



## 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

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<sub>2</sub> 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<sub>2</sub> 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].

## 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

Metrosep A Supp 20 - 150/4.0 column with a carbonate eluent.

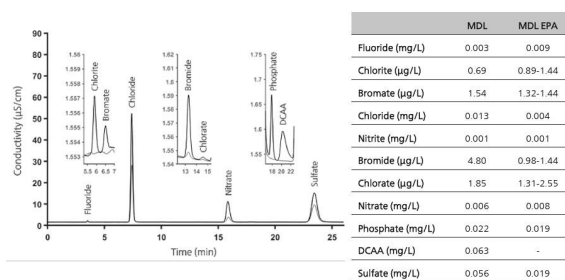
DCA is the acetate form of DCAA (dichloroacetic acid) and can be present in treated drinking water, as well as in groundwater and swimming pools, as a reaction product from organic material during the chlorination process [3, 8]. The provisional WHO guideline for DCA in drinking water is 0.05 mg/L, as 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.



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

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).



**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.

## REFERENCES

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

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## CONFIGURATION



### Metrosep A Supp 20 - 150/4.0

Die Metrosep A Supp 20 - 150/4.0 ist eine fortschrittliche Trennsäule für die Anionenchromatographie, die für überragende Trenneigenschaften in regulatorischen und anspruchsvollen Anwendungen entwickelt wurde. Dank ihrer hervorragenden Trennleistung eignet sie sich ideal für Methoden, die eine präzise Bestimmung von Standardanionen und Oxyhalogeniden erfordern, darunter US EPA 300.1, Teile A und B, sowie ISO 10304, Teile 1 und 4. Mit ihrer zuverlässigen Leistung bei verschiedenen Probenotypen bietet sie Laboren eine stabile Lösung sowohl für die routinemässige als auch für die Compliance-bedingte Anionenanalyse.

Die auf einem langlebigen Polystyrol/Divinylbenzol-Trägermaterial basierende Metrosep A Supp 20 - 150/4.0 ist hinsichtlich ihrer Selektivität für den Einsatz mit isokratischen Carbonat-Eluenten optimiert und bietet eine besonders robuste und benutzerfreundliche Lösung für die täglichen Workflows in der Anionenchromatographie. Das gewährleistet eine hervorragende Langzeitstabilität sowie umfassende Kompatibilität mit gängigen IC-Methoden.

Dank ihrer hohen Anionenaustauschkapazität deckt die Metrosep A Supp 20 - 150/4.0 das gesamte Anwendungsspektrum ab, das typischerweise von Anionensäulen mit hoher Kapazität übernommen wird, einschliesslich der Bestimmung von Oxyhalogeniden, Standardanionen und Dichloracetat. Die kürzere Variante der Metrosep A Supp 20-Reihe, die Version 150/4.0, ermöglicht eine schnelle und genaue Analyse verschiedener Probenotypen und eignet sich für die meisten Bestimmungen.





### Metrosep A Supp 20 Guard/4.0

Die Metrosep A Supp 20 Guard/4.0 bietet zuverlässigen Schutz für Metrosep A Supp 20 Trennsäulen, indem sie verhindert, dass Verunreinigungen aus Probe oder Eluent in die Trennsäule gelangen. Diese Vorsäule ist mit derselben stationären Phase wie die entsprechenden Trennsäulen gepackt und in einem chemikalienbeständigen PEEK-Gehäuse untergebracht. Sie sichert die Leistungsfähigkeit der Säule und verlängert die Lebensdauer der Haupttrennsäule, ohne die chromatographische Qualität zu beeinträchtigen.

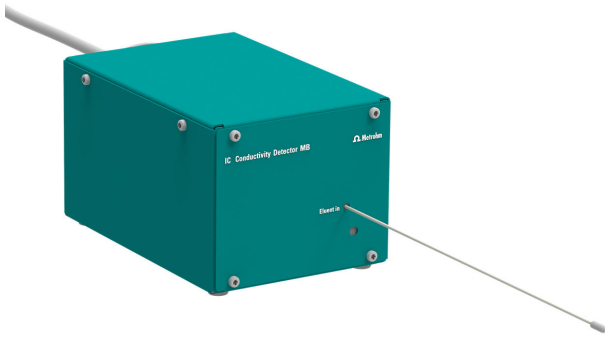


### 930 Compact IC Flex Oven/SeS/PP/Deg

Der 930 Compact IC Flex Oven/SeS/PP/Deg ist das intelligente Compact-IC-Gerät mit **Säulenofen**, **sequenzieller Suppression** und **Peristaltikpumpe** zur Suppressorregeneration, sowie eingebautem **Degasser**. Das Gerät kann mit beliebigen Trenn- und Detektionsmethoden eingesetzt werden.

Typische Anwendungsgebiete:

- Anionen- oder Kationenbestimmungen mit sequenzieller Suppression und Leitfähigkeitsdetektion



### IC Conductivity Detector MB

Kompakter und intelligenter Hochleistungs-Leitfähigkeits-Detektor zu den intelligenten IC Geräten. Optimiert für Microboresäulen. Hervorragende Temperaturkonstanz, die gesamte Signalverarbeitung innerhalb des geschützten Detektorblocks und DSP – Digital Signal Processing – der letzten Generation garantieren höchste Präzision der Messung. Dank dem dynamischen Arbeitsbereich sind keine (auch nicht automatische) Bereichswechsel notwendig.

#### Typische Anwendungsgebiete:

- Anionen- oder Kationenbestimmungen mit chemischer Suppression, sequenzieller Suppression oder ohne Suppression und Leitfähigkeitsdetektion
- Optimierte für Microbore (2mm) Applikationen, ideal geeignet für Kupplungstechniken (IC-MS or IC-ICP/MS)

#### Spezifikation auf einen Blick:

- 0 ... 15000  $\mu\text{S}/\text{cm}$  ohne Bereichsumschaltung
- Zellvolumen: 0.3  $\mu\text{L}$
- Ringförmige Elektroden aus Edelstahl X2CrNiMo17-12-2 (316 L), kompatibel mit MSA
- Maximaler Betriebsdruck: 10.0 MPa (100 bar)
- Zelltemperatur: 20 ... 50  $^{\circ}\text{C}$  in Schritten von 5  $^{\circ}\text{C}$
- Temperaturstabilität: 0.001  $^{\circ}\text{C}$
- Basislinienrauschen: 0.2 nS/cm typisch für sequenzielle Suppression
- Kapillaren: ID 0.18 mm

Unterstützt mit MagIC Net 4.1 und höher



### 858 Professional Sample Processor

Der 858 Professional Sample Processor verarbeitet Proben von 500  $\mu\text{L}$  bis 500 mL. Der Proben transfer erfolgt entweder mittels Peristaltikpumpe am 850 Professional IC System oder durch einen 800 Dosino.