Determination of Haloacetic Acids in Water by GC/µECD Using Agilent J&W DB-35ms Ultra Inert and DB-XLB Columns

Application Note

Environmental, Water Quality

Authors

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Abstract

Haloacetic acids (HAAs) in water samples are effectively extracted and concentrated with Agilent's Bond Elut SAX solid phase extraction (SPE) sorbent. A dual column GC/µECD approach, using Agilent J&W DB-35ms Ultra Inert (UI) and DB-XLB columns, provided consistent and sensitive analysis for the derivatized HAAs. The detection limits for most of the HAAs were 0.05–0.5 ng/mL. Analyte recoveries at three fortification levels (0.2–2, 1–10, and 4–40 ng/mL) ranged from 82.5–116.5% with relative standard deviations (RSDs) < 3.5%.

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Introduction

The most widely used method for disinfecting water for public consumption is chlorination. During chlorination, oxidizing agents such as hypochlorite can react with any natural organic matter or bromide present in the raw water to form disinfection byproducts (DBPs). Many of these DBPs have been classified as possible human carcinogens and are regulated by the US Environmental Protection Agency (EPA) under the Stage 1 Disinfectants/Disinfection Byproducts Rule [1,2]. Haloacetic acids (HAAs) make up the second largest group of DBPs, after the trihalomethanes (THMs). The nine HAAs (HAA9) recommended for monitoring include monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and dibromochloroacetic acid (DBCAA). The first five acids are grouped and regulated as the sum HAA5, which has an established maximum contaminant level (MCL) of 60 ng/mL [3]. Although no current MCL has been set for the remaining acids, monitoring for all nine haloacetic acids (HAA9) is encouraged. EPA Method 552.3 is currently used for compliance monitoring of HAA9, along with the chlorinated herbicide dalapon in drinking water [4].

Due to their low volatility and polar nature, haloacetic acids must be converted to their methyl ester derivatives prior to GC analysis. The revised EPA Method 552.3 involves liquid-liquid extraction of the HAAs with MTBE, followed by esterification with acidic methanol. The resultant methyl esters are partitioned into the organic phase, the extract neutralized, and the upper ether layer removed for analysis by GC/µECD.

Although liquid-liquid extraction (LLE) is typically used for HAAs analysis, solid-phase extraction (SPE) offers several advantages, including high selectivity, high capacity, reduced solvent use, reduced preparation time, and reduced cost per analysis. Recent studies have shown successful utilization of SPE for HAAs extraction [5,6,7]. Because haloacetic acids are anionic at pH values above their pKa, a strong anion exchanger (SAX) can be used effectively to retain and preconcentrate these analytes. In this application note, a silica-based quaternary ammonium strong anion exchanger, Agilent's Bond Elut SAX, was used as the SPE sorbent.

Quantitative determination of the methylated HAAs was achieved by GC/µECD using a dual-column approach. Agilent's J&W DB-35ms Ultra Inert GC column was chosen for primary analysis of the methyl esters. Column and liner inertness were critical to achieving reproducible, reliable results, especially for the brominated trihaloacetic acids, which were particularly susceptible to interaction with active sites in the inlet or on the column. Confirmatory analysis was performed using an Agilent J&W DB-XLB column, which provided a complementary separation with a less polar stationary phase than the primary column, to help verify analyte identity.

Because incomplete esterification can occur for some of the haloacetic acids, a procedural standard technique is employed by EPA Method 552.3 to establish the calibration curves. This technique requires that the calibration standards be treated as samples and processed through the sample extraction and derivatization procedure prior to analysis. This method compensates for less than 100% conversion of the acids to the methyl esters.

Experimental

An Agilent 7890A GC system equipped with dual µECD detection and an Agilent 7683B autosampler was used for this study. An inert tee was used to split the effluent 1:1 to the primary and confirmation columns. Table 1 lists the chromatographic conditions used for these analyses. Table 2 lists flow path consumable supplies, and Table 3 lists the SPE sample preparation supplies used in these experiments.

