

Automated wet chemical analysis

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

Authors

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Keywords

Gallery Aqua Master discrete analyzer, discrete analyzer, automated sulfate test methods, test methods for EPA SDWA compliance measurement, drinking water

Application benefits

- Provides a novel discrete analyzer-based automated method for drinking water sulfate testing for compliance measurements that follows the United States Environmental Protection Agency (U.S. EPA) Safe Drinking Water Act (SDWA)
- Meets the performance requirements of the EPA-approved reference method: Standard Method SM4500-SO₄²⁻-E. Turbidimetric Method¹
- Minimizes used volumes of reagents and their associated costs
- Automation and ready-to-use reagents save time and reduce errors compared to manual approaches

Goals

- Establish an automated sulfate analysis method for drinking water samples using the Thermo Scientific™ Gallery™ and Gallery™ Plus Aqua Master Discrete Analyzers in compliance with the U.S. 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 SM4500-SO₄²⁻-E. Turbidimetric Method
- Analyze spiked water samples to verify that the Gallery Aqua Master discrete analyzer-based automated method is applicable to different types of tap and source 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 U.S., the quality of drinking water is regulated and supervised by the U.S. 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.²

Measuring sulfate levels in drinking water is important, even though sulfate itself is not a health concern in the concentrations normally found in drinking water.³ However, high levels of sulfate cause bad tasting water.^{3,4} Water with sulfate concentrations exceeding 500 mg/L can have a mild laxative effect, especially if there are other osmotically active substances present. In the absence of these substances, the laxative effects are unlikely at concentrations up to about 1,000 mg/L of sulfate.⁴ The U.S. EPA sets the Secondary Maximum Contaminant Level (SMCL) for sulfate at 250 mg/L.^{4,5} In addition, the chloride-to-sulfate mass ratio (CSMR) is important to monitor because it has been linked with lead release into drinking water from the distribution system via galvanic corrosion.^{6,7} Galvanic corrosion of lead in water distribution systems occurs when lead pipe or lead solder is in contact with a dissimilar metal such as copper. If the source water entering those systems has a relatively elevated CSMR, the potential for galvanic corrosion is elevated, especially in water with low alkalinity.⁷

Traditional manual turbidimetric methods are well known but come with disadvantages. Because the turbidity used to measure sulfate can rapidly settle after its formation, uniform sample mixing and accurate timing of analyte measurement after reagent addition is required. In addition, manual turbidimetric methods are time-consuming and contain additional manual steps that are potential sources of measurement inaccuracies. These challenges have triggered the need to develop a better way of performing the analysis.

The [Thermo Scientific Drinking Water Method: Drinking Water Sulphate for Thermo Scientific Gallery Discrete Analyzer](#)⁸ is a turbidimetric method that uses ready-to-use reagents and fully automated test workflows for measuring sulfate. In the method, the sulfate ions in the sample form a barium sulfate suspension under controlled conditions. The formed suspension is stabilized with gelatin and sodium chloride, and the turbidity of the reaction mixture is measured with 420 nm wavelength.

This method references the SM4500-SO₄²⁻ E. Turbidimetric 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 reagent (part # 984648 Sulphate R1) and test procedures. The method makes it possible to monitor sulfate 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 potentially 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 is provided in the Thermo Scientific Drinking Water Method: Drinking Water Sulphate for Thermo Scientific Gallery Discrete Analyzer.⁸

Equipment

- Gallery Plus Aqua Master automated photometric discrete analyzer.
- Gallery Aqua Master photometric discrete analyzer can be used as an optional piece of equipment.

Reagents

Thermo Scientific system reagent for environmental and industrial analysis, part # 984648 Sulphate R1, was used. The kit contains a ready-to-use reagent for analyzing sulfate with the Gallery discrete analyzers.

Deionized water was also used.

