



Application Note AN-M-015

# Trace haloacetic acids, dalapon, and bromate measurement in drinking water

## Robust analysis with IC-MS/MS according to US EPA 557

Chlorinating drinking water helps reduce pathogens, but it can also form potentially carcinogenic byproducts, e.g., haloacetic acids (HAAs), dalapon, and bromate [1,2]. The US Environmental Protection Agency (EPA) and the EU set a maximum contamination limit for the sum of five HAAs (HAA5: MCAA, MBAA, DCAA, DBAA, TCAA) of 60 parts per billion (60 µg/L) [3]. EPA Method 557 describes their quantification in the µg/L range in a wide variety of water types [4]. Here, the analysis is accomplished with a Metrohm ion chromatograph (IC) coupled to a

triple quadrupole Agilent mass spectrometer (MS). This sensitive method requires no sample extraction, and the Metrohm Suppressor Module eliminates any eluent interferences. Analytes are well-resolved from matrix components with the Metrosep A Supp 19 column. Matrix spike recoveries for 1 µg/L of all analytes were between 65–115% even in heavily loaded water samples. Minimum reporting levels (MRL) were 0.025–0.25 µg/L. The presented IC-MS/MS method fulfills all requirements of EPA Method 557.

## SAMPLE AND SAMPLE PREPARATION

Water samples included tap water (from eastern Switzerland) and mineral water (Evian containing  $c(\text{hydrogen carbonate}) = 360 \text{ mg/L}$ ,  $c(\text{sulfate}) = 14 \text{ mg/L}$ ,  $c(\text{chloride}) = 10 \text{ mg/L}$ , and  $c(\text{nitrate}) = 3.8 \text{ mg/L}$ ). Additionally, the laboratory synthetic sample matrix (LSSM) according to EPA 557 ( $c(\text{ammonium chloride}) = 100 \text{ mg/L}$ ,  $c(\text{nitrate}) = 20 \text{ mg/L}$ ,

$c(\text{hydrogen carbonate}) = 150 \text{ mg/L}$ ,  $c(\text{chloride}) = 250 \text{ mg/L}$ , and  $c(\text{sulfate}) = 250 \text{ mg/L}$ ) was analyzed. Samples were stabilized with 0.1% methanol (v/v) and cooled to 4 °C. Internal standards were added at a concentration of 4 µg/L (here: MCAA-<sup>13</sup>C and MBA-<sup>13</sup>C).

## EXPERIMENTAL

The hyphenation of HPLC with mass spectrometry has commonly focused on the study of organic molecules. Hyphenating ion chromatography (IC) with mass spectrometry (MS) opens up the field to highly sensitive analysis of ionic and more polar substances in aqueous solutions or salt-containing matrices. Using the 889 IC Sample Center – cool guarantees stable and reproducible sample processing at 4 °C (Figure 1) by preventing the decay of the degradation-sensitive HAAs.



**Figure 1.** Instrumental setup to measure haloacetic acids, dalapon, and bromate including an 889 IC Sample Center – cool (Metrohm), 940 Professional IC Vario (Metrohm), and 6475 Triple Quadrupole LC/MS with Jet Stream Technology Ion Source (Agilent). A Dosino was used for direct infusion to the MS during method optimization.

## EXPERIMENTAL

The metal-free microbore ion chromatograph 940 Professional IC Vario with a Metrosep A Supp 19 column, sequential suppression, and an IC Conductivity Detector MB accomplished chromatographic separation without any interferences and a reduced void volume. Sensitive and selective detection of haloacetic acids was carried out with an Agilent 6475 Triple Quadrupole LC/MS equipped with an Agilent Jet Stream Technology Ion Source, operated in dynamic multiple reaction monitoring (dMRM) acquisition mode. Conductivity detection can be used to quantify common anions like fluoride, chloride, nitrate, or sulfate in parallel. An additional Dosino enables direct infusion of standard solutions to the MS for method optimization, i.e., finding the best MS parameters to detect the analytes of interest.

The 948 Continuous IC Module, CEP precisely produces a potassium hydroxide eluent in concentrations from 15–100 mmol/L potassium hydroxide (KOH) (Figure 2). The IC was operated with the software MagIC Net, and the MS by MassHunter software. Synchronization of both instruments was controlled via a remote cable. Table 1 lists the most important instrument settings.



