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 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], 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 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 highly selective Metrosep A Supp 7 column fulfills these requirements in a single-run analysis, increasing lab efficiency and saving money while keeping analytical quality high.

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. Certified reference standards from Merck were used for the standard as well as spiking. All solutions, i.e. samples and standards, were automatically filtered applying Metrohm Inline Ultrafiltration (8.000.5341). 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.

EXPERIMENTAL

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

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].

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

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 2). 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 2).

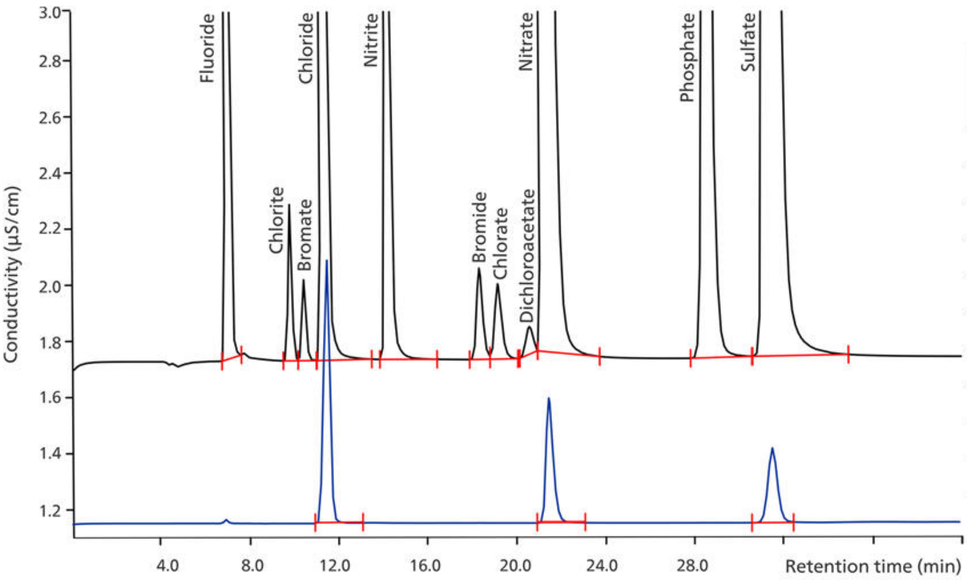
The surrogate DCA was not detected in any of the tap waters but it could be separated from the predominant nitrate (30 mg/L) in the mixed standard with a resolution of 1.2 (Figure 2).

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 2) [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.

The analytical procedure is also suitable for both EN ISO 10304-1: bromide and nitrate (working range ≥0.05 mg/L), chloride, fluoride, nitrate, orthophosphate, and sulfate (working range ≥0.1 mg/L) and EN ISO 10304-4: chlorate (working range ≥0.03 mg/L), chloride (working range ≥0.1 mg/L), and chlorite (working range ≥0.05 mg/L). With the excellent separation achieved using the Metrosep A Supp 7 column, all requirements for possible anionic interferences mentioned in these norms are fulfilled. In contrast to the EPA, ISO allows usage of UV/VIS detection (bromide, nitrate, nitrite, chlorite) or amperometric detection (chlorite) to achieve a higher sensitivity if needed. DCA is not covered by ISO 10304-1 or 4.

RESULTS



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 2. 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].

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.	-	-	-

CONCLUSION

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 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 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 1).

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. The analytical procedure is also in line with the requirements for **EN ISO 10304 parts 1 and 4** and can be modified by using UV/VIS detection for higher sensitivity. Further integration of Metrohm Inline Sample Preparation (MISP) techniques (8.940.5004) such as Ultrafiltration or Inline Dilution provides additional benefits to laboratories by increasing the analytical efficiency through the reduction of analysis time.

REFERENCES

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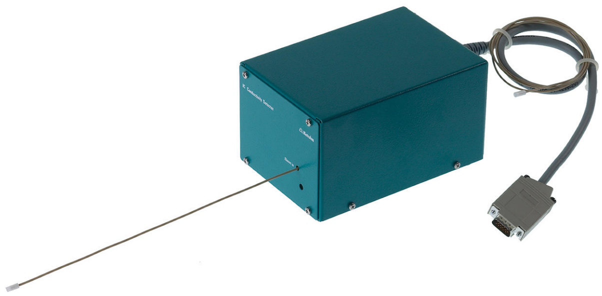
CONFIGURATION

940 Professional IC Vario ONE/SeS/PP

The 940 Professional IC Vario ONE/SeS/PP is the intelligent IC instrument with **sequential suppression** and a **peristaltic pump** for suppressor regeneration. 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
- Trace analysis for anions or cations
- Online monitoring for anions or cations

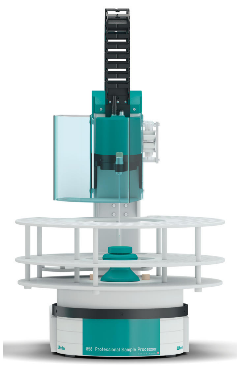


IC Conductivity Detector

Compact and intelligent high performance conductivity detector for intelligent IC instruments. 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.

Metrosep A Supp 7 - 250/4.0

Disinfection byproducts from water treatment are suspected not only of being health hazards but even of being carcinogenic. Oxyhalides have therefore become the subject of many investigations and standards (e.g., EPA 300.1 Part B, EPA 317.0, EPA 326.0). Of primary concern is bromate, which forms from bromide during the ozonization of drinking water. The Metrosep A Supp 7 - 250/4.0 is a high-performance separation column for the parallel determination of standard anions, oxohalides and dichloroacetic acid. With this column, these ions are determined with certainty and precision down to the lower µg/L range. The high detection sensitivity is achieved through the use of the 5 µm polyvinyl alcohol polymer, with which extremely high plate numbers and thus outstanding separation and detection properties are achieved. In addition, the separation can be adapted to the specific requirements of the application by modifying the temperature.



858 Professional Sample Processor – Pump

The 858 Professional Sample Processor – Pump processes samples from 500 µL to 500 mL. The sample transfer takes place either with the installed bidirectional two-channel peristaltic pump or with an 800 Dosino.

MagIC Net

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Professional PC program for controlling one intelligent Compact IC instrument, one detector and one Autosampler, or one 771 Compact Interface. The software permits checks, data acquisition, data evaluation and data monitoring as well as report generation of ion chromatographic analyses.

Graphical user interface for routine operations, extensive database programs, method development, configuration and manual system control; very flexible user management, powerful database operations, extensive data export functions, individually configurable report generator, control and monitoring of all system components and the chromatography results.

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