

「Promising Solution_Application Note」

Analysis of Haloacetic Acids as Chlorination Disinfection Byproducts in Drinking Water by ChroZen GC/MS

• GC/MS Application



Abstract

Haloacetic Acids (HAAs) are major chlorination disinfection byproducts (DBPs) of drinking water, which can be formed when the chlorine reacts with organic matter in water. They may cause toxic effects to the nervous system and increase the development of liver-related tumors. Dichloroacetic Acids, as one of HAAs, are classified as carcinogens and have been strictly regulated in drinking water.

In this study, the analysis of haloacetic acids in drinking water was determined by a gas chromatograph-mass spectrometer referring to the standard method for drinking water_ES 05552. 1a [Analysis of haloacetic acids by GC/MS]

As a promising solution, one-fourth of the sample amount indicated in the standard method was used as well as the standards and reagents, which saves the time and cost of the overall analysis. The use of ChroZen GC/MS provides superior sensitivity in spite of use of a small amount of sample while assuring the goal value of quality control.



Fig 1. PAL-ChroZen

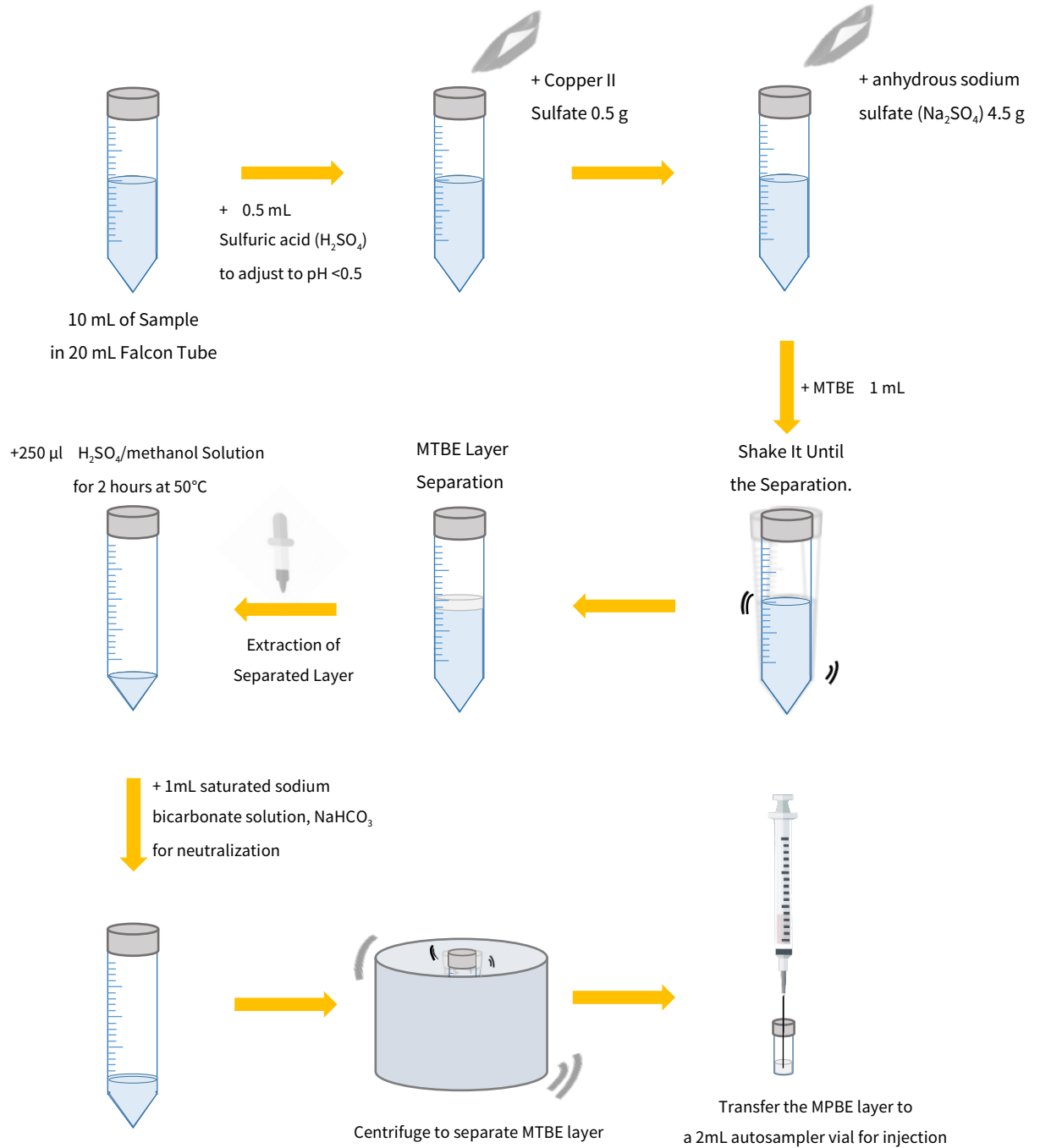
Instruments and Software

· ChroZen GC/MS System

Item	Description	Part No.
Oven	ChroZen GC Mainframe Assembly for Mass Spectrometer	6701012500
Inlet	Capillary Inlet Assembly for ChroZen GC	6701012550
Detector	ChroZen MS for ChroZen GC incl. built-in turbomolecular pump - Single Quadropole - EI source (UEIS: Ultimated Efficiency Ion Source) - Turbo pump(240 L/sec) - Include fore pump and spares kit - Higher Sensitivity (S/N for OFN 2500:1)	6901012110
