INTERNATIONAL STANDARD

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Water quality — Determination of phosphorus — Ammonium molybdate spectrometric method

Qualité de l'eau — Dosage du phosphore — Méthode spectrométrique au molybdate d'ammonium

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Foreword

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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 6878 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 6878:1998), which has been technically revised.

Introduction

This International Standard specifies the determination of different forms of phosphorus compounds present in ground, surface and waste waters in various concentrations in the dissolved and undissolved state.

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

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WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard 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. It is absolutely essential that tests conducted according to this International Standard be carried out by suitably qualified staff. Molybdate and antimony waste solutions should be disposed of properly.

1 Scope

This International Standard specifies methods for the determination of

— orthophosphate (see Clause 4);

— orthophosphate after solvent extraction (see Clause 5);

— hydrolysable phosphate plus orthophosphate (see Clause 6);

— total phosphorus after decomposition (see Clauses 7 and 8).

The methods are applicable to all kinds of water including seawater and effluents. Phosphorus concentrations within the range of 0,005 mg/l to 0,8 mg/l may be determined in such samples without dilution.

A solvent extraction procedure allows smaller phosphorus concentrations to be determined with a detection limit of about 0,000 5 mg/l.

2 Interferences

See Annex A for some known interferences. There may be others and it is recommended to verify whether any such interferences exist and take action to eliminate them.

3 Principle

Reaction of orthophosphate ions with an acid solution containing molybdate and antimony ions to form an antimony phosphomolybdate complex.

Reduction of the complex with ascorbic acid to form a strongly coloured molybdenum blue complex. Measurement of the absorbance of this complex to determine the concentration of orthophosphate present.

Polyphosphate and some organophosphorus compounds are determined if converted to molybdate reactive orthophosphate formed by sulfuric acid hydrolysis.

Many organophosphorus compounds are converted to orthophosphate by mineralization with peroxodisulfate. Nitric acid-sulfuric acid mineralization is used if a more vigorous treatment is required.

4 Determination of orthophosphate

4.1 Reagents

During the analysis, use only reagents of recognized analytical grade and only water having a phosphate content that is negligible compared with the lowest concentration to be determined in the samples.

For low phosphate contents, double-distilled water from an all-glass apparatus is recommended.

4.1.1 Sulfuric acid solution, $c(H_2SO_4) \approx 9$ mol/l.

Add 500 ml ± 5 ml of water to a 2 l beaker. Cautiously add, with continuous stirring and cooling, 500 ml ± 5 ml of sulfuric acid, $\rho = 1{,}84$ g/ml. Mix well and allow the solution to cool to room temperature.

4.1.2 Sulfuric acid solution, $c(H_2SO_4) \approx 4{,}5$ mol/l.

Add 500 ml ± 5 ml of water to a 2 l beaker. Cautiously add, with continuous stirring and cooling, 500 ml ± 5 ml of sulfuric acid (4.1.1). Mix well and allow to cool to room temperature.

4.1.3 Sulfuric acid solution, $c(H_2SO_4) \approx 2$ mol/l.

Add 300 ml ± 3 ml of water to a 1 l beaker. Cautiously add 110 ml ± 2 ml of sulfuric acid solution (4.1.1), with continuous stirring and cooling. In a measuring flask, dilute to 500 ml ± 2 ml with water and mix well.

4.1.4 Sodium hydroxide solution, $c(NaOH) = 2$ mol/l.

Dissolve 80 g ± 1 g of sodium hydroxide pellets in water, cool and dilute to 1 l with water.

4.1.5 Ascorbic acid solution, $\rho = 100$ g/l.

Dissolve 10 g ± 0,5 g of ascorbic acid ($C_6H_8O_6$) in 100 ml ± 5 ml water.

NOTE The solution is stable for 2 weeks if stored in an amber glass bottle in a refrigerator and can be used as long as it remains colourless.

4.1.6 Acid molybdate, Solution I.

Dissolve 13 g ± 0,5 g of ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$] in 100 ml ± 5 ml of water. Dissolve 0,35 g ± 0,05 g of antimony potassium tartrate hemihydrate [$K(SbO)C_4H_4O_6{\cdot}½H_2O$] in 100 ml ± 5 ml of water.

Add the molybdate solution to 300 ml ± 5 ml of sulfuric acid (4.1.1) with continuous stirring. Add the tartrate solution and mix well.

