Automated wet chemical analysis

# Automated method to detect orthophosphate in drinking water using the Thermo Scientific Gallery discrete analyzer

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Keywords

Gallery Aqua Master Discrete Analyzer, discrete analyzer, automated orthophosphate test methods, EPA SDWA compliant test methods, reduced manual handling errors, high-throughput nutrient analysis, automated water testing, drinking water, electrochemical measurement, photometric measurement

## Application benefits

- Meets the requirements of regulated methods for orthophosphate testing in drinking water.
- Automation and ready-to-use reagents save time and reduce errors compared to manual approaches.

## Goals

- Analyze phosphate in drinking water samples using the Thermo Scientific™ Gallery™ discrete analyzer platform in compliance with the United States Environmental Protection Agency (U.S. EPA) Safe Drinking Water Act (SDWA).
- Demonstrate that results obtained using the Gallery discrete analyzer-based automated method are equivalent or better than the reference method 4500-P E: Phosphorous by Ascorbic Acid Method and Standard Methods for the Examination of Water and Wastewater.
- Analyze spiked drinking water from different sources to establish that the Gallery discrete analyzer-based automated method is applicable to different types of 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. In the United States, the quality of drinking water is regulated and supervised by the U.S. EPA. The water-quality parameters of health concerns and their analysis are regulated under the 40 CFR Part 141 National Primary Drinking Water Regulations.[1]

Water utilities treat drinking water by adding orthophosphate to prevent the corrosion that can cause metals, particularly copper and lead, to dissolve and leak into water systems. In 2016, the U.S. EPA approved the first discrete analyzer method for testing orthophosphate in drinking water, which uses the Gallery discrete analyzers.[2,3] The Thermo Scientific drinking water method: Drinking Water Orthophosphate for the Thermo Scientific Gallery Discrete Analyzer describes the EPA-approved alternative method for testing drinking water for orthophosphate.[4] The method is based on the well-established and EPA-approved reference method SM 4500-P E: Phosphorous by Ascorbic Acid Method. Standard Methods for the Examination of Water and Wastewater.[5] In this method, orthophosphate is reacted with ammonium molybdate and antimony potassium tartrate in an acidic medium to form an antimony-phospho-molybdate complex. The complex is subsequently reduced by ascorbic acid to form an intensely blue complex that is measured photometrically at 880 nm.

The method is easily automated using the Gallery discrete analyzers, which allow simultaneous analysis of multiple parameters in the same sample aliquot. Ready-to-use Thermo Scientific™ Gallery™ system reagents and test procedures further streamline analyses. The Thermo Scientific™ Gallery™ and Gallery™ Plus Aqua Master discrete analyzers provide equivalent performance and are therefore also applicable to the Thermo Scientific method. The Gallery Aqua Master discrete analyzers add additional capabilities including automatic spiking, flexible test, and quality control (QC) parameter configuration, and flexible results reporting with versatile features for configuring report templates.[6]

## Experimental

### Materials and methods

Additional details about the necessary equipment and supplies; reagents, calibrators, and control preparation; and test parameters are provided in the Thermo Scientific drinking water method: Drinking water orthophosphate for the Thermo Scientific Gallery discrete analyzer.[4]

### Equipment

- Gallery or Gallery Plus automated photometric discrete analyzer. Note: The Gallery and Gallery Plus Aqua Master discrete analyzers provide equivalent performance and can also be used to carry out the Thermo Scientific method.
- Other necessary laboratory equipments and supplies are listed in the Thermo Scientific method.[4]

### Reagents

Ready-to-use Thermo Scientific system reagents for environmental and industrial analysis:

- Phosphate R1 (Part# 984366)
- Phosphate R2 (Part# 984368)

and deionized water.

### Calibrator and controls

- 984729 Phosphate (as P) Std, 1000 ppm, 500 mL standard solution was used to prepare the calibrator and continuing calibration check samples.
- 984726 Phosphate (as PO4) Std, 1000 ppm, 500 mL (326.2 mg/L as P) was used to prepare the QC samples and ongoing QC samples.

### Test parameters

Table 1 provides the automated test flow using the Gallery system reagents. Table 2 provides the calibration parameters. As an integrated and automated platform, the Gallery discrete analyzers increase laboratory productivity by freeing staff to work on other tasks.

