SHIMADZU

WP 276

Quantification of 8 chlorination disinfectant byproducts from water by LLE and Gas Chromatography-Mass Spectrometry

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1. Introduction

- Disinfection of water is normally carried out by adding chemicals such as chlorine/chloramine which reacts with naturally occurring amino acids and other labile organic chemicals to form a range of disinfection byproducts (DBPs) [1].
- Chronic exposure to disinfection byproducts (DBPs) can heighten the likelihood of cancer development, liver damage, and reduced nervous system activity [2]. To assess DBP levels in water, we utilized the USEPA 551.1 method. According to EPA 551.1 guidelines, quantification involves employing Gas Chromatography with an Electron Capture Detector (GC-ECD), while qualitative confirmation necessitates Gas Chromatography Mass Spectrometry (GC-MS) [3].
- This article showcases the use of the Shimadzu GCMS-QP2020 NX (Fig. 1) for both quantification and qualification of eight significant DBPs, comprising four haloacetonitriles.
- The chemical structure of the various targeted DBPs are shown in Fig. 2.

Fig. 1 GCMS-QP2020 NX.

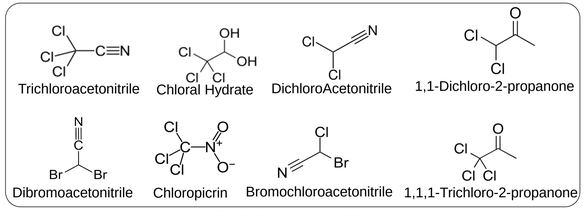

Fig. 2 Structure of DBPs.

2. Materials and methods

◆ Preparation of calibration standards.

The stock standard solution containing 8 DBP analytes, the surrogate standard of decafluorobiphenyl, and the internal standard solution of p-bromofluorobenzene in acetone were obtained from Accustandard (catalog numbers: M-551.1B, M-551.1-SS, and M-551.1-IS, respectively). A working stock solution containing standards and surrogates at a concentration of 500 ppb is prepared using MTBE as a diluent. From this standard stock, eight levels of calibration standards were prepared, each containing 1 ppm of internal standard. The concentrations of the different standards are presented in Table 1. Only in L6, the surrogate standard is spiked to achieve a resulting concentration of 10 ppb. This adjustment is made to assess the surrogate standard's area for comparison with that in the recovery sample.

Name	Rt (min)	Target m/z	Concentration (ppb)								Linearity coefficient r^2
			L1	L2	L3	L4	L5	L6	L7	L8	
Trichloroacetonitrile	3.258	108.0	1	5	10	20	40	80	160	200	0.9955
Chloral Hydrate	3.909	82.0	1	5	10	20	40	80	160	200	0.9950
DichloroAcetonitrile	4.240	74.0	1	5	10	20	40	80	160	200	0.9980
1,1-Dichloro-2-propanone	4.343	43.0	1	5	10	20	40	80	160	200	0.9953
Chloropicrin	5.715	117.0	1	5	10	20	40	80	160	200	0.9936
Bromochloroacetonitrile	8.042	74.0	1	5	10	20	40	80	160	200	0.9931
1,1,1-Trichloro-2-propanone	8.741	43.0	1	5	10	20	40	80	160	200	0.9944
Dibromoacetonitrile	16.702	118.0	1	5	10	20	40	80	160	200	0.9925
p-Bromofluorobenzene (IS)	16.496	95.0	1	1	1	1	1	1	1	1	----
Decafluorobiphenyl (SS)	19.186	334.0	0	0	0	0	0	10	0	0	----

Table. 1 Analyte m/z and concentration chart.

◆ Preparation of water sample and spike recovery sample.

Prior to analysis, the water sample is treated with preservatives to maintain a pH between 4.8 and 5.5, as recommended by the EPA. This is achieved by adding 1g of phosphate buffer—a mixture comprising 1% sodium phosphate dibasic and 99% potassium phosphate monobasic—to 50mL of the water sample contained in a separating funnel. The funnel is then shaken until all salts are dissolved.
Following this, the solution is fortified with 50µL of a 10ppm surrogate standard. Subsequently, 3mL of MTBE (methyl tert-butyl ether) is added to the solution and shaken vigorously for 2 minutes.
Next, 10g of NaCl (sodium chloride) is introduced into the solution, and the separating funnel is shaken rigorously for 10 minutes. The mixture is then allowed to settle for 20 minutes to facilitate phase separation, resulting in the formation of two distinct layers: an upper organic layer consisting of MTBE and a lower aqueous layer.
Once the layers have settled, the lower aqueous layer is carefully drained, while the upper organic layer is meticulously transferred into a clean 5mL vial using a pipette. From this organic layer, 990µL is pipetted into a LabTotal vial. Subsequently, 10µL of a 100ppm internal standard is added to the vial and mixed thoroughly.
A recovery test is conducted using 50mL of water. The analytes are spiked at two different concentrations: 2.5 and 5ppb after the addition of 1g of phosphate buffer. The extraction of analytes is performed following the same procedure as outlined for the sample extraction and is illustrated in Fig 3.