**Figure 2.** The 948 Continuous IC Module, CEP automatically produces KOH eluent from ultrapure water and a KOH concentrate. The electrochemical eluent production takes place at a membrane in the eluent producer cartridge.

**Table 1.** This table lists the most important method parameters for haloacetic acid determination with IC-MS/MS.

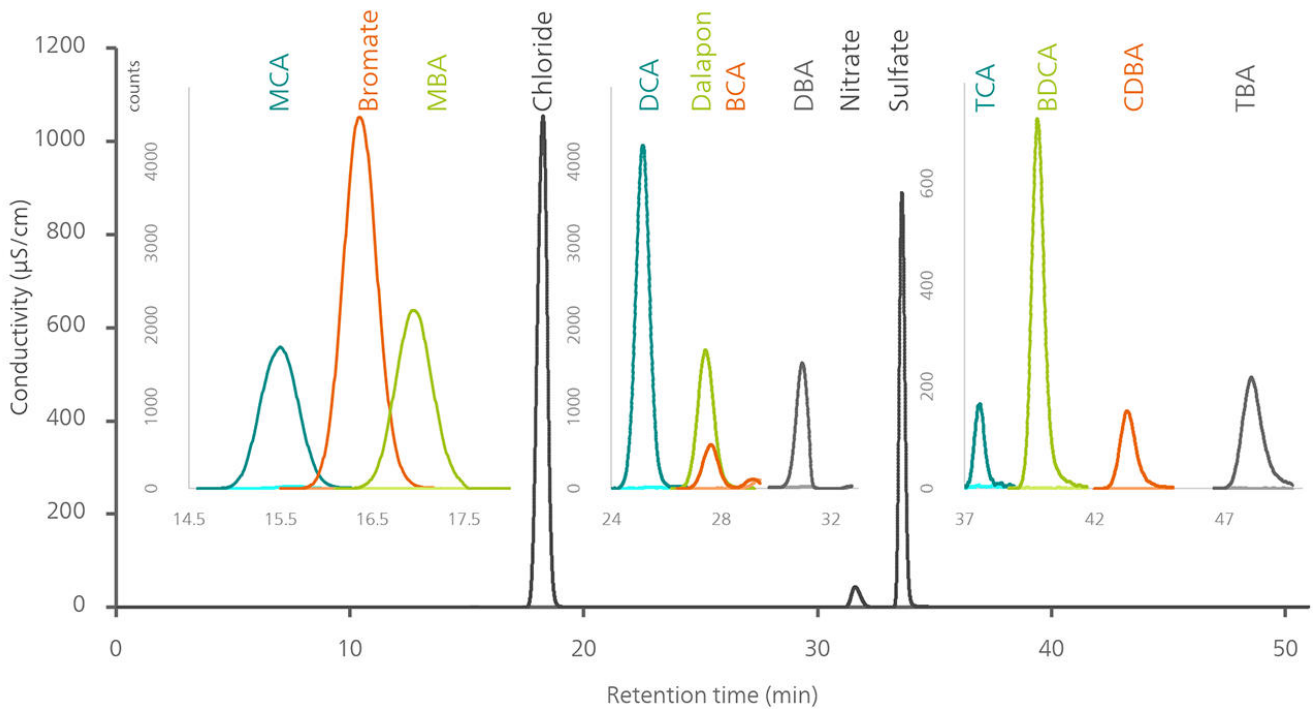
| IC Column              | Metrosep A Supp 19 - 150/4.0                |
|------------------------|---|
| Eluent/gradient        | 15–100 mmol/L KOH + 10% methanol            |
| Flow rate              | 0.5 mL/min                                  |
| Column temperature     | 15 °C                                       |
| Injection volume       | 100 µL                                      |
| Suppression            | sequential                                  |
| Ion polarity           | negative                                    |
| Gas flow               | 12 L/min                                    |
| Sheath gas flow        | 12 L/min                                    |
| Gas temperature        | 150 °C                                      |
| Sheath gas temperature | 245 °C                                      |
| Detection              | dMRM (dynamic Multiple Reaction Monitoring) |