**Table 1. Automated test workflow**

| Automated test flow: DW o-PO4P | |
|---|---|
| Sample | 120 µL |
| Incubate | 18 s |
| Blank | 880 nm |
| Phosphate R1 | 14 µL |
| Incubate | 120 s |
| Phosphate R2 | 6 µL |
| Incubate | 540 s |
| End point measurement | 880 nm |

**Table 2. Calibration parameters**

| | |
|---|---|
| Test range | Up to 0.5 mg/L as P |
| Primary range | Up to 5 mg/L as P |
| Calibration | 2nd order |
| QC | Automated calibration QC, ongoing QC and spike samples |

## Samples

In addition to analyzing several different standard samples, the study included analysis of different tap water samples spiked with known amounts of analyte. Tap water 1 used lake water as the source water, tap water 2 originated from a ground water source, and tap water 3 was obtained from a ferry drinking water reservoir.

## Results and discussion

### Calibration and calibration verification

Calibrator stock solution was prepared from a standard phosphate solution. Using the Gallery discrete analyzer, the calibrator levels were automatically diluted and analyzed according to the test parameters. The Gallery discrete analyzer automatically plots the responses against the standard concentrations to create the calibration curve. Figure 1 presents the calibration curve obtained.

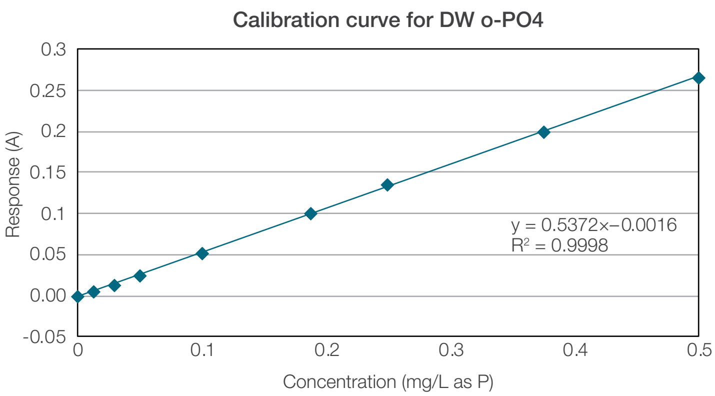


**Figure 1. Calibration curve obtained per the Thermo Scientific drinking water method: Drinking water orthophosphate for the Thermo Scientific Gallery discrete analyzer.**

Each calibration was verified by the analysis of second-source standard samples against the preset limits of the Thermo Scientific method. Table 3 presents the results from the Thermo Scientific method, including the percent recovery for the quality control samples (QCS). Overall, the results obtained showed good accuracy with a recovery nearly 100% and very good precision (% RPD) for the QC sample duplicates.

**Table 3. Results for quality control samples (QCS)**

| Phosphate as phosphorous | | |
|---|---|---|
| **QCS-sample** | **Duplicate % RPD** | **% Recovery** |
| PO4-P 0.1 mg/L | 0.1% | 97% |
| PO4-P 0.4 mg/L | 0.2% | 98% |

### Method detection limit (MDL)

The MDL was defined using low-concentration standard samples per the EPA approach described in 40 CFR Part 136, Appendix B.[7] The MDL results are presented in Table 4.

**Table 4. Thermo Scientific method results**

| MDL Sample: 0.01 mg/L PO4-P Std, 7 replicates | |
|---|---|
| Average, mg/L | 0.0079 (0.0077–0.0080) |
| % Recovery | 79% (77–80%) |
| Std. deviation (SD), mg/L | 0.00011 |
| **MDL, mg/L** | **0.00036** |

### Minimum reporting level (MRL)

The MRL was estimated to be at the level of the lowest calibrator, 0.0125 mg P/L. Seven replicate laboratory-fortified blank (LFB) samples at just below 0.0125 mg P/L were analyzed to confirm the MRL. The MRL confirmation results are presented in Table 5.

**Table 5. MRL confirmation results**

| Sample: 0.01 mg/L PO4-P Std, 7 replicates | |
|---|---|
| % Recovery | 97% (94–101%) |
| % RSD (n=7) | 2.4% |
| **The MRL was confirmed at level 0.010 mg/L**<br>**The MRL was applied at level 0.0125 mg/L**** | |

** Because the lowest calibrator level for the method was 0.0125 mg/L, the 0.010 mg/L limit could not be applied. The MRL confirmation procedure was done per EPA requirements.[8]

### Accuracy and precision

Phosphate standard samples were analyzed in replicates of ten to determine within-run method accuracy and precision. The accuracy and precision obtained are presented in Table 6.

