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APPLICATION NOTE 71728

Determination of water pollutants using photometric analysis

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Keywords

DA, Automated analysis, ISO 15923-1, water analysis, discrete analysis

Goal

To demonstrate compliance with the ISO 15923-1 standard for the determination of water pollutants using an automated photometric procedure.

Introduction

Clean water in sufficient amounts is an ongoing global challenge. Water resources are experiencing increasing pressure in many parts of the world, requiring countries to improve the management and protection of water ecosystems. In 2000, the European Union's (EU) Water Framework Directive (WFD) announced an integrated approach to protecting water quality, quantity, and the role of habitat. As a result, governmental bodies of different EU member states are required to work with one another to ensure that the requirements of the directive are met and water quality is maintained. Quality criteria include nutritional composition as well as chemical composition, i.e. the level of pollutants.

The International Organization of Standardization (ISO) develops standards to benefit state authorities, regulatory bodies, and industry for the purpose of equitably and durably managing shared water resources. As a network composed of 163 countries, ISO published more than 19,500 international standards covering almost every industry from technology and food safety to agriculture and healthcare. More than 550 standards currently exist to address water issues and these quality standards provide a common language for water sampling, reporting, and monitoring in order to ensure purity and other desired characteristics that apply to industrial processes as well as natural water.

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Part 1 of the ISO standard 15923 describes methods for automated photometric determinations of ammonium, chloride, nitrate, nitrite, orthophosphate, silicate and sulfate specifically using a discrete analysis system to analyze water, i.e., ground, potable, surface, waste, eluates and boiler water.

In this study, the methods and performance of Thermo Scientific™ Gallery™ and Thermo Scientific™ Aquakem™ discrete analyzers are described according to the analysis guidelines of ISO 15923-1. All data is generated using the automated Gallery, Thermo Scientific™ Gallery Plus™, or Aquakem discrete analyzers and Thermo Scientific™ system reagents and applications.

According to the standard, a large number of different parameters need to be determined with a single instrument in which the desired tests can be specified for each sample type. Samples falling outside the normal measuring range can be automatically diluted or measured again using a different range. Both the Gallery and Aquakem discrete analyzers are within the desired category of acceptable instruments. Beyond the analytes discussed in the standard, these analyzers can perform other methods, such as alkalinity, calcium, chromium (VI), fluoride, ferrous iron, magnesium, nitrate (with enzymatic or vanadium chloride reduction), total hardness, and urea. The Gallery discrete analyzer is equipped with an electrochemical unit capable of measuring pH and conductivity.

Experimental

Materials and methods

Reagents

Thermo Scientific system reagents, their composition, and references are listed in Table 1. For convenience and flexibility, reagents are bar-coded, traceable, ready-to-use, and are available in 4 × 20 mL packages.

Table 1. Preparation of calibration standards.

Analyte	Product	Composition of System Reagent	Compliance with the ISO 15923- 1 Reagent Composition	Reference Standards
Ammonia	Ammonia R1 (984362)	sodium salicylate, trisodium citrate, sodium nitroprusside	Yes	ISO 15923- 1 ISO 7150-1
	Ammonia R2 (984363)	sodium hydroxide, sodium dichloroisocyanurate	Yes	ISO 15923- 1 ISO 7150
Chloride	Chloride R1 (984364)	methanol, iron (III) nitrate, mercury dithiocyanate, nitric acid	Yes	ISO 15923- 1 ISO 15682
Total Oxidized Nitrogen (TON) (Nitrate + Nitrite) Nitrate by calculation	TON R1 (984369)	sodium hydroxide	Yes	ISO 15923- 1 SM4500 NO3-H
	TON R2 (984370)	hydrazine, copper sulfate, zinc sulfate	Yes	ISO 15923- 1 SM4500 NO3-H
	TON R3 (984371)	phosphoric acid, sulfanilamide, NEDD	Yes	ISO 15923- 1 SM4500 NO3-H
Nitrite	TON R3 (984371)	phosphoric acid, sulfanilamide, NEDD	Yes	ISO 15923- 1 SM4500 NO2-B
Phosphate	Phosphate R1 (984366)	sulphuric acid, antimony potassium tartrate, ammonium molybdate	Yes	ISO 15923- 1 ISO 6878 including instruction for orthophosphate digestion
	Phosphate R2 (984368)	ascorbic acid	Yes	ISO 15923- 1 ISO 6878
Silica	Silica R1 (984625)	ammonium molybdate, sulfuric acid	Yes	ISO 15923- 1 SM4500-SiO2 D ISBN 0117515574
	Silica R2 (984626)	oxalic acid	Yes	ISO 15923- 1 SM4500-SiO2 D ISBN 0117515574
	Silica R3 (984627)	ascorbic acid	Yes	ISO 15923- 1 SM4500-SiO2 D ISBN 0117515574
Sulfate	Sulfate R1 (984648)	barium chloride, hydrochloric acid, stabilizers	Yes	ISO 15923- 1 SM4500 $SO4^{2}$-E