Autosampler	ChroZen PAL LSI system for liquid injection	6501011590
	Mounting Kit for ChroZen GC	PAL3-Kit-YI6700
CDS	YL-Clarity software for single instrument of YL GC	5301011020
	MS module of YL-Clarity	5301011180
	Autosampler control of YL-Clarity	5301011040
	Library(NIST/EPA/NIH 2020 edition)-350,643 spectra	9781119750291
Column	DB-5 (30m, 0.2 mm, 0.33 μ m)	-
ACC	Start-up kit (Installation kit)	1601011110
	Big Universal Trap, 1/8" fttgs, Helium	RMSH-2
	ChroZen PAL System Vial 2CV, 1.5ml Clear Glass with Label, designed for the YL PAL Autosampler. 12x32mm, 1st Class Hydrolytic Glass, fits ND9 Screw Caps, Pk of 100 Pcs	Vial-1.5-ND9-CG-100
	ChroZen PAL System Screw Cap 2CV, designed for the YL PAL Autosampler. ND9, Magnetic, Gold, Silicone/PTFE Septa 1.0mm, Pk of 100 pcs	Cap-ND9-St-SP10-100

Water Samples Preparation

Promising Solution



Consumption of Sample, Reagent, Standard



Productivity



Methods of Analysis

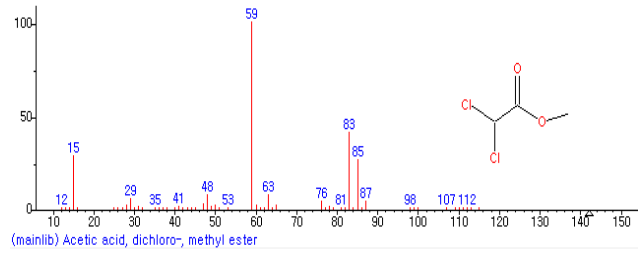
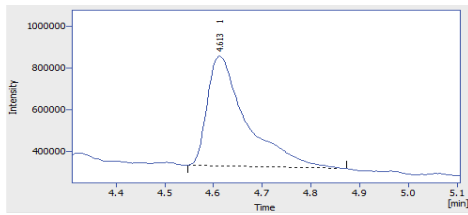
Table 2. GC/MS conditions

GC conditions	MS conditions
Column: DB-5 (30 m x 0.2 mm i.d. x 0.33 μ m)	Ion source 230°C, Transfer Line 280°C Detection: SIM mode
Inlet: 1 mL/min, split ratio: 1/10, 250°C	
Oven temperature program: 40°C, 6min, 5°C/min to 100°C, 30°C/min to 280°C, 3min	

Table 3. GC/MS chromatographic conditions

	Compound	Molecular Weight	Selected ions, m/z
1	Acetic acid, dichloro-, methyl ester	142	59, 83, 85
2	Acetic acid, trichloro-, methyl ester	176	59, 117, 119