Calibrator and controls

- A certified standard solution containing 1,000 mg/L of sulfate was used as a 1,000 mg/L calibration stock solution. This solution was used to prepare calibrators and continuing calibration verification samples.
- Thermo Scientific standard material part # 984727 Sulphate Std, 1,000 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 part # 984648 Sulphate system reagent for the low range and high range of sample sulfate concentrations. Table 2 provides the calibration parameters for the low range and high range of sulfate concentrations.

Table 1. Automated test workflow for low and high range of sample sulfate concentrations

	DW SO ₄ L (low range)	DW SO ₄ H (high range)
Sample	120 µL	100 µL (+20 µL water)
Incubate	18 s	18 s
Blank measurement	420 nm	420 nm
Sulphate R1 (part # 984648)	40 µL	40 µL
Incubate	300 s	300 s
End-point measurement	420 nm	420 nm

Table 2. Calibration parameters for low and high range of sulfate concentrations

	DW SO ₄ L (low range)	DW SO ₄ 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 different types of water samples spiked with known amounts of analyte. Certified reference material ERA #698, Inorganics, PotableWatR™ was also tested.

Turbid samples were filtered with GF/A cat 1820-150/Whatman filters.

Three tap water samples, two surface water samples, and two ground water samples were spiked with known concentrations of part # 984727 Sulphate Std:

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 (251 mg CaCO₃/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
4. Lake water 1 and 2 and Well water 1 and 2 from various sources

Results and discussion

Calibration and calibration verification

Calibrators of different concentrations were individually and separately prepared from a standard sulfate solution via automated dilutions 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 both the low (L) and high (H) calibration ranges. The correlation coefficients (R²) were 0.9992 or higher, demonstrating good calibration correlations.

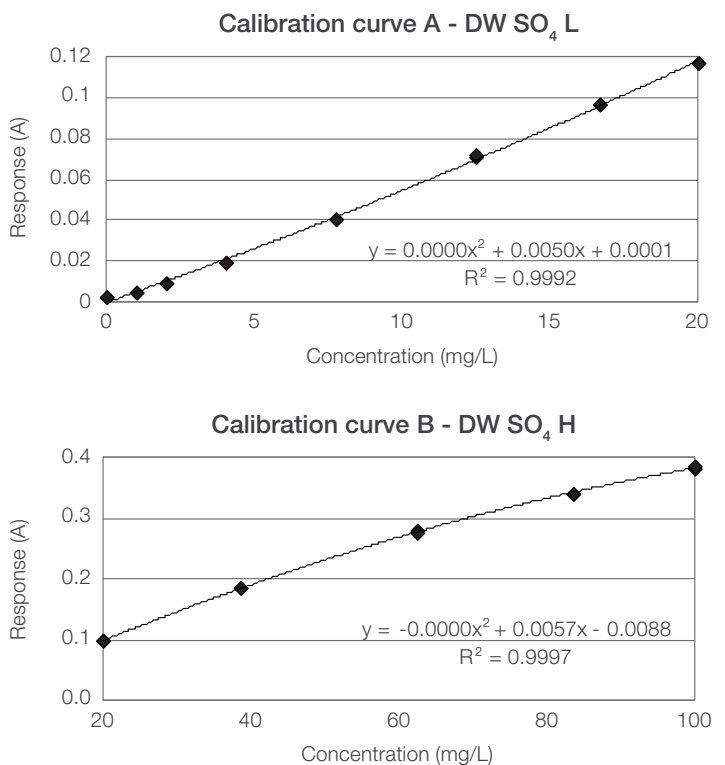


Figure 1. Example calibration curves obtained from the Thermo Scientific Drinking Water Method: Drinking Water Sulphate for Thermo Scientific Gallery Discrete Analyzer, A) low-range calibration, and B) high-range calibration.

Each calibration was made using a certified standard solution and was verified by the analysis of quality control samples prepared from part # 984727 Sulphate Std. Table 3 lists the results of the verification. The calculated recoveries were from 94% to 108% for all samples.

