

# Determination of Haloacetic Acids in Water by GC/μECD and Strong Anion Exchange SPE

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## Introduction

- 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 EPA under the Stage 1 Disinfectants/ Disinfection Byproducts Rule [1]
- Haloacetic acids (HAAs) make up the second largest group of DBPs, after the trihalomethanes (THMs)
- The nine HAA (HAA9) recommended for monitoring include monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (BBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and dibromochloroacetic acid (DBCAA)

### Current EPA Method 552.3

- Current method uses LLE to extract analytes from water
- Haloacetic acids (HAAs) must be converted to their methyl ester derivatives prior to GC analysis
- Lower recoveries typically seen for brominated trihaloacetic acids
  - Suspected Factors
    - Low methylation efficiencies for the brominated trihaloacetic acids, attributed to steric hindrance of the SN<sub>2</sub> intermediate during esterification [2]
    - Hydrolysis/ decarboxylation of trihaloacetic acids methyl esters to haloforms [3]

### Application Development for Determination of Haloacetic Acids in Water by GC/μECD

- DB-35ms UI and DB-XLB columns used for analyte separation
  - Dual column analysis allows primary and confirmatory analysis from a single injection
- Bond Elut® SPE used for extraction and pre-concentration of analytes
  - SPE offers advantages over LLE including selectivity and reduced solvent use
  - Haloacetic acids are anionic at pH values above their pKa, a strong anion exchanger (SAX) can be effectively used to retain and preconcentrate these analytes

## Experimental and Results

Table 1. Haloacetic Acid Standards Used in Application

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
Dibromochloroacetic acid (DBCAA)	1002	5.0
Dalapon	401.9	2.0

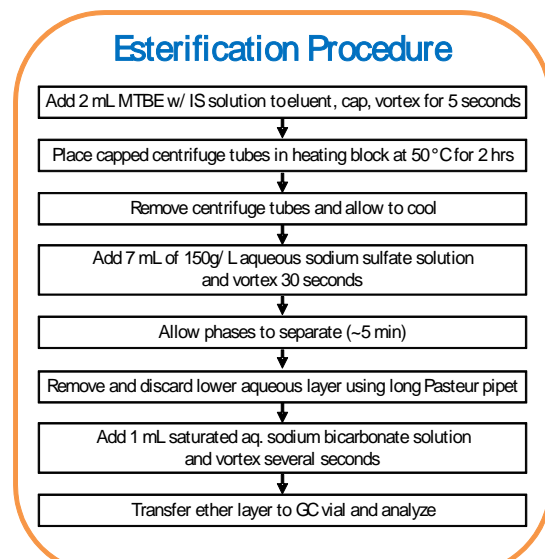
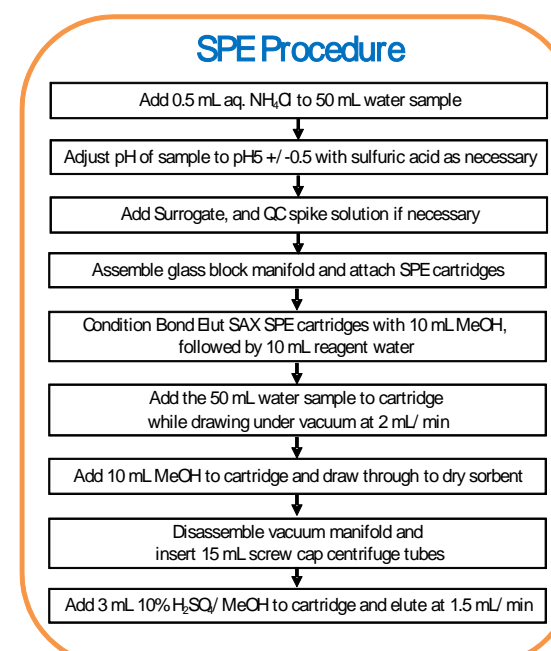


