Application note | 002395

Automated wet chemical analysis

Automated method to detect chloride in drinking water using the Thermo Scientific Gallery Aqua Master discrete analyzer

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Keywords

Gallery Aqua Master discrete analyzer, discrete analyzer, automated chloride test methods, EPA SDWA compliant test methods, drinking water

Application benefits

- Provides a novel discrete analyzer-based automated method for drinking water chloride testing for compliance measurements that follows the United States Environmental Protection Agency (US EPA) Safe Drinking Water Act (SDWA)
- Meets the performance requirements of other EPA approved chloride methods
- Minimizes used volumes of hazardous reagents and their associated costs
- Automation and ready-to-use reagents save time and reduce errors compared to manual approaches

Goals

- Establish an automated chloride analysis method for drinking water samples using the Thermo Scientific™ Gallery™ and Gallery™ Plus Aqua Master Discrete Analyzers in compliance with the US EPA SDWA
- Demonstrate that results obtained using the Gallery Aqua Master discrete analyzer-based automated method correlate well with and meet the quality control (QC) acceptance criteria in the EPA-approved Standard Method SM4500-Cl- B. Argentometric Method
- Analyze spiked tap waters to verify that the Gallery Aqua Master discrete analyzer-based automated method is applicable to different types of tap water samples

Introduction

Compliance with standards and regulations is essential in a world continuously faced with environmental challenges. In particular, analysis of drinking water for contaminants such as inorganic anions, cations, heavy metals, organic pollutants, and nutrients is required to protect public health. It is also important to provide drinking water with good aesthetic quality without causing damage to the distribution system. In the US, the quality of drinking water is regulated and supervised by the US EPA. Guidelines including analyses of water-quality parameters other than those concerning health are given under the 40 CFR Part 143, Subpart A. National Secondary Drinking Water Regulations.[1]

Measuring chloride levels in drinking water is important, even though chloride itself is not a heath concern.[2] In addition to causing a salty taste, excessive concentrations of chloride can contribute to drinking-water distribution-network corrosion and, in the worst cases, can result in copper and lead release into drinking water.[3] The US EPA sets the Secondary Maximum Contaminant Level (SMCL) for chloride at 250 mg/L.[4] Traditional methods based on titrimetry are well known and accurate. However, these methods are time-consuming and contain manual steps that are potential sources of measurement inaccuracies. These challenges have triggered the need to develop a different way of doing the analysis.

The Thermo Scientific Drinking Water Method: Drinking Water Chloride for Thermo Scientific Gallery Discrete Analyzer[5] is a photometric method that uses ready-to-use reagents and fully automated test workflows for measuring chloride. In the method, the chloride present releases thiocyanate ions from mercury (II) thiocyanate. The released thiocyanate ions react further with iron (III) nitrate in acidic medium and form a red/brown iron (III) thiocyanate complex. The intensity of the stable color produced is measured photometrically at a wavelength of 480 nm and is proportional to the original chloride concentration.

This method references SM4500-Cl- B. Argentometric Method which is EPA approved under 40 CFR Appendix A to subpart C of Part 141 and compliant to National Secondary Drinking Water Regulations (NSDWR) based on the SDWA.

The Thermo Scientific method uses the Gallery or Gallery Plus Aqua Master discrete analyzer in combination with ready-to-use reagents (part # 984364 or 984365 Chloride) and test procedures. The method makes it possible to monitor chloride levels following the SDWA regulations while accessing the benefits of discrete analyzer technology. The method is easily automated and allows simultaneous analysis of multiple parameters from the same sample aliquot, automatic spiking procedures, flexible test and QC parameter configuration, and flexible result reporting with versatile features for configuring report templates. As an integrated and automated platform, the Gallery Aqua Master discrete analyzer workflow eliminates the need to handle hazardous reagents and increases laboratory productivity by freeing staff to work on other tasks.

Experimental

Materials and methods

A detailed description of the necessary equipment and supplies; reagents, calibrators, and control preparation; and test parameters are provided in the Thermo Scientific Drinking Water Method: Drinking Water Chloride for Thermo Scientific Gallery Discrete Analyzer.[5]

Equipment

Gallery Plus Aqua Master automated photometric discrete analyzer

Reagents

Thermo Scientific system reagent for environmental and industrial analysis, part # 984364 Chloride, was used. The kit contains the ready-to-use reagent for analyzing chloride with the Gallery discrete analyzers.

Deionized water was also used.

Calibrator and controls

- 1000 mg/L calibration stock solution was prepared from sodium chloride (≥99.8%): 0.3299 g per liter of laboratory reagent water. This solution was used to prepare calibrators and continuing calibration verification samples.
- Thermo Scientific standard material 984721 Chloride Std, 1000 ppm, 500 mL was used to prepare the quality control (QCS), initial and ongoing QC samples.