Table 3. Examples of quality control sample (QCS) results

QCS	Test	Result (mg/L)	Recovery (%)
SO ₄ QCS 4 mg/L	DW SO ₄ L	3.8	94
SO ₄ QCS 18 mg/L	DW SO ₄ L	18.1	101
SO ₄ QCS 30 mg/L	DW SO ₄ H	30.6	102
SO ₄ QCS 90 mg/L	DW SO ₄ H	96.8	108

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.⁹ The MDL achieved in this study was 0.8 mg/L. The results are listed in Table 4.

Table 4. Results for defining MDL

Sample	Result (mg/L) 0.5 mg/L LFB	Result (mg/L) LRB
Average	0.61	0.44
Min	0.56	0.38
Max	0.70	0.55
n	7	7
Std. deviation (SD)	0.06	0.06
MDL (LFB /LRB)	0.80	0.63
MDL applied	0.80	

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 procedure¹⁰ (Table 5). The MRL was confirmed to be 2.00 mg/L. The recoveries were from 89% to 94% for all samples, with a relative standard deviation (RSD) of 2.1%.

Table 5. MRL confirmation results

Sample: 2.0 mg/L SO ₄ Std, 7 replicates	
Recovery (%)	92 (89–94)
RSD (% , n=7)	2.1

Operational range

The operational range was verified by analyzing part # 984727 Sulphate Std. samples for three different method ranges. The results are shown in Figure 2. Recoveries of samples within initial and extended calibration ranges were 90% to 104%.

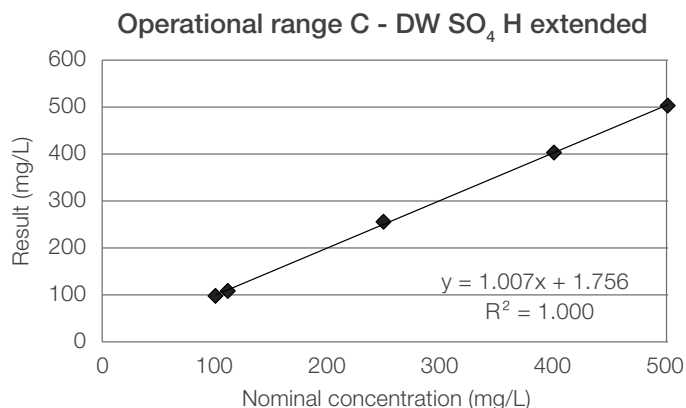
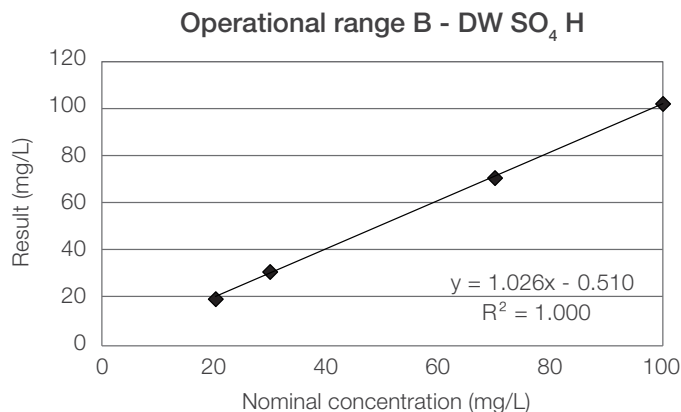
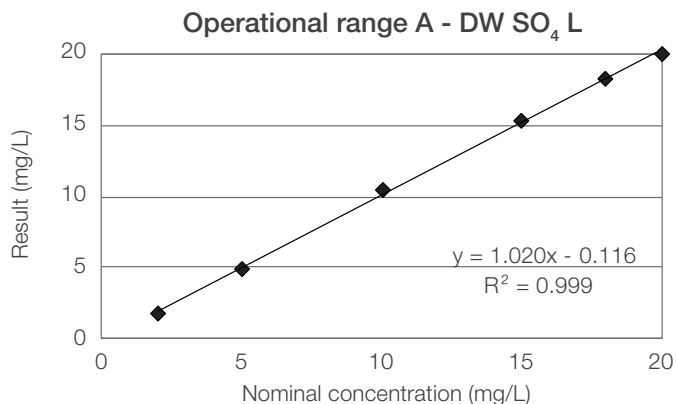


Figure 2. Correlation of results and the nominal values of the operational range samples, A) low-range concentration, B) high-range concentration, and C) extended range concentration.