Table 1. Chromatographic Conditions

GC/µECD	Agilent 7890A GC system
Sampler	Agilent 7683B, 5.0 µL tapered syringe (p/n G4513-80206)
CFT device	Inert Tee (p/n G3184-60065) Split Ratio 1:1
Retention gap	2 m × 0.25 mm id High Temp deactivated fused silica tubing (p/n 160-2845-10)
Inlet	1 µL splitless; 180 °C, Purge flow 60 mL/min at 0.15 min
Column 1	DB-35ms UI 30 m × 0.25 mm, 0.25 µm (p/n 122-3832UI)
Column 2	DB-XLB 30 m x 0.25 mm, 0.5 µm (p/n 122-1236)
Carrier	Helium, constant flow 3.2 mL/min at 40 °C
Oven	40 °C (0.5 min), 12 °C/min to 95 °C, 25 °C/min to 200 °C, 35 °C/min to 325 °C (1.25 min)
µECD	340 °C, Constant column + makeup (N_2) = 30 mL/min

Table 2. Flow Path Supplies

Vials and caps	MS- certified amber crimp top glass vials and caps kit (p/n 5190-2283)
Vial inserts	250 µL glass/polymer feet (p/n 5181-8872)
Syringe	5 µL tapered (p/n G4513-80206)
Septum	Advanced green (p/n 5183-4759)
Inlet liner	Helix double taper splitless deactivated liner (p/n 5188-5398)
Ferrules	0.4 mm id short; 85/15 Vespel/graphite (p/n 5181-3323)
CFT fittings	Internal nut (p/n G2855-20530)
CFT ferrules	SilTite ferrules, 0.25 mm id (p/n 5188-5361)
20x magnifier	20x Magnifier loop (p/n 430-1020)

Table 3. SPE Sample Prep Supplies

SPE cartridge	Agilent Bond Elut SAX, 500 mg, 6 mL (p/n 12102144)
SPE adapter	3 and 6 mL adapters (p/n 12131001)
SPE reservoirs	60 mL capacity (p/n 12131012)

Reagents and chemicals

All reagents and solvents were ACS or Ultra Resi grade. Methanol, MTBE, and sodium sulfate from JT Baker were purchased through VWR International (West Chester, PA, USA). Sulfuric acid was bought from Sigma-Aldrich, sodium bicarbonate from Fisher Scientific (Fair Lawn, NJ), and ammonium chloride from Mallinckrodt (Phillipsburg, NJ). The haloacetic acids and their methyl esters, surrogate, and internal standards were purchased from Ultra Scientific (West Chester, PA, USA). The individual analyte concentrations are listed in Table 4.

Table 4. Individual Analyte Concentrations of the Commercially Prepared HAAs Stock Solution and the Primary Dilution Standard

Haloacetic Acid Standards

Analyte	Commercial stock std µg/mL	Primary dilution std µg/mL
chloroacetic acid (MCAA)	600.5	3.0
dichloroacetic acid (DCAA)	600.0	3.0
trichloroacetic acid (TCAA)	201.0	1.0
bromoacetic acid (MBAA)	400.2	2.0
dibromoacetic acid (DBAA)	201.0	1.0
tribromoacetic acid (TBAA)	2002	10.0
bromochloroacetic acid (BCAA)	402.0	2.0
bromodichloroacetic acid (BDCAA)	400.0	2.0

Solutions and Standards

An aqueous ammonium chloride solution was prepared at a 10 mg/mL concentration. This solution was added to the sample during collection to convert residual disinfectants such as hypochlorite present in the matrix to chloramines, to minimize additional DBP formation.

The analyte primary dilution standard was prepared by diluting the commercially prepared haloacetic acid stock solution with MTBE to yield the analytes at a varied concentration of 1–10 µg/mL. This solution was used to fortify reagent water for calibration and recovery standards. A surrogate standard, 2-bromobutanoic acid, was prepared at concentrations of 1 and 20 µg/mL in MTBE and added to the samples prior to extraction. An MTBE extraction solvent containing 1,2,3-trichloropropane as an internal standard was prepared by dilution in MTBE to yield a final concentration of 500 ng/mL internal standard. This solution was used to extract the samples.

A 10% acidic methanol solution was prepared by adding 10 mL sulfuric acid dropwise to a 100 mL volumetric flask containing approximately 60 mL MeOH in a cooling bath. The solution was allowed to reach room temperature, then diluted to volume with MeOH and mixed thoroughly.

An aqueous sodium sulfate solution was prepared at a concentration of 150 g/L. A saturated sodium bicarbonate solution was prepared by addition of sodium bicarbonate to a volume of water until a small amount of undissolved bicarbonate remained despite further mixing.

The HAAs primary dilution standard and surrogate standard spiking solutions were used to prepare the calibration curves in the reagent water by appropriate dilution.