Test parameters

Table 1 provides the automated test workflow using the Chloride system reagents (part # 984364). Table 2 provides the calibration parameters.

Table 1. Automated test workflow

Automated test flow	DW CL- L (low range)	DW CL- H (high range)
Chloride R1	120 µL	120 µL
Incubate	240 s	240 s
Blank measurement	480 nm	480 nm
Sample	100 µL	80 µL
Incubate	240 s	240 s
End-point measurement	480 nm	480 nm

Table 2. Calibration parameters

	DW CL- L (low range)	DW CL- H (high range)
Test range	Up to 20 mg/L	Up to 500 mg/L with automated secondary dilution 1+4
Primary (calibration) range	Up to 20 mg/L	Up to 100 mg/L
Calibration type	2nd order	2nd order
Calibrator dilution	Automated from 100 mg/L solution	Automated from 500 mg/L solution
QC	Automated calibration QC, ongoing QC	Automated calibration QC, ongoing QC

Samples

In addition to analyzing several different standard samples, the study included analysis of three different tap waters, spiked with known amounts of analyte. Certified reference material ERA #698 was also tested.

Results and discussion

Calibration and calibration verification

Calibrators were prepared from a standard chloride solution and analyzed using the Gallery Aqua Master discrete analyzer. The analyzer automatically calculates blank-subtracted responses for each analyzed sample and plots the responses against standard concentrations to create the calibration curve. Figures 1A and 1B present examples of the calibration curves obtained for low (L) and high (H) ranges.

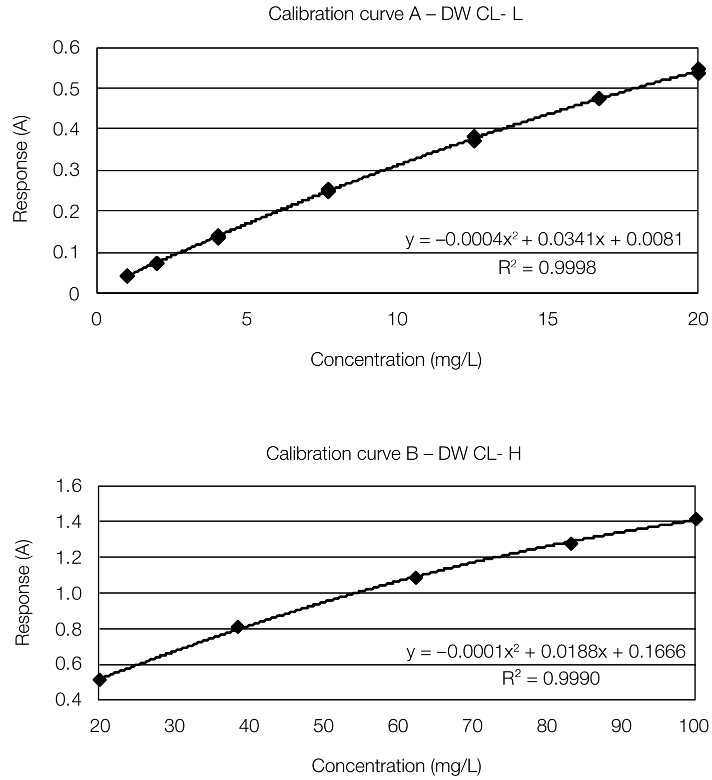

Figure 1. Example calibration curves obtained from the Thermo Scientific Drinking Water Method: Drinking Water Chloride for Thermo Scientific Gallery Discrete Analyzer, A) low-range calibration, and B) high-range calibration.

Each calibration was verified by the analysis of second-source standard samples. Table 3 lists the results of the verification.

Table 3. Quality control sample (QCS) results

QCS-sample	Test	Result (mg/L)	% Recovery
Cl- QCS 4 mg/L	DW CL- L	3.9	**97%**
Cl- QCS 18 mg/L	DW CL- L	17.7	**98%**
Cl- QCS 30 mg/L	DW CL- H	31.4	**105%**
Cl- QCS 90 mg/L	DW CL- H	87.8	**98%**

Method detection limit (MDL)

The MDL was defined using low-concentration standard samples (LFB) and blank samples (LRB) following the EPA approach described in 40 CFR Part 136 Appendix B.[6] The MDL results are listed in Table 4.

Table 4. Results for defining MDL

Sample	Results (mg/L) 0.4 mg/l LFB	Results (mg/L) LRB
Average	0.41	0.13
Min	0.37	0.09
Max	0.43	0.16
n	7	7
Std. deviation (SD)	0.02	0.02
MDL (LFB/LRB)	**0.07**	**0.06**
MDL applied	**0.1**	

Minimum reporting level (MRL)

The MRL was estimated to be at the lowest calibrator level. Seven replicate standard samples (LFB) were analyzed at this concentration to confirm the MRL according to the EPA recommended procedure[7] (Table 5). The MRL was confirmed to be 1.0 mg/L.

