SLOVENSKI STANDARD
SIST EN 1189:1997

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Kakovost vode - Določanje fosforja - Spektrofotometrijska metoda z amonmolibdatom

Water quality - Determination of phosphorus - Ammonium molybdate spectrometric method

Wasserbeschaffenheit - Bestimmung von Phosphor - Photometrisches Verfahren mittels Ammoniummolybdat

Qualité de l'eau - Dosage du phosphore - Dosage spectométrique a l'aide du molybdate d'ammonium

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English version

Water quality - Determination of phosphorus - Ammonium molybdate spectrometric method

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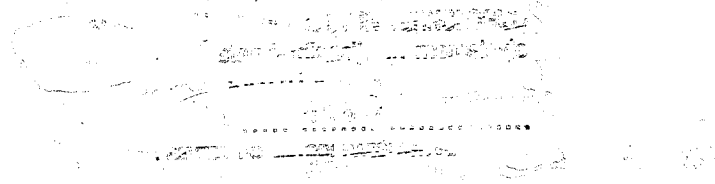
Wasserbeschaffenheit - Bestimmung von Phosphor - Photometrisches Verfahren mittels Ammoniummolybdat



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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart,36 B-1050 Brussels

Contents

Foreword

This European Standard is based on ISO 6878-1:1986. This European Standard has been prepared by CEN/TC 230 "Water analysis" the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 1997, and conflicting national standards shall be withdrawn at the latest by April 1997.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, United Kingdom.

Annexes designated "informative" are given only for information. In this Standard Annex A, B, and C are informative.

Introduction

This European 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.

1 Scope

This European Standard specifies methods for the determination of

- orthophosphate (see clause 3);
- orthophosphate after solvent extraction (see clause 4);
- hydrolysable phosphate plus orthophosphate (see clause 5);
- total soluble phosphorus and total phosphorus after decomposition (see clauses 6 and 7).

The methods are applicable to all kinds of water including seawater and effluents. Phosphorus contents within the range of 0,005mg/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 0,0005 mg/l .

See annex B for some known interferences. There may be others and it is recommended to verify whether any such exist and take action to remove them.

2 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 persulfate. Nitric acid-sulfuric acid mineralization is used if a more vigorous treatment is required.

3 Determination of orthophosphate

3.1 Reagents

3.1.1 General

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

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

3.1.2 **Sulfuric acid**, solution, $c(H_2SO_4)$ = 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 , ρ = 1,84 g/ml. Mix well and allow the solution to cool to room temperature.

3.1.3 Sulfuric acid, solution, $c(H_2SO_4)$ = 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 (see 3.1.2). Mix well and allow to cool to room temperature.

3.1.4 Sulfuric acid, solution, $c(H_2SO_4)$ = 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 (see 3.1.2), with continuous stirring and cooling. Dilute to 500 ml ± 2 ml with water and mix well.

3.1.5 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.

3.1.6 Ascorbic acid, solution, ρ = 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.

3.1.7 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 $[K(SbO)C_4H_4O_6 \cdot 1/2H_2O]$ in 100 ml ± 5 ml of water.

Add the molybdate solution to 300 ml ± 5 ml of sulfuric acid (see 3.1.2) 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.

3.1.8 Acid molybdate, solution II

Add 230 ml ± 0,5 ml of sulfuric acid (see 3.1.2) 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 $[K(SbO)C_4H_4O_6 \cdot 1/2H_2O]$ 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 (see 3.1.3) (see clause 5, 6 and 7).

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

3.1.9 Turbidity-colour compensation solution

On a volume/volume basis, mix two parts of sulfuric acid (see 3.1.3) and one part of ascorbic acid (see 3.1.6).

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

3.1.10 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.

3.1.11 Orthophosphate, stock standard solution , ρ = 50 mg/l

Dry a few grams of potassium dihydrogen phosphate to constant mass at 105 °C. Dissolve 0,2197 g ± 0,0002 g of KH_2PO_4 in about 800 ml ± 10 ml of water in a 1000 ml volumetric flask. Add 10 ml ± 0,5 ml of sulfuric acid (see 3.1.2) and make up to the mark with water.

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

3.1.12 Orthophosphate, standard solution ρ = 2 mg/l

Pipette 20 ml ± 0.01 ml of orthophosphate stock standard solution (see 3.1.11) into a 500 ml volumetric flask. Make up to the mark with water and mix well.

Prepare and use this solution each day it is required.

