



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  $\mu$ L. 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.

Sequential suppression, i.e. the combination of chemical and CO<sub>2</sub> 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<sub>2</sub> 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 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).

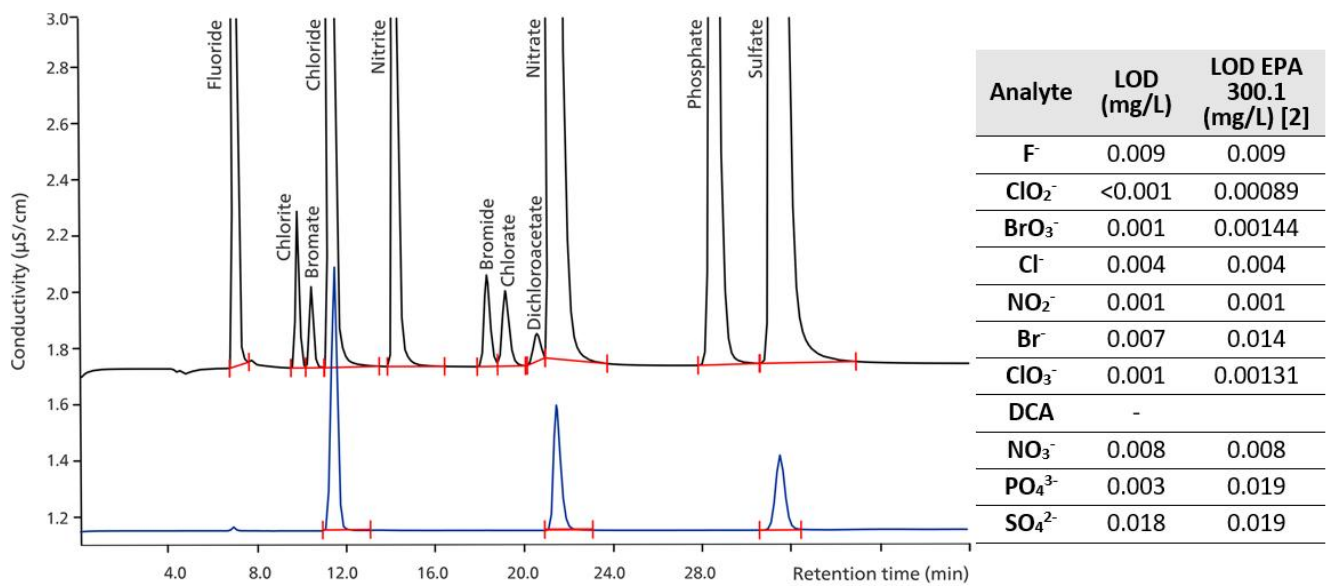
The relative standard deviations (RSDs) for repeated tap water analysis below 2.5% (Table 1, with exceptions for chlorite and bromate) and spike recoveries of 82–120% are within the common quality criteria and highlight the **repeatability, accuracy, and robustness** of the method. The determined detection limits (LODs) (according to DIN 62645) fit the EPA requirements (Figure 2) [8].



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

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.



**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 µ L). 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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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.

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## CONFIGURATION

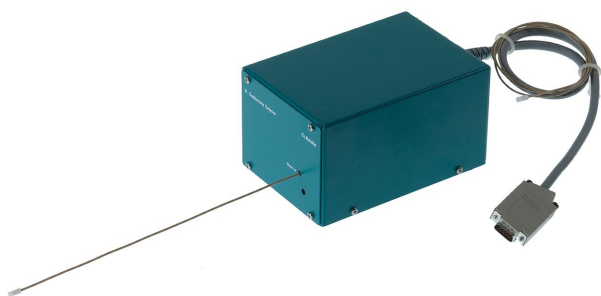


### 940 Professional IC Vario ONE/SeS/PP

940 フロフェッショナル IC Vario ONE/SeS/PP は連続サフレーションとサフレッサー再生のためのヘリスタリックホンフを備えたインテリシエントIC装置です。この装置は任意の分離メソッドおよび検出メソッドによって使用することかできます。

典型的な使用領域:

- 連続サフレーションおよび電気電導度検出器による陰イオンの測定
- 陰イオンのトレース分析
- 陰イオンのオンラインモニタリング



### IC Conductivity Detector

インテリシエントIC装置のためのコンパクトかつインテリシエントな高出力電気伝導度検出器。優れた温度安定性、保護された検出器フロック内の総合的な信号処理、最新版のDSP (Digital Signal Processing) が高精度の測定を保証します。稼動範囲がダイナミックなので測定範囲の変更は(自動のものも含めて)必要ありません。



### Metrosep A Supp 7 - 250/4.0

水処理における副産物 (消毒副産物) は、健康を害するだけではなく発がん性も疑われています。そのため、オキシハライトは、多くの調査や規格の対象となっています (例えば EPA 300.1 Part B、EPA 317.0、EPA 326.0 など)。その際、何よりも問題となっているのは、飲料水をオゾン処理する際に臭化物から生成される臭素酸塩です。Metrosep A Supp 7 - 250/4.0は、標準陰イオン、オキシハライトおよびシクロ酢酸の並行測定に高性能を発揮する分離カラムです。このカラムを用いることで、これらのイオンを  $\mu\text{g/L}$  の低い範囲まで、確実かつ精密に測定できます。5- $\mu\text{m}$  ホリヒニルアルコール・ホリマーを使用することで、検出感度が高まり、極端に高い理論段数を示し、その結果傑出した分離特性および検出特性を実現することかできます。さらに、温度変化によって、アプリケーション特有の条件に分離を順応させることかできます。



### 858 Professional Sample Processor – Pump

858 フロフェッショナルサンプルプロセッサ - ホンプは、500  $\mu$ Lから500 mLまでのサンプルを処理します。サンプルは内蔵式双方向性の2チャンネルのヘリスタリックホンプまたは800 トシーノ電動ヒュレットによって転送されます。

# MagIC Net

### MagIC Net 4.0 Compact: 1

インテリシエントなCompact IC装置、検出器、オートサンフラーあるいは771 Compact Interfaceの制御用のフロフェッショナルなPCプログラム。このソフトウェアにより、イオンクロマトグラフィー分析のチェック、データ記録・評価・モニタリングならびにレポート作成が可能。

ルーチンオペレーションのためのグラフィック ユーザーインターフェース、広範なデータベースプログラム、メソッド開発、コンフィクレーションならびに手動のシステム制御; 非常にフレキシブルなユーザー管理、高性能なデータベースオペレーション、広範なデータエクスポート機能、独自設定可能なレポート作成機能、全システムコンポーネントおよびクロマトグラフィー結果のコントロールおよびモニタリング。

MagIC Net CompactはFDA規定21 CFR ハート11およびGLPに完全に準拠。

MagIC Net は16のタイアロク言語で使用可能です: ドイツ語、英語、中国語 (繁体、簡体)、フランス語、イタリア語、スペイン語、ホルトカル語、フルカリア語、チェコ語、ハンカリー語、日本語、韓国語、ロシア語、スロハキア語、ホーランド語

1 ライセンス。

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