Table 5. MRL confirmation results

Sample: 1.0 mg/L Cl- Std, 7 replicates	
% Recovery	93% (92–94%)
% RSD (n=7)	0.5%

Operational range

The operational range was verified by analyzing standard samples for three different method ranges. The results are shown in Figure 2. Recoveries of samples within initial and extended calibration ranges were 96–106%.

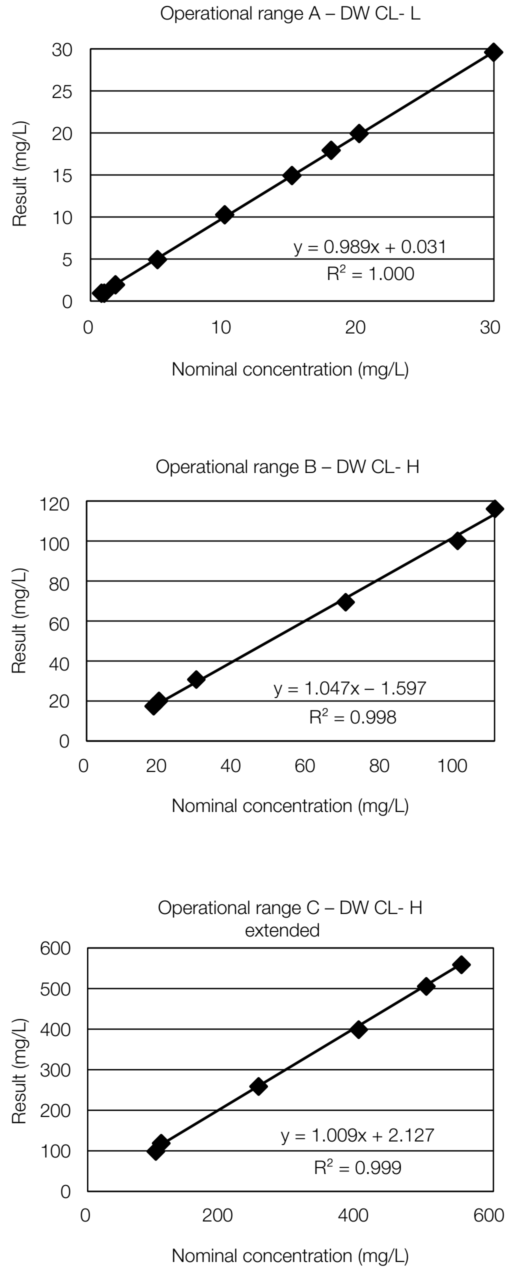

Figure 2. Correlation of results and the nominal values of the operational range samples. A) low-range concentration, B) high-range concentration, and C) extended range concentration.

Ongoing QC

To control method performance between calibrations, chloride standard samples were automatically analyzed by the Gallery Plus Aqua Master discrete analyzer in sample intervals of ten. Both the low and high test had two levels of standard samples (LFB) – low and high. 300 mg/L LFB was analyzed only with samples that were analyzed at the extended range. Results from this ongoing QC procedure, also known as the ongoing precision and recovery (OPR), are provided in Table 6.

Spike samples

Accuracy of the method in sample matrix was tested by analyzing spiked samples, also known as Laboratory Fortified Matrix (LFM).

Three tap water samples were spiked with known concentrations of chloride standard:

1. Tap water 1: treated drinking water sample from a surface water source.
2. Tap water 2: treated drinking water sample from a ground water source with high hardness (254 mg $CaCO_3$/L).
3. Tap water 3: treated drinking water sample from a surface water source with high total organic carbon (TOC) of 2.3 mg/L.

The results of the spike sample analyses are provided in Table 7.

Certified reference material (CRM)

To verify the accuracy of the method a NIST-traceable reference material (CRM) was analyzed in four replicates diluted to both calibration ranges. The CRM results are presented in Table 8.

Table 6. Precision and accuracy data for ongoing QC analyses (OPR)

Sample	Test	Average % recovery	Min. % recovery	Max. % recovery	Number of results	% RSD
Cl- LFB 2	DW CL- L	96%	94%	99%	22	1.2%
Cl- LFB 4	DW CL- L	97%	94%	98%	7	1.8%
Cl- LFB 18	DW CL- L	100%	97%	102%	33	1.3%
Cl- LFB 30	DW CL- H	104%	101%	106%	23	1.5%
Cl- LFB 90	DW CL- H	101%	98%	104%	20	1.9%
Cl- LFB 300 (dil. 1+4)	DW CL- H	103%	102%	103%	4	0.2%

Table 7. Laboratory Fortified Matrix (LFM) sample results. Each of the three tap water samples were spiked with 10 and 50 mg/L of chloride. D = duplicate sample.

