

Determining Inorganic Anions in Drinking Water

by Barbara Van Cann, Product Specialist Chromatography Software at Thermo Fisher Scientific, Takkebijsters 1, Breda, Netherlands

Water is essential to maintaining life and as such, drinking water needs to be safe for human consumption. Often sourced from ground, precipitation and surface water, there will inherently be impurities within it, which need to be maintained at concentrations low enough not to pose any risk to human health. Inorganic ions and oxyhalides in drinking water can lead to conditions such as fluorosis and methemoglobinemia, which is why the U.S. Environmental Protection Agency (EPA), and similar health and environmental standards agencies in other industrialised countries, have introduced ion chromatography as an approved method for compliance monitoring [1]. Environmental analysis labs are therefore faced with the challenge of accurately monitoring drinking water in line with these guidelines. However, traditional manual analysis methods using spreadsheets for result calculations can be unsafe and prone to human error. The introduction of chromatography software, where all data is held, analysed and reported using preconfigured and adaptable method specific templates, ensures that compliance is adhered to and data integrity is maintained.

Determining common inorganic ions and oxyhalides in drinking water is an extremely important ion chromatography (IC) application. This technique is approved by the Environmental Protection Agency (EPA Method 300.1) and similar health and environmental standards in other

industrialised countries, for compliance monitoring of inorganic anions in drinking water [1]. In addition many standards agencies such as the International Organization for Standardization (ISO), the American Society for Testing and Materials (ASTM) and the American Water Works

Association (AWWA) have validated IC methods for this use [2,3].

Due to their toxicity, the concentrations of inorganic anions in drinking water are regulated. For example:

- High levels of fluoride can cause skeletal

The screenshot displays the Thermo Scientific AppsLab interface. At the top, there is a navigation bar with 'Search', 'Find One-Click Workflows', and 'Run' buttons. Below this, a search bar contains the text '300.1'. The interface shows a list of search results for '300.1' with columns for 'Find a method', 'AU 126: Detect Diethanolamine in Surface Fin Scrubber Solu...', 'AU 131: Detect Nitrate in Drinking Water Using Ion Chromatography', and 'AU 166: Detect in Chondroitin Dietary Supplement'. A green circle 'A' is overlaid on the search bar. Below the search results, there are filters for 'Matrix', 'Column Manufacturer', 'Column Model', 'Column Length', 'Column Diameter', 'Column Particle Size/Film Thickness', and 'Column Stationary Phase'. A green circle 'B' is overlaid on the filter section. On the right side, there is a list of methods with a 'Download' button. A chromatogram showing peaks at 12, 13, 14, and 15 minutes is displayed. A green circle 'C' is overlaid on the download button. The chromatogram has a y-axis labeled 'Response' and an x-axis labeled 'Minutes'. The peaks are labeled with their retention times: 12, 13, 14, and 15. A green circle 'C' is overlaid on the download button.

Figure 1: Search (A), find (B) and download (C) methods in AppsLab Library

and dental fluorosis

- Nitrite/nitrate can cause methemoglobinemia, a condition which can be fatal to infants
- Ozonation of drinking water containing bromide can result in the formation of bromate, a potential carcinogen, even at low $\mu\text{g/L}$ concentrations

Even secondary contaminants, such as chloride and sulphate, can affect odour, colour and other aesthetic characteristics of drinking water.

EPA Method 300.1 describes in detail the entire analytical process for the determination of common inorganic anions and oxyhalides in drinking water. To generate reliable, accurate, and repeatable results when adhering to this methodology, quality control (QC) is essential. The QC procedures detailed within EPA Method 300.1 consist of an initial demonstration of performance, assessing laboratory performance within every analysis batch, and assessing analyte recovery and data quality. In addition, the procedures for calibration, standardisation, data analysis and calculations are described. The challenge that environmental analysis laboratories face is to correctly implement these guidelines. First an

