

Trace Level Determination of Volatile Organic Components (VOC's) in packaged drinking water by HSGCMS

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Introduction

VOC's in drinking water include compounds already present in natural water sources, as well as contaminants produced by industry and during daily activities. These are pollutants from agricultural activity, water purification chemicals, pesticides used for public health initiatives and pharmaceutical products.

VOC's are known to be responsible for many human health hazards. In general, exposure to low levels of certain VOC's over a long period of time may lead to impaired immune system function, liver damage and increased risk of cancer. At elevated levels, even short-term exposure to

certain VOC's can cause central nervous system depression. As a result, in order to maintain a fixed drinking water quality, each country sets regulations and analyzes for chemical contaminants in drinking water. In India, Bureau of Indian Standard (BIS) has established safe drinking water standards.

This study reports a sensitive analytical method using Shimadzu GCMS-QP2020 NX single quadrupole system with HS-20 dynamic headspace autosampler (Figure 1) to determine 51 VOC's at trace level.



Figure 1. GCMS-QP2020 NX with HS-20 headspace autosampler

Methods of Analysis

Procedure

- **Standard Stock Solution :**
VOC's standard was procured from Restek®. Stock solution of 100 ppm was prepared in high purity grade water.
- **Calibration Levels:**
Standard stock solution was further diluted with high purity grade water (JT Baker) to prepare the concentration levels of 0.025 ppb, 0.050 ppb, 0.100 ppb, 0.250 ppb and 0.500 ppb. 10.0 mL of each standard solution was then transferred to 20 mL headspace vial and calibration curve was plotted.
- **Sample Preparation:**
About 10.0 mL of commercially available packaged drinking water was taken in headspace vial.
- **Spike Sample Preparation:**
For recovery studies, 10.0 mL of commercially available packaged drinking water was spiked with VOC's Standard solution at 0.05 ppb, 0.075 ppb and 0.100 ppb concentration levels.

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GC-MS Analytical Conditions

The analysis was carried out on Shimadzu GCMS-QP2020 NX equipped with HS-20 headspace sampler as per the conditions given in Table 1.

Table 1. Analytical conditions

Chromatographic parameters

Column

Injection Mode

Split Ratio

Carrier Gas

Flow Control Mode

Linear Velocity

Column Flow

Injection Volume

Total Program Time

Column Temp. Program

: VMS (60 m L x 0.45 mm I.D. x 2.55 µm)

: Split

: 3

: Helium

: Linear Velocity

: 44.0 cm/sec

: 3.0 mL/min

: Not applicable

: 40.00 min

:

Rate (°C /min)	Temperature (°C)	Hold time (min)
-	35.0	5.00
5.00	150.0	2.00
15.00	230.0	4.67

Headspace parameters

HS Mode

HS Oven Temp.

Sample Line Temp.

Transfer Line Temp.

Gas Pressure

Equilibrating Time

Load Time

Injection Time

Needle Flush Time

GC Cycle Time

Trap Cooling Temp

Trap Desorb Temp.

Multi Injection Count

: Trap

: 60.0 °C

: 200.0 °C

: 220.0 °C

: 50 kPa

: 30 min

: 0.2 min

: 40.0 min

: 40.0 min

: 55.0 min

: -10.0 °C

: 150.0 °C

: 10

Mass Spectrometry parameters

Ion Source Temp.

Interface Temp.

Ionization Mode

Acquisition Mode

: 220.0 °C

: 230.0 °C

: EI (Electron Ionization)

: SCAN

Method development

The standards for many of the VOC's commonly found in water, measured in parts per billion(ppb). Hence, it is imperative to have a method to quantitatively evaluate their presence at trace levels in environmental water

samples. Analysis of VOC's in water using HS-20 trap (dynamic headspace) with GCMS was as an alternative for purge & trap GCMS technique.

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Key Features of GCMS-QP2020 NX equipped with HS-20 Headspace

- With Peltier cooling, trap column (Tenax TA) was cooled up to - 10.0 °C for efficient adsorption of high volatile components from the water sample
- With multiple injection count feature, VOCs from water sample were extracted for 10 times from same vial and concentrate on the trap column (Tenax TA)
- ASSP™ (Advanced Scanning Speed Protocol) enables high-speed scan and data acquisition for accurate quantitation at 20,000 u/sec
- LabSolutions Insight significantly improves the efficiency of reporting for multi-component analysis

Results

About 1 ppm standard was analysed in scan mode and the components were identified with the help of NIST-17 library. Further retention time and SIM ions were determined from the scan data.. The quantitative analysis of commercially available package bottled water sample was done by using above method. The data was statistically evaluated with respect to linearity, precision and recovery.