Figure 1. Sample Preparation Steps for Haloacetic Acids in Water

### Haloacetic Acids EPA Method 552.3

Chromatographic Conditions	
ID:	Agilent 7890A with dual μECD detection
Model:	Agilent 7890B
File:	2 mL (0.5 min) 100 Temp. 300.000000
DT:	100.000000
DT:	100.000000
Column 1:	DB-35ms UI, 30m (125mm x 0.25mm) (Agilent part # 122-38034)
Column 2:	DB-XLB, 30m (125mm x 0.25mm) (Agilent part # 122-1028)
Carrier:	Helium, constant flow 3.2 mL/min @ 40°C
Temp:	14.000000, 30.000000
Inlet:	Purge flow: 60 mL/min at 0.15 min
OVEN:	40.000000 min @ 120.000000 °C, 30.000000 min @ 120.000000 °C, 35.000000 min @ 120.000000 °C
Detector:	μECD
Detector:	Constant cell + make-up (N2) = 30 mL/min

Consumable Supplies	
Sample:	50 μL, septum Agilent part # G1813-80300
Method:	100.000000
Method:	100.000000
SPE:	500 mg, 6 mL, Agilent part # 121021446

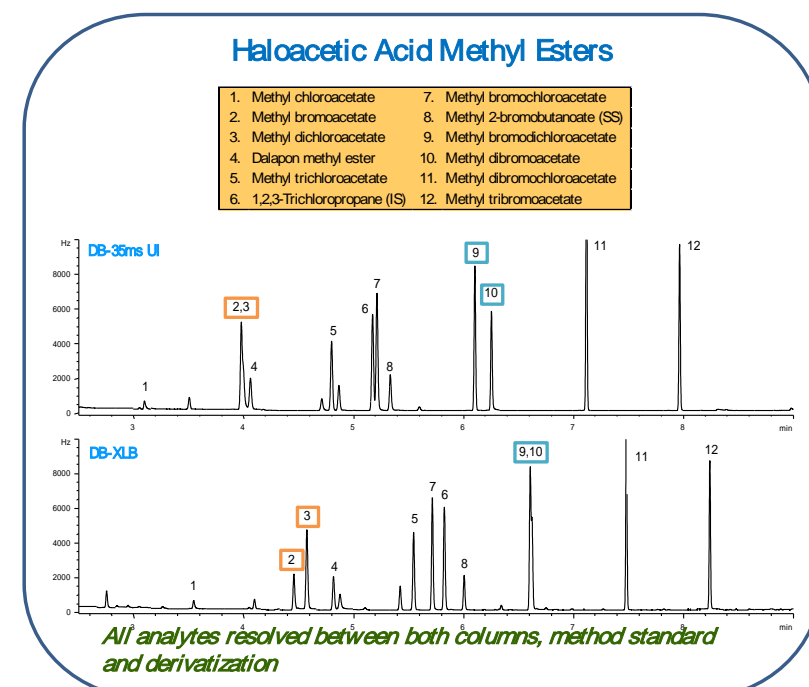


Figure 2. GC/μECD chromatogram for the haloacetic acids standard after derivatization; chromatographic conditions and sample preparation identified (left) employed for all experimentation

### Trace Level Methylated HAAs Standard

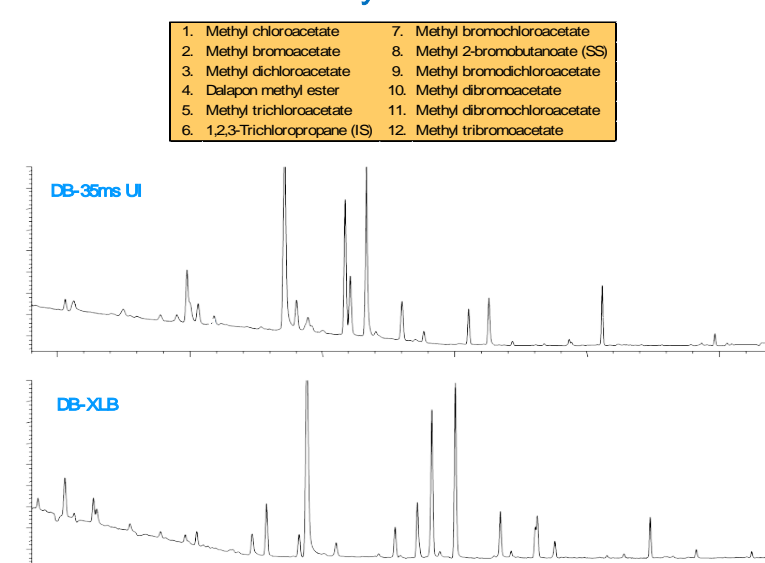


Figure 4. Enlarged section of the GC/μECD chromatogram of a 0.05-0.5 ng/mL esterified haloacetic acid standard