1. Acetic acid, dichloro-, methyl ester



2. Acetic acid, trichloro-, methyl ester

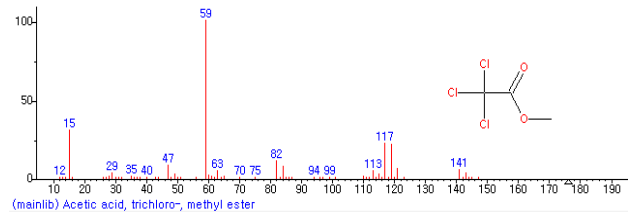
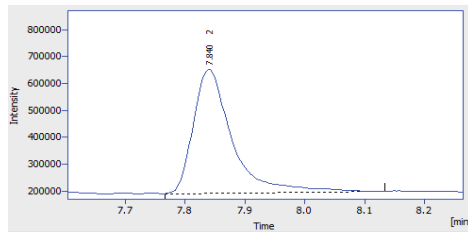


Fig 2. STD Chromatogram & Spectrum

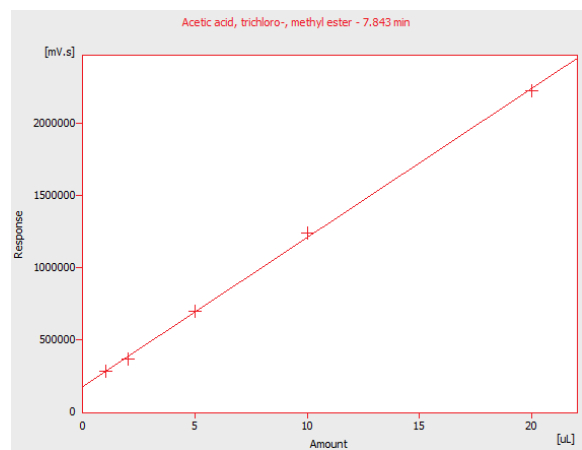
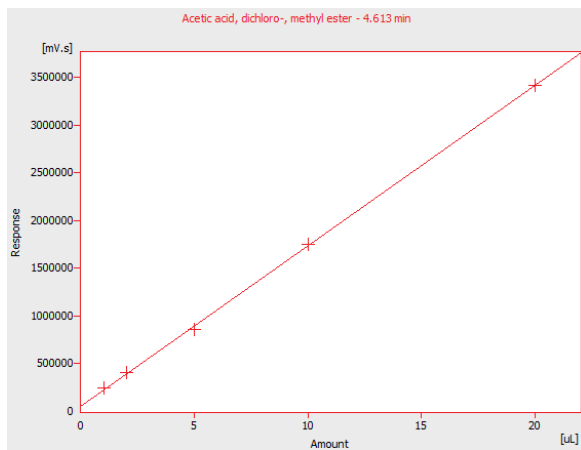


Fig 3. Calibration (1, 2, 5, 10, 20 ppb)

Result

Table 4. Accuracy and Precision of Haloacetic Acids

Analyte	Sample name	Resp.	Calc. Conc (ppb)	Accuracy (%)	Precision (%)
Acetic acid, dichloro-, methyl ester	QC-1	1713838.553	9.861	99.54	0.84
	QC-2	1747667.478	10.063		
	QC-3	1730120.909	9.958		
	QC-4	1725659.131	9.932		
Acetic acid, trichloro-, methyl ester	QC-1	1198210.956	9.903	99.36	1.04
	QC-2	1201670.344	9.937		
	QC-3	1215850.741	10.075		
	QC-4	1190298.591	9.827		

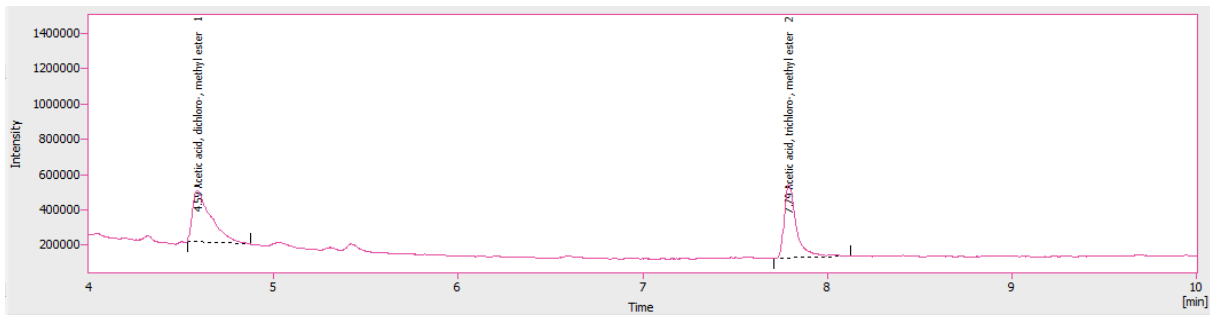
Table 5. MDL(Method Detection Limit) & LOQ(Limit of Quantitation) of Haloacetic Acids

