Application Note AN-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 considered a human right by the World Health Organization [1]. Policies, standards, and robust analytical methods are required to protect water quality and 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, US EPA method 300.0 has outlined the analytical requirements for the determination of major inorganic anions (Part A) and harmful inorganic disinfection byproducts (DBPs) in Part B [2–5], corresponding largely to EN ISO 10304-1 and 10304-4, respectively. Inorganic DBPs like chlorite and chlorate are primarily formed via 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 US EPA method [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 high-capacity Metrosep A Supp 20 column fulfills these requirements in a single-run analysis, increasing lab efficiency, saving money, and maintaining high analytical quality.

EXPERIMENTAL

Drinking and tap water samples from sites in Herisau, Switzerland, and commercial mineral waters 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. For the analysis, US EPA Method 300.1 Parts A and B were combined into a single method using a common injection volume of 50 µL. Major anions, oxyhalides, and the surrogate dichloroacetate (DCA) were separated under isocratic conditions on a Metrosep A Supp 20 - 150/4.0 column with a carbonate eluent.

DCA is the acetate form of DCAA (dichloroacetic acid) and can be present in treated drinking water, as well as in groundwater and 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, as it poses potential health hazards [1]. Therefore, it must be separated from the other ions to guarantee appropriate resolution and quantification. In US EPA Method 300.1, DCA is defined as a surrogate and must be spiked to the samples at a concentration of 1 mg/L.

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

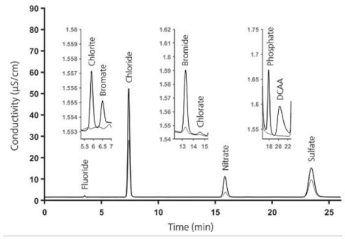
Sequential suppression, i.e., the combination of chemical and CO_2 suppression, reduces background conductivity and therefore improves the signal-to-noise ratio. Typically, background conductivities below 1.6 µS/cm are achieved by completely removing CO_2 and carbonic acid from the eluent. This enables the analysis of very low concentrations, and fulfills the US EPA requirements for baseline noise (<5 nS/cm) and drift (<5 nS/(cm x min)) [8].

Figure 1. Compact, user-friendly Metrohm IC instrumentation to quantify oxyhalides besides standard anions in drinking water.

RESULTS

The analyzed water samples contained high concentrations (i.e., mg/L range) of chloride (9-11 mg/L), sulfate (5-14 mg/L), and nitrate (4-9 mg/L) (Table 1, Table 2, and Figure 2). Bromide and fluoride were detected in minor concentrations (<0.006 mg/L and <0.07 mg/L, respectively), while the toxic disinfection byproducts chlorate, bromate, and chlorite, as well as nitrite, were not detected (with one exception where 0.003 mg/L chlorate was detected, Table 2).

Also, the surrogate DCA was not detected in any of the samples. However, DCA (10 mg/L) could be well separated with a resolution of 2.8 in a mixed standard solution with a 10-fold concentration of sulfate (100 mg/L) (Figure 2).



	MDL	MDL EPA
Fluoride (mg/L)	0.003	0.009
Chlorite (µg/L)	0.69	0.89-1.44
Bromate (µg/L)	1.54	1.32-1.44
Chloride (mg/L)	0.013	0.004
Nitrite (mg/L)	0.001	0.001
Bromide (µg/L)	4.80	0.98-1.44
Chlorate (µg/L)	1.85	1.31-2.55
Nitrate (mg/L)	0.006	0.008
Phosphate (mg/L)	0.022	0.019
DCAA (mg/L)	0.063	-
Sulfate (mg/L)	0.056	0.019

Figure 2. Chromatograms for the highly mineralized commercial mineral water (lower line) and the spiked water sample (upper line) (see Table 1 and Table 2 for average concentrations). Anions were separated on a Metrosep A Supp 20 - 150/4.0 column (eluent: 5.6 mmol/L sodium carbonate, 3.1 mmol/L sodium bicarbonate, flow rate 0.85 mL/min, column temperature 30 °C, injection volume 50 µL). The conductivity signal was recorded after sequential suppression. The Method Detection Limits (MDL) were determined in accordance with US EPA 300.1 (number of replicates = 2).[8].