Ongoing QC

To control method performance between calibrations, samples prepared from part # 984727 Sulphate Std were automatically analyzed by the Gallery Plus Aqua Master discrete analyzer in sample intervals of ten. Both the low and the 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. The average recoveries were from 92% to 103%. The OPR precision was evaluated by calculating the RSDs, which ranged from 0.5% to 2.6%.

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

Sample (mg/L)	Average recovery (%)	Min. recovery (%)	Max. recovery (%)	Number of results	RSD (%)
SO ₄ LFB 3	92	89	98	28	2.3
SO ₄ LFB 4	93	89	95	17	1.9
SO ₄ LFB 18	101	100	102	44	0.5
SO ₄ LFB 30	103	98	106	21	1.9
SO ₄ LFB 90	102	98	108	21	2.6
SO ₄ LFB 300	102	101	103	4	1.0

Spike samples

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

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

The spike recoveries were from 92% to 107%. The precision (RPD) ranged from 0.1% to 4.8%.

Table 7. Laboratory Fortified Matrix (LFM) sample results. Each of the samples were spiked with different amounts of sulfate (4, 10, 30, or 50 mg/L). D refers to duplicate sample.

Sample	Test	Results (mg/L)	Theoretical value, mg/L (corrected for spike volume)	Spike recovery (%)	Relative percent difference (RPD) (%)
Tap water 1	DW SO ₄ H	23.6	23.6	—	—
Tap water 1 + 10	DW SO ₄ H	34.2	33.6	102	0.1
Tap water 1 + 10 D	DW SO ₄ H	34.3	33.6	102	
Tap water 1 + 50	DW SO ₄ H	74.3	72.5	103	0.2
Tap water 1 + 50 D	DW SO ₄ H	74.4	72.5	103	
Tap water 2	DW SO ₄ H	31.0	31.0	—	—
Tap water 2 + 10	DW SO ₄ H	40.8	41.0	100	0.8
Tap water 2 + 10 D	DW SO ₄ H	40.5	41.0	99	
Tap water 2 + 50	DW SO ₄ H	79.3	79.5	100	0.6
Tap water 2 + 50 D	DW SO ₄ H	79.7	79.5	100	
Tap water 3	DW SO ₄ L	6.5	6.5	—	—
Tap water 3 + 10	DW SO ₄ L	17.2	16.5	105	0.9
Tap water 3 + 10 D	DW SO ₄ L	17.1	16.5	104	—
Tap water 3 + 50	DW SO ₄ H	58.9	55.3	106	0.7
Tap water 3 + 50 D	DW SO ₄ H	59.3	55.3	107	
Lake water 1	DW SO ₄ L	12.5	12.5	—	—
Lake water 1 + 4	DW SO ₄ L	16.7	16.5	101	1.8
Lake water 1 + 4 D	DW SO ₄ L	16.4	16.5	99	
Lake water 2	DW SO ₄ H	37.5	37.5	—	—
Lake water 2 + 30	DW SO ₄ H	65.1	66.4	98	3.0
Lake water 2 + 30 D	DW SO ₄ H	63.2	66.4	95	
Well water 1	DW SO ₄ L	6.2	6.2	—	—
Well water 1 + 4	DW SO ₄ L	10.4	10.2	102	0.7
Well water 1 + 4 D	DW SO ₄ L	10.3	10.2	101	
Well water 2	DW SO ₄ H	23.8	23.8	—	—
Well water 2 + 30	DW SO ₄ H	50.9	53.1	96	4.8
Well water 2 + 30 D	DW SO ₄ H	48.5	52.6	92	

Certified reference material (CRM)

To verify the accuracy of the method, a NIST-traceable reference material (CRM) was analyzed in four replicates diluted to the low and high calibration ranges. The CRM results are presented in Table 8. The RSDs for the low and high calibration ranges were 0.2% and 0.3%, respectively. The recoveries were 101% and 102%, respectively.