Application Document	Title	EPA Method 300.1 Part	Thermo Scientific™ Dionex™ Columns
AN133	Determination of Inorganic Anions in Drinking Water by Ion Chromatography	A	IonPac AS4A-SC, Analytical, 4 × 250 mm IonPac AG4A-SC, Guard, 4 × 50 mm
AN154	Determination of Inorganic Anions in Environmental Waters Using a Hydroxide-Selective Column	A	IonPac AS18 Analytical, 4 × 250 mm IonPac AG18 Guard, 4 × 50 mm
AN167	Determination of Trace Concentrations of Oxyhalides and Bromide in Municipal and Bottled Waters Using a Hydroxide Selective Column with a Reagent-Free Ion Chromatography System	B	IonPac AS19 Analytical, 4 × 250 mm IonPac AG19 Guard, 4 × 50 mm
AN184	Determination of Trace Concentrations of Chlorite, Bromate, and Chlorate in Bottled Natural Mineral Waters	B	IonPac AS19 Analytical, 4 × 250 mm IonPac AG19 Guard, 4 × 50 mm IonPac AS23 Analytical, 4 × 250 mm IonPac AG23 Guard, 4 × 50 mm
AN208	Determination of Bromate in Bottled Mineral Water Using the CRD 300 Carbonate Removal Device	B	IonPac AS23 Analytical, 4 × 250 mm IonPac AG23, Guard, 4 × 50 mm
AN1113	Determination of Chloride and Sulphate in Water and Soil	A	IonPac AS18-4 μm Analytical, 2 × 250 mm IonPac AG18-4 μm Guard, 2 × 50 mm IonPac AS22 Analytical, 2 × 250 mm IonPac AG22 Guard, 2 × 50 mm
AU196	Anion Determinations in Municipal Drinking Water Samples Using EPA Method 300.1 (A) on an Integrated IC System	A	IonPac AS22 Analytical, 4 × 250 mm IonPac AG22 Guard, 4 × 50 mm
AU198	Improved Determination of Trace Concentrations of Oxyhalides and Bromide in Drinking Water Using a Hydroxide-Selective Column	B	IonPac AS27 Analytical, 4 × 250 mm IonPac AG27 Guard, 4 × 50 mm

Table 1: Overview of application documents describing analysis according to U.S. EPA Method 300.1

3.1 ANALYSIS BATCH -- A group of no more than 20 field samples (Field sample analyses include only those samples derived from a field sample matrix. These include the initial and duplicate field samples as well as all Laboratory Fortified Sample Matrices). The analysis batch must include an Initial Calibration Check Standard, an End Calibration Check Standard, Laboratory Reagent Blank, and a Laboratory Fortified Blank. Within an ANALYSIS BATCH, for every group of ten field samples, at least one Laboratory Fortified Matrix (LFM) and either a Field Duplicate, a Laboratory Duplicate or a duplicate of the LFM must be analyzed. When more than 10 field samples are analyzed, a Continuing Calibration Check Standard must be analyzed after the tenth field sample analysis.

The screenshot shows the 'EPA 300.1 2014-12-22 15-47-10' interface. It features a table with columns for 'Name', 'Type', 'Level', and '*Analysis_Type'. The table lists various samples and standards, including Laboratory Reagent Blank, Calibration Standards 1-6, Initial Calibration Check Standard, Laboratory Fortified Blank, Field Samples 10-27, Laboratory Fortified Matrix, Continuing Calibration Check Standard, and End Calibration Check Standard. A 'Sequence Preview' window is also visible, showing a detailed view of the sequence items.

The screenshot shows the 'rflow Editor - EPA Method 300.1 Templates' interface. It features a table with columns for 'Name', 'Type', 'Level', and '*Analysis_Type'. The table lists various samples and standards, including Laboratory Reagent Blank, Calibration Standards 1-6, Initial Calibration Check Standard, Laboratory Fortified Blank, Field Samples 10-27, Laboratory Fortified Matrix, Continuing Calibration Check Standard, and End Calibration Check Standard. A 'Sequence Preview' window is also visible, showing a detailed view of the sequence items.

Figure 2: From EPA method to sequence.