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

3.1.13 Hydrochloric acid, ρ (HCl) = 1,12 g/ml

3.1.14 Hydrochloric acid, c(HCl) = 2 mol/l

Add 200 ml ± 10 ml of hydrochloric acid (see 3.1.13) to 500 ml ± 10 ml of water. Mix and cool to room temperature. Make up to 1 000 ml with water.

3.2 Apparatus

3.2.1 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 can 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.

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

3.2.3 Preparation of glassware

Before use, all glassware shall be washed with hydrochloric acid (see3.1.13) at approximately 40 °C to 50 °C and rinsed thoroughly with water. Detergents containing phosphate shall not be used.
Preferably the glassware should be used only for the determination of phosphorus. After use it shall be cleaned as above and kept covered until needed again.

Glassware used for the colour development stage shall be rinsed occasionally with sodium hydroxide solution (see 3.1.5) to remove deposits of the coloured complex which has a tendency to stick as a thin film on the wall of glassware.

3.3 Sampling and Samples

3.3.1 Sampling

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

3.3.2 Preparation of the test sample

The laboratory sample (see 3.3.1) shall be filtered 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 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 (see 3.4.4).

If the filtrate is not within the range of pH 3 to 10, adjust it with sodium hydroxide solution (see 3.1.5) or sulfuric acid (see 3.1.4).

NOTE 1: The filtration time should not exceed 10 min. If necessary, a larger diameter filter should be used.

NOTE 2: 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.

3.4 Procedure

3.4.1 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

3.4.2 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.

3.4.3 Calibration

3.4.3.1 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 (see 3.1.12) to 50 ml volumetric flasks. Dilute with water to about 40 ml. These solutions represent orthophosphate concentrations ρ_P = 0,05 mg/l to 0,5 mg/l.

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

3.4.3.2 Colour development

Add to each flask, while swirling, 1 ml ascorbic acid (see 3.1.6) followed by 2 ml of acid molybdate solution I (see 3.1.7). Make up to the mark with water and mix well.

3.4.3.3 Spectrometric measurements

Measure the absorbance of each solution using the spectrometer (see 3.2.1) at 880 nm after between 10 min and 30 min, or if a loss of sensitivity can be accepted, at 700 nm. Use water in the reference cell.

3.4.3.4 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. Run an independently prepared calibration solution with each series of samples.

3.4.4 Determination

3.4.4.1 Colour development

Pipette the selected volume of test portion into a 50 ml one-mark volumetric flask and if necessary dilute to 40 ml ± 2 ml with water. Proceed as specified in 3.4.3.2.

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 1 ml of ascorbic acid solution (see 3.1.6), and 1 ml of thiosulfate solution (see 3.1.10). Mix and allow the reduction to proceed for 10 min ± 1 min. Add 2 ml acid molybdate solution II (see 3.1.8). Make up to the mark with water. Mix well. Proceed as described in clause 3.4.3.2.

NOTE 1: If the test sample is turbid and/or coloured, the procedure described below is recommended.

Add 3 ml of the turbidity-colour compensation reagent (see 3.1.9) to the selected volume of test portion. Dilute to 50 ml and measure the absorbance. Subtract the absorbance of this solution from the value measured according to 3.4.3.3.

NOTE 2: Absorbance measured at 700 nm represents a loss of about 30 % of the sensitivity at 880 nm.

3.4.4.2 Spectrometric measurements

See 3.4.3.3.

If, due to interference by arsenate, the test portion has been treated with thiosulfate, measurements should be taken within 10 min; otherwise the colour will fade.

3.5 Expression of Results

3.5.1 Calculation

Calculate the orthophosphate concentration, ρ_P, expressed in milligrams per litre, using the equation

$$\rho P = \frac{(A - A_0) \cdot V_{max}}{f \cdot V_s}$$

where:

A is the absorbance of the test portion;
A_0 is the absorbance of the blank test;
f is the slope of the calibration graph (3.4.3.4), in litres per milligrams;
V_{max} is the reference volume, of the test portion (50 ml), in millilitres;
V_s is the actual volume of the test portion, in millilitres.

Report the mass concentrations of phosphorus as follows, but to not more than three significant figures:

ρ P < 0,1 mg/l ± 0,001 mg/l;
0,1 mg/l ± 0,01 mg/l ≤ ρ P < 10 mg/l ± 0,01 mg/l;
ρ P ≥ 10 mg/l ± 0,1 mg/l.

3.5.2 Precision

The precision data in Table A.1 were obtained in an interlaboratory trial involving 16 laboratories.

NOTE: For interferences, see annex B.

