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Application Note

Quantification of 8 Disinfection Byproducts from Water by Liquid-Liquid Extraction and Gas Chromatography-Mass Spectrometry

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Environment

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■ Abstract

Disinfection byproducts (DBPs) are chemical byproducts formed during the disinfection process of water. One of the approved methods by the US Environmental Protection Agency (US EPA) for the quantification of selected DBPs in drinking water is method EPA 551.1. According to this method, the target compounds are analyzed by Gas Chromatography with Electron Capture Detector (GC/ECD)[1]. Because of the limited selectivity of GC/ECD, the method requires confirmation of the results by either using the same detector with a dissimilar column or by using Gas Chromatography with Mass Spectrometry (GC/MS). In this article, we demonstrate the performance of the Shimadzu single quadrupole GCMS-QP2020 NX for the analysis of 8 DBPs (Fig. 1) after liquid-liquid extraction as sample preparation.

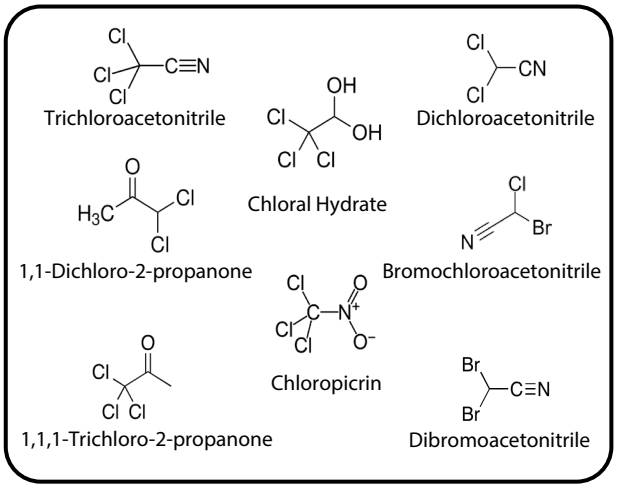


Fig. 1 Structure of DBPs.

1. Introduction

Disinfectants such as chlorine and chloramine are widely used to eliminate microorganisms in water. However, these disinfectants react with naturally occurring chemical constituents, such as amino acids and other labile organic chemicals, forming a range of disinfection byproducts (DBPs). Chronic exposure to DBPs elevates the risk of developing cancer, liver damage, and decreased nervous system activity. Hence, accurate detection and quantification of DBPs in water is crucial.

Although official recommended method for measuring DBPs is based on GC/ECD, GC/MS offers significant advantages in terms of simultaneous quantification and identification of both known and unknown compounds in a single analysis, providing comprehensive data on complex water samples. Unlike ECD, which has a limited dynamic range and can only detect electroactive compounds, MS offers a broader dynamic range, allowing the detection of analytes at varying concentrations. Additionally, GC/MS provides superior sensitivity, specificity, and structural information, making it the ideal method for detailed, high-precision analysis of disinfection byproducts and other water contaminants.

2. Materials and methods

The mixed standard solution for the 8 DBPs, the internal standard (IS) (p-bromofluorobenzene), and the surrogate standard (SS) (decafluorobiphenyl) were obtained from AccuStandard, with catalog numbers M-551.1B, M-551.1-IS, and M-551.1-SS, respectively.

Fig. 2 GCMS-QP2020 NX

Methyl-tert-butyl ether (MTBE), with a purity of ≥99.5 % (Laboratory Reagent grade), was used as the extraction solvent. The inorganic salts—sodium phosphate dibasic (Na_2HPO_4), potassium phosphate monobasic (KH_2PO_4), and sodium chloride (NaCl)—used in sample preparation were of Analytical Reagent grade. Tap water was analyzed to evaluate the method performance; the target analytes were quantified in unspiked samples. The analysis was performed on Shimadzu GCMS-QP2020 NX (Fig. 2).

2.1. Sample preparation

Preparation of calibration standards:

Stock solutions of standards and surrogate were prepared at a concentration of 500 ppb using MTBE as a diluent. From the standard stock, six calibration standards were prepared ranging from 5 ppb to 200 ppb, each containing 1 ppm of internal standard. To verify the efficiency of the sample extraction process, 166 ppb of the surrogate standard was spiked into level 4 of the linearity standards. The peak area of the surrogate measured in the level 4 standard was then compared with that observed in the samples, and the difference was used to correct the recovery.

Preparation of water sample and spike recovery sample:

Prior to analysis, 50 mL of water sample was buffered with 1 g of phosphate buffer (1 % Na_2HPO_4 and 99 % KH_2PO_4) to maintain a pH between 4.8 and 5.5, as stated in EPA method 551.1. in a separating funnel. The funnel was then shaken until all salts were dissolved. The solution was fortified with 50 µL of a 10 ppm surrogate standard. Subsequently, 3 mL of MTBE were added to the solution and shaken vigorously for 2 minutes. Afterwards, 10 g of NaCl was added into the solution, and the separating funnel was shaken rigorously for 10 minutes. The mixture was 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 had settled, the lower aqueous layer was carefully drained, while the upper organic layer was meticulously transferred into a clean 5 mL vial using a pipette. 990 µL of the organic layer was pipetted into a LabTotal vial. Subsequently, 10 µL of a 100 ppm internal standard was added to the vial and mixed thoroughly.