Calibration solutions

Thermo Scientific 1000 ppm Standard solutions: Ammonium as nitrogen (N), Chloride, Nitrite as N, Nitrate as N, Phosphate as P, and Sulfate were used.

Equipment

The Thermo Scientific Gallery, Gallery Plus and Aquakem discrete analyzers were used.

Applications

- The instrument's programmed applications were applied.
- For low methods, 120 µL sample volumes were used. The maximum single reagent addition per test was 120 µL.
- Tests were performed at 37 °C and read at a range from 340 to 880 nm; actual wavelengths are listed in Figures 1–6.
- The calibration curves used were non-linear, polynomial/2nd order, or linear.

Blanking

All tests were blanked according to the ISO 15923-1 Annex A instructions. The blank measurement was done after dispensing the sample and, if applicable, after one or more reagents (not the chromogenic reagent) produced a color change in the sample. This blank value was subtracted from the final absorption of the measuring solution with consideration for the ratio between various volumes of the measuring solutions. All standards were measured the same way.

Thermo Scientific system methods except chloride were blanked to eliminate the color eluting from the sample. If required, the software is flexible and allows methods to be altered after validation by the laboratory.

Results and discussion

Calibration requirements

As required by ISO 15923-1, methods were calibrated using a zero calibration solution. Examples of the calibration graphs are shown in Figures 1-6. According to the ISO 15923-1 standard, procedures may be modified for different instruments.

Validated Gallery and Aquakem discrete analyzer system methods are performed with linear, non-linear, or 2nd order/ polynomial calibrations. A wide range of other calibration options are also available such as: no calibration, linear, bias, factor, 2nd order, spline, logit-log4, logit-log5, and point-to-point.

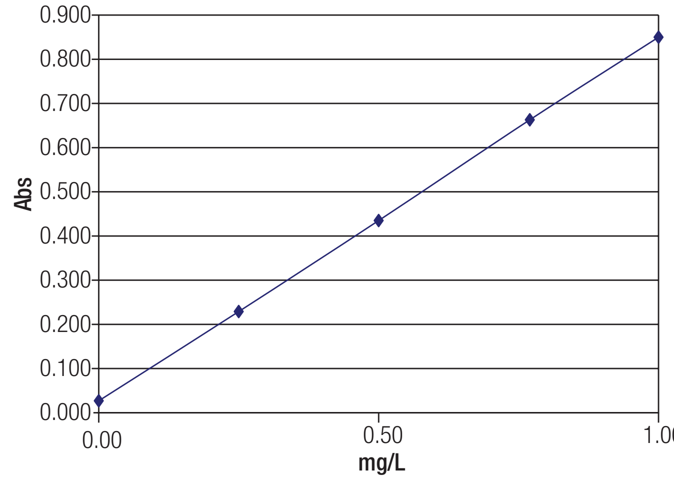

Figure 1. Calibration example for the ammonia method.

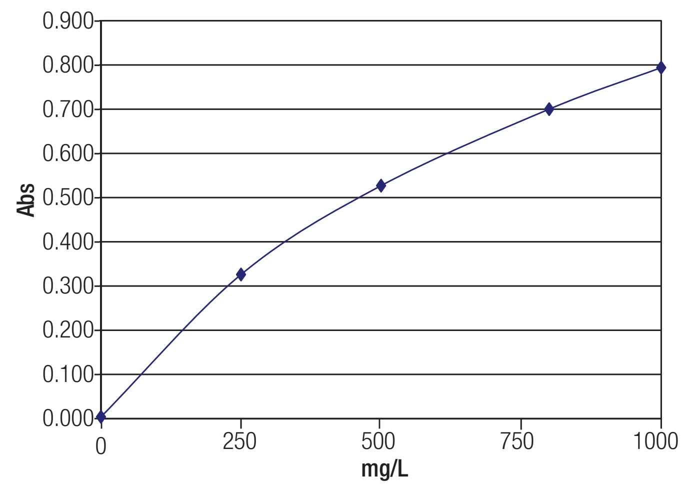

Figure 2. Calibration example for the chloride method.