Table 8. CRM results (n = 4)

Sample	ERA CRM 698	
Target value (mg/L)	249	
Test	DW SO ₄ L	DW SO ₄ H
Dilution	25x	5x
Average (mg/L)	251	253
RSD (%)	0.2	0.3
Recovery (%)	101	102

Method comparison

The results for tap water samples and the CRM sample measured using the Gallery discrete analyzer method were compared to results obtained from the EPA-approved reference method: SM4500-SO₄²⁻ E. Turbidimetric Method. The results are shown in Table 9. The recoveries ranged from 93% to 104%.

Table 9. Correlation of the Gallery discrete analyzer method results with the reference method results for tap water samples and a CRM sample

QCS	Result Gallery Method (mg/L)	Result Reference Method (mg/L)	Recovery (%)
CRM-ERA 698	252.9	242.7	104
Tap water 2	31.0	33.4	93
Tap water 3	6.5	6.2	104

Conclusions

Table 10 summarizes the results from the performance study of the Thermo Scientific Drinking Water Method: Drinking Water Sulphate 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-SO₄²⁻ E. Turbidimetric Method. By using the Gallery discrete analyzer method, it is possible to reach lower detection and reporting limits than the reference method.

The Thermo Scientific Drinking Water Method: Drinking Water Sulphate for Thermo Scientific Gallery Discrete Analyzer offers laboratories an easy approach for sulfate compliance measurements*. The discrete analyzers automate the entire workflow, including liquid handling, incubation, mixing, and results measurement, delivering high-throughput results without having to use time-consuming, laborious and error-prone manual methods. This high level of automation eliminates operator-caused variation, ensuring results are more consistent. As it is essential for turbidimetric tests to prevent precipitate settling, the consistent incubation times and mixing performed by the Gallery Aqua Master analyzers provide a substantial advantage compared to traditional turbidimetric methods. Convenient ready-to-use reagents reduce the need to handle hazardous chemicals, improving work safety and removing another 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 10. Performance of the Thermo Scientific Drinking Water Method: Drinking Water Sulphate for Thermo Scientific Gallery Discrete Analyzer compared to the EPA-approved reference method acceptance criteria and performance. The Pass/Fail conclusion is for the Gallery discrete analyzer performance compared to QC acceptance criteria.

	QC acceptance criteria for Reference Method SM4500-SO ₄ ²⁻ E. Turbidimetric Method	Performance results for Reference Method SM4500-SO ₄ ²⁻ E. Turbidimetric Method	Performance of Thermo Scientific Drinking Water Sulphate Method for the Gallery Discrete Analyzer	Pass/Fail
MDL	To be done according to 40 CFR Part 136. Appendix B. ⁹	2.21 mg/L	0.80 mg/L when done according to 40 CFR Part 136. Appendix B. ⁹	Pass
MRL	NA	8.00 mg/L	2.00 mg/L	Pass
Method blank	≤½ MRL	Max. 2.03 mg/L	Max. 0.60 mg/L	Pass
Recovery (%) operational range	±10% when c > 5 × MRL ±20% when c > 2 and ≤ 5 × MRL ±50% when c ≤ 2 × MRL	NA	97–104% 90% when c ≤ 2 × MRL	Pass
Recovery (%) QCS	±10%	98–99%	90–108%	Pass
Recovery (%) OPR	NA (Proficiency test limits for sulfate ±15%) ¹¹	91–111% 87–98% when c ≤ 2 × MRL	98–108% 89–98% when c ≤ 2 × MRL	Pass
Recovery (%) spike sample	NA (Wider limits may be used than for IPR)	101–113%	92–107%	Pass
RSD (%) OPR	NA (Industry acceptable max. 20%) ¹²	7.3–8.2%	0.5–2.6%	Pass
RPD (%) spike duplicates	NA (Industry acceptable max. 20%) ¹²	1.0–3.1%	0.1–4.8%	Pass

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