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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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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

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

This second edition cancels and replaces the first edition (ISO 15681-2:2003), which has been technically revised. The main changes compared to the previous edition are as follows:

a) the reagents have been adjusted to decrease the pH to enhance the colour reaction;

b) the figures in Annex A have been revised.

A list of all parts in the ISO 15681 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Methods of determining water quality using flow analysis automated wet chemical procedures 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)[6][8] or continuous flow analysis (CFA)[9]. 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 document 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 document should be familiar with normal laboratory practice. This document 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.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this document be carried out by suitably qualified staff.

1 Scope

This document specifies continuous flow analysis (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 and in References [4], [5] and [7], or with an integrated ultraviolet (UV) digestion and hydrolysis unit.

This document is applicable to various types of water, such as ground, drinking, surface, leachate and waste water. The range of application can be changed by varying the operating conditions.

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

It is also applicable to analysis using 10 mm to 50 mm cuvettes depending on the desired range. For extreme sensitivity, 250 mm and 500 mm long way capillary flow cells (LCFCs) can be used. However, the method is not validated for these two uses. Changes in sensitivity and calibration solutions could be required.

Annex A provides examples of a CFA system. Annex B gives performance data from interlaboratory trials. Annex C gives information of determining orthophosphate-P and total-P by CFA and tin(II) chloride reduction.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 — Specification and test methods*

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

ISO 5667-3:2018, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 6878:2004, *Water quality — Determination of phosphorus — Ammonium molybdate spectrometric method*

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*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Interferences

4.1 General interferences

Refer to ISO 6878:2004, Annex A for a list of general interferences. In addition, or contrary to the cited standard, the following applies:

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 for by measuring, in addition to the sample signal (9.6), 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 10).

4.2 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 or during 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 (6.22). In this case, the sample should be diluted.

5 Principle

5.1 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][7]. The pH of the reaction mixture shall be between pH 0,6 and pH 0,9[3].

5.2 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 5.1. The samples can be neutralized manually in accordance with 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.

5.3 Total phosphorus with integral UV digestion and hydrolysis

The sample is mixed with potassium peroxodisulfate and passed through a UV digester, followed by acid digestion to hydrolyse polyphosphates. The resulting orthophosphate is measured using the colour reaction described in 5.1. The pH of the reaction mixture shall be between pH 0,6 and pH 0,9[3]. The pH of the reaction mixture is critical to avoid interferences from silicate.

6 Reagents

Use analytical grade chemicals unless otherwise specified. Molybdate and antimony waste solutions should be disposed properly.

6.1 Water, conforming to grade 1 of ISO 3696.

The phosphate blank value shall be checked (see 9.3).

6.2 Sulfuric acid, H_2SO_4.

6.2.1 Sulfuric acid I, ρ = 1,84 g/ml; 95 % to 98 %.

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

To approximately 800 ml of water (6.1), carefully add 136 ml of sulfuric acid I (6.2.1) while stirring. Cool and dilute to 1 000 ml with water (6.1).

6.2.3 Sulfuric acid III, $c(H_2SO_4)$ = 2,45 mol/l.

To 1 000 ml of sulfuric acid II (6.2.2), add 1 g of sodium dodecyl sulfate (6.7) and mix.

6.3 Sodium hydroxide, NaOH.

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

6.5 Antimony potassium tartrate trihydrate, $K_2(SbO)_2C_8H_4O_{10}{\cdot}3H_2O$.

6.6 Ascorbic acid, $C_6H_8O_6$.

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

6.8 Potassium peroxodisulfate, $K_2S_2O_8$.

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

6.10 Potassium pyrophosphate, $K_4P_2O_7$.

6.11 Organophosphorus compounds, to check the UV digestion.

6.11.1 Pyridoxal-5-phosphate monohydrate, $C_8H_{10}NO_6P{\cdot}H_2O$.

6.11.2 Disodium phenylphosphate, $C_6H_5Na_2PO_4$.

6.12 Surfactant solutions.

6.12.1 Surfactant solution I, see (A) or (B) in Figure A.1.

Dissolve 1 g of sodium dodecyl sulfate (6.7) in about 800 ml of water (6.1) and dilute to 1 000 ml with water (6.1).

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

6.12.2 Surfactant solution II, see (A) or (B) in Figure A.1.

Dissolve 10 g of sodium dodecyl sulfate (6.7) in about 800 ml of water (6.1) and dilute to 1 000 ml with water (6.1).

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

6.13 Molybdate solution.

Dissolve 40 g of ammonium heptamolybdate tetrahydrate (6.4) in about 800 ml of water (6.1) and dilute to 1 000 ml with water (6.1).

Do not use a metal spatula when weighing the ammonium heptamolybdate tetrahydrate (6.4). The solution is stable for three months if stored at room temperature. Avoid any contact between metal and the ammonium heptamolybdate.

6.14 Antimony potassium tartrate solution.

Dissolve 2,5 g of antimony potassium tartrate trihydrate (6.5) in about 800 ml of water (6.1) and dilute to 1 000 ml with water (6.1).

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

6.15 Antimony tartrate molybdate reagents.

6.15.1 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 (6.2.2), 150 ml of molybdate solution (6.13) and 50 ml of antimony potassium tartrate solution (6.14).

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