Sample Preparation

A 50 mL water sample was extracted using SPE, esterified with acidic methanol, and the resultant methyl esters extracted into MTBE for GC analysis. Figure 1 illustrates the SPE sample preparation and esterification procedure graphically.

A 50 mL aliquot of water was collected and 0.5 mL of 10 mg/mL aqueous ammonium chloride was added to convert any residual free chlorine to chloramines. The pH of the sample was adjusted to a pH of 5 ± 0.5 with sulfuric acid as necessary. Quality control samples were spiked with appropriate amounts of spiking solutions to yield QC samples with varied analyte concentrations of 0.2–2, 1–10, and 4–40 ng/mL.

After assembling the vacuum manifold system, the Agilent Bond Elut SAX SPE cartridges were attached and conditioned by slowly drawing through 10 mL MeOH, followed by 10 mL reagent water. After conditioning, adapters and reservoirs were attached to the cartridges and the 50 mL sample was

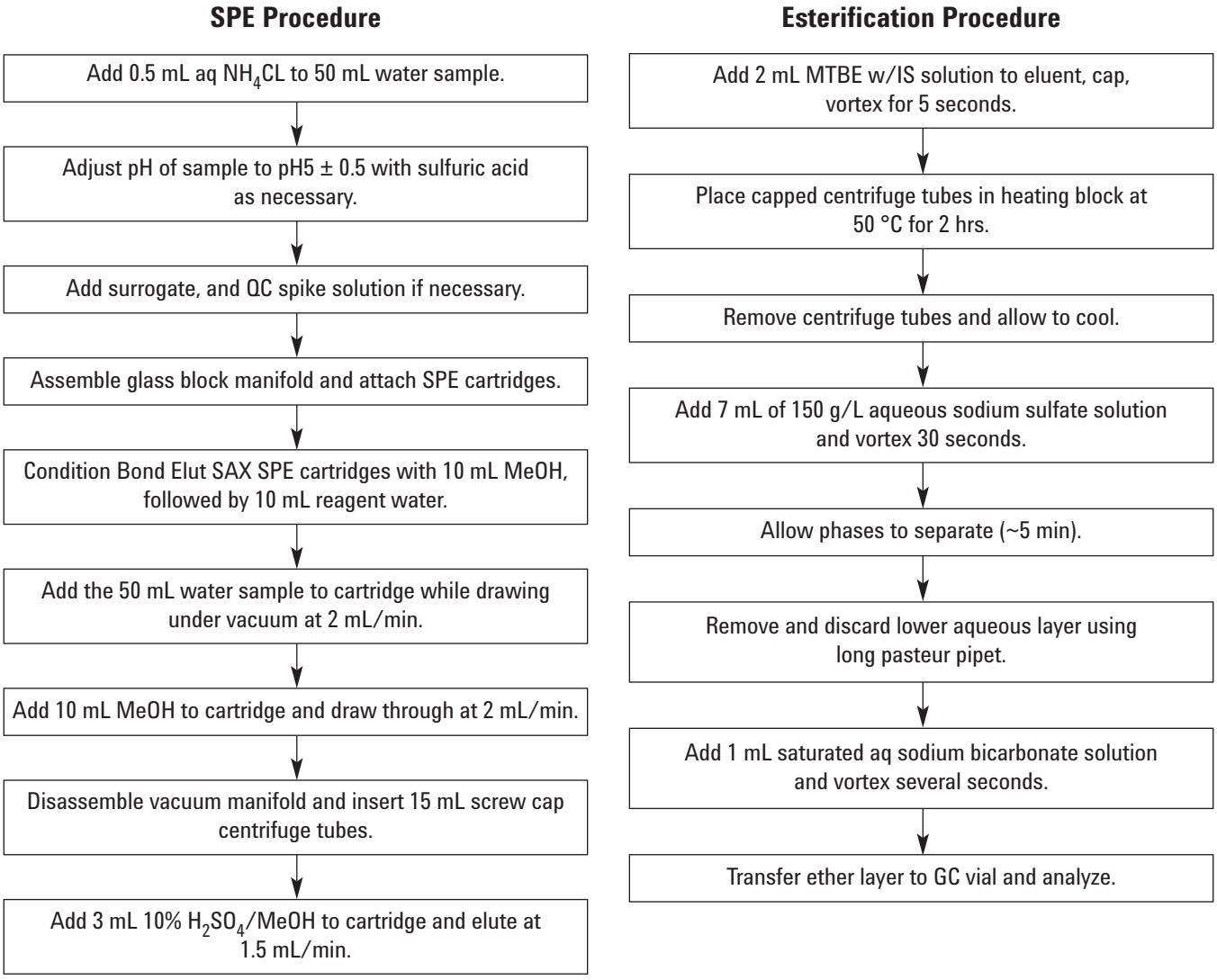

Figure 1. Flow chart for SPE sample preparation and derivatization for haloacetic acids in water.

