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Water quality — Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) —

Part 2: Method by continuous flow analysis (CFA)

Qualité de l'eau — Dosage des orthophosphates et du phosphore total par analyse en flux (FIA et CFA) —

Partie 2: Méthode par analyse en flux continu (CFA)

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Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15681-2 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

ISO 15681 consists of the following parts, under the general title *Water quality — Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA)*:

— *Part 1: Method by flow injection analysis (FIA)*

— *Part 2: Method by continuous flow analysis (CFA)*

Introduction

Methods of determining water quality using flow analysis automated wet chemical procedures and are particularly suitable for the processing of many analytes in water in large sample series at a high analysis frequency.

Analysis can be performed by flow injection analysis (FIA) [1], [2] or continuous flow analysis (CFA) [3]. Both methods share the feature of an automatic dosage of the sample into a flow system (manifold) where the analyte in the sample reacts with the reagent solutions on its way through the manifold. The sample preparation may be integrated in the manifold. The amount of reaction product is measured in a flow detector (e.g. flow photometer). This part of ISO 15681 describes the CFA method.

The user should be aware that particular problems could require the specification of additional marginal conditions.

Water quality — Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) —

Part 2:
Method by continuous flow analysis (CFA)

WARNING — Persons using this part of ISO 15681 should be familiar with normal laboratory practice. This part of ISO 15681 does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions. Molybdate and antimony waste solutions should be disposed of properly. It is absolutely essential that tests conducted according to this part of ISO 15681 be carried out by suitably qualified staff.

1 Scope

This part of ISO 15681 specifies CFA methods for the determination of orthophosphate in the mass concentration range from 0,01 mg/l to 1,00 mg/l P, and total phosphorus in the mass concentration range from 0,10 mg/l to 10,0 mg/l P. The method includes the digestion of organic phosphorus compounds and the hydrolysis of inorganic polyphosphate compounds, performed either manually as described in ISO 6878 [5], [6] or with an integrated UV digestion and hydrolysis unit.

This part of ISO 15681 is applicable to various types of water (such as ground, drinking, surface, leachate and waste water). The range of application may be changed by varying the operating conditions.

This method is also applicable to the analysis of seawater, but with changes in sensitivity, by adaptation of the carrier and calibration solutions to the salinity of the samples.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specifications and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design on sampling programmes*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

ISO 6878:—[1)], *Water quality — Determination of phosphorus — Ammonium molybdate spectrometric method*

1) To be published.

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

3 Interferences

3.1 General interferences

ISO 6878:—, Annex B gives a list of general interferences. In addition, or contrary to the cited standard, the following guidelines apply.

a) Arsenate causes serious interference. 100 µg/l As, present as arsenate, results in a response comparable to approximately 30 µg/l P.

b) If the silicate concentration in samples is not greater than 60 times the phosphorus concentration, interferences by silicate can be neglected.

c) Fluoride interference is significant above 50 mg/l.

d) Nitrite interference is significant above 5 mg/l. The interference can be eliminated by acidifying samples after collection.

e) For samples containing high concentrations of oxidizing agents, the amount of added reduction reagent can be insufficient. In this case, remove the oxidizing material prior to digestion.

f) The self-absorption of the sample can be compensated by measuring, in addition to the sample signal (8.6), the signal of the sample without the admixture of the reagents. In this case, the difference of the two responses is used for the evaluation (Clause 9).

3.2 Interferences in the determination of total-P

Samples containing solids or suspended particles can show low values when analysed by the UV method, if the particles are not completely transported into the UV unit. The error can be minimized by stirring the sample immediately before sampling, in order to ensure that a representative sample is delivered into the analyser, and by reducing the particle size.

The interferences from silicate, nitrite, fluoride and iron described for the orthophosphate determination are generally not observed in the UV method, due to the pre-digestion and the higher analytical range.

The efficiency of the UV digestion can be affected for water samples with chemical oxygen demand (COD) values of more than 10 times the highest concentrations of the calibration solutions (5.21). In this case, the sample should be diluted.