Sample	Spike % recovery	% RPD
Tap water 1 (5 mg/l)		
Tap water 1 +10	99%	0.6%
Tap water 1+10 D	98%	
Tap water 1 +50	103%	1.2%
Tap water 1 +50 D	102%	
Tap water 2 (126 mg/L)		
Tap water 2 +10	98%	0.4%
Tap water 2 +10 D	104%	
Tap water 2 +50	112%	0.5%
Tap water 2 +50 D	111%	
Tap water 3 (27 mg/L)		
Tap water 3 +10	107%	0.5%
Tap water 3 +10 D	109%	
Tap water 3 +50	104%	0.7%
Tap water 3 +50 D	103%	

Table 8. CRM results

Sample: ERA #698, target: 118 mg/L *(analyzed in four replicates diluted to both calibration ranges)*		
	DW CL- L	DW CL- H
% recovery	97%	101%
% RSD (n=4)	1.0%	0.3%

Method comparison

The results for tap water samples measured using the Gallery discrete analyzer method were compared to results obtained from the EPA approved reference method: SM4500-Cl- B. Argentometric Method. The results are shown in Figure 3.

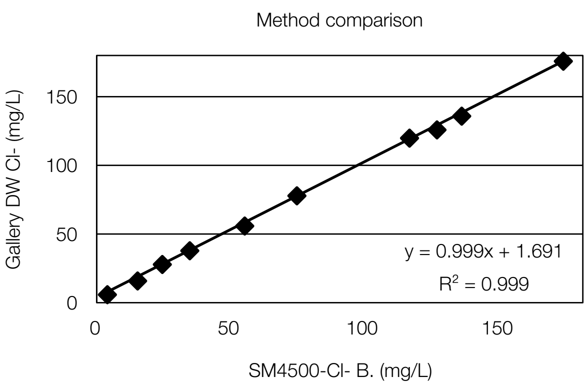

Figure 3. Correlation of the Gallery discrete analyzer method results with the reference method results for the tap water samples.

Conclusions

Table 9 summarizes the results from the performance study of the Thermo Scientific Drinking Water Method: Drinking Water Chloride for Thermo Scientific Gallery Discrete Analyzer. The results demonstrate that the Gallery Aqua Master discrete-analyzer-based automated method meets and, in many cases, exceeds the QC acceptance criteria of the EPA approved reference method: SM4500-Cl- B. Argentometric Method. Using the Gallery discrete analyzer method, it is possible to reach lower detection and reporting limits and better precision than with the reference method. Most importantly, good correlation with the EPA approved reference method was obtained.

The Thermo Scientific Drinking Water Method: Drinking Water Chloride for Thermo Scientific Gallery Discrete Analyzer offers laboratories an easy approach for chloride compliance measurements* that minimize the challenges associated with traditional titrimetric methods. The discrete analyzers automate the entire analysis, delivering high-throughput results without having to use time-consuming and laborious titration. Convenient ready-to-use reagents reduce the need to handle hazardous chemicals, improving work safety, and removing a source of experimental error.

*Each laboratory is responsible for validating their analytical methods for compliance measurements and for getting approval for the method from the corresponding authority if required.

Table 9. Performance of the Drinking Water Chloride method for Gallery discrete analyzer compared to EPA approved reference method acceptance criteria.

	QC acceptance criteria for reference method SM4500-Cl- B. Argentometric Method	Performance results for reference method SM4500-Cl- B. Argentometric Method	Performance of Thermo Scientific Drinking Water Chloride method for the Gallery Discrete Analyzer	Pass/Fail
MDL	To be done according to 40 CFR Part 136. Appendix B.[6]	2.0 mg/L	0.1 mg/L when done according to 40 CFR Part 136. Appendix B.[6]	Pass
MRL	NA	3 mg/L with EPA recommended procedure[7]	1.0 mg/L with EPA recommended procedure[7]	Pass
Method blank	≤ ½ MRL	-1.5–0.5 mg/L	max. 0.2 mg/L	Pass
% Recovery operational range	±10% when c > 5 × MRL ±20% when c > 2 and ≤ 5 × MRL ±50% when c ≤ 2 × MRL	NA	96–106% 92–99% when c ≤ 2 × MRL	Pass
% Recovery QCS	±10%	NA	96–105%	Pass
% Recovery OPR	NA (Proficiency test limits for chloride ±15%[8])	93–110%	94–106%	Pass
% Recovery spike sample	NA (Wider limits may be used than for IPR)	101–115%	98–112%	Pass
% RSD OPR	NA (Industry acceptable max. 20%)[9]	0.4–5.6%	0.2–1.9%	Pass
Relative percent difference (% RPD) Spike duplicates	NA (Industry acceptable max. 20%)[9]	0.4–7.3%	0.4–1.2%	Pass

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