



Application Note AN-M-016

Resolving haloacetic acids in water

Increased sensitivity thanks to coupling IC with a MS detector

During drinking water disinfection with chlorine, chloramine, or ozone, potentially toxic halogenated byproducts can be formed. The disinfectants can react with naturally occurring bromide and/or organic matter in the source water and form one of the most common disinfection byproducts (DBPs): haloacetic acids (HAAs).

HAAs are highly toxic water-soluble compounds. Mono- to tri-halogenated acetic acids mainly contain bromine and/or chlorine. To protect human health, their maximum tolerable levels in drinking waters are regulated. Currently the EPA states a maximum contamination level of 60 µg/L for drinking water

(EPA 816-F-09-004) for five HAAs («HAA5»): dichloroacetic acid (0 mg/L), trichloroacetic acid (20 µg/L), monochloroacetic acid (70 µg/L), with both bromoacetic and dibromoacetic acid having no defined contamination levels.

EPA Method 557 specifies the analysis of HAAs by ion chromatography coupled to mass spectroscopy (IC-MS) with LODs varying from 0.02–0.11 µg/L. In this manner, the HAAs can be separated and determined at the required low levels due to an increased sensitivity by mass detection. Even with single MS, a high sensitivity is achieved to determine the current MCLs within an adequate accuracy.

SAMPLE AND SAMPLE PREPARATION

Spiked and unspiked mineral water samples are measured to simulate contaminated water sources. The samples are spiked with the following components in varying concentrations: bromate, chlorite, monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA),

dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), tribromoacetic acid (TBAA), chlorodibromoacetic acid (CDBAA), and trichloroacetic acid (TCAA). Recoveries are calculated by comparing spiked and unspiked sample equivalents. All samples are stabilized with ammonium chloride.

EXPERIMENTAL

The measurements are conducted with an IC equipped with a gradient pump coupled to a mass spectrometer (MS) (Waters SQ Detector 2) (Fig. 1). The separation of the individual components is performed with a Metrosep A Supp 5 - 250/2.0 column in combination with a Metrosep A Supp 10 column guard. The 2 mm diameter column allows a low eluent flow, which enables a direct measurement with the subsequent MS without any additional flow splitter. The high pressure gradient of the mobile

phase (composed of a mixture of potassium hydroxide, sodium carbonate, and acetonitrile) has been optimized to separate the individual components.

Instrument control and data evaluation is performed with Empower™. The Metrohm Driver 2.1 for Empower™ promotes the analyses with this powerful software and of course handling of hyphenated techniques as a single-software solution.

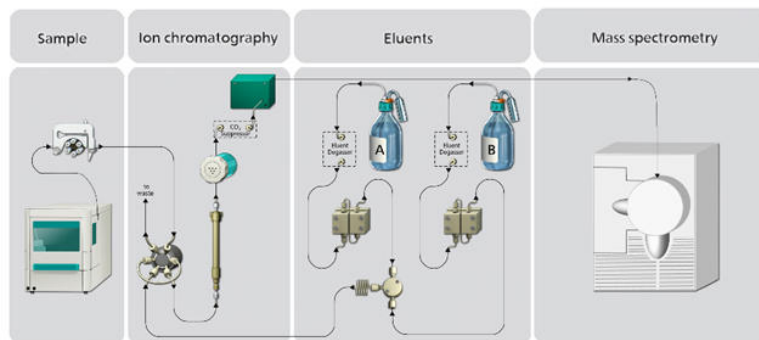


Figure 1. Flow path for the hyphenation of ion chromatography with mass spectrometry. The application requires an ion chromatograph with gradient pumps and sequential suppression. The suppression is required so that the eluent does not interfere with ion spray performance of the MS. An autosampler with a cooling function guarantees sample stability by limiting the decay of the HAAs over time. Beside the mass detection, conductivity detection occurs simultaneously.

RESULTS

The separation of nine HAAs is performed in less than 40 minutes. **Figure 2** shows the separation of the five relevant HAAs for EPA 816-F-09-004, often named as «HAA5». The spiking tests exhibit acceptable recoveries within a range of 74–124%. The estimated limits of detection are well within the EPA requirements for EPA method 557 regarding MCAA and MBAA (0.2 and 0.064 µg/L, respectively). To achieve a higher sensitivity for the other compounds,

hyphenation with a triple quadrupole MS is mandatory and can be used to entirely fulfill EPA 557. However, the recent maximum contamination levels for drinking water (EPA 816-F-09-004) for the five HAAs (DCAA, TCAA, MCAA, MBAA, and DBAA) are in sum 60 µg/L. Compared to the estimated LODs (**Table 1**), these are two orders of magnitude lower, showing the suitability of the present single quadrupole IC-MS method for drinking water quality measurements.

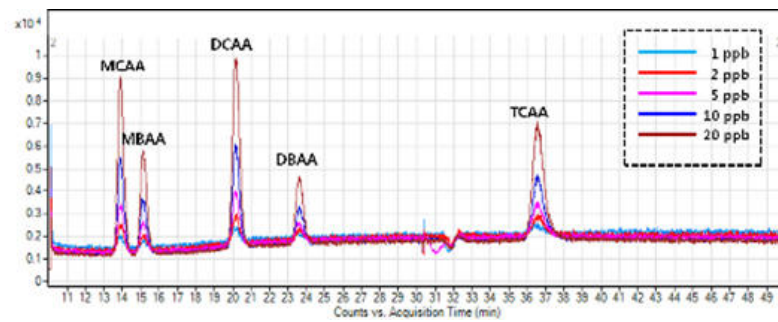


Figure 2. Overlay of multiple mass channels of 25 µg/L HAAs in ultrapure water (injection volume 100 µL). Mass-specific signal detection enhances the specificity for the individual HAAs, avoiding peak overlaps and increasing sensitivity for the individual compounds.

Table 1. Estimated limits of detection (LOD) for the haloacetic acids based on three times the signal-to-noise ratio.

| Analyte | LOD (µg/L) |
|---------|------------|
| MCAA | 0.045 |
| MBAA | 0.045 |
| DCAA | 0.45 |
| BCAA | 0.60 |
| DBAA | 0.15 |
| TCAA | 1.5 |
| BDCAA | 1.5 |
| CDBAA | 1.5 |
| TBAA | 1.5 |

CONCLUSION

The coupling of ion chromatography and mass spectroscopy is an ideal combination to achieve low detection limits and increase the specificity of analyses. The unique Metrohm Suppressor Module provides enhanced flexibility for the eluent choice, as the solvent is modified by post-column suppression in

order to make it suitable for the ion spray and the MS specifications. For many different applications, especially in the environmental sector, this combination can provide a more detailed insight than other techniques and expands the field of applications significantly.

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