4 Principle

4.1 Determination of orthophosphate

The sample is mixed with a surfactant solution, followed by an acidic solution containing molybdate and antimony ions. The resulting phospho-antimony-molybdate complex is reduced by ascorbic acid to molybdenum blue [4], [5].

4.2 Total phosphorus with manual digestion

Phosphorus compounds in the sample are oxidized manually with a potassium peroxodisulfate solution, in accordance with ISO 6878, or with an equivalent procedure. The resulting orthophosphate is determined by the molybdenum blue reaction using the colour reaction described in 4.1. The samples can be neutralized manually according to ISO 6878 or by taking into account the amount of acid used in this procedure when calculating the acid to be used in the molybdenum reagent.

4.3 Total phosphorus with integral UV digestion and hydrolysis

The sample is mixed with potassium peroxodisulfate and passed through a UV digestor, followed by acid digestion to hydrolyse polyphosphates. The resulting orthophosphate is measured using the colour reaction described in 4.1.

5 Reagents

Use analytical grade chemicals unless otherwise specified.

5.1 Water complying to grade 1 of ISO 3696.

The phosphate blank value shall be checked (8.3).

5.2 Sulfuric acid, H_2SO_4.

5.2.1 Sulfuric acid (I), $\rho = 1{,}84$ g/ml; 98 % (mass fraction).

5.2.2 Sulfuric acid (II), $c(H_2SO_4) = 2{,}45$ mol/l.

To approximately 800 ml of water (5.1), carefully add 136 ml of sulfuric acid (I) (5.2.1) while stirring. Cool and dilute to 1 000 ml with water (5.1).

5.3 Ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$.

5.4 Antimony potassium tartrate hemihydrate, $K(SbO)C_4H_4O_6 \cdot 0{,}5\ H_2O$.

5.5 Ascorbic acid, $C_6H_8O_6$.

5.6 Sodium dodecyl sulfate, $NaC_{12}H_{25}SO_4$.

5.7 Potassium peroxodisulfate, $K_2S_2O_8$.

5.8 Potassium dihydrogen phosphate, KH_2PO_4, dried at 105 °C ± 5 °C to constant mass.

5.9 Potassium pyrophosphate, $K_4P_2O_7$.

5.10 Organophosphorus compounds to check the UV digestion.

5.10.1 Pyridoxal-5-phosphate monohydrate, $C_8H_{10}NO_6P \cdot H_2O$ *or alternatively*:

5.10.2 Disodium phenylphosphate, $C_6H_5Na_2PO_4$.

5.11 Surfactant solutions

5.11.1 Surfactant solution I, [see (A) in Figure A.1].

Dissolve 1 g of sodium dodecyl sulfate (5.6) in about 800 ml of water (5.1) and dilute to 1 000 ml.

The solution is stable for 6 months if stored at room temperature.

5.11.2 Surfactant solution II, [see (B) in Figure A.1, and S1 in Figure A.2].

Dissolve 10 g of sodium dodecyl sulfate (5.6) in about 800 ml of water (5.1) and dilute to 1 000 ml.

The solution is stable for 6 months if stored at room temperature.

5.12 Molybdate solution

Dissolve 40 g of ammonium heptamolybdate tetrahydrate (5.3) in about 800 ml of water (5.1) and dilute to 1 000 ml with water (5.1).

The solution is stable for 3 months if stored at room temperature.

5.13 Antimony potassium tartrate solution

Dissolve 2,5 g of antimony potassium tartrate hemihydrate (5.4) in about 800 ml of water (5.1) and dilute to 1 000 ml with water (5.1).

The solution is stable for 3 months if stored at room temperature.

5.14 Antimony tartrate molybdate reagents

5.14.1 Antimony tartrate molybdate reagent I, for determination of orthophosphate and total P after manual digestion (R1 in Figure A.1).

