

# Chromeleon CDS Workflow for Determination of Inorganic Anions in Drinking Water According to U.S. EPA Method 300.1

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## Keywords

Disinfection Byproduct, EPA Method 300.1, Ion Chromatography, Water Analysis, Chromeleon 7.2 CDS

## Goal

Demonstrate the use of a complete Chromeleon CDS solution for determination of inorganic anions in drinking water according to U.S. EPA Method 300.1.

## Introduction

The determination of common inorganic anions and oxyhalides in drinking water is one of the most important ion chromatography (IC) applications worldwide. IC has been approved for compliance monitoring of inorganic anions in United States (U.S.) drinking water since the mid-1980s, as described in U.S. Environmental Protection Agency (EPA) Method 300.1.<sup>1</sup> Many other industrialized countries have similar health and environmental standards and a considerable number of regulatory IC methods have been published worldwide (e.g., in Germany, France, Italy, and Japan). In addition, many standards organizations, including the International Organization for Standardization (ISO), American Society for Testing and Materials (ASTM), and American Water Works Association (AWWA), have validated IC methods for the determination of inorganic anions in drinking water.<sup>2,3</sup>

The concentrations of some anions in drinking water are regulated due to their toxicity. For example, high levels of fluoride can cause skeletal and dental fluorosis, and nitrite and nitrate can cause methemoglobinemia, which can be fatal to infants. Ozonation of drinking water containing bromide can result in the formation of the disinfection byproduct bromate, a potential human carcinogen even at low  $\mu\text{g/L}$  concentrations. Other common anions, such as chloride and sulfate, are considered secondary contaminants and can affect odor, color, and certain aesthetic characteristics in drinking water.



## U.S. EPA Method 300.1

EPA Method 300.1 describes in detail the entire analytical process for determination of common inorganic anions and oxyhalides in drinking water. This includes descriptions of the practical execution of the analysis, like equipment, supplies, reagents, and standards, and procedure for collecting, preservation and storage of water samples. To generate reliable results when using IC in environmental analysis, quality control (QC) is essential. EPA Method 300.1 provides detailed instructions on the QC procedures to be implemented, consisting of three parts:

- Initial demonstration of performance (outside scope of presented solution)
- Assessing laboratory performance within every analysis batch
- Assessing analyte recovery and data quality

Finally, the procedures for calibration, standardization, data analysis, and calculations are described.

The laboratory's challenge is to correctly execute the guidelines as described in the EPA method, including calculating and assessing the final results. Often data is manually transferred to an external spreadsheet which is a time consuming and error prone process. Additionally, there is often poor control over these spreadsheets with no automatic tracking or versioning available.

This technical note presents a complete Thermo Scientific™ Dionex™ Chromeleon™ 7.2 Chromatography Data System (CDS) workflow solution to perform the determination of inorganic anions according to the requirements as described in EPA Method 300.1.

## Experimental

The experimental conditions for execution of U.S. EPA Method 300.1 are described in several application documents, which are listed in Table 1.

Because of the variety of Thermo Scientific™ Dionex™ instruments and columns to perform successful analysis according to EPA Method 300.1, the Chromeleon workflow solution does not contain an instrument method and run parameters.

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

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 Sulfate in Water and Soil	A	IonPac AS18-4µm Analytical, 2 × 250 mm IonPac AG18-4µm 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 AG27Guard, 4 × 50 mm

A Chromeleon eWorkflow is an electronic procedure that provides guidance throughout an entire analysis batch, from initial samples to final results. It assists in creating an appropriate sequence with predefined associated files and a well-defined structure. The processing method and report templates ensure the data is processed correctly and final calculations and checks are readily available. A dedicated eWorkflow for EPA Method 300.1 has been created for both parts A and B (Figure 1).

EPA Method 300.1 provides a detailed description about which order the field samples, standards, and other related solutions such as duplicates of fortified samples etc. should be injected (Figure 2A). The sequence also depends on the total number of field samples. The EPA eWorkflow (Figure 2B) predefines the order of injections, and if the number of field samples varies, automatically adjusts to have the correct number of calibration check standards. Because the eWorkflow automatically adjusts based on the number of samples, the result is a consistent sequence table with the correct structure that conforms to the EPA requirements (Figure 2C).