9.4.3 FIELD OR LABORATORY DUPLICATES -- The laboratory must analyze either a field or a laboratory duplicate for a minimum of 10% of the collected field samples or at least one with every analysis batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and insure the quality of the data. If none of the samples within an analysis batch have measurable concentrations, the LFM should be employed as a laboratory duplicate.

9.4.3.1 Calculate the relative percent difference (RPD) of the initial quantitated concentration (I_c) and duplicate quantitated concentration (D_c) using the following formula.

$$RPD = \frac{(I_c - D_c)}{((I_c + D_c)/2)} \times 100$$

9.4.3.2 Duplicate analysis acceptance criteria

Concentration range	RPD Limits
MRL to 10xMRL	+/- 20 %
10xMRL to highest calibration level	+/- 10 %

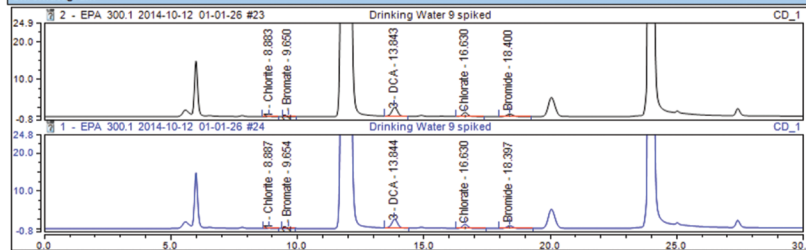
9.4.3.3 If the RPD fails to meet these criteria, the samples must be reported with a qualifier identifying the sample analysis result as yielding a poor duplicate analysis RPD. This should not be a chronic problem and if it frequently recurs (>20% of duplicate analyses) it indicates a problem with the instrument or individual technique.

Field or Laboratory Duplicates

Injection Details

Injection Name:	Drinking Water 9 spiked	Injection Date/Time:	30/Jun/14 17:34
Vial Number:	BD2	Run Time (min):	30.00
Injection Type:	Unknown	Injection Volume:	250.00
Analysis Type:	Duplicate	Channel:	CD_1
Instrument Method:	EPA 300.1 AS27	Dilution Factor:	1.0000
Processing Method:	EPA 300.1 Part B	Sample Weight:	1.0000

Chromatogram



LFB Results

No.	Peak Name	Ret. Time min	Area $\mu\text{S}^2\text{min}$	Height μS	Amount $\mu\text{g/L}$	MRL $\mu\text{g/L}$	RPD Limit %
1	Chlorite	8.89	0.015	0.079	14.368	9.970	20.0
2	Bromate	9.65	0.001	0.005	1.851	0.980	20.0
3	DCA	13.84	0.611	2.328	983.227	n.a.	10.0
4	Chlorate	16.63	0.260	1.081	186.760	10.670	10.0
5	Bromide	18.40	0.188	0.691	186.687	15.010	10.0

LFM Recovery Results

Injection Name	Duplicate	Amount $\mu\text{g/L}$					
		Chlorite	Bromate	DCA	Chlorate	Bromide	
Drinking Water 9 spiked	Duplicate 1	14.407	1.853	986.730	187.218	187.117	
Drinking Water 9 spiked	Duplicate 1	14.368	1.851	983.227	186.760	186.687	
	RPD (%)	0.1	0.0	0.1	0.1	0.1	
	Result	Passed	Passed	Passed	Passed	Passed	

analytical method, including experimental conditions suitable for instrumentation available in the laboratory, needs to be identified and implemented. Next the guidelines as described in the EPA method, including calculating and assessing the final results, need to be executed correctly. This can prove challenging, since data is often manually transferred to an external spreadsheet, a process which can be both time consuming and open to errors. These spreadsheets are uncontrolled, with no automatic tracking or versioning of changes.

Here we look at how a system, such as an eWorkflow in the Thermo Scientific™ Dionex™ Chromeleon™ 7.2 Chromatography Data System (CDS) software, performs the determination of inorganic anions according to the requirements as described in EPA Method 300.1.