The US EPA 300.1 Parts A and B have a few requirements that need to be met:

- Spiking recoveries must lie between 85% and 115% for high concentrations (mg/L) and between 75% and 125% for lower concentrations (maximum 10 times the «minimum reporting level», which corresponds to the lower calibration standard, lower µg/L-range).

As can be seen in Table 1 and Table 2, spike recoveries were between 80–104%, with the exception of phosphate in the commercial mineral water (70%), presumably due to the presence of metal ions chelating phosphate and reducing its recovery.

- The Peak Gaussian Factor (PGF) of the surrogate peak DCA must be between 0.80 and 1.15. The spiking recovery of DCA must be between 90% and 115%.

Across all measurements, the PFG for DCA ranged from 0.85 to 1.02. Recoveries for DCA were between 90% and 91%.

- A minimum of 10% of the samples must be analyzed twice. Therefore, the relative percent difference (RSD) between measurement replicates must be below 10% for high concentrations and below 20% for lower concentrations.

The relative standard deviations (RSDs) for the water and spiked water samples (n = 4) for major anions (fluoride, chloride, nitrate, phosphate, sulfate, and DCA) were below 0.5% (Table 1 and Table 2, except for phosphate in the mineral water sample, <2%). For oxyhalides (chlorite, bromate, chlorate), nitrite, and bromide, occurring in low concentrations (i.e., single digit µg/L range), the RSDs were between <0.1 and 9%).

- The US EPA 300.1 Parts A and B do not explicitly mention minimum resolutions. However, even in highly concentrated matrices, adequate separation must be ensured.

Matrix compatibility and high carbonate levels can create significant challenges and affect analysis quality. When the column capacity is exceeded, peak broadening or shifts in retention time can occur. Within the scope of this work, separation was demonstrated in various drinking and commercially available waters, as well as in artificial matrices with high concentrations of chloride (up to 250 mg/L), nitrate (up to 50 mg/L), sulfate (up to 250 mg/L), and carbonate (up to 300 mg/L).

Table 1: Results for repeated water analysis (n = 4) and spike recoveries (n = 4) for Herisau tap water. The spike had the following analyte concentrations: 10 mg/L chloride, nitrate, sulfate, 1 mg/L phosphate, dichloroacetate (DCAA), 100 µg/L fluoride, nitrite, bromide, and 5 µg/L chlorite, bromate, and chlorate. Analytes which were not detected in the tap water are indicated with «n. d.».

	Result [µg/L]	RSD [%]	Result spiked [µg/L]	RSD [%]	Spike recovery [%]
Fluoride	53	0.5	146	0.4	97.6
Chlorite	n. d.		5	2.9	93.0
Bromate	n. d.		4	9.2	82.1
Chloride	8865	0.1	18444	<0.1	103.
Nitrite	n. d.		104	2.1	103.9
Bromide	6	5.7	109	0.7	104.3
Chlorate	n. d.		5	5.6	91.4
Nitrate	8787	0.1	18325	<0.1	103.3
Phosphate	n. d.		972	0.3	97.2
DCAA	n. d.		9.19	0.4	91.3
Sulfate	4804	0.2	14430	<0.1	100.6

Table 2: Results for repeated water analysis (n = 4) and spike recoveries (n = 4) for a commercial mineral water sample. The spike had the following analyte concentrations: 10 mg/L chloride, nitrate, sulfate, 1 mg/L phosphate, dichloroacetate (DCAA), 100 µg/L fluoride, nitrite, bromide, and 5 µg/L chlorite, bromate, and chlorate. Analytes which were not detected in the tap water are indicated with «n. d.».