transferred and extracted under vacuum at a rate of 2 mL/min. Once the sample was extracted, 10 mL of MeOH was added to the cartridge and passed through to remove interferences. The vacuum manifold was then disassembled, and 15 mL screw top conical centrifuge tubes inserted to collect the eluent. A 3 mL aliquot of 10% H_2SO_4/MeOH solution was added to the cartridge to elute the HAAs at a rate of 1.5 mL/min.

The centrifuge tubes were removed and 2 mL of the MTBE extraction solvent was added to the acidic methanol eluent. The capped tubes were vortexed and placed in a heating block at 50 °C (± 2 °C) for two hours for methylation of the analytes.

After the derivatization, the centrifuge tubes were removed and allowed to cool.

Once cool, 7 mL of 150 g/L sodium sulfate solution was added, and the tube vortexed for several seconds. The phases were allowed to separate and the bottom aqueous layer was removed and discarded. The MTBE phase was then neutralized by adding 1 mL of saturated sodium bicarbonate solution and vortexing.

The ether extract was then analyzed by GC/μECD using the chromatographic conditions in Table 1.

Results and Discussion

The targeted dalapon and haloacetic acid methyl esters were resolved on the DB-35ms UI primary analysis column and DB-XLB confirmation column in less than nine minutes. The chromatogram of the haloacetic acid methyl esters standard shown in Figure 2 exhibits good peak shape and separation of the esters, with one coelution found on each column. The coeluting peaks are baseline resolved on the counterpart column, allowing confirmation of their presence and interference-free quantitation.

A six point calibration curve was produced using a procedural calibration technique as per EPA Method 552.3. Reagent water standards fortified with varying amounts of the acids over the targeted concentration range were treated as samples and processed through the sample extraction and derivatization procedure prior to analysis. The six standard solutions were prepared from 0.1–1 ng/mL to 5–50 ng/mL of varied analyte concentrations, then extracted and derivatized following the method procedure in Figure 1, and analyzed by GC/μECD.