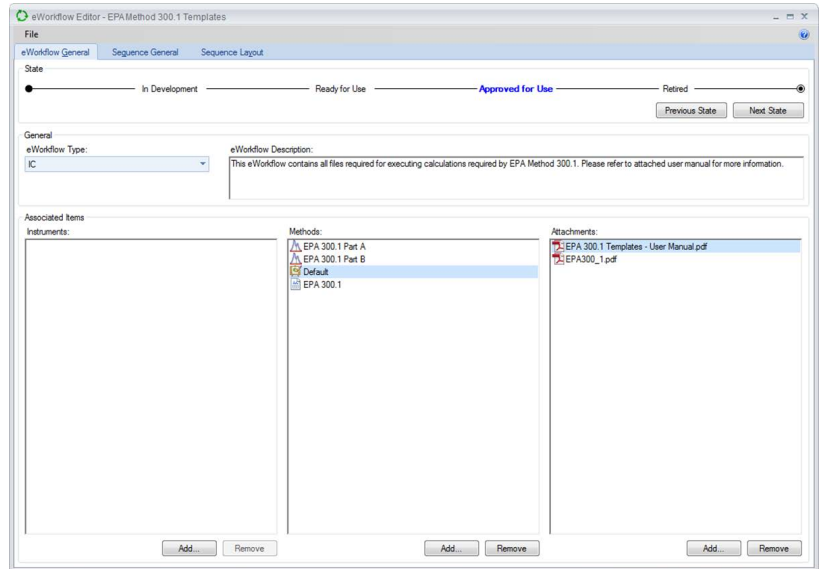


Figure 1. Chromeleon eWorkflow for EPA Method 300.1.

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 Laboratory Fortified Sample Matrices). The analysis batch must include an Initial Calibration Check Standard, and 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.

Chromatogram	No. of Inj	Name	Type	Level	*Analysis_Type	*Fortified	*Duplicate	Pos
<b>Sequence Header - 8 items</b>								
n.A	1	Laboratory Reagent Blank	Unknown		Laboratory Reagent Blank (LRB)	LFB Set		
n.A	1	Calibration Standard 1	Calibration Standard	01	Initial Calibration Standard (CAL)			
n.A	1	Calibration Standard 2	Calibration Standard	02	Initial Calibration Standard (CAL)			
n.A	1	Calibration Standard 3	Calibration Standard	03	Initial Calibration Standard (CAL)			
n.A	1	Calibration Standard 4	Calibration Standard	04	Initial Calibration Standard (CAL)			
n.A	1	Calibration Standard 5	Calibration Standard	05	Initial Calibration Standard (CAL)			
n.A	1	Calibration Standard 6	Calibration Standard	06	Initial Calibration Standard (CAL)			
		Standard 01			Initial Calibration Check Standard (CCS)			
		Standard 02			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 03			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 04			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 05			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 06			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 07			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 08			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 09			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 10			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 11			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 12			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 13			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 14			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 15			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 16			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 17			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 18			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 19			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 20			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 21			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 22			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 23			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 24			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 25			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 26			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 27			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 28			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 29			Laboratory Fortified Blank (LFB)	LFB Set		
		Standard 30			Laboratory Fortified Blank (LFB)	LFB Set		

Figure 2. From EPA method to sequence.

Name	Type	Level	*Analysis_Type	*Fortified	*Duplicate
Std 5	Calibration Standard	05	Initial Calibration Standard (CAL)		
Std 1 ICCS	Check Standard	01	Initial Calibration Check Standard (CCS)		
Fortified Blank	Unknown		Laboratory Fortified Blank (LFB)	LFB Set	
Drinking Water 1	Unknown		Field Sample		
Drinking Water 2	Unknown		Field Sample		
Drinking Water 3	Unknown		Field Sample		
Drinking Water 4	Unknown		Field Sample		
Drinking Water 5	Unknown		Field Sample		
Drinking Water 6	Unknown		Field Sample		
Drinking Water 7	Unknown		Field Sample		
Drinking Water 8	Unknown		Field Sample		
Drinking Water 9	Unknown		Field Sample	LFM Set 1	
Drinking Water 9 spiked	Unknown		Laboratory Fortified Sample Matrix (LFM)	LFM Set 1	Duplicate 1
Drinking Water 9 spiked	Unknown		Duplicate		Duplicate 1
Std 3 CCCS	Check Standard	03	Continuing Calibration Check Standard (CCS)		
Drinking Water 10	Unknown		Field Sample		
Drinking Water 11	Unknown		Field Sample		

Figure 3. Injection identification columns.