Experimental Methods and Results

The experimental conditions for the execution of the EPA Method 300.1 are described in detail across several application documents, which can be found in Thermo Scientific™ AppsLab Library of Analytical Applications (Figure 1) and are listed in Table

1 below. Each experiment was performed using Thermo Scientific instruments and columns to meet the different EPA Method Part A or B criteria.

For method execution, an electronic workflow (eWorkflow) was used, to provide guidance throughout an entire analysis batch, from initial sample to final results. The eWorkflow assists in creating an appropriate sequence of actions, with predefined associated files and the correct injection order. The processing method and report templates are included to ensure that the data is processed correctly and final calculations and checks are readily available. A dedicated eWorkflow for the EPA Method 300.1 can be downloaded from the AppsLab Library. This ensures that every step of the EPA specified protocol is undertaken in the correct order, without error.

EPA Method 300.1 provides a detailed description about which order the field samples, standards and other related solutions need to be injected (Figure 2A). This order is also dependent on the total number of field samples and therefore subject to change. The dedicated EPA eWorkflow defines the order of injections (Figure 2B) and if the field number varies, it automatically adjusts to have the correct number of calibration checks and

standards. Due to this automatic adjustment functionality, the result is a consistent sequence table with the correct structure that conforms to the EPA requirements (Figure 2C).

The generated sequence contains specific columns to identify the individual injections (analysis type, fortified and duplicate), and the component table of the processing method contains columns to enter parameters specific for the EPA Method 300.1, such as minimum detection and reporting limits. Combining the information present in the sequence and processing method with calculations in the spreadsheet-based report of the software, provides a complete solution that converts all information as described in the EPA Method 300.1 to a final analysis report (Figure 3), eliminating the need to transfer any data to an external spreadsheet. As a result, the likelihood of errors being introduced is minimised and data integrity is ensured.

Figure 3a shows EPA Method 300.1, Chapter 9.4.3, and details the calculation and evaluation of the field or laboratory duplicates. Section 9.4.3.1 defines the calculation for the relative percentage difference (RPD), which can be performed within the software's reporting tools. Then the RPD limit should be determined, since