**Table 6. Method precision and accuracy for the standard samples**

| | PO4-P 0.1 mg P/L | PO4P 0.3 mg P/L | PO4P 0.4 mg P/L |
|---|---|---|---|
| % Recovery | 103% | 102% | 102% |
| n | 10 | 10 | 10 |
| % RSD | 0.2% | 1.1% | 0.2% |

## Ongoing QC

To control method performance between calibrations, continuous calibration verification (CCV) and laboratory reagent blank (LRB) samples were automatically analyzed in intervals of ten using two Gallery discrete analyzers to verify the reliability of results. Results from this procedure, also known as ongoing precision and recovery (OPR), are provided in Table 7. The LRB sample results are presented in Table 8.

**Table 7. PO4P continuous calibration verification (CCV) results Sample: PO4P CCV, concentration 0.25 mg/L**

| | Analyzer 1 | Analyzer 2 |
|---|---|---|
| % Recovery | 102% (100–105%) | 102% (101–105%) |
| n | 20 | 6 |
| % RSD | 1.3% | 1.9% |

**Table 8. PO4P LRB sample results**

| | Analyzer 1 | Analyzer 2 |
|---|---|---|
| Average, mg/L | 0.0029 (0.0016–0.0035) | 0.0019 (0.0016–0.0024) |
| n | 20 | 7 |
| SD, mg/L | 0.0004 | 0.0003 |

## Spike samples

The accuracy of the method in the sample matrix was tested by analyzing spike samples. Three different tap water samples were spiked with known concentrations of phosphate standard to create the laboratory-fortified matrix samples (LFM): Tap water 1 (lake water source), tap water 2 (groundwater source), and tap water 3 (ferry drinking water reservoir source). The method accuracy results are presented in Table 9.

**Table 9. Method accuracy for LFM samples**

| Sample | Results mg/L | Spike % Recovery |
|---|---|---|
| Tap water 1 | 0.0026 | — |
| Tap water 1 +0.1 mg/L | 0.0944 | 92% |
| Tap water 1 +0.4 mg/L | 0.3943 | 98% |
| Tap water 2 | 0.0028 | — |
| Tap water 2 +0.1 mg/L | 0.0989 | 96% |
| Tap water 2 +0.4 mg/L | 0.3754 | 93% |
| Tap water 3 | 0.0021 | — |
| Tap water 3 +0.1 mg/L | 0.0946 | 92% |
| Tap water 3 +0.4 mg/L | 0.3906 | 97% |

## Conclusions

Table 10 summarizes the results from the performance study of the Thermo Scientific drinking water method: Drinking water orthophosphate for the Thermo Scientific Gallery discrete analyzer. The performance study results showed the automated method meets the QC acceptance criteria in the reference method. The Thermo Scientific orthophosphate method showed a good correlation to the well-established EPA-approved reference method 4500-P E: Phosphorous by Ascorbic Acid Method. The study also demonstrated that when performed using the Gallery discrete analyzers, the method is suitable for analyzing different types of water samples.

The Thermo Scientific discrete analyzer method offers laboratories an automated, high-throughput option for regulated testing for orthophosphate in drinking water. Walk-away automation simplifies drinking water analyses and reduces errors. Ready-to-use Gallery system reagents are convenient and likewise, decrease the costs and errors associated with manual processes. The Gallery and Gallery Plus Aqua Master discrete analyzers provide equivalent performance and can also be applied to the Thermo Scientific method.

**Table 10. Performance of the Thermo Scientific drinking water method: Drinking water orthophosphate for the Thermo Scientific Gallery discrete analyzer compared to the reference method acceptance criteria**

| | QC acceptance criteria for reference method: standard method 4500-P E. | Performance of drinking water ortho-PO4P method for the Gallery discrete analyzer |
|---|---|---|
| MDL | Minimum 7 replicates of MDL sample, conc. 1–5 × MDL estimate, analyzed in 3 days, ideally by different users. Recoveries should be 50–150% and % RSD ≤20%. | 0.00036 mg P/L when the procedure in 40 CFR part 136, Appendix B was used. The procedure is similar to reference method. |
| MRL | Set at or above the lowest calibrator and verified with QC sample at 1 to 2 times the MRL conc. Result is acceptable if precision and accuracy meet laboratory method requirements. | 0.0125 mg P/L. The MRL confirmation procedure was done per EPA requirements.[8] |
| Method blank | <1/2 MRL | Max. 0.0035 mg/L |
| % Recovery continuing calibration verification (CCV) | ±10%ß´ | 100–105% |
| % Recovery QCS | ±15% | 97–98% |
| % Recovery spike sample | Laboratory specific | 92–98% |
| % RSD CCV | Laboratory specific | 1.3–1.9% |

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