NOTE The reagent is stable for at least 2 months if stored in an amber glass bottle.

4.1.7 Acid molybdate, Solution II.

Cautiously add 230 ml ± 0,5 ml of sulfuric acid (4.1.1) to 70 ml ± 5 ml of water, cool. Dissolve 13 g ± 0,5 g of ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$] in 100 ml ± 5 ml of water. Add to the acid solution and mix well. Dissolve 0,35 g ± 0,05 g of antimony potassium tartrate hemihydrate [$K(SbO)C_4H_4O_6{\cdot}½H_2O$] in 100 ml ± 5 ml of water. Add to the molybdate-acid solution and mix well.

This reagent is used when the sample is acidified with sulfuric acid (4.1.2) (see also Clauses 6, 7 and 8).

NOTE The reagent is stable for at least 2 months if stored in an amber glass bottle.

4.1.8 Turbidity-colour compensation solution.

On a volume/volume basis, mix two parts of sulfuric acid (4.1.2) and one part of ascorbic acid (4.1.5).

NOTE The reagent is stable for several weeks if stored in an amber glass bottle in a refrigerator.

4.1.9 Sodium thiosulfate pentahydrate solution, ρ = 12,0 g/l.

Dissolve 1,20 g ± 0,05 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) in 100 ml ± 5 ml of water. Add 0,05 g ± 0,005 g of anhydrous sodium carbonate (Na_2CO_3) as preservative.

NOTE The reagent is stable for at least 4 weeks if stored in an amber glass bottle.

4.1.10 Orthophosphate stock standard solution, ρ_P = 50 mg/l.

Dry a few grams of potassium dihydrogen phosphate to constant mass at 105 °C. Dissolve 0,219 7 g ± 0,000 2 g of KH_2PO_4 in about 800 ml ± 10 ml of water in a 1 000 ml volumetric flask. Add 10 ml ± 0,5 ml of sulfuric acid (4.1.2) and make up to the mark with water.

Alternatively, use a commercially available stock solution.

The solution is stable for at least 3 months if stored in a well stoppered glass bottle. Refrigeration to about 4 °C is recommended.

4.1.11 Orthophosphate standard solution, ρ_P = 2 mg/l.

Pipette 20 ml ± 0,01 ml of orthophosphate stock standard solution (4.1.10) into a 500 ml volumetric flask. Make up to the mark with water and mix well.

Prepare and use this solution each day as required.

NOTE 1 ml of this standard solution contains 2 µg P.

4.1.12 Hydrochloric acid, ρ(HCl) = 1,19 g/ml.

4.1.13 Hydrochloric acid, c(HCl) = 2,5 mol/l.

Cautiously add 200 ml ± 10 ml of hydrochloric acid (4.1.12) to 500 ml ± 10 ml of water. Mix and cool to room temperature. Make up to 1 000 ml with water.

4.2 Apparatus

4.2.1 Spectrometer, "prism"- or "grating-type" or filter type, capable of accepting optical cells of thickness 10 mm to 50 mm.

The spectrometer chosen shall be suitable for measuring absorbance in the visible and near infra-red regions of the spectrum. The most sensitive wavelength is 880 nm, but if a loss of sensitivity can be accepted, absorbance may be measured at 700 nm.

NOTE The detection limit of the method is lower if a spectrometer capable of accepting 100 mm optical cells is available.

4.2.2 Filter assembly, to hold a membrane filter of nominal pore size 0,45 µm.

4.2.3 Glassware.

Before use, wash all glassware, for example with hydrochloric acid (4.1.13), at approximately 40 °C to 50 °C and rinse thoroughly with water. Detergents containing phosphate shall not be used.

Preferably the glassware should be used only for the determination of phosphorus. After use, clean it as described above and keep covered until needed again.

Rinse glassware used for the colour development stage occasionally with sodium hydroxide solution (4.1.4), followed by thorough rinsing with water (4.1), to remove deposits of the coloured complex which has a tendency to stick as a thin film on the wall of glassware.

4.3 Sampling and samples

4.3.1 Sampling

Collect the laboratory samples in polyethene, polyvinylchloride or preferably glass bottles. In the case of low phosphate concentrations, use glass bottles.

The use of sampling bottles with cap lines should be avoided as these may contain phosphorus.