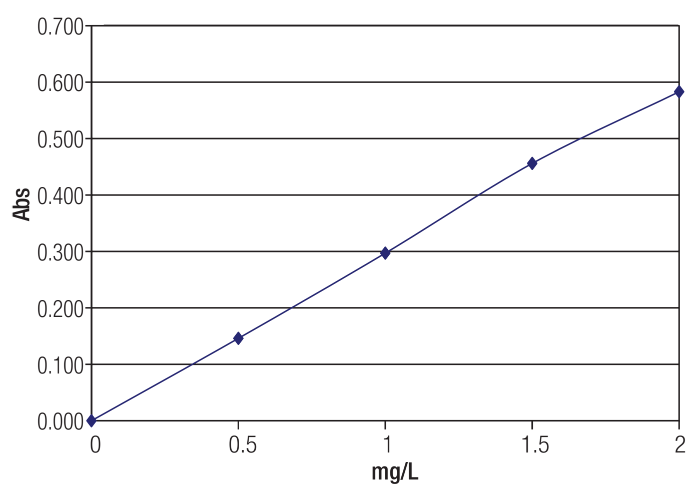

Figure 3. Calibration example for the phosphate method.

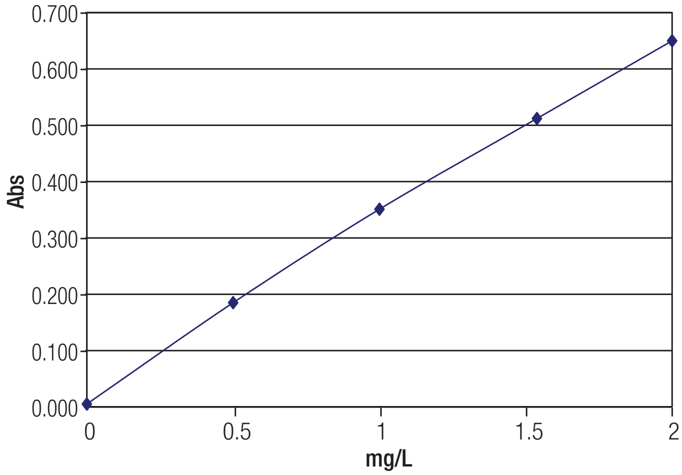

Figure 4. Calibration example for the TON method.

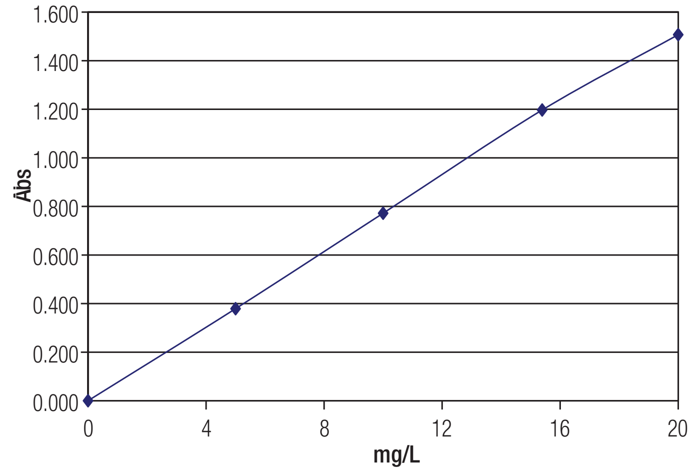

Figure 5. Calibration example for the silica method.