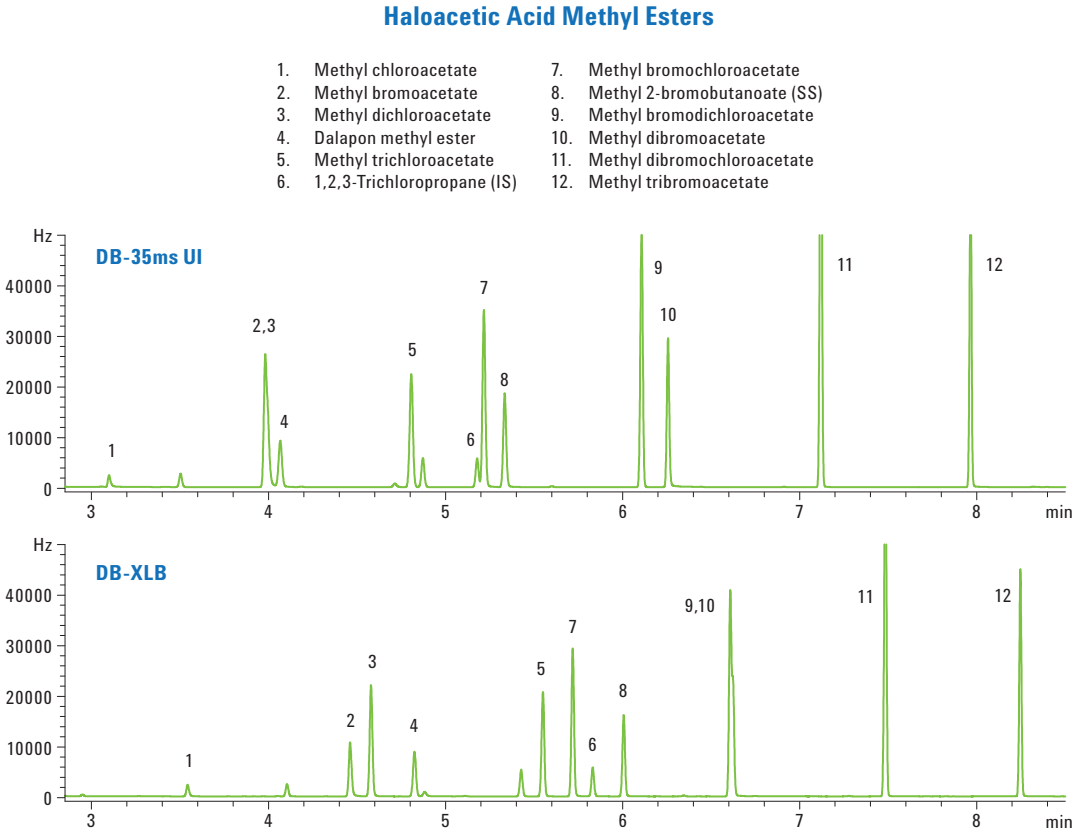

Figure 2. GC/μECD chromatogram of esterified haloacetic acids analyzed on an Agilent J&W DB-35ms UI 30 m × 0.25 mm, 0.25 μm column (p/n 122-3832UI) and DB-XLB 30 m × 0.25 mm, 0.5 μm column (p/n 122-1236). This standard was prepared by the method standard preparation and derivatization listed in Figure 1. Chromatographic conditions are listed in Table 1.

Linearity as defined by the correlation coefficient (R^2) of the calibration curve can be used to evaluate the performance of a gas chromatographic column. Brominated trihaloacetic acid methyl esters tend to be unstable and can undergo degradation by debromination, hydrolysis, and decarboxylation, making them chromatographically challenging. A nonlinear response can be indicative of breakdown or adsorption of the compound in the inlet or column. The performance of the DB-35ms UI and DB-XLB columns yielded excellent linearity with $R^2 \geq 0.998$ over the calibration range of this study. The individual haloacetic acid methyl ester analyte values are shown in Table 5.

The method was able to detect the methylated HAAs with a high level of sensitivity at trace levels. Figure 3 depicts the excellent peak response of an extracted and derivatized 0.05–0.5 ng/mL fortified reagent water sample on the DB-35ms UI and DB-XLB columns. The observed levels are at or below the recommended levels reported in EPA Method 552.3.

Table 5. Correlation Coefficients for the Derivatized HAA Calibration Standards Analyzed by GC/µECD

Excellent Linearity of Methylated HAAs with Agilent's J&W DB-35ms UI and DB-XLB columns

	R^2 Values	
Compound	**DB-35ms UI**	**DB-XLB**
Methyl chloroacetate	0.9993	0.9990
Methyl bromoacetate	*	0.9998
Methyl dichloroacetate	*	1.0000
Dalapon methyl ester	1.0000	1.0000
Methyl trichloroacetate	0.9997	0.9999
Methyl bromochloroacetate	1.0000	1.0000
Methyl bromodichloroacetate	0.9985	**
Methyl dibromoacetate	1.0000	**
Methyl dibromochloroacetate	0.9982	0.9992
Methyl tribromoacetate	0.9994	0.9996
Methyl 2-bromobutanoate (SS)	0.9997	0.9995

*Coelute on DB-35ms UI
**Coelute on DB-XLB

Trace Level Methylated HAAs Standard

1. Methyl chloroacetate
2. Methyl bromoacetate
3. Methyl dichloroacetate
4. Dalapon methyl ester
5. Methyl trichloroacetate
6. 1,2,3-Trichloropropane (IS)
7. Methyl bromochloroacetate
8. Methyl 2-bromobutanoate (SS)
9. Methyl bromodichloroacetate
10. Methyl dibromoacetate
11. Methyl dibromochloroacetate
12. Methyl tribromoacetate