## RESULTS

The presented method is capable of determining all relevant haloacetic acids, bromate, and dalapon in drinking water according to EPA 557 (**Table 2**). Separation on the column Metrosep A Supp 19 - 150/4.0 with a hydroxide eluent was robust and reproducible. This combination enabled sufficient resolution between highly concentrated matrix peaks (i.e., chloride, nitrate, bicarbonate, and sulfate) and the analytes (**Figure 3**). The matrix was diverted to the waste to avoid ion suppression in the MS. A further advantage of this setup is the solvent-stable suppressor. Using 10% methanol in the eluent helps the transfer from aqueous to gas phase and has no

impact on the suppressor. Thus, no further post-column addition of organic solvents with a secondary pump was necessary to improve evaporation of analytes in the MS.

Calibration from 0.1–40 µg/L with quadratic fits resulted in  $R^2$  values in the range of 0.996–0.999. Determination of the lowest concentration minimum reporting levels (LCMRL) was done as per EPA 557, chapter 9.2.4 (**Table 2**). Seven replicates were successfully analyzed for the upper and lower PIR (prediction interval of results) limit (acceptable range 50–150%).



**Figure 3.** Overlay of a chromatogram of laboratory synthetic sample matrix (LSSM) according to EPA 557 with  $c(\text{ammonium chloride}) = 100 \text{ mg/L}$ ,  $c(\text{nitrate}) = 20 \text{ mg/L}$ ,  $c(\text{hydrogen carbonate}) = 150 \text{ mg/L}$ ,  $c(\text{chloride}) = 250 \text{ mg/L}$ , and  $c(\text{sulfate}) = 250 \text{ mg/L}$  (light colored lines), and of LSSM spiked with  $1 \mu\text{g/L}$  of all analytes (intensely colored lines). Injection volume was  $100 \mu\text{L}$ .

Water samples were directly analyzed (no dilution needed). **Table 3** shows that spiking recoveries of  $1 \mu\text{g/L}$  were in the range of 65–115% (for LSSM), 46–112% (for tap water), and 87–150% (for Evian water). Replicates for tap water ( $n = 7$ ) were in the range of 0.7–6.8% RSD (relative standard deviation). For mineral water (Evian) ( $n = 6$ ) and for LSSM ( $n = 7$ ) RSD values were in the range of 1.6–6.3% and 1.0–36.5%, respectively. Most values were  $\leq 5\%$ , except for TCAA (which elutes close to sulfate). Critical pairs were DBA/nitrate and TCAA/sulfate. The diverter windows must be accurately set to acquire

complete data for the analytes DBAA and TCAA and divert both nitrate and sulfate to the waste. Sample degradation at room temperature was visible after one day and considerable degradation occurred after four to five days. The samples must be measured in a timely manner or a sampler with cooling function must be used (e.g., 889 IC Sample Center – cool). A Metrohm  $\text{CO}_2$ -suppressor (MCS) was used in this setup as it improved the conductivity background and hence reduced the number of interfering ions in the MS.

**Table 2.** Determination of lowest concentration minimum reporting levels (LCMRL) was done as per EPA 557, chapter 9.2.4 minimum reporting level (MRL) confirmation. Seven replicates were analyzed for the upper and lower PIR (prediction interval of results) limit (acceptable range 50–150%). \*Concentrations lower than 0.025 µg/L were not tested, but signal-to-noise ratio was >10 and showed that the minimum limit was not reached.

| Analyte                  | Abbreviation     | Retention time [min] | Precursor or <i>m/z</i> | Product <i>m/z</i> | Concentration for minimum reporting level [µg/L] | PIR limits [%] |
|--------------------------|------------------|----------------------|-------------------------|--------------------|--|----------------|
| Monochloroacetic acid    | MCAA             | 15.8                 | 93                      | 34.9               | 0.025*   | 91–109         |
| Monobromoacetic acid     | MBAA             | 17.2                 | 137                     | 79                 | 0.025*   | 88–112         |
| Bromate                  | BrO <sub>3</sub> | 16.7                 | 127                     | 111                | 0.025*   | 84–116         |
| Dichloroacetic acid      | DCAA             | 25.6                 | 127                     | 83                 | 0.025  | 84–116         |
| Dalapon                  | DAL              | 28.0                 | 141                     | 97                 | 0.025  | 74–126         |
| Bromochloroacetic acid   | BCAA             | 28.0                 | 173                     | 81                 | 0.05   | 74–126         |
| Dibromoacetic acid       | DBAA             | 31.4                 | 217                     | 173                | 0.025  | 75–125         |
| Trichloroacetic acid     | TCAA             | 37.9                 | 161                     | 117                | 0.25   | 62–131         |
| Bromodichloroacetic acid | BDCAA            | 40.2                 | 163                     | 81                 | 0.025  | 79–121         |
| Chlorodibromoacetic acid | CDBAA            | 43.5                 | 207                     | 79                 | 0.025  | 52–148         |
| Tribromoacetic acid      | TBAA             | 49.1                 | 251                     | 79                 | 0.025  | 62–138         |