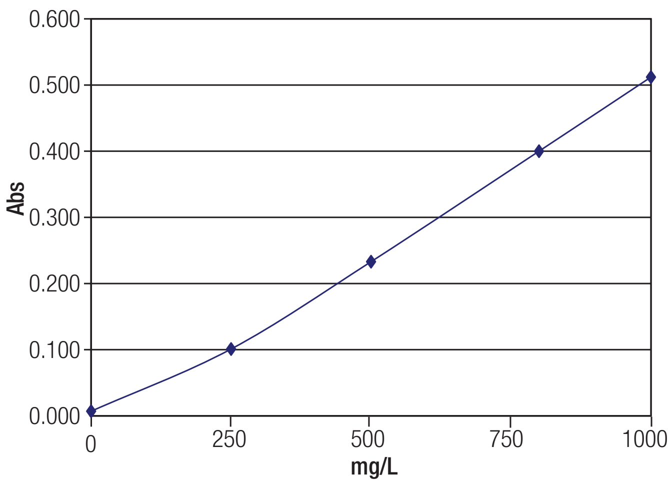

Figure 6. Calibration example for the sulfate method.

Test limits and MDL data

Method detection limit (MDL) values and upper ranges of method linearity for the Gallery and Aquakem discrete analyzers are shown in Table 2. Theoretical MDL values are calculated in two ways in order to support different customer requirements. Since the limit of detection (LOD) and limit of quantitation (LOQ) are matrix, method, and analyte dependent, only theoretical MDL values are listed since the samples analyzed were not standard matrix samples.

The ISO 15923-1 standard low application requirement is 0.05 mg/L as N for Ammonia, 0.1 mg/L as N for Nitrate, 0.01 mg/L as N for Nitrite, 5 mg/L for Chloride, 0.01 mg/L as P for Phosphate, 5 mg/L for Sulfate and 0.05 mg/L for Silica. The Gallery and Aquakem analyzer methods meet or exceed these detection limits.

Table 2. MDL values and upper ranges of method linearity for the Gallery and Aquakem discrete analyzers.

Test	Theoretical MDL (3.14 × SD (blank sample, n=7)	Theoretical MDL (3 × SD + average (blank sample, 3 batches, n=30-50)	Linearity
Ammonia low	0.5 µg/L as N	1.6 µg/L as N	up to 1000 µg/L
Ammonia high	n/a	n/a	up to 375 mg/L
Chloride low	0.035 mg/L	0.349 mg/L	up to 1000 mg/L
Nitrite	0.4 µg/L as N	1.2 µg/L as N	up to 2500 µg/L as N
Phosphate low	0.4 µg/L as P	3.6 µg/L as P	up to 1 mg/L
Phosphate high	n/a	n/a	up to 10 mg/L
Silica	0.01 mg/L	0.05 mg/L	up to 80 mg/L
Sulfate low	0.26 mg/L	n/a	up to 100 mg/L
Sulfate high	n/a	n/a	up to 500 mg/L
TON low	0.6 µg/L as N	11.5 µg/L as N	up to 2.5 mg/L
TON high	n/a	n/a	up to 50 mg/L

Automating the analysis

As required by the ISO 15923-1 standard, methods are calibrated using a zero calibration solution. Further, the requirement to analyze a control standard solution every 20th sample or less can be fulfilled using the automated quality control function and pre-programming the QC test. The discrete analyzer calculates results automatically based on calibration data. These systems are designed to trace the reagent lot through the software to final results and calibration details. The requirement of a correction factor to accommodate for inherent sample color is eliminated with the use of a sample blanking step.

To correct for inherent sample color, the ISO 15923-1 standard suggests the use of blanking and compensating solutions. The Gallery and Aquakem discrete analyzer software supports creation of a test flow containing a compensating solution (a true sample blank) however; current system applications do not require the use of this feature.

The Gallery discrete analyzer software also contains a feature called "standard addition." This is used in instrumental analysis to determine the concentration of a substance in an unknown sample by comparing it to a set of samples with known concentration and is similar to using a calibration curve. Standard addition can be applied to most analytical techniques and is used instead of a calibration curve to solve the matrix effect problem.

Analysis performance variability as standard deviation (SD) and variability of the data points expressed as coefficient of variation (CV %) are shown in Table 3.

Table 3. Method precision data presented as within run, between run, and as total.