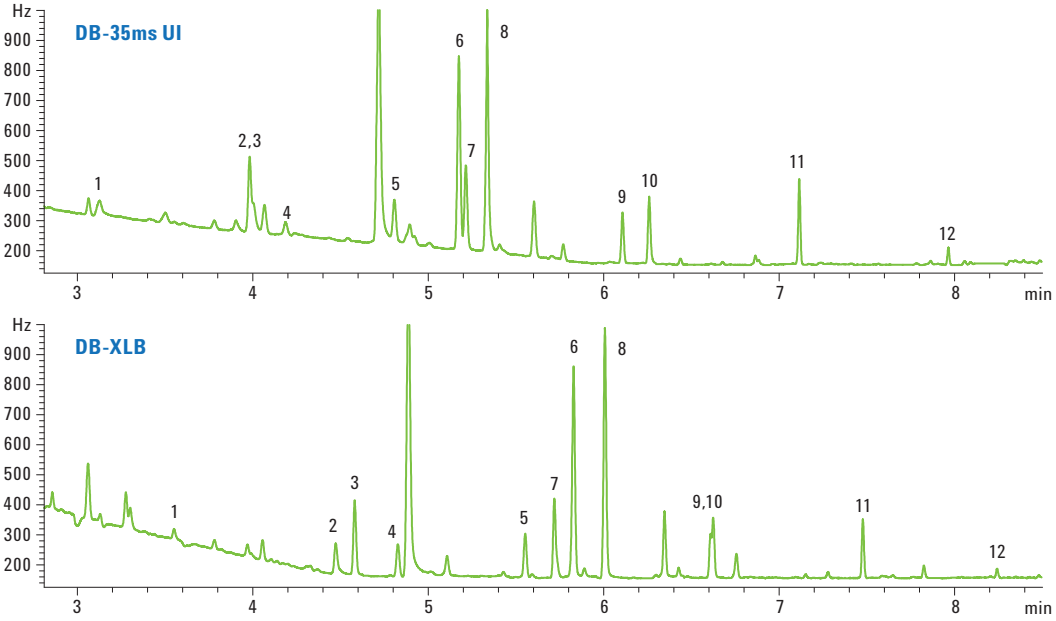

Figure 3. Enlarged section of the GC/µECD chromatogram of a 0.05-0.5 ng/mL esterified haloacetic acids standard analyzed on an Agilent J&W DB-35ms UI 30 m × 0.25 mm, 0.25 µm column and DB-XLB 30 m × 0.25 mm, 0.5 µm column. Internal standard is at a 50 ng/mL level for better illustration. The chromatographic conditions are listed in Table 1.

Sample preparation using Agilent Bond Elut SAX SPE was effective in retaining and preconcentrating the haloacetic acids in the spiked water samples. This allowed for a lower level of detection while maintaining a small sample volume. The pH of the water sample was adjusted with sulfuric acid as necessary to a pH 5 ± 0.5, to ensure ionization of the haloacetic acids. Figure 4 shows a reagent water sample which was fortified with the haloacetic acids and prepared using the method sample preparation and derivatizing procedure.

The accuracy of the method was demonstrated by determination of percent recovery at a known level of spiking. Recoveries were conducted at 1x, 5x, and 20x spike levels. The recoveries of the acids were greater than 82% with RSDs below 3.5%. Recoveries for the individual HAAs are listed in Table 6. These results indicate effective extraction of HAAs with SPE and consistent quantitative analysis by GC/μECD.

