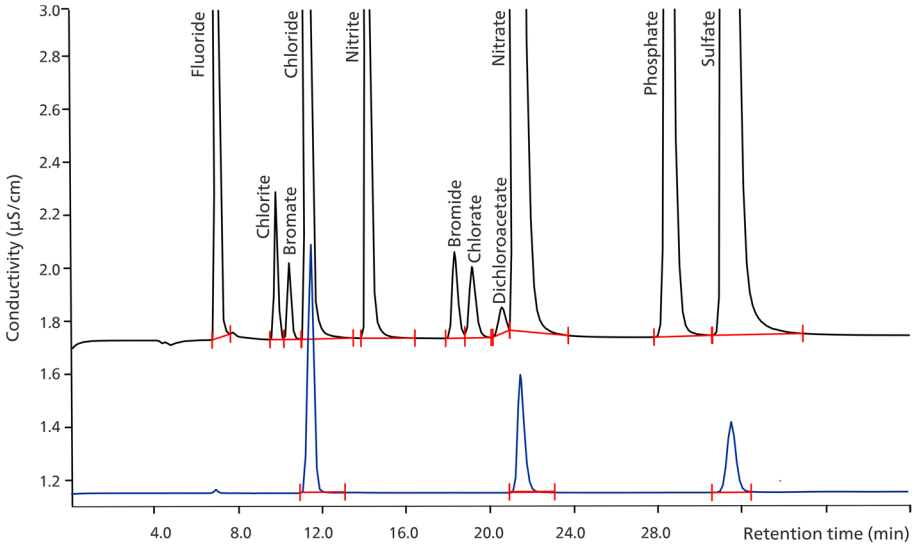
IC APPLICATION NOTE S-236

Drinking water quality by EPA 300.1

Combining EPA method 300.1 parts A and B in a single IC run

Clean drinking water is cited as a human right by the World Health Organization [1]. Policies as well as standards and robust analytical methods are required to safeguard water quality, and by extension, public health. In Europe, the EU Drinking Water Directive regulates water quality, while the Safe Drinking Water Act (SDWA) is responsible in the US. The SDWA authorized the US EPA to develop minimum drinking water standards and the respective standardized analytical methods. Since the 1980s, EPA method 300.0 has outlined the analytical requirements for determination of major inorganic anions (part A) and harmful inorganic disinfection byproducts (DBPs) in Part B [2–5]. Inorganic DBPs like chlorite and chlorate are primarily formed during chlorination processes, while bromate is created through ozonation of naturally present bromide [2, 5–7]. When maximum contaminant levels (MCLs) of DBPs were revised, so was the EPA method (1997) [5, 6]. To reach the method detection limits (MDLs), different injection volumes are required for parts A and B due to relative concentration differences [8]. Ion chromatography with suppressed conductivity detection using the highly selective Metrosep A Supp 7 column fulfills these requirements in a single-run analysis, increasing laboratory efficiency and saving money while keeping analytical quality high.



Analyte	LOD (mg/L)	LOD EPA 300.1 (mg/L) [2]
F^-	0.009	0.009
ClO_2^-	<0.001	0.00089
BrO_3^-	0.001	0.00144
Cl^-	0.004	0.004
NO_2^-	0.001	0.001
Br^-	0.007	0.014
ClO_3^-	0.001	0.00131
DCA	-	
NO_3^-	0.008	0.008
PO_4^{3-}	0.003	0.019
SO_4^{2-}	0.018	0.019

Figure 1. Chromatograms for a tap water sample (Herisau, Switzerland, blue—see **Table 1** for average concentrations) and a standard (black) containing the relevant analytes with high concentrations of major anions for EPA 300.1 (fluoride 2.0 mg/L, chloride 10.0 mg/L, nitrite 5.0 mg/L, nitrate 30.0 mg/L, phosphate 15.0 mg/L, and sulfate 40 mg/L) beside low concentrations for disinfection byproducts and bromide (chlorite 1.0 mg/L, bromate 1.0 mg/L, bromide 1.0 mg/L, chlorate 1.0 mg/L, and dichloroacetate 1.0 mg/L). Anions were separated on a Metrosep A Supp 7 - 250/4.0 column (eluent: 3.6 mmol/L sodium carbonate, flow rate 0.8 mL/min, column temperature 45 °C, sample volume 20 µL). The conductivity signal was recorded after sequential suppression. The limits of detection (LODs, on the right) determined by DIN 62645 are in line with the EPA requirements **[8]**.