Mix 500 ml of sulfuric acid (II) (5.2.2), 150 ml of molybdate solution (5.12) and 50 ml of antimony potassium tartrate solution (5.13).

The solution is stable for 2 weeks if stored at room temperature.

5.14.2 Antimony tartrate molybdate reagent II, for total phosphorus determination after integrated UV digestion (R3 in Figure A.2).

Dissolve 20 g of ammonium heptamolybdate tetrahydrate (5.3) and 50 mg of antimony potassium tartrate hemihydrate (5.4) in about 800 ml of water (5.1), add 100 ml of surfactant solution II (5.11.2) and bring to a volume of 1 000 ml with water (5.1).

The solution is stable for 2 weeks if stored at room temperature.

5.15 Ascorbic acid solution I, (R2 in Figure A.1).

Dissolve 1 g of ascorbic acid (5.5) in about 80 ml of water (5.1) and bring to a volume of 100 ml with water (5.1). Store in the dark. Prepare the solution daily before use.

5.16 Ascorbic acid solution II, (R4 in Figure A.2).

Dissolve 3,5 g of ascorbic acid (5.5) in about 80 ml of water (5.1), add 0,1 g of sodium dodecyl sulfate (5.6) and dilute with water (5.1) to 100 ml. Store in the dark. Prepare the solution daily before use.

5.17 Digestion reagents for the determination of total phosphorus after integrated UV digestion.

5.17.1 Digestion reagent I, working range 0,10 mg/l to 1,00 mg/l [line (D) in Figure A.2].

Dissolve 10 g of potassium peroxodisulfate (5.7) in about 600 ml of water (5.1). While stirring, carefully add 340 ml of sulfuric acid (II) (5.2.2), cool and dilute with water (5.1) to 1 000 ml.

The solution is stable for 2 weeks if stored at room temperature.

5.17.2 Digestion reagent II, working range 1,00 mg/l to 10,0 mg/l [line (C) in Figure A.2].

Dissolve 2,5 g of potassium peroxodisulfate (5.7) in about 600 ml of water (5.1). While stirring, carefully add 85 ml of sulfuric acid (II) (5.2.2), cool and dilute with water (5.1) to 1 000 ml.

The solution is stable for 2 weeks if stored at room temperature.

5.18 Orthophosphate stock solution I, $\rho = 50{,}0$ mg/l orthophosphate-P.

Dissolve 220 mg $\pm$ 1 mg of potassium dihydrogenphosphate (5.8) in water (5.1) and dilute with water (5.1) to 1 000 ml. Store in a tightly closed glass bottle.

The solution is stable for 2 months if stored at 4 °C $\pm$ 2 °C.

5.19 Orthophosphate stock solution II, $\rho = 10{,}0$ mg/l P.

Dilute 20 ml of solution (5.18) to 100 ml with water (5.1). Prepare fresh daily.

5.20 Orthophosphate stock solution III, $\rho = 1{,}00$ mg/l P.

Dilute 2 ml of solution (5.18) to 100 ml with water (5.1). Prepare fresh daily.

5.21 Calibration solutions.

Prepare at least five calibration solutions by diluting solutions 5.18 to 5.20 according to the range required.

Ranges:

For orthophosphate-P:	range II:	0,01 mg/l to 0,10 mg/l P
	range I:	0,10 mg/l to 1,00 mg/l P
For total-P:	range II:	0,10 mg/l to 1,00 mg/l P
	range I:	1,00 mg/l to 10,0 mg/l P

Tables 1 to 3 give examples for the preparation of 10 calibration solutions for the above-mentioned ranges.

Table 1 — Example for the preparation of 10 calibration solutions for the orthophosphate range II (0,01 mg/l to 0,10 mg/l P)

Millilitres of orthophosphate stock solution III (5.20) diluted to 100 ml	1	2	3	4	5	6	7	8	9	10
Concentration of calibration solutions, mg/l P	0,01	0,02	0,03	0,04	0,05	0,06	0,07	0,08	0,09	0,10