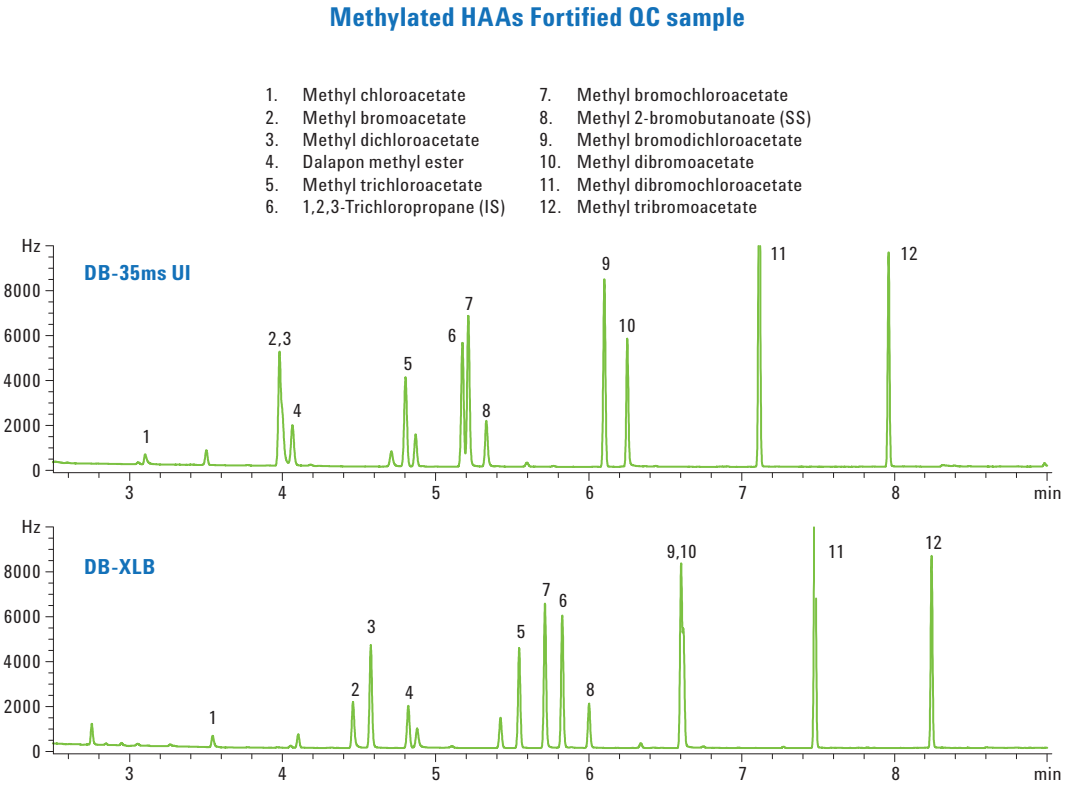

Figure 4. GC/μECD chromatograms of a 1–10 ng/mL fortified reagent water sample prepared according to method procedure and analyzed on an Agilent J&W DB-35ms UI (p/n 122-3832UI) and DB-XLB (p/n 122-1236) capillary GC columns. Chromatographic conditions are listed in Table 1.

Table 5. Recovery and Repeatability of Haloacetic Acids in Fortified Reagent Water Using Agilent's Bond Elut SAX SPE for Extraction and J&W DB-35ms UI (p/n 122-3832UI) and DB-XLB (p/n 122-1236) GC Columns for Quantitative Analysis

Recovery and Repeatability of Haloacetic Acids on DB-35ms UI column

	Spike	1 x Spike fortified QC		5 x Spike fortified QC		20 x Spike fortified QC	
Analytes	**ng/mL**	**% Recovery**	**RSD (n=6)**	**% Recovery**	**RSD (n=6)**	**% Recovery**	**RSD (n=6)**
Methyl chloroacetate	0.60	108.8	1.8	102.4	0.6	95.8	0.7
Methyl bromoacetate/Methyl dichloroacetate*	1.00	98.2	1.6	98.2	0.7	95.9	0.6
Dalapon methyl ester	0.40	95.5	2.1	99.4	0.9	96.1	0.7
Methyl trichloroacetate	0.20	96.7	1.7	88.4	2.0	92.2	1.4
Methyl bromochloroacetate	0.40	91.9	2.6	95.0	1.8	93.4	1.3
Methyl bromodichloroacetate	0.40	113.0	1.1	88.9	1.7	93.9	1.8
Methyl dibromoacetate	0.20	82.5	3.4	92.1	2.3	93.6	1.6
Methyl dibromochloroacetate	1.00	116.5	1.0	89.5	1.7	94.3	1.9
Methyl tribromoacetate	2.00	101.4	2.1	84.6	2.1	90.4	2.2
Methyl 2-bromobutanoate (SS)	0.50	104.4	2.5	105.5	1.2	106.9	0.7

Recovery and Repeatability of Haloacetic Acids on DB-XLB column

	Spike	1 x Spike fortified QC		5 x Spike fortified QC		20 x Spike fortified QC	
Analytes	**ng/mL**	**% Recovery**	**RSD (n=6)**	**% Recovery**	**RSD (n=6)**	**% Recovery**	**RSD (n=6)**
Methyl chloroacetate	0.60	83.5	2.8	98.9	0.7	91.9	0.8
Methyl bromoacetate	0.40	85.2	0.8	92.7	0.4	88.5	0.7
Methyl dichloroacetate	0.60	94.2	1.0	98.9	0.3	94.9	0.5
Dalapon methyl ester	0.40	95.3	0.4	99.6	0.2	96.2	0.4
Methyl trichloroacetate	0.20	106.1	0.8	100.8	0.5	99.7	0.6
Methyl bromochloroacetate	0.40	103.8	1.1	107.8	0.9	102.7	1.2
Methyl bromodichloroacetate/Methyl dibromoacetate*	0.60	109.2	1.0	104.0	0.8	102.8	1.2
Methyl dibromochloroacetate	1.00	116.2	1.0	101.0	0.9	102.8	1.2
Methyl tribromoacetate	2.00	107.2	2.0	95.9	1.2	98.7	1.6
Methyl 2-bromobutanoate (SS)	0.50	109.5	0.7	108.6	0.5	108.3	0.9