#	Name	Ret.Time	Window	*MDL	*MRL	*Add. LFB	*Add. LFM	*LFM Rec. Limit Low	*LFM Rec. Limit High
1	Chlorite	8.900	2.500 RG	0.8900 [µg/L]	9.9700 [µg/l]	47.960 [µg/l]	9.970 [µg/l]	75 [%]	125 [%]
2	Bromate	9.700	2.500 RG	1.4400 [µg/L]	0.9800 [µg/l]	4.900 [µg/l]	0.980 [µg/l]	75 [%]	125 [%]
3	DCA	13.900	2.500 RG			983.800 [µg/l]	983.800 [µg/l]	75 [%]	125 [%]
4	Chlorate	16.700	2.500 RG	1.4400 [µg/L]	10.6700 [µg/l]	48.970 [µg/l]	102.200 [µg/l]	75 [%]	125 [%]
5	Bromide	18.500	2.500 RG	1.3100 [µg/L]	15.0100 [µg/l]	48.970 [µg/l]	102.200 [µg/l]	75 [%]	125 [%]

Figure 4. Component columns for EPA specific parameters.

The generated sequence contains specific columns to identify the individual injections; Analysis Type (Figure 3A) as specified in chapter 3.1 of EPA Method 300.1, Fortified (Figure 3B) to identify fortified sample sets, and Duplicate (Figure 3C) to identify duplicate sample sets.

Additionally, the component table of the processing method contains columns to enter parameters specific for EPA Method 300.1 (Figure 4), such as minimum detection and reporting limits, and additions to fortified samples with corresponding recovery limits.

Combining the information present in the sequence and processing method with calculations in the spreadsheet-based reporting capabilities of Chromeleon CDS, provides a complete solution that converts all information as described in the method (Figure 5A) to a final analysis report (Figure 5B), without the need to transfer data to an external spreadsheet. This minimizes the possibility of human error and ensures data integrity.

Figure 5 shows an example of EPA Method 300.1, Chapter 9.4.3, detailing the calculation and evaluation of the field or laboratory duplicates. Section 9.4.3.1 defines the calculation for the relative percent difference (RPD). This calculation is performed in the Chromeleon CDS report template (Figure 5-1). Subsequently the RPD limit should be determined, as this depends on the concentration of the analyte relative to its minimum reporting limit (MRL) (Figure 5-2). Finally the calculated RPD for the duplicate injection set is compared to the RPD limit and the evaluation result is reported (Figure 5-3).

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 have measurable concentrations, the LFM should be employed as a laboratory duplicate.

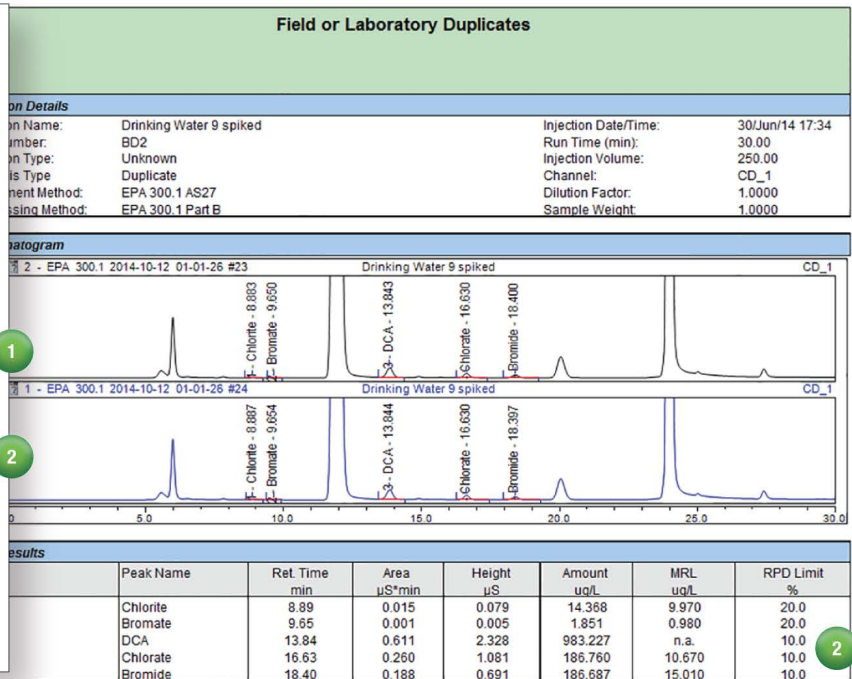
9.4.3.1 Calculate the relative percent difference (RPD) of the initial quantitated concentration ( $I_c$ ) and duplicate quantitated concentration ( $D_c$ ) using the following formula,