**Table 3.** Three types of water samples were spiked with 1 µg/L of all listed analytes and determined with IC-MS/MS. Analytes were not evaluated in the original unspiked samples. They were either not detected or below 0.1 µg/L. Concentration values are averaged over at least six replicates.

| Analyte                       | Concentration [µg/L] in samples spiked with 1 µg/L of all analytes |                       |                |
|-------------------------------|--|-----------------------|----------------|
|                               | Tap water (eastern Switzerland)                                    | Mineral water (Evian) | LSSM (EPA 557) |
| MCAA                          | 1.12   | 1.41                  | 1.15           |
| MBAA                          | 1.00   | 0.97                  | 0.87           |
| BrO <sub>3</sub> <sup>-</sup> | 0.88   | 0.86                  | 0.84           |
| DCAA                          | 0.88   | 1.03                  | 0.80           |
| DAL                           | 0.88   | 0.93                  | 0.76           |
| BCAA                          | 0.87   | 0.87                  | 0.71           |
| DBAA                          | 0.88   | 1.22                  | 0.79           |
| TCAA                          | 0.46   | 1.50                  | 0.65           |
| BDCAA                         | 0.89   | 0.91                  | 0.87           |
| CDBAA                         | 0.88   | 1.00                  | 0.88           |
| TBAA                          | 0.88   | 1.43                  | 0.84           |

The presented method fulfills all analytical requirements of US EPA 557 [4]. The robust setup of hyphenating Metrohm IC and Agilent MS guarantees the highest sensitivity and selectivity for all relevant haloacetic acids, dalapon, and bromate, even in complex drinking water matrices. The five

representative substances (mono-, di-, and trichloroacetic acid, and mono- and dibromoacetic acid) were precisely quantified in the sub µg/L concentration range for various water samples. The requirements of EPA 557 [4] and the EU directive [5] are met with this method.

## REFERENCES

1. Zhao, H.; Yang, L.; Li, Y.; et al. Environmental Occurrence and Risk Assessment of Haloacetic Acids in Swimming Pool Water and Drinking Water. *RSC Adv* 10 (47), 28267–28276. DOI:10.1039/d0ra02389b
2. Sinha, R.; Gupta, A. K.; Ghosal, P. S. A Review on Trihalomethanes and Haloacetic Acids in Drinking Water: Global Status, Health Impact, Insights of Control and Removal Technologies. *Journal of Environmental Chemical Engineering* 2021, 9 (6), 106511. DOI:10.1016/j.jece.2021.106511
3. US EPA, O. *National Primary Drinking Water Regulations*. <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations> (accessed 2022-09-19).
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5. *Directive - 2020/2184 - EN - EUR-Lex*. <https://eur-lex.europa.eu/eli/dir/2020/2184/oj> (accessed 2024-03-11).

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## CONFIGURATION



### 940 Professional IC Vario TWO/SeS/PP/MB

El 940 Professional IC Vario TWO/SeS/PP es el aparato CI inteligente de **dos canales** con **supresión secuencial** (un canal) y una **bomba peristáltica** para la regeneración de supresores. Este aparato puede emplearse con cualquier método de separación o de detección.

