

## Analysis of chlorinated and brominated acetic acids as environmental contaminants in different water matrices by HPLC-ICPMS/MS

**H**alogenated acetic acids (HAAs) are among the most common water disinfection byproducts. Since these are presumably harmful to health, the US Environmental Protection Agency (EPA) regulates the levels of five haloacetic acids (monochloro-, dichloro-,

trichloro-, monobromo- and dibromoacetic acid) to an overall maximum of 60 µg/L. The regulations of the European Union include another four haloacetic acids, with a maximum concentration of 80 µg/L for all nine HAAs combined [1].



High performance liquid chromatography coupled with electrospray ionisation tandem mass spectrometry (HPLC-ESI-MS/MS) is commonly used to achieve high sensitivity and selectivity. However, this detection technique is prone to matrix effects due to ion suppression or enhancement in the ionisation source.

This application note will demonstrate the analysis of nine HAAs by using inductively coupled plasma tandem mass spectrometry (ICPMS/MS) for detection, which is less prone to matrix effects [2]. Different types of water samples from Austria were analysed: tap water from Graz, groundwater from the Leutschach well and river water from the Mur.

Table 1: Chromatographic conditions [2].

Column:	YMC-Triart C18 (3 µm, 12 nm) 150 x 3.0 mm ID
Part No.:	TA12S03-1503WT
Eluent:	22 mM oxalic acid in pure water (pH 1.8)
Flow rate:	0.5 mL/min
Temperature:	40 °C
Injection:	50 µL
Samples:	Tap (Graz), ground (Leutschach well) and river (Mur) water Spiked with EPA 552.2 standard 2.0 mg/L of each HAA: chloroacetic acid (CAA), dichloroacetic acid (DCAA), bromoacetic acid (BAA), chlorobromoacetic acid (CBAA), trichloroacetic acid (TCAA), dibromoacetic acid (DBAA), dichlorobromoacetic acid (DCBAA), chlorodibromoacetic acid (DBCBA), tribromoacetic acid (TBAA) all samples: acidified to a final concentration of 50 mM oxalic acid
Detection:	ICPMS/MS

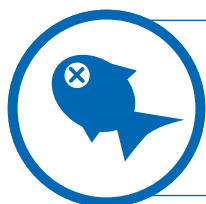


Figure 1 shows the baseline separation of nine HAAs, each spiked with 2.0 mg/L EPA 552.2 reference material, in about 15 min. A high injection volume is used to achieve the lowest possible limit of detection (LOD). Therefore, the alkaline hard water samples (pH = 7.1–7.9) must be acidified to reduce the pH difference with the mobile phase.

The LOD ranges from 1.8–2.0 µg Cl/L and 1.0–1.5 µg Br/L, while the limit of quantification varies between 4.6 and 12 µg/L.

The recoveries obtained show that ICPMS/MS detection is less prone to matrix effects compared to ESI-MS/MS because interfering ions with high carbon load (e.g. bicarbonate) are separated from the analytes as they elute with the dead volume. Therefore, an internal standard (IS) is not required unlike ESI-MS/MS, where an isotopically labelled IS for each analyte is preferable.

Furthermore, ICPMS/MS detection can also be performed using non-volatile buffers containing phosphate, sulphate, chloride or sodium.