3.6 Test report

The test report shall contain the following information:

a) all information necessary for complete identification of the sample;

b) a reference to this European Standard;

c) a reference to the method used, and the number of the clause;

d) the results obtained and

e) details of any operations not included in this section or regarded as optional, together with any incidents likely to have an influence upon the results.

4 Determination of orthophosphate after solvent extraction

This method can be applied only if the phosphate concentration in the sample is less than 0,01 mg/l P. The method is especially suitable for marine water.

4.1 Reagents

Use the reagents specified in 3.1.6 and 3.1.7, and in addition:

4.1.1 1-Hexanol ($C_6H_{13}OH$)

4.1.2 Ethanol (C_2H_5OH)

4.1.3 **Orthophosphate**, Standard solution, ρ = 0,5 mg/l P.

Pipette 5,0 ml ± 0,01 ml of orthophosphate stock standard solution (see 3.1.11) into a 500 ml one-mark volumetric flask. Make up to the mark with water and mix well.

Prepare and use this solution each day it is required.

4.2 Sampling and Samples

See 3.3.

4.3 Procedure

4.3.1 Test portion

Transfer, by means of a measuring cylinder, 350 ml ± 5 ml of the test sample (see 3.3) to a 500 ml separating funnel.

4.3.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, using the same quantities of all reagents as in the determination, but using 350 ml of water instead of the test portion.

4.3.3 Calibration

4.3.3.1 Preparation of calibration solutions

Add 300 ml ± 10 ml of water to five individual separating funnels. From a microburette add 1,4 ml; 2,8 ml; 4,2 ml; 5,6 ml and 7,0 ml of orthophosphate standard solution (see 4.1.3) to each 500 ml separating funnel. Dilute each solution to 350 ml ± 10 ml with water, stopper, swirl, and mix. These solutions represent orthophosphate concentrations, ρ_P, of 0,002 mg/ml; 0,004 mg/ml; 0,006 mg/ml; 0,008 mg/ml and 0,01 mg/l respectively.

4.3.3.2 Colour development

To each separating funnel, with swirling, add 7,0 ml ± 0,1 ml of ascorbic acid solution (see 3.1.6) and 14,0 ml ± 0,1 ml of acid molybdate solution I (see 3.1.7).

After 15 min add 40,0 ml ± 0,1 ml of 1-hexanol (see 4.1.1) to each separating funnel and stopper. Shake vigorously for 1 min. Allow the phases to separate and pipette 30 ml ± 0,01 ml of each of the upper 1-hexanol extracts into a series of dry 50 ml one-mark volumetric flasks. Add 1,0 ml ± 0,2 ml ethanol (see 4.1.2) to each flask and dilute each solution to the mark with 1-hexanol.

4.3.3.3 Spectrometric measurements

Measure the absorbance of each 1-hexanol solution at 680 nm in optical cells of thickness 40 mm or 50 mm against 1-hexanol in the reference cell.

4.3.3.4 Plotting the calibration graph

Plot a graph of absorbance (as the y-axis) against the phosphorus content (as the x-axis), in milligrams per litre, of the calibration solutions. Determine the slope of the graph.

Verify the linearity of the calibration curve periodically, especially if new batches of chemicals are used.

4.3.4 Determination

4.3.4.1 Colour development

Treat the test portions (see 4.3.1) as specified in 4.3.3.2 for the calibration solutions.

4.3.4.2 Spectrometric measurements

See 4.3.3.3.

4.4 Expression of results

Calculate the orthophosphate concentration ρ_P, expressed in milligrams per litre, using the equation:

$$\rho P = \frac{A - A_0}{f}$$

where:

A is the absorbance of the test portion;
A_0 is the absorbance of the blank test;
f is the slope of the calibration graph (see 4.3.3.4), in litres per milligrams.

Report the value to the nearest 0,0001 mg/l but give values below 0,0005 mg/l as $\rho_P < 0{,}0005$ mg/l.

NOTE: For interferences, see annex B.

4.5 Test report

The test report shall contain the following information:

a) all information necessary for complete identification of the sample;

b) a reference to this European Standard;

c) a reference to the method used, and the number of the clause;

d) the results obtained and

e) details of any operations not included in this section or regarded as optional, together with any incidents likely to have an influence upon the result.

5 Determination of hydrolysable phosphate and orthophosphate

5.1 Reagents

Use the reagents specified in 3.1.3, 3.1.6 , 3.1.7, and 3.1.8.

5.2 Apparatus

See 3.2.