### Methylated HAAs Fortified QC sample

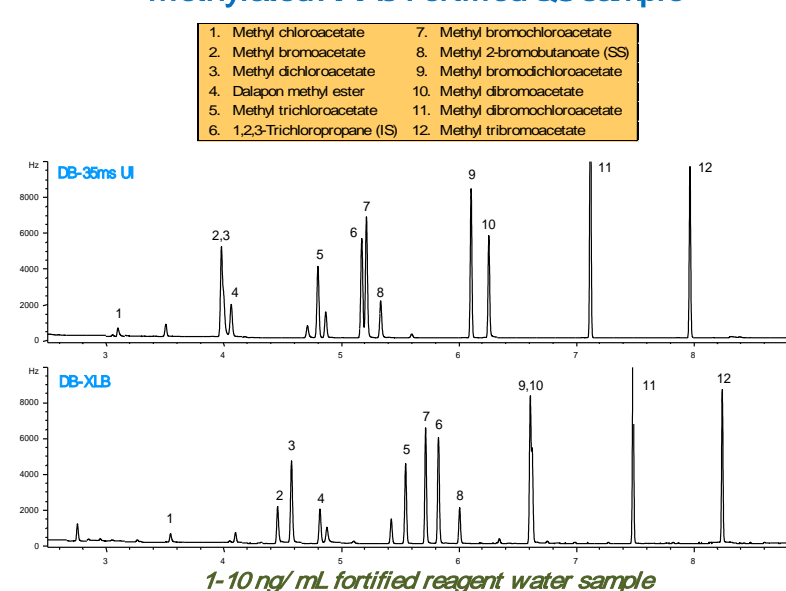


Figure 5. GC/μECD chromatogram fortified QC water sample

Table 2. Correlation Coefficients for the Derivatized HAA Standards Analyzed by GC/μECD

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



Table 3. Recovery and Repeatability of Haloacetic Acids in Fortified Reagent Water Using Bond Elut SAX SPE and GC/μECD

### Recovery and Repeatability

Evaluation of the Bond Elut SAX SPE method and analysis by GC/μECD of unknown water samples