EXPERIMENTAL

Drinking and tap water samples from sites in Herisau, Switzerland were analyzed according to the requirements of US EPA Method 300.1 **[8]**. Additionally, standards and spiked samples showing the full analyte range (i.e., fluoride, chlorite, bromate, chloride, nitrite, bromide, chlorate, dichloroacetate (DCA), nitrate, phosphate, and sulfate) were injected for quantification and quality control. All solutions, i.e. samples and standards, were automatically filtered applying Metrohm Inline Ultrafiltration (8.000.5341EN). EPA Method 300.1 Parts A and B are combined in a single method and use a common injection volume of 20 µL. The anions, including the surrogate dichloroacetate (DCA), were separated on a Metrosep A Supp 7 - 250/4.0 using a carbonate eluent.

DCA is the acetate form of DCAA (dichloroacetic acid) and can be present in treated drinking waters, but also in groundwater or swimming pools as a reaction product from organic material during the chlorination process **[3, 8]**. The provisional WHO guideline for DCA in drinking water is 0.05 mg/L because it exhibits potential health hazards **[1]**. Therefore, it must be separated from the other ions to guarantee appropriate resolution and quantification.

The signal detection for the analysis was performed with a conductivity detector after sequential suppression and quantified using the MagIC Net software.

Figure 2. Compact, user-friendly Metrohm IC instrumentation to quantify oxyhalides besides standard anions in drinking water.

Sequential suppression, i.e. the combination of chemical and CO_2 suppression, reduces the background conductivity and therefore improves the signal-to-noise ratio. Typical background conductivities below 1 µS/cm are reached by completely removing CO_2 and carbonic acid from the eluent. Thus, analysis of very low concentrations is enabled and requirements of the US EPA regarding drift and baseline noise are fulfilled (<5 nS per min over background conductivity) **[8]**.

RESULTS

The analyzed tap waters contained high concentrations (i.e., mg/L range) of chloride (13 mg/L), sulfate (4 mg/L), and nitrate (8 mg/L) (**Table 1** and **Figure 1**). Bromide and fluoride were detected in minor concentrations (<0.06 mg/L), while the toxic disinfection byproducts chlorate, bromate, and chlorite, as well as nitrite could not be detected. The peak resolutions of >1.5 reveal that the anions are baseline separated (example shown in **Figure 1**).

The surrogate DCA was not detected in any of the tap waters but it could be separated from the predominant nitrate (30 mg/L) in the mixed standard with a resolution of 1.2 (**Figure 1**).

The relative standard deviations (RSDs) for repeated tap water analysis below 2.5% (**Table 1**, with exceptions for chlorite and bromate) and spike recoveries of 82–120% are within the common quality criteria and highlight the **repeatability**, **accuracy**, and **robustness** of the method. The determined detection limits (LODs) (according to DIN 62645) fit the EPA requirements (**Figure 1**) **[8]**.

Aside from the applicability to surface, ground, and finished drinking waters as specified in the EPA Method 300.1 **[8]**, the presented setup was approved for a variety of different waters including bottled water, mineral water, and swimming pool water.

Table 1. Results for repeated tap water analysis (n = 6) with 5 µg/L spikes (indicated by *) of the oxyhalides chlorite, bromate, and chlorate, which were not contained in the unspiked tap water. Analytes which were not detected in the tap water are indicated with «n. d.».