Nitrite precision

	Tap Water (µg/L N)		Lake Water (µg/L N)	
	N	30	N	30
	Mean	56	Mean	308
	SD	CV %	SD	CV %
Within run	0.177	0.3	1.041	0.3
Between run	0.849	1.5	4.096	1.3
Total	0.867	1.5	4.227	1.4

Phosphate precision

	Pond Water (µg/L P)		Spiked Lake Water (µg/L P)		Spiked Tap Water (µg/L P)	
	N	40	N	40	N	40
	Mean	9.5	Mean	59.0	Mean	167.6
	SD	CV %	SD	CV %	SD	CV %
Within run	0.362	3.8	0.991	1.7	2.667	1.6
Between run	0.103	1.1	3.554	6.0	2.746	1.6
Total	0.376	4.0	3.690	6.3	3.828	2.3

TON precision

	Lake Water (µg/L N)		Pond Water (µg/L N)		Tap Water (µg/L N)	
	N	50	N	50	N	50
	Mean	61	Mean	292	Mean	404
	SD	CV %	SD	CV %	SD	CV %
Within run	1.557	2.6	5.531	1.9	7.968	2.0
Between run	4.581	7.5	13.071	4.5	4.779	1.2
Total	4.838	7.9	14.193	4.9	9.291	2.3

Chloride precision

	Pond Water (mg/L)		Tap Water (mg/L)		Pond Water (mg/L)	
	N	50	N	50	N	50
	Mean	2.53	Mean	4.91	Mean	16.50
	SD	CV %	SD	CV %	SD	CV %
Within run	0.031	1.2	0.030	0.6	0.075	0.5
Between run	0.011	0.4	0.020	0.4	0.224	1.4
Total	0.033	1.3	0.036	0.7	0.236	1.4

Ammonia precision

	Pond Water (µg/L N)		Tap Water (µg/L N)	
	N	50	N	50
	Mean	17	Mean	189
	SD	CV %	SD	CV %
Within run	0.340	1.9	0.849	0.4
Between run	0.786	4.5	0.871	0.5
Total	0.856	4.9	1.216	0.6

Sulfate precision

	Tap Water (mg/L)		Pond Water (mg/L)	
	N	50	N	50
	Mean	24.0	Mean	72.0
	SD	CV %	SD	CV %
Within run	0.254	1.1	0.320	0.4
Between run	0.063	0.3	0.282	0.4
Total	0.262	1.1	0.427	0.6

Silica precision

	Tap water (mg/L)		Natural water (mg/L)		Well water (mg/L)	
	N	50	N	50	N	50
	Mean	5.52	Mean	7.91	Mean	12.61
	SD	CV %	SD	CV %	SD	CV %
Within run	0.007	0.3	0.016	0.2	0.033	0.3
Between run	0.007	0.3	0.022	0.3	0.074	0.6
Total	0.010	0.4	0.027	0.3	0.081	0.6

As shown by the data, all methods demonstrate very good precision at higher concentrations. The Gallery discrete analyzers provide repeatable results between runs while full automation improves quality and efficiency. Bar-coded traceable system reagents save technician time and reduce errors, thus ensuring confidence in the quality of the results. Software features, such as an automated QC analysis after the insertion of reagent vials, enable full control.

Analysis throughput

The Aquakem and Gallery discrete analyzers rapidly perform each of the seven required ISO 15923-1 tests from one sample; results for one sample are available in 18 minutes. In another example, performance of 100 sulfate tests is complete in only 25 minutes.

Both the Gallery and Aquakem discrete analyzers have several washing features allowing random access analysis to methods. Analysis of low ammonia should be performed in a batch due to the on-board instability of very volatile ammonia reagents.

Summary

For this study, Thermo Scientific system reagent compositions were described and analytical performance was analyzed. The ISO 15923-1 standard allows for some flexibility in the actual method used, therefore with the allowance for slight modifications, all Thermo Scientific system reagents are in compliance with the standard. In addition, bar-coded reagent vials are designed for long shelf life, traceability, and ease-of-use. All method parameters are included in the analyzer database and include automatic dilution limits and method linearity limits. The discrete analyzer software fully supports the requirements listed in the standard.
In case an exact application according to the ISO 15923-1 standard is required, the analyzer's software allows access and contains tools for such modifications. These analyzers are designed to use small volumes of water and reagents and are therefore environmentally friendly solutions for determination of ions and several other water quality parameters, such as: alkalinity, total hardness, pH, and conductivity.

References

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