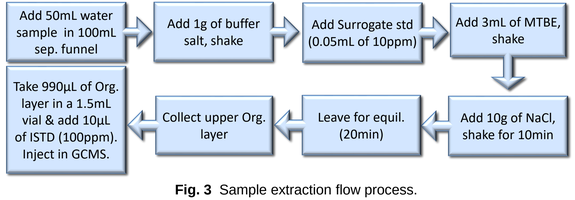

Fig. 3 Sample extraction flow process.

◆ Preparation of instrument and analysis.

The details of instrument parameters are shown in Table 2. At first, the mix standards, internal standard and surrogate standard peaks are identified by NIST GC/MS library and the m/z for the target and reference masses for each analytes are then selected to finalize for the Scan/SIM method. This is facilitated by utilizing the UFMS feature of the GCMS-QP2020 NX (20,000 u/sec), and the "Creation Of Automatic Scan/SIM Table" (COAST) wizard within the GCMS Solutions software. The compound table thus obtained is then used for the quantification and reporting of analysis data. The calibration standards are analyzed, and the linearity curve is then plotted by internal standard method.

GC inlet parameters		
Injector Temperature	240 °C	Analytical column: SH-I-5Sil MS (P/N: 221-75954-30) (30 m x 0.25 mm; df: 0.25 µm)
Injection mode	Splitless	
Injection volume	2.0 µL	
Flow Control Mode	Linear Velocity (39.4cm/s)	
Column Flow	1.2 mL/min	
Purge Flow	1.0 mL/min	

Column Oven Program		
Rate	Temperature (°C)	Hold Time (min)
-	35.00	16.00
40.00	220.0	4.37

Table. 2 Instrument parameters.

Analyte	% Recovery		10ppb Surrogate STD spiked sample
	2.5ppb	5.0ppb	Sample 1
Trichloroacetonitrile	93.5	86.9	----
Chloral Hydrate	63.0	61.7	----
DichloroAcetonitrile	111.3	104.9	----
1,1-Dichloro-2-propanone	97.8	92.3	----
Chloropicrin	103.4	104.0	----
Bromochloroacetonitrile	111.3	107.3	----
1,1,1-Trichloro-2-propanone	109.0	102.6	----
Dibromoacetonitrile	111.4	106.9	0.07
Decafluorobiphenyl (SS)	110.9	110.3	11.46

Table. 3 Recovery results.

3.Results

- The method developed on GCMS-QP2020 NX can quantify even 1ppb concentration in sample.
- Good linear response for all the analytes are observed with r^2 > 0.99. The linearity results for all the compounds are shown in Table 1 and the linearity chromatograms of all the analytes are given in Fig. 4.
- The area responses for the 10ppb surrogate standard spiked in the 50mL sample solution is closely matching with that spiked in the 6th level standard.
- The 2.5ppb and 5ppb recovery sample produced acceptable results with recovery between 80-120% for all compounds except for Chloral hydrate (50-60%). The recovery results is summarized in Table 3.

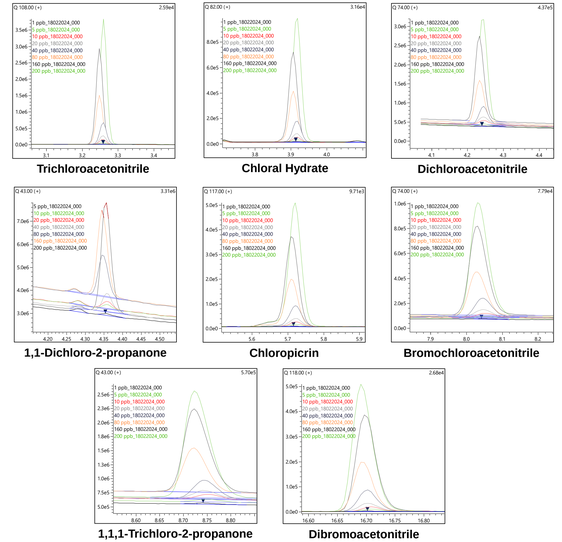

Fig. 4 Linearity chromatograms of 8 targeted DBPs.

4. Conclusion

- A highly sensitive GC/MS method is developed for 8 halogenated DBPs using Shimadzu GCMS-QP2020 NX following USEPA 551.1 sample preparation protocol.
- Excellent linearity results and recovery results at 2.5 & 5.0ppb concentrations for all the analytes proves the method and the instrument is highly efficient.
- Low recovery obtained for Chloral hydrate can be attributed to the analyte stability during the extraction process.

References
1) https://en.wikipedia.org/wiki/Disinfection_by-product
2) https://www.cdc.gov/biomonitoring/THM-DBP_FactSheet.html.
3) https://www.epa.gov/sites/default/files/2015-06/documents/epa-551.1.pdf