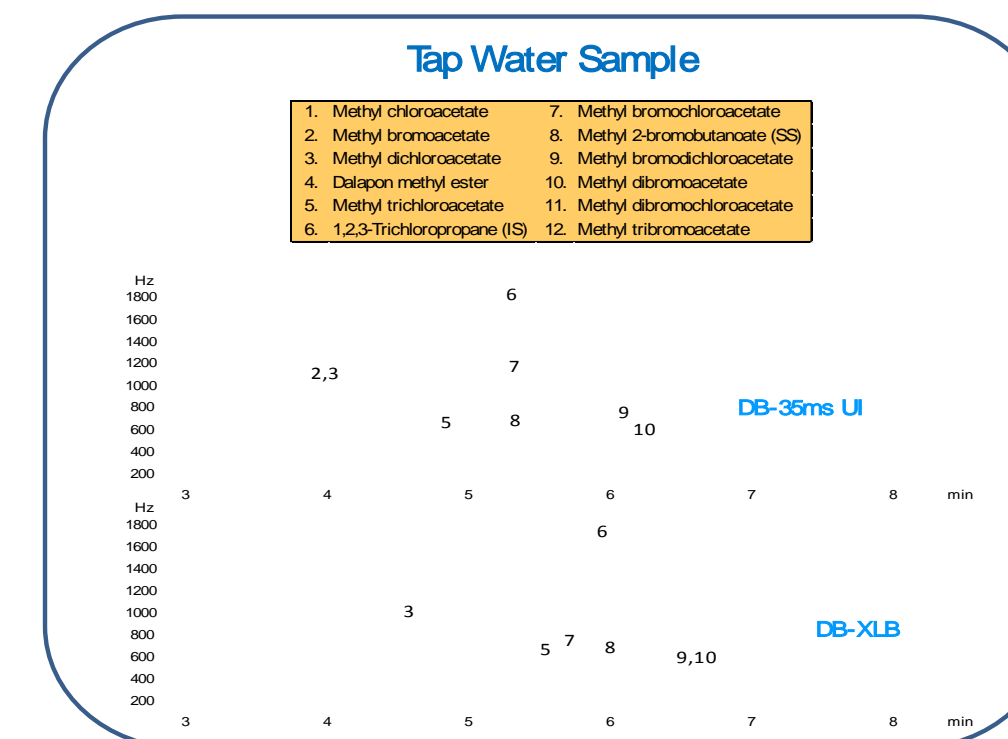


Figure 5. GC/μECD chromatogram for tap water sample

## Experimental and Results

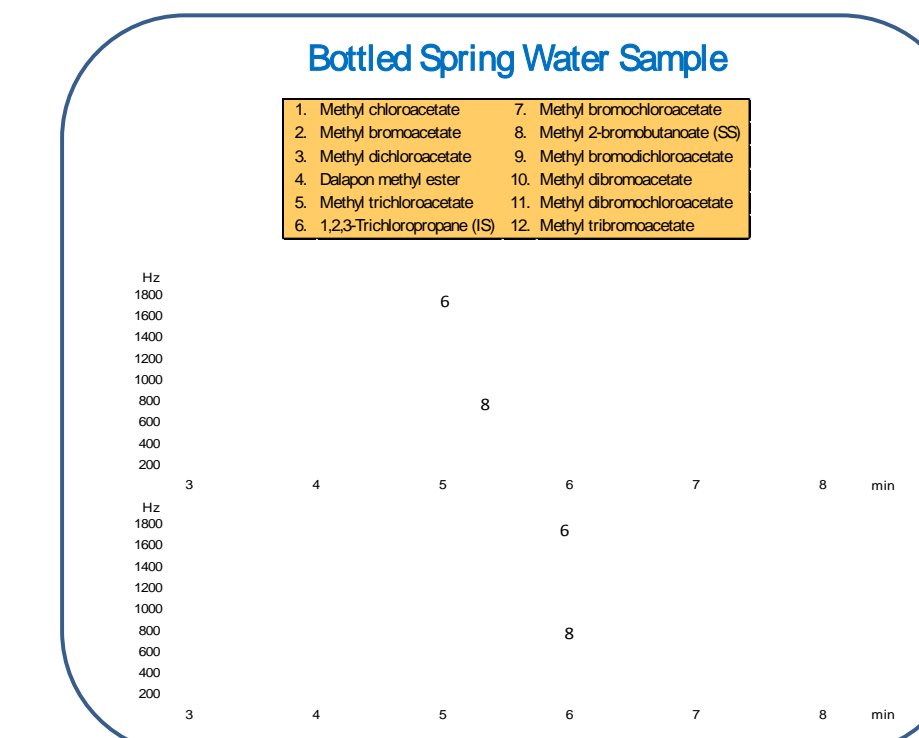


Figure 6. GC/μECD chromatogram of bottled water sample

## Conclusions

- Haloacetic acids (HAAs) in water samples are effectively extracted and concentrated with Agilent Bond Elut SAX SPE sorbent
- A dual column GC/μECD approach using an Agilent J&W DB-35ms Ultra Inert (UI) and DB-XLB 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%

## References

- U.S. EPA (U.S. Environmental Protection Agency), December 16, 1988a. National Primary Drinking Water Regulations. Disinfectants and Disinfection Byproducts. Final Rule. Fed Reg. 63:241:69406.
- M.M. Domino, B.V. Pepich, D.J. Munch, and P.S. Fair, *J. Chromatogr. A*, 1035 (2004) 9-16.
- E.T. Urbansky, *J. Environ. Monit.*, 2 (2000) 285-291.