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.

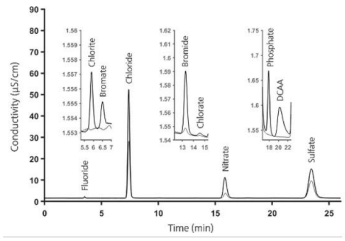
DCA is the acetate form of DCAA (dichloroacetic acid) and can be present in treated drinking water, as well as in groundwater and swimming pools, as a reaction product from organic material during the chlorination process [3, 8]. The provisional WHO guideline for DCA in drinking water is 0.05 mg/L, as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

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.

CONTACT

瑞士万通中国
北京市海淀区上地东路1号
院1号楼7层702
100085 北京

marketing@metrohm.com.cn

CONFIGURATION

Metrosep A Supp 20 - 150/4.0

Metrosep A Supp 20 - 150/4.0 是一款先进的阴离子色谱柱,设计用于为合规及高级应用提供高质量分离。其卓越的分离效率使其非常适用于需要精确测定标准阴离子和含氧卤化物的方法,包括 US EPA 300.1 A 和 B 部分以及 ISO 10304 第 1 和第 4 部分等标准。凭借在不同样品类型中稳定可靠的性能,它为实验室在常规分析和合规性要求的阴离子检测方面提供了稳定的解决方案。

Metrosep A Supp 20 - 150/4.0 基于耐用的聚苯乙烯/二乙烯基苯基材,其选择性针对等度碳酸盐淋洗液进行了优化,为日常阴离子色谱工作流程提供了尤为稳定且易于操作的解决方案。这确保了出色的长期稳定性,并与广泛应用的离子色谱方法完全兼容。

凭借其高阴离子交换容量,Metrosep A Supp 20 - 150/4.0 能够覆盖通常由高容量阴离子色谱柱处理的全范围应用,包括含氧卤化物、标准阴离子和二氯乙酸盐的测定。作为 Metrosep A Supp 20 系列的短柱型号,150/4.0 类型可为各种样品类型提供快速、准确的分析,适用于大多数测定。

Metrosep A Supp 20 Guard/4.0

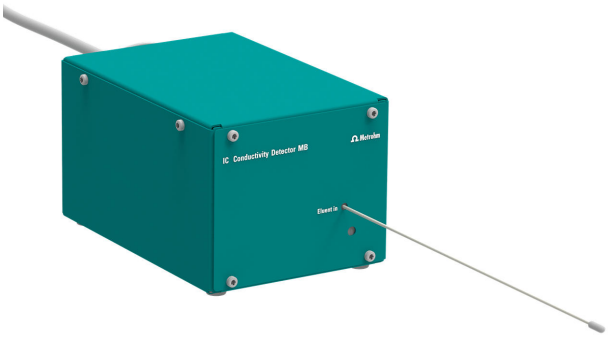
Metrosep A Supp 20 Guard/4.0 可有效阻挡样品或淋洗液中的污染物进入分离柱,为 Metrosep A Supp 20 分析柱提供可靠保护。该保护柱装填与对应分析柱相同的固定相,采用化学稳定性优异的 PEEK 柱管,可在不影响色谱分离质量的前提下,保护色谱柱性能并延长主分析柱使用寿命。

930 Compact IC Flex Oven/SeS/PP/Deg

930 Compact IC Flex Oven/SeS/PP/Deg 是智能型 Compact 离子色谱仪器,带有**柱加热炉**、**序列抑制**和**蠕动泵**用于抑制器再生,以及内置的**脱气装置**。该仪器可使用各种分离和检测方法。

典型的应用范围:

- 阴离子或阳离子测定,序列抑制法及电导检测



IC Conductivity Detector MB

用于智能型离子色谱仪的紧凑智能型高性能电导检测器。针对微孔柱经过优化。卓越的温度稳定性,在受保护的检测器端子板内完成整个信号处理过程以及最新一代的 DSP(数字式信号处理)均能确保测量的最高精确性。归功于动态工作范围,无需进行(也包括非自动)范围变更。

典型的应用范围:

- 阴离子或阳离子测定,化学抑制、序列抑制法或无抑制及电导检测
- 针对微孔 (2mm) 应用经过优化,尤其适合耦合技术(IC-MS 或 IC-ICP/MS)

规格说明书概览:

- 0 ... 15000 µS/cm 无区段切换
- 测量池容量:0.3 µL
- 由不锈钢 X2CrNiMo17-12-2 (316 L) 制成的环形电极,与 MSA 兼容
- 最大工作压力:10.0 MPa (100 bar)
- 池温:20 ... 50 ° C,步幅为 5 ° C
- 温度稳定性: 0.001 ° C
- 基线噪音:° 0.2° nS/cm,是使用序列抑制法的典型值
- 毛细管:ID 0.18 mm

支持 MagIC Net 4.1 和以上版本

858 Professional Sample Processor

858 Professional Sample Processor 可处理体积在 500 µL 至 500 mL 之间的样品。进行样品转移时,既可以使用 850 Professional IC System 上的蠕动泵、也可通过 800 Dosino 来进行。