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

9.4.3.2 Duplicate analysis acceptance criteria  
 Concentration Range  
 MRL to 10×MRL  
 10×MRL to highest calibration level

RPD Limits  
 +/- 20%  
 +/- 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.



Injection Name	Duplicate	Chlorite	Bromate	Amount µg/L 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

Figure 5. Translation of EPA Method 300.1 Chapter 9.4.3 to Chromeleon CDS reporting.

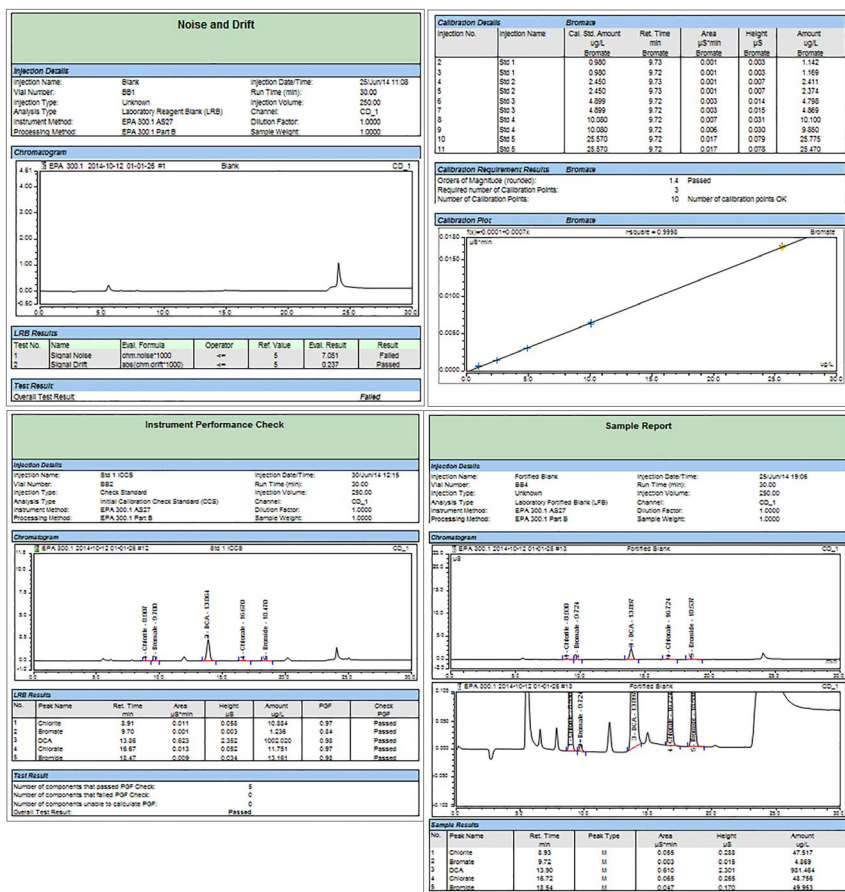


Figure 6. Example pages of the final report.

As a last step in the process the final report can be created, reporting the results for each individual section of EPA Method 300.1 (Figure 6). The report template is preconfigured to report the correct sheets for the correct analysis types.

### Conclusion

The eWorkflow in Chromeleon 7.2 CDS offers a user-friendly approach to analysis setup and data handling for the determination of inorganic anions and oxyhalides in drinking water according to U.S. EPA Method 300.1. The general settings included in the eWorkflow can easily be adapted to suit the demands of any laboratory. The U.S. EPA Method 300.1 eWorkflow ensures the analysis is executed according to all guidelines as described in the EPA method. The built-in reporting template provides instant and error free reporting, without the need to export the data to an external spreadsheet.

### References

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