A recovery test was conducted by spiking 5 ppb of target analytes and 10 ppb of surrogate compound in 50 mL of water, after the addition of 1 g of phosphate buffer.

The extraction of analytes was performed following the same procedure as outlined earlier in this section.

2.2. Analytical Conditions

Preparation of instrument and analysis:

The analytical method was established, and the instrument parameters are detailed in Table 1. Prior to the analysis, both the instrument and the column were conditioned. The "High-Sensitivity" autotune mode of the GCMS-QP2020 NX was used for the analysis. A standard solution containing 500 ppb of the target analytes, surrogate, and internal standard was injected using the MS full scan mode to determine the retention times.

Table. 1 Instrument parameters GC-MS

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	: 1.0 µL	
Flow Control Mode	: Linear Velocity (39.4 cm/s)	
Column Flow	: 1.2 mL/min	
Purge Flow	: 1.0 mL/min	
Column Oven Program		
Rate (°C/min)	**Temperature (°C)**	**Hold Time (min)**
-	35.00	16.00
40.00	220.00	4.37
MS parameters		
Ion Source Temperature	: 290 °C	
Interface Temperature	: 290 °C	
Solvent Cut Time	: 2.5 min	
Detector Voltage	: 0.6 kV (relative to tune result)	
Event Time	: 0.3 s (scan) , 0.05 s (SIM)	
Scan Range	: 35.0 - 600.0 m/z	

The peaks corresponding to the target compounds, internal standard, and surrogate were identified using the NIST GC/MS library. Quantifier and qualifier ions for each analyte were selected, and a compound table was created accordingly and the same was used to develop a Scan/SIM method using the "Creation of Automatic Scan/SIM Table" (COAST) wizard within the GCMSsolution™ software. The ultra-fast scanning capability (20,000 u/s) of the GCMS-QP2020 NX enables simultaneous acquisition of Scan and SIM events without compromising data quality.

The newly created Scan/SIM method was used for the quantification and reporting of analytical data. Calibration standards were analyzed. The data and the calibration curve, using the internal standard method, were processed using LabSolutions Insight™ software which enables the analysis of large numbers of data simultaneously. Following this, both the unspiked and spiked (5 ppb) samples were analyzed and quantified.

3. Result and Discussion

A 6-point calibration curve was created for all target analytes. A good linear response, with correlation coefficients (r^2) greater than 0.99, and accuracy within 80-120% was observed for all analytes. A signal-to-noise ratio (S/N) ≥ 10 was observed for all analytes at 5 ppb standard. The results are shown in Table 2.

Table. 2 Target details

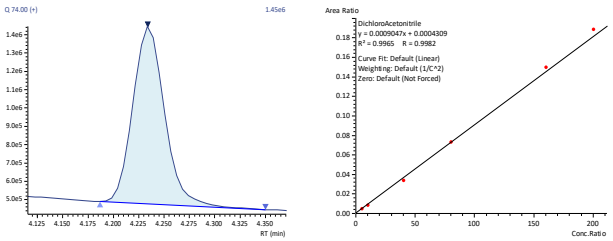
Name	Rt (min)	Target m/z	S/N (5 ppb)	Linearity coefficient $(r)^2$
Trichloroacetonitrile	3.25	108	513	0.9989
Chloral Hydrate	3.91	82	53	0.998
Dichloroacetonitrile	4.24	74	26	0.9965
1,1-Dichloro-2-propanone	4.35	63	13	0.9989
Chloropicrin	5.72	117	56	0.9988
Bromochloroacetonitrile	8.03	74	16	0.9983
1,1,1-Trichloro-2-propanone	8.72	125	49	0.9984
Dibromoacetonitrile	16.7	118	24	0.9979

The area responses of the spiked surrogate standard in the samples were comparable to those in level 4, demonstrating the efficiency of the extraction procedure. Furthermore, the 5 ppb recovery sample produced acceptable results, with recoveries ranging from 70–120% for all compounds. Lower recovery obtained for Chloral hydrate (70%) as compared to the other targets (92-116%) can be attributed to the analyte limited stability during the extraction process. The recovery results are provided in Table 3.

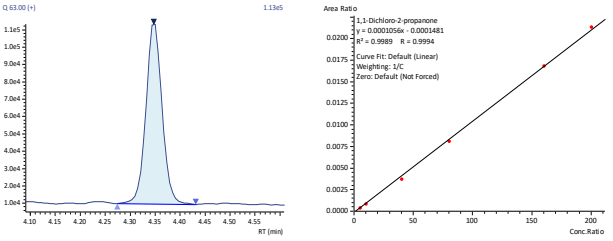
Table. 3 Recovery results

Analyte	Sample	Spiked Conc.	Conc.	% Recovery
Trichloroacetonitrile	----	5	4.6	92
Chloral Hydrate	----	5	3.5	70
Dichloroacetonitrile	----	5	5.7	114
1,1-Dichloro-2-propanone	----	5	4.9	98
Chloropicrin	----	5	5.5	110
Bromochloroacetonitrile	----	5	5.8	116
1,1,1-Trichloro-2-propanone	----	5	5.6	112
Dibromoacetonitrile	----	5	5.8	116
Decafluorobiphenyl (SS)	11.3	10	9.2	92