Linearity for standards ranging from 0.025 ppb, 0.050 ppb, 0.100 ppb, 0.250 ppb and 0.500 ppb concentration level was plotted with weighted linear regression (1/C). Linear response with $r^2 \geq 0.99$ was obtained for most of the components.

The Relative Standard deviation (RSD) for six replicate injections of 0.100 ppb VOC's standard were found to be less than 20% for most of the components.

Since VOC's were not detected in package water bottle sample, recovery studies at various concentration levels were carried out by spiking standard solutions in same water sample. For all the levels, recovery was found to be in between 70% to 130% for most of the components.

Statistical data of linearity and accuracy were listed in table 2, showed that the method was sensitive, accurate and reproducible.

Chromatographic overlay of all linearity levels, calibration curve and quantitative chromatogram for m-Xylene were shown in figure 2,3 and 4.

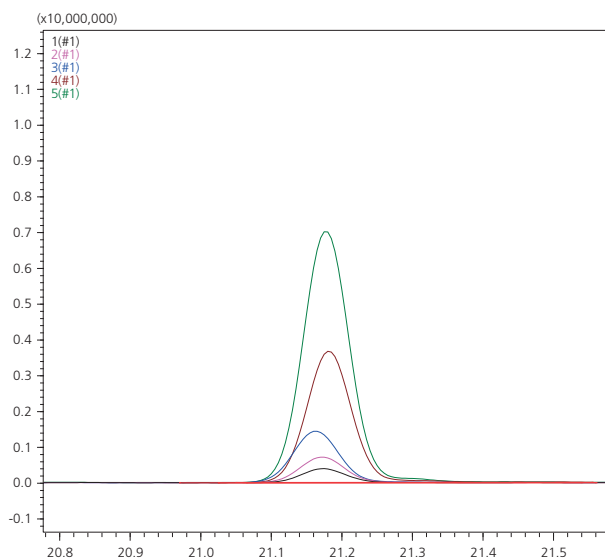


Figure 2. Linearity overlay for m-Xylene

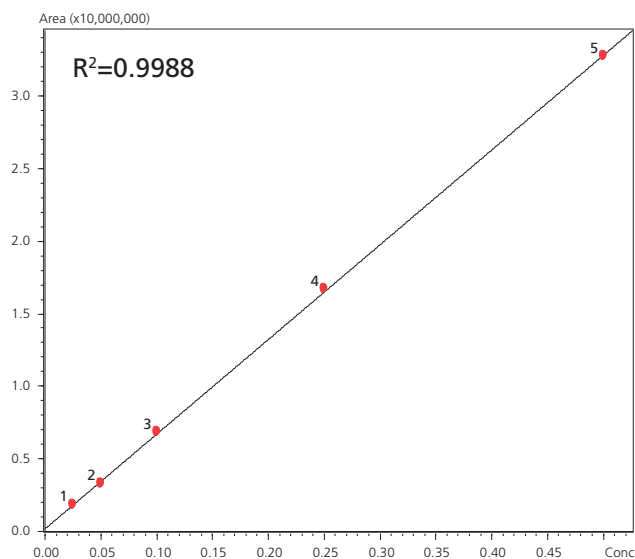


Figure 3. Calibration curve for m-Xylene

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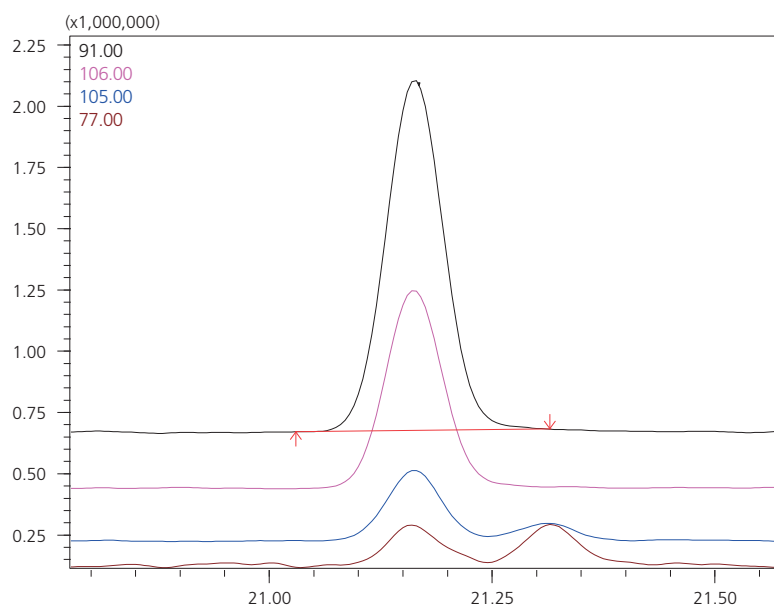