	Result [µg/L]	RSD [%]	Result spiked [µg/L]	RSD [%]	Spike recovery [%]
Fluoride	65	0.5	153	0.5	93.7
Chlorite	n. d.		5	6.0	92.1
Bromate	n. d.		4	8.5	80.3
Chloride	11300	0.1	20602	<0.1	103.2
Nitrite	n. d.		106	1.8	106
Bromide	6	5.7	110	0.4	103.8
Chlorate	3	10.9	7	5.7	94.1
Nitrate	3681	<0.1	13296	0.1	99.5
Phosphate	n. d.		687	1.9	68.7
DCAA	n. d.		899	0.5	89.9
Sulfate	13717	0.1	22806	0.1	103.2

CONCLUSION

The greatest challenge involved with combining the requirements of EPA 300.1 Parts A and B within a single method is 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 degree of detector linearity is required. Here, the Metrohm conductivity detector exhibited 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 that provides high resolution, especially for the oxyhalides (i.e., the DPBs) and in highly concentrated water matrices.

The high-capacity anion-exchange column, Metrosep A Supp 20 - 150/4.0, shows very high resolution, especially for the oxyhalides. It separates all ions of interest, including DCA, in a single isocratic method. This keeps the analysis straightforward and the setup simple (Figure 1).

US EPA method 300.1 [8] is the primary standard

method for the analysis of oxyhalides and common anions in drinking water and is broadly accepted worldwide. The requirement of using two injections, one for the standard anions and a second one for the trace anions, dramatically reduces the sample throughput for laboratories.

Metrohm offers a comprehensive way to combine the two parts of EPA 300.1 without loss of quality by using a setup with the Metrosep A Supp 20 - 150/4.0 separation column, followed by conductivity detection after sequential suppression. The analytical procedure is also in line with the requirements of EN ISO 10304 Parts 1 and 4. Further integration of Metrohm Inline Sample Preparation (MISP) techniques (8.940.5002EN), such as Ultrafiltration or Inline Dilution, provides additional benefits to laboratories by increasing analytical efficiency through reduced analysis time.

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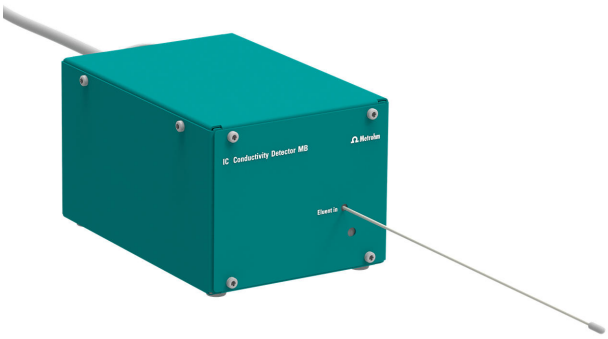
CONFIGURATION

930 Compact IC Flex Oven/SeS/PP/Deg

The 930 Compact IC Flex Oven/SeS/PP/Deg is the intelligent Compact IC instrument with **column oven**, **sequential suppression**, **peristaltic pump** for suppressor regeneration and built-in **degasser**. The instrument can be used with any separation and detection methods.

Typical areas of application:

- Anion or cation determinations with sequential suppression and conductivity detection



IC Conductivity Detector MB

Compact and intelligent high performance conductivity detector for intelligent IC instruments. Optimized for microbore columns. Outstanding temperature stability, the complete signal processing within the protected detector block and the latest generation of DSP – Digital Signal Processing – guarantee the highest precision of the measurement. No change of measuring ranges (not even automatic ones) is required, due to the dynamic working range.

Typical areas of application:

- Anion or cation determinations with chemical suppression, sequential suppression or without suppression and conductivity detection
- Optimized for microbore (2 mm) applications, ideally suitable for coupling techniques (IC-MS or IC-ICP/MS)

Specification at a glance:

- 0–15000 µS/cm without range switching
- Cell volume: 0.3 µL
- Ring-shaped electrodes made of stainless steel X2CrNiMo17-12-2 (316 L), compatible with MSA
- Maximum operating pressure: 10.0 MPa (100 bar)
- Cell temperature: 20–50 °C in increments of 5 °C
- Temperature stability: 0.001 °C
- Baseline noise: 0.2 nS/cm typical for sequential suppression
- Capillaries: ID 0.18 mm

Supported with MagIC Net 4.1 and higher

858 Professional Sample Processor

The 858 Professional Sample Processor processes samples from 500 µL to 500 mL. The sample transfer takes place either by means of a peristaltic pump on the 850 Professional IC system or with an 800 Dosino.