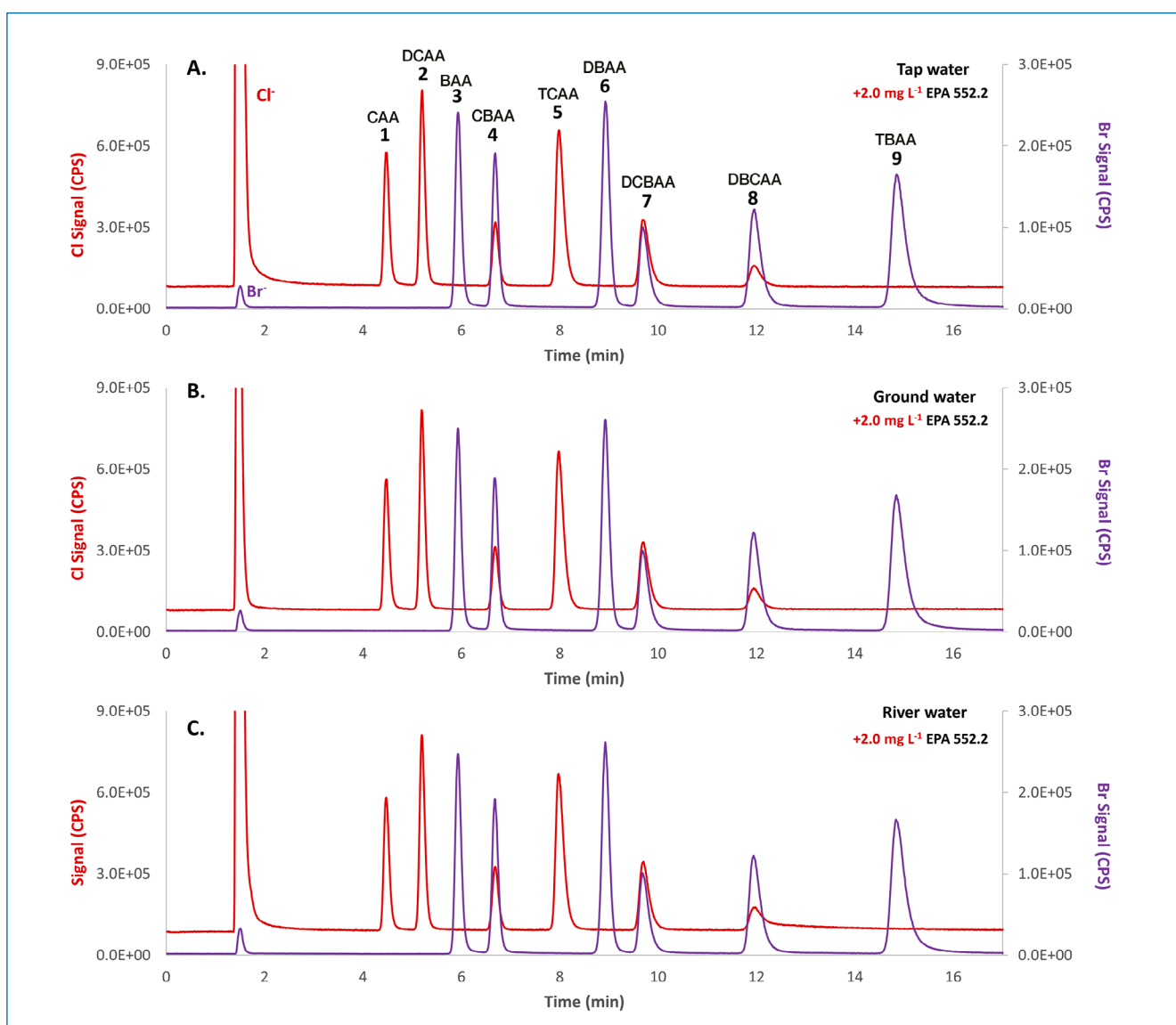


Figure 1: separation of haloacetic acids in tap (A), ground (B), and river water (C) samples spiked with the EPA 552.2 certified reference material [2].

[1] European Parliament. Quality of water intended for human consumption \*\*\*I  
[https://www.europarl.europa.eu/doceo/document/TA-8-2018-0397\\_EN.html](https://www.europarl.europa.eu/doceo/document/TA-8-2018-0397_EN.html) (accessed 08.2024)

[2] Bassam Lajin and Walter Goessler, Analytical Chemistry 2020 92 (13), 9156-9163, DOI: 10.1021/acs.analchem.0c01456.