Tap water n = 5	Result (mean ± SD) [mg/L]	RSD [%]	Spike conc. [mg/L]	Recovery %
Fluoride	0.064 ± 0.002	2.5	-	-
Chlorite *	0.004 ± <0.001	8.3	0.005	82
Bromate *	0.006 ± <0.001	5	0.005	113
Chloride	12.5 ± 0.1	1.0	-	-
Nitrite	n. d.	-	-	-
Bromide	0.008 ± <0.001	1.6	-	-
Chlorate *	0.006 ± <0.001	1.9	0.005	120
Nitrate	7.9 ± 0.1	1.5	-	-
Sulfate	3.9 ± 0.06	1.5	-	-
Phosphate	n. d.	-	-	-

CONCLUSIONS

The greatest challenge involved with combining the requirements of EPA 300.1 parts A and B within a single method was to separate and measure high concentrations of inorganic anions (e.g., chloride, nitrate, and sulfate in the mg/L range) beside lower concentrations of DBPs (i.e., bromate, chlorite, and chlorate) and nitrite. To measure such analytes accurately over a very large concentration range (five orders of magnitude or more), **a high linearity of the detector is required**. Here, the Metrohm conductivity detector showed an excellent performance with a linearity range of 0–15,000 µS/cm. Additionally, the separation of the analytes listed in EPA Method 300.1 parts A and B requires a **dedicated analytical column** which shows a high resolution, especially for the oxyhalides (i.e., the DPBs).

The Metrosep A Supp 7 column shows a very high resolution, especially for the oxyhalides. It separates all ions of interest including dichloroacetate in an isocratic method. This keeps the analysis straightforward and the setup simple (**Figure 2**).

US EPA method 300.1 **[8]** is the main standard method for the analysis of oxyhalides and common anions in drinking water with global acceptance. The requirement of using two injections, one for the standard anions and a second for the trace anions, dramatically reduces the sample throughput for laboratories.

Metrohm offers a very comprehensive way to combine the two parts of EPA 300.1 **without any quality losses** by using a setup with the Metrosep A Supp 7 - 250/4.0 separation column in combination with conductivity detection after sequential suppression. Further application of Metrohm Inline Sample Preparation (MISP) techniques (8.025.5003EN) such as Ultrafiltration or Inline Dilution provides additional benefits to laboratories by increasing the analytical efficiency through the reduction of analysis time.

REFERENCES

[1] World Health Organization. *Guidelines for Drinking-Water Quality: First Addendum to the Third Edition, Volume 1 : Recommendations*; Geneva: WHO, 2006.

[2] Boorman, G. A. Drinking Water Disinfection Byproducts: Review and Approach to Toxicity Evaluation. *Environ. Health Perspect.* **1999**, *107* (suppl 1), 207–217.

[3] Evans, S.; Campbell, C.; Naidenko, O. V. Analysis of Cumulative Cancer Risk Associated with Disinfection Byproducts in United States Drinking Water. *Int. J. Environ. Res. Public. Health* **2020**, *17* (6), 2149.

[4] *Some Drinking-Water Disinfectants and Contaminants, Including Arsenic IARC Monographs on the Evaluation of Carcinogenic Risks to Humans Volume 84*; International Agency for Research on Cancer, Ed.; IARC monographs on the evaluation of carcinogenic risks to humans; IARC: Lyon, 2004.

[5] Jackson, P. E. Ion Chromatography in Environmental Analysis. In *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; John Wiley & Sons, Ltd: Chichester, UK, 2000; p a0835.

[6] EPA National Primary Drinking Water Regulations: Disinfectants, and Disinfection Byproducts. *Fed. Regist.* **1998**, *63* (241), 69389–69476.

[7] Singer, P. C. Control of Disinfection By-Products in Drinking Water. *J. Environ. Eng.* **1994**, *120* (4), 727–744.

[8] EPA Method 300.1 - Determination of Inorganic Anions in Drinking Water by Ion Chromatography. In *Methods for the Determination of Organic and Inorganic Compounds in Drinking Water*; United States Environmental Protection Agency: USA, 2000; p 300.1-1–300.1-42.

Analytes:	**Halogens – chloride, chlorite, chlorate, bromide, bromate, fluoride; Haloacetic acids (HAA); Nitrogen – nitrate, nitrite; Phosphorus – phosphate; Sulfur – sulfate**
Matrix:	**Water – drinking water, tap water, others**
Method:	**Ion Chromatography**
Industry:	**Food & beverage; Environmental**
Standards:	**EPA Method 300.1 Part A; EPA Method 300.1 Part B**

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