. *Table 3* shows the recovery of the most volatile target, Chlorodifluoromethane in the CCCs analyses.

Table 3: Recovery of Chlorodifluoromethane which is the most volatile compound of the analysis in the Continuing Calibration Checks was within the QC check criteria.

Injection	Recovery Requirement (%)	Actual Recovery (%)
1	70 - 130	74
2	70 - 130	93
3	70 - 130	98
4	70 - 130	89
5	70 - 130	87

Internal Standards

EPA Method 524.3 is quantitated based on the Internal Standards. Internal Standards were spiked into all calibration standards, CCCs and field samples. Stability of internal standards is crucial to obtain precise response factor of the analytes which will be used to plot the calibration curve. Internal standard peak areas of all analyses should not deviate more than 50% for the lowest calibration level and 30% of other calibration levels from the most recent CCC. Figure 5 shows the stability of internal standards for the analysis of 10 field samples.

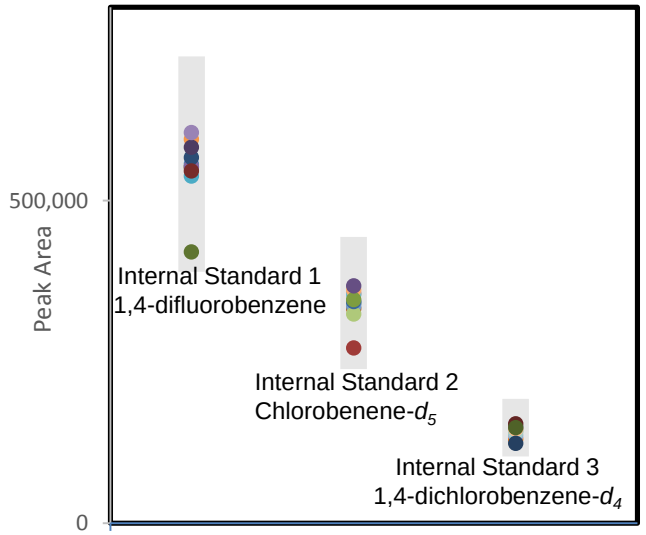

Figure 5: Peak areas of Internal Standards in all the field samples are within ±30% of peak areas (highlighted region) of internal standard in CCCs.

Surrogate Recovery

In order to evaluate the matrix interference on sample, surrogates are spiked into the field samples prior to analyses. Surrogates are compounds which are chemically similar to the target analytes and thus behave similarly in the matrix. In the EPA Method 524.3, methyl-t-butyl ether-d_3, 4-bromofluorobenzene, and 1,2-dichlorobenzne-d_4 were fortified as Surrogate Standards for all analyses including calibration standards, CCCs and field samples. The surrogate standards were closely monitored to confirm that the recovery percentage of samples were within the range of 70% to 130%. Figure 6 shows the recovery of all surrogates in 10 field samples analyses.

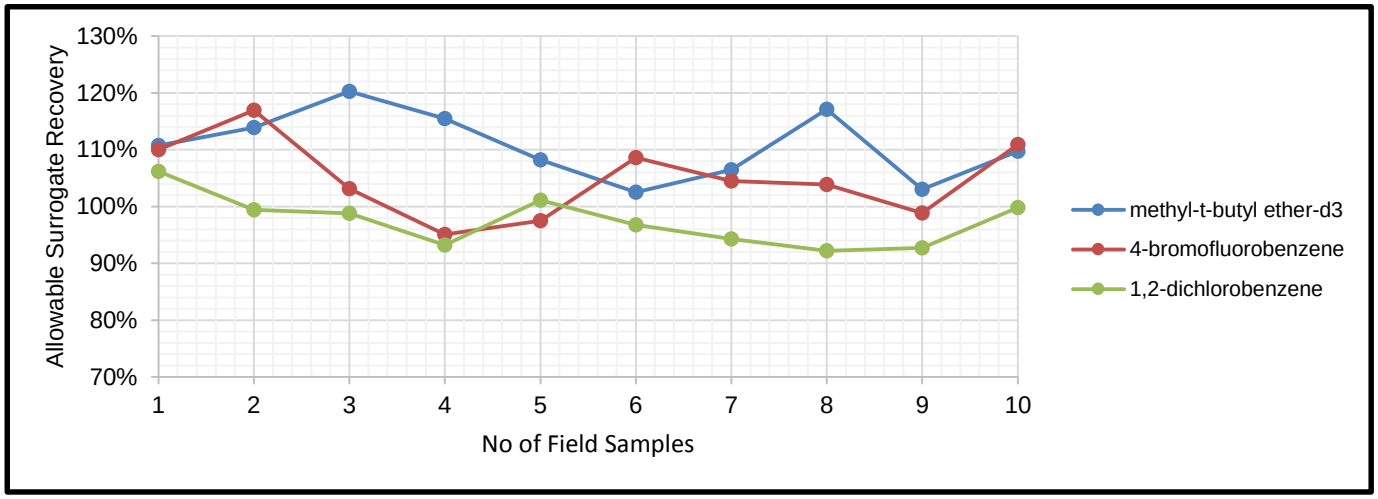

Figure 6: Recovery of all surrogates, namely methyl-t-butyl ether-d_3(Surrogate 1), 4-bromofluorobenzene(Surrogate 2), and 1,2-dichlorobenzene-d_4(Surrogate 3) of all 10 CCCs are within the acceptable QC criteria (70 – 130%).

❑ Conclusions

The results shows that the HS-20 Trap mode is a viable alternative method in analysis of VOCs following EPA 524.3. The correlation coefficient, recovery and RSD obtained in this study complies with the EPA Method 524.3. Matrix effect of the real samples is insignificant as recoveries of the internal standards and surrogate standards are within the limits of the standard method. In brief, the system of Shimadzu HS-20 Trap sampler coupled with GCMS-QP2010 Ultra provide another choice for analysis of VOCs in drinking and underground water samples.

❑ Reference

B.Prakash, A.D. Zaffiro, M. Zimmerman, D. J. Munch and B.V. Pepich, Method 524.3 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, EPA Document # EPA 815-B-009, Version 1.0, June 2009

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SHIMADZU (Asia Pacific) Pte. Ltd
79 Science Park Drive, #02-01/08, Cintech IV, Singapore 118264
www.shimadzu.com.sg
Tel: +65-6778 6280 Fax: +65-6778 2050