Analyte	QC name	Data Conc.(ppb)	STDEV	MDL (ppb)	LOQ (ppb)
Acetic acid, dichloro-, methyl ester	MDL-1	4.872	0.0583	0.18	0.58
	MDL-2	4.949			
	MDL-3	5.048			
	MDL-4	4.933			
	MDL-5	5.018			
	MDL-6	4.993			
	MDL-7	4.979			
Acetic acid, trichloro-, methyl ester	MDL-1	4.832	0.0789	0.25	0.79
	MDL-2	4.993			
	MDL-3	5.036			
	MDL-4	4.930			
	MDL-5	4.979			
	MDL-6	4.830			
	MDL-7	4.918			

Table 6. Results for Sample Analysis

Sample name	Analyte	Calc. Conc (ppb)
A	Acetic acid, dichloro-, methyl ester	9.863
	Acetic acid, trichloro-, methyl ester	14.89
B	Acetic acid, dichloro-, methyl ester	18.072
	Acetic acid, trichloro-, methyl ester	22.485

Sample A



Sample B

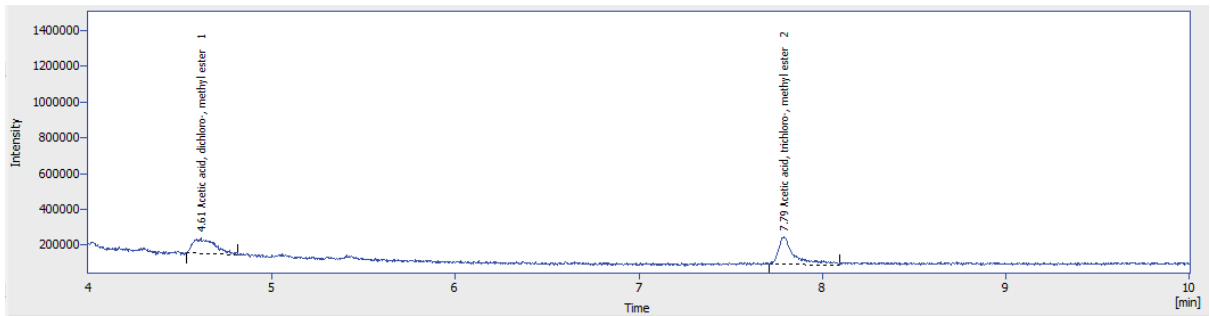


Fig 4. Chromatogram of Sample A & B

Conclusion

Analysis of haloacetic acids in drinking water was conducted by ChroZen GC/MS coupling with PAL system in reference to the Korean standard method for drinking water_ES 05552. 1a. The derivatization by methanol was confirmed by the MS spectrum. [Fig. 2]

The linearity, accuracy, and precision of all analytes were evaluated to verify the validity of analysis results. The accuracy was 99 % and the precision resulted within 2%, of which analytes recoveries meet between 75% and 125% for accuracy and within 25% for precision. [Table 4]

The method detection limit (MDL) and the limit of quantitation (LOQ) were calculated according to the standard method. The LOQ was calculated at 0.00058 mg/L for Dichloroacetic acids and 0.00079 mg/L for Trichloroacetic acids, which are lower than 0.001 mg/L indicated in the standard method. [Table 5]

Sample A and B were collected from tap water in 2 different places and derivatized by methanol. The success of derivatization was confirmed by the detection of Dichloroacetic acids and Trichloroacetic acids. [Fig 4][Table 6]

In this study, the reduction of sample amount

to one-fourth enables to save the sample preparation time and cost to enhance productivity.

As a result, ChroZen GC/MS with PAL system ensures that the data reliability of haloacetic acids analysis and the indicated promising solution for sample preparation works successfully.

Reference

- Standard method for drinking water_ES 05552. 1a [Analysis of Chlorine disinfection byproducts by GC/MS]
- EPA 552.2 Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatization and gas chromatography with electron-capture detection.



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