*Coelute; % Recovery is based on sum of both analytes

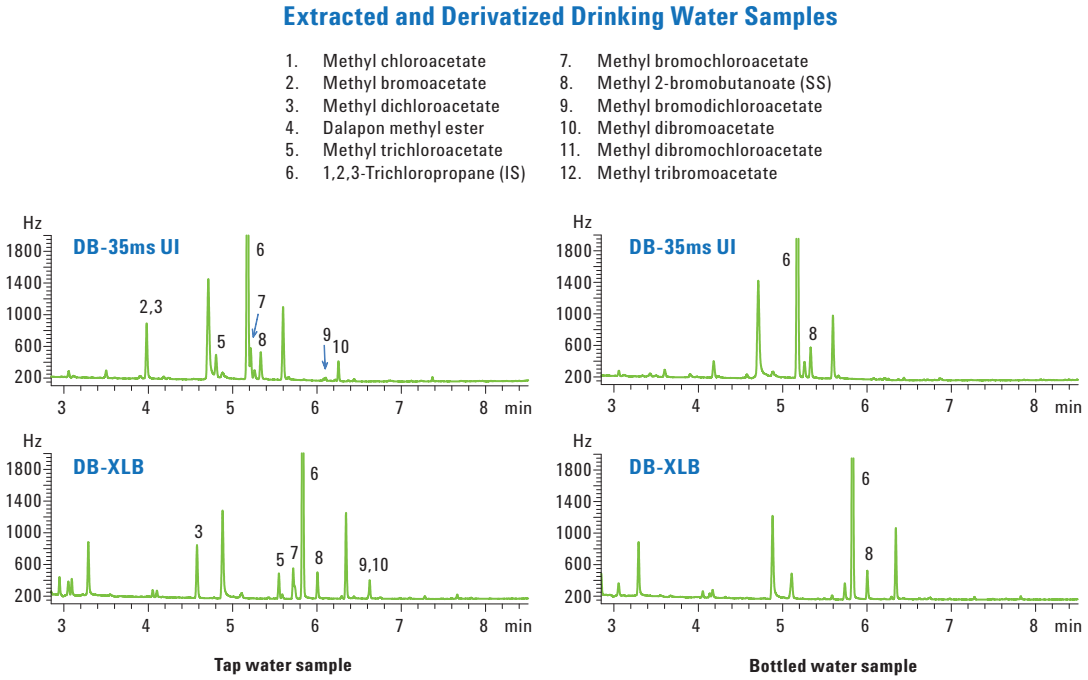

Figure 5. GC/μECD chromatograms for two water samples prepared according to method procedure and analyzed using Agilent's J&W DB-35ms UI (p/n 122-3832UI) and DB-XLB (p/n 122-1236) GC columns. Chromatographic conditions are listed in Table 1.

Two drinking water samples were analyzed for HAAs using this method. A tap water and bottled spring water sample were collected and prepared according to the sample preparation and derivatization steps shown in Figure 1. DCAA (peak 3) was detected in the tap water sample at 0.3 ng/mL. Four other HAAs (TCAA, BCAA, BDCAA, and DBAA) were detected in the tap water sample, but were below the calibrated range of this study. No HAAs were detected in the bottled spring water. Chromatograms for the two samples shown in Figure 5.

Conclusion

This application note successfully demonstrates a quick and efficient analytical method to monitor low and trace level haloacetic acids in water samples. Agilent J&W DB-35ms UI and DB-XLB capillary columns adequately resolve the targeted HAA methyl esters and provide excellent sensitivity, yielding reliable quantitation at low levels. Levels were detectable well below the EPA maximum contaminant levels (MCLs) for HAAs in water. Calibration standards yielded regression coefficients $R^2 \geq 0.998$ and recoveries of fortification studies were 82.5% to 116.5% with an average RSD < 3.5%, further demonstrating the effectiveness of using J&W DB-35ms UI and DB-XLB columns for low level haloacetic acids.

Agilent Bond Elut SAX SPE sorbent successfully extracts and preconcentrates haloacetic acids from water samples, allowing for improved trace level analyte detection. The SPE method offers a reliable alternative to LLE with the advantage of fast and easy sample preparation, reduced solvent use, and reduced cost.

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