Figure 4. Quantitative chromatogram for m-Xylene

Table 2. Analytical results

No.	Name	Retention Time (min)	Linearity (r2)	% Accuracy at 0.100 ppb
1	Dichloromethane	6.540	0.9966	87
2	cis-1,2-Dichloroethene	6.892	0.9958	92
3	1,1-Dichloroethane	8.219	0.9992	88
4	trans-1,2-Dichloroethene	9.358	0.9978	85
5	2,2-Dichloropropane	9.567	0.9833	79
6	Bromochloromethane	9.766	0.9992	97
7	Chloroform	9.979	0.9997	102
8	Carbon tetrachloride	10.220	0.9909	105
9	1,1,1-Trichloroethane	10.360	0.9972	99
10	1,1-Dichloropropene	10.648	0.9934	85
11	Benzene	11.180	0.9990	89
12	1,2-Dichloroethane	11.597	0.9966	99
13	Dibromomethane	13.373	0.9993	96
14	1,2-Dichloropropane	13.620	0.9997	110
15	Bromodichloromethane	13.793	0.9988	91
16	cis-1,3-Dichloropropene	15.254	0.9957	93
17	Toluene	15.829	0.9930	101
18	Tetrachloroethylene	16.719	0.9986	114
19	trans-1,3-Dichloropropene	16.843	0.9997	91

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Table 2. Analytical results

No.	Name	Retention Time (min)	Linearity (r2)	% Accuracy at 0.100 ppb
20	1,1,2-Trichloroethane	17.210	0.9940	86
21	Dibromochloromethane	17.618	0.9974	92
22	1,3-Dichloropropane	17.867	0.9997	99
23	1,2-Dibromoethane	18.156	0.9980	98
24	Chlorobenzene	19.533	0.9995	95
25	o-Xylene/ Ethyl Benzene	19.678	0.9916	90
26	1,1,1,2-Tetrachloroethane	19.724	0.9994	83
27	p-Xylene	20.073	0.9996	89
28	m-Xylene	21.187	0.9985	93
29	Bromoform	21.303	0.9982	103
30	Styrene	21.328	0.9975	117
31	Isopropylbenzene	22.055	0.9965	91
32	Bromobenzene	22.989	0.9988	99
33	n-Propylbenzene	23.199	0.9947	95
34	1,1,2,2-Tetrachloroethane	23.389	0.9993	98
35	2-Chlorotoluene	23.550	0.9979	82
36	1,2,3-Trichloropropane	23.700	0.9964	89
37	1,2,4-Trimethylbenzene	23.782	0.9968	93
38	4-Chlorotoluene	24.018	0.9967	96
39	tert-Butylbenzene	24.636	0.9959	102
40	1,3,5-Trimethylbenzene	24.855	0.9969	111
41	sec-Butylbenzene	25.152	0.9909	95
42	p-Isopropyltoluene (p-Cymene)	25.610	0.9925	97
43	1,4-Dichlorobenzene	25.676	0.9928	110
44	1,3-Dichlorobenzene	25.926	0.9914	119
45	n-Butylbenzene	26.826	0.9952	96
46	1,2-Dichlorobenzene	27.132	0.9984	88
47	1,2-Dibromo-3-chloropropane	29.606	0.9999	83
48	1,2,3-Trichlorobenzene	31.794	0.9981	92
49	Hexachlorobutadiene	31.808	0.9935	99
50	Naphthalene	32.611	0.9934	101
51	1,2,4-Trichlorobenzene	33.043	0.9977	95

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Conclusion

A sensitive, reproducible and accurate method was successfully developed for quantitative determination of VOCs in commercially available packaged drinking water sample by using Shimadzu GCMS-QP2020 NX with HS-20 headspace autosampler.

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