4.3.2 Preparation of the test sample

Filter the laboratory sample (4.3.1) within 4 h after sampling. If the sample has been kept cool in the meantime, bring to room temperature before filtration.

Wash a membrane filter of nominal pore size 0,45 µm to ensure it is free of phosphate by passing 200 ml of water, previously heated to approximately 30 °C to 40 °C. Discard these washings. Filter the sample and reject the first 10 ml of sample filtrate. Collect the remainder in a clean, dry glass bottle for the immediate determination of orthophosphate (4.4.4).

If the filtrate is not within the range of pH 3 to pH 10, adjust it with sodium hydroxide (4.1.4) or sulfuric acid solution (4.1.3).

The filtration time should not exceed 10 min. If necessary, a larger diameter filter should be used.

The membrane filter should either be checked for phosphorus content or washed as described. Commercially available membrane filters that are sold free from phosphorus should be washed as described.

4.4 Procedure

4.4.1 Test portion

Take a volume of test portion not exceeding 40 ml. This maximum volume is suitable for the determination of orthophosphate concentrations of up to ρ_p = 0,8 mg/l, when using an optical cell of thickness 10 mm. Smaller test portions shall be used in order to accommodate higher phosphate concentrations as shown in Table 1. Similarly, low phosphate concentrations can be determined by measuring the absorbance in an optical cell of thickness 40 mm or 50 mm.

Table 1 — Sample volumes and concentrations

Orthophosphate concentration mg/l	Volume of test portion ml	Thickness of optical cell mm
0,0 to 0,8	40,0	10
0,0 to 1,6	20,0	10
0,0 to 3,2	10,0	10
0,0 to 6,4	5,0	10
0,0 to 0,2	40,0	40 or 50

4.4.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, using the same quantities of all the reagents as in the determination, but using the appropriate volume of water instead of the test portion.

4.4.3 Calibration

4.4.3.1 Preparation of calibration solutions

Transfer, by means of a volumetric pipette, appropriate volumes, for example, 1,0 ml, 2,0 ml, 3,0 ml, 4,0 ml, 5,0 ml, 6,0 ml, 7,0 ml, 8,0 ml, 9,0 ml and 10,0 ml of the orthophosphate standard solution (4.1.11) to 50 ml volumetric flasks. Dilute with water to about 40 ml. These solutions represent orthophosphate concentrations ρ_P = 0,04 mg/l to 0,4 mg/l.

Proceed accordingly for other ranges of phosphate concentrations shown in Table 1.

4.4.3.2 Colour development

Add to each flask, while swirling, 1 ml of ascorbic acid (4.1.5) followed by 2 ml of acid molybdate Solution I (4.1.6). Make up to the mark with water and mix well.

NOTE Absorbance measured at 700 nm causes a loss of about 30 % of the sensitivity at 880 nm.

4.4.3.3 Spectrometric measurements

Measure the absorbance of each solution using the spectrometer (4.2.1) at 880 nm after a period between 10 min and 30 min, or, if a loss of sensitivity can be accepted, at 700 nm. Use water in the reference cell.

4.4.3.4 Plotting the calibration graph

Plot a graph of absorbance (as the y-axis) against the phosphorus content (as the x-axis) in milligrams of phosphorus per litre of the calibration solutions. The relationship between absorbance and concentration is linear. Determine the slope of the graph.

Verify the graph from time to time for linearity, especially if new batches of chemicals are used.

4.4.4 Determination

4.4.4.1 Colour development

4.4.4.1.1 Standard procedure

Pipette the selected volume of test portion (4.4.1), V_S , into a 50 ml one-mark volumetric flask and, if necessary, dilute to approximately 40 ml ± 2 ml with water. Proceed as specified in 4.4.3.2.

If the test sample contains arsenate, this should be reduced to arsenite with thiosulfate in acidic medium. The reduction to arsenite is quantitative for arsenate concentrations up to at least 2 mg/l As, as described below.

Transfer, by means of a volumetric pipette, up to a maximum of 40 ml of the test sample to a 50 ml volumetric flask. Add 0,4 ml of sulfuric acid (4.1.2), 1 ml of ascorbic acid solution (4.1.5), and 1 ml of thiosulfate solution (4.1.9). Mix and allow the reduction to proceed for 10 min ± 1 min. Add 2 ml acid molybdate Solution II (4.1.7). Make up to the mark with water. Mix well. Proceed as described in 4.4.3.3.