#### Ámbitos típicos de aplicación:

- Aparato estándar para determinaciones en paralelo de cationes y aniones
- Análisis de trazas para aniones y cationes
- Supervisión online para aniones y cationes
- Optimizado para aplicaciones microbore (2 mm), ideal para técnicas de acoplamiento (IC-MS o IC-ICP/MS)

Compatible con MagIC Net 4.1 y versiones superiores

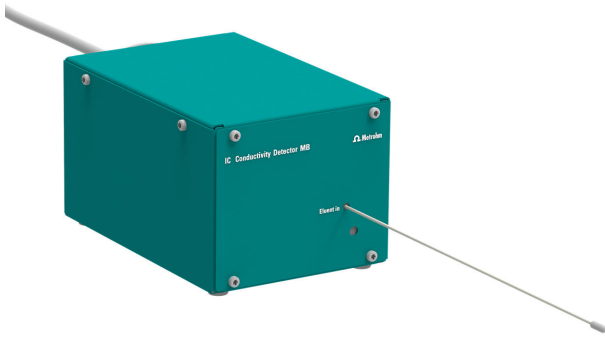


### Metrosep A Supp 19 - 150/4,0

Excelentes propiedades de separación y alta capacidad: estas son las cualidades que distinguen claramente a la familia de productos Metrosep A Supp 19 de las demás integrantes de la cartera de columnas. Destaca por tener las mejores simetrías de picos y su gran selectividad, así como por su elevada estabilidad térmica, mecánica y química, lo que le confiere extrema robustez y resistencia ante presiones y flujos más altos.

La versión de 150 mm es considerada la columna estándar para la cromatografía aniónica, pues resuelve con seguridad la gran mayoría de aplicaciones y puede utilizarse con mucha versatilidad. En virtud de su gran capacidad, la columna de separación Metrosep A Supp 19 - 150/4,0 resulta particularmente adecuada, incluso para aplicaciones complejas con exigentes matrices. Por sus excelentes propiedades de separación, el campo de utilización de la Metrosep A Supp 19 - 150/4,0 es muy versátil y abarca, entre otras, las siguientes aplicaciones:

- Determinación de aniones estándar (fluoruro, cloruro, nitrito, bromuro, nitrato, fosfato y sulfato) en las más diversas muestras de agua;
- Determinación de aniones estándar y ácidos orgánicos en complejas matrices de muestras como, por ejemplo, muestras tomadas del medioambiente o muestras de alimentos;
- Determinación de aniones estándar y ácidos orgánicos en el agua de alimentación de calderas para garantizar la seguridad de las operaciones en centrales eléctricas;
- Determinación de aniones estándar en muestras farmacéuticas.



### IC Conductivity Detector MB

Detector de conductividad de alto rendimiento, inteligente y compacto para aparatos CI inteligentes. Optimizado para columnas microbore. La extraordinaria constancia de temperatura, el tratamiento completo de la señal dentro del bloque detector protegido y DSP (tratamiento digital de la señal) de última generación garantizan la máxima precisión de la medida. Gracias a la zona de trabajo dinámica, no es necesario el cambio de la zona (ni siquiera automático).

#### Ámbitos típicos de aplicación:

- Determinaciones de cationes o aniones con supresión química, supresión secuencial o sin supresión y detección de conductividad
- Optimizado para aplicaciones microbore (2 mm), ideal para técnicas de acoplamiento (IC-MS o IC-ICP/MS)

#### Resumen de la especificación:

- 0...15 000  $\mu\text{S}/\text{cm}$  sin conmutación de gama
- Volumen de celda: 0,3  $\mu\text{L}$
- Electrodo de forma anular de acero fino X2CrNiMo17-12-2 (316 L), compatibles con MSA
- Presión máxima de servicio: 10,0 MPa (100 bar)
- Temperatura de la celda: 20...50  $^{\circ}\text{C}$  en pasos de 5  $^{\circ}\text{C}$
- Estabilidad térmica: < 0,001  $^{\circ}\text{C}$
- Ruido de la línea de base: < 0,2 nS/cm típico en la supresión secuencial
- Capilares: d. i. 0,18 mm

Compatible con MagIC Net 4.1 y versiones superiores



### 889 IC Sample Center – cool

El 889 IC Sample Center - cool es la solución de automatización perfecta para cuando se dispone de muy poca cantidad de muestra. A diferencia del 889 IC Sample Center, también dispone de una función de refrigeración que lo convierte en el cambiador de muestras ideal para muestras inestables térmicamente o bioquímicamente relevantes.