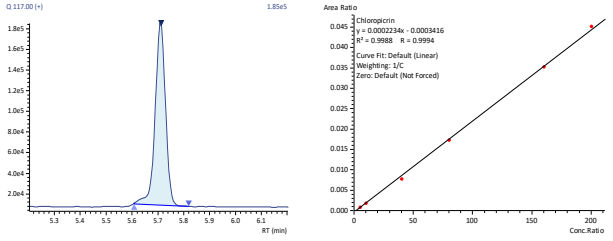
A representative chromatogram of target compounds and their respective calibration curve are presented in Fig. 3, while representative chromatograms of the internal standard and surrogate compound are shown in Fig. 4.



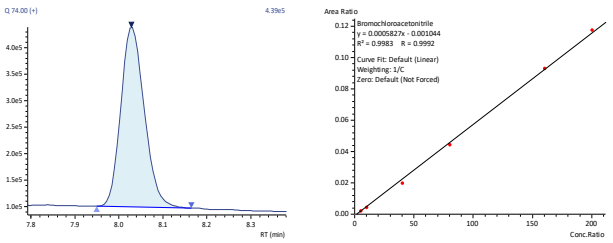
DichloroAcetonitrile



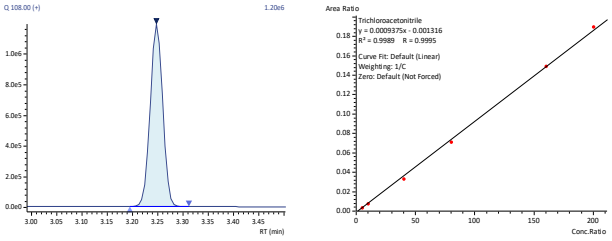
1,1-Dichloro-2-propanone



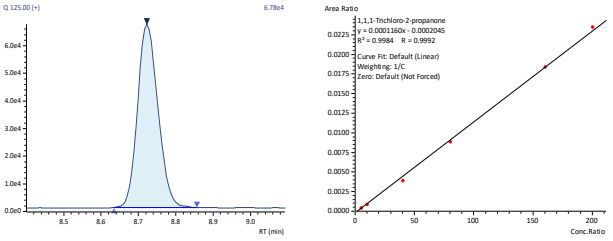
Chloropicrin



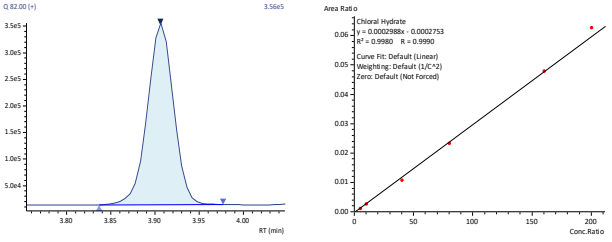
Bromochloroacetonitrile



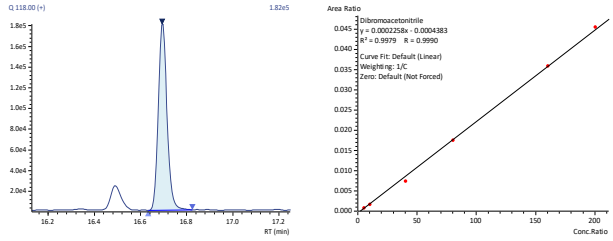
Trichloroacetonitrile



1,1,1-Trichloro-2-propanone

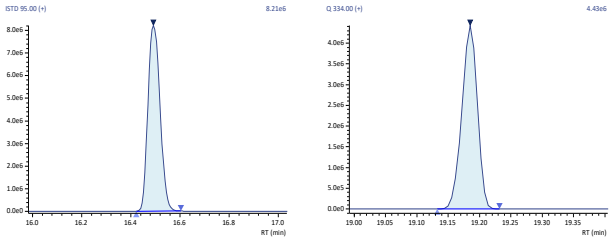


Chloral Hydrate



Dibromoacetonitrile

Fig. 3 Linearity and Chromatograms of 80 ppb std



p-Bromofluorobenzene (IS) Decafluorobiphenyl (SS)

Fig. 4 Chromatograms of IS and SS in 80 ppb std

4. Conclusion

- A highly sensitive GC/MS method was developed for 8 halogenated DBPs using Shimadzu GCMS-QP2020 NX following USEPA 551.1 sample preparation protocol.
- Excellent linearity results and recovery results at 5.0 ppb concentration for all the analytes demonstrate that the analytical workflow is suitable for analyzing the listed DBPs in tap water using GC/MS technique at a low concentration level.

5. References

1. EPA METHOD 551.1 : Determination of chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron-capture detection. https://www.epa.gov/sites/default/files/2015-06/documents/epa-551.1.pdf (accessed 28-10-2025)

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