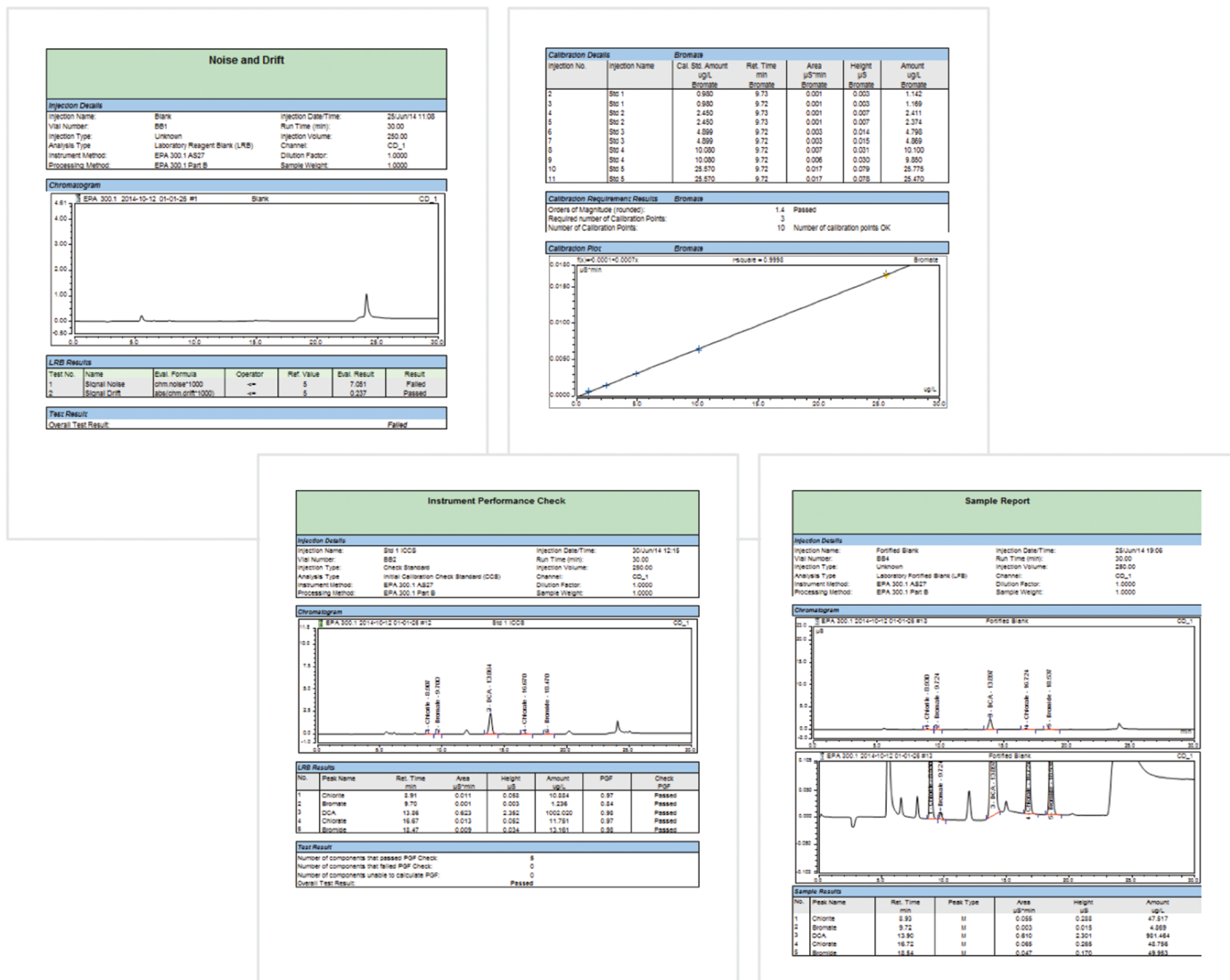


Figure 4: Example pages of the final report

this depends on the concentration of the analyte relative to its minimum reporting limit (MRL). The calculated RPD for the duplicate injection set is compared to the RPD limit and the evaluation result is reported. To complete the process, a final report can be created, which details the results for each individual section of the EPA Method 300.1 (Figure 4).

Conclusion

The analysis of drinking water in compliance with guidelines such as those set by the US EPA is an important part of environmental analysis, and one which can be greatly simplified through the use of chromatography software. In order to get the full benefit of such software, advanced application expertise is often required to ensure that method development is optimised. There are few online portals offering complete application data and methods, and those that do typically require adaptation to

the methods to make them usable in the lab. The AppsLab Library is the only online application search engine providing downloadable, ready to run analytical methods, including EPA Method 300.1.

The combination of AppsLab Library and Chromeleon CDS enables analysts to unite their chromatography software with an extensive repository of applications and eWorkflows, simplifying the path to compliance with regulatory requirements. By the EPA Method 300.1 eWorkflow, environmental analysis laboratories can make sure that analyses are executed according to all guidelines for the determination of inorganic anions and oxyhalides in drinking water, ensuring compliance. The built-in reporting template provides error-free results without the need to export to an external spreadsheet removing time-consuming and error-prone manual transcriptions.

www.thermoscientific.com/chromeleon

www.thermoscientific.com/appslab

References

1. Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography; U.S. Environmental Protection Agency, National Exposure Research Laboratory, Office of Research and Development: Cincinnati, Ohio, 1997. [Online] http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_300_1.pdf (accessed May 19, 2015).
2. Greenberg, A. E.; Clesceri, L. S.; Eaton, A. D., Eds.; Standard Methods for the Examination of Water And Wastewater, 18th ed.; American Public Health Association: Washington, DC, 1992.
3. Standard Test Methods for Anions in Water by Chemically Suppressed Ion Chromatography; American Society for Testing and Materials; West Conshohocken, PA; 1999, D4327-97, Vol. 11.01, 420–427.