

British Standard

Water quality

Part 2. Physical, chemical and biochemical methods

Section 2.28 Methods for the determination of phosphorus: ammonium molybdate spectrometric method

[ISO title: Water quality — Determination of phosphorus — Part 1 : Ammonium molybdate spectrometric method]

Qualité de l'eau

Partie 2. Méthodes physiques, chimiques et biochimiques

Section 2.27 Dosage du phosphore: dosage spectrométrique à l'aide du molybdate d'ammonium

Wasserqualität

Teil 2. Physikalische, chemische und biochemische Verfahren

Abschnitt 2.27 Verfahren zu phosphorbestimmung: Spektrometrie mit Ammoniummolybdat

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National foreword

This Section of this British Standard, which has been prepared under the direction of the Environment and Pollution Standards Committee, is identical with ISO 6878/1-1986 'Water quality — Determination of phosphorus — Part 1 : Ammonium molybdate spectrometric method'. The international standard was prepared by Subcommittee 2, Physical, chemical and biochemical methods of Technical Committee 147, Water quality, of the International Organization for Standardization (ISO) as a result of discussion in which the UK participated.

This British Standard is being published in a series of Parts subdivided into Sections that will generally correspond to particular international standards. Sections are being, or will be, published in Parts 1 to 6 which, together with Part 0, are as follows:

- Part 0. Introduction
- Part 1. Glossary
- Part 2. Physical, chemical and biochemical methods
- Part 3. Radiological methods
- Part 4. Microbiological methods
- Part 5. Biological methods
- Part 6. Sampling

Terminology and conventions. The text of the international standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

The comma has been used as a decimal marker. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

Wherever the words 'part of ISO 6878' appear, referring to this standard, they should be read as 'Section of this British Standard'.

In British Standards it is current practice to use the symbol 'L' for litre (and in its submultiples) rather than 'l', and to use the spelling 'sulphur', etc., instead of 'sulfur', etc.

Textual error. When adopting the text of the international standard, the textual error given below was discovered. It has been marked in the text and has been reported to ISO in a proposal to amend the text of the international standard.

In 23.1, line 2, the word 'efficient' should read 'effective'.

Additional information. The responsible technical committee has reviewed the consequences of the last sentence of paragraph 2 of clause 3, and considers that this requirement is superfluous as it is clearly stated immediately above that distilled or double-distilled water shall be used. Accordingly this anomaly is being reported to ISO in a proposal to delete this sentence.

The tests described in this British Standard should only be carried out in laboratories with suitable facilities and by suitably qualified persons with an appropriate level of chemical expertise and knowledge of the necessary safety precautions. Standard chemical procedures should be followed throughout.

Warning. Continuous cooling of the solution when making the sulphuric acid solutions referred to in 3.1 and 3.2 will help minimize the risk of localized boiling.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

0 Introduction

This part of ISO 6878 deals with the determination of phosphorus compounds present in ground, surface, and waste waters in various concentrations in the dissolved and undissolved state.

A spectrometric method after mineralization with sulfuric acid and perchloric acid, for heavily polluted waste water, will form the subject of ISO 6878/2.

1 Scope and field of application

This part of ISO 6878 specifies methods for the determination of

orthophosphate (see **section one**);

orthophosphate after extraction (see **section two**);

hydrolysable phosphate plus orthophosphate (see **section three**);

total soluble phosphorus and total phosphorus after decomposition (see **section four**).

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

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

See the annex for some known interferences. There may be others and it is necessary 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 to determine the concentration of orthophosphate present.

Polyphosphates and some organophosphorus compounds are determined if converted to the molybdate reactive orthophosphate form 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.

Section one : Determination of orthophosphate

3 Reagents

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 necessary. Deionized water shall be checked according to the procedures given in the bibliography.

3.1 Sulfuric acid, solution, $c(\text{H}_2\text{SO}_4) = 9 \text{ mol/l}$.

Add $500 \pm 5 \text{ ml}$ of water to a 2 l beaker. Cautiously add, with continuous stirring, $500 \pm 5 \text{ ml}$ of sulfuric acid ($\rho = 1,84 \text{ g/ml}$).

3.2 Sulfuric acid, solution, $c(\text{H}_2\text{SO}_4) = 4,5 \text{ mol/l}$.

Add $500 \pm 5 \text{ ml}$ of water to a 2 l beaker. Cautiously add, with continuous stirring, $500 \pm 5 \text{ ml}$ sulfuric acid (3.1) and mix well.

3.3 Sulfuric acid, solution, $c(\text{H}_2\text{SO}_4) = 2 \text{ mol/l}$.

Add $300 \pm 3 \text{ ml}$ of water to a 1 litre beaker. Cautiously add $110 \pm 2 \text{ ml}$ of sulfuric acid solution (3.1), with continuous stirring and cooling. Dilute to $500 \pm 2 \text{ ml}$ with water and mix well.

3.4 Sodium hydroxide, solution, $c(\text{NaOH}) = 2 \text{ mol/l}$.

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

3.5 Ascorbic acid, 100 g/l solution.

Dissolve 10 g of ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) in 100 ml water.

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.

3.6 Acid molybdate, solution I.

Dissolve 13 g ammonium heptamolybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ in 100 ml water. Dissolve 0,35 g anti-mony potassium tartrate hemihydrate $[\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}]$ in 100 ml water.

Add the molybdate solution to 300 ml of 9 mol/l sulfuric acid (3.1) with continuous stirring. Add the tartrate solution and mix well.

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

3.7 Acid molybdate, solution II.

Add 230 ml 9 mol/l sulfuric acid (3.1) to 70 ml water, cool, then add molybdate and tartrate solutions as in 3.6.

This reagent is used when samples are acidified with 1 ml of 4,5 mol/l sulfuric acid (3.2) per 100 ml (see sections three and four).

The reagent is stable for at least 2 months.

3.8 Turbidity-colour compensation solution.

Mix two parts by volume of 9 mol/l sulfuric acid (3.1) and one part by volume of ascorbic acid (3.5).

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

3.9 Sodium thiosulfate pentahydrate, 12,0 g/l solution.

Dissolve 1,20 g sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 100 ml water. Add about 50 mg anhydrous sodium carbonate (Na_2CO_3) as preservative.

This reagent is stable for several weeks if stored in an amber glass bottle.

3.10 Orthophosphate, stock standard solution corresponding to 50 mg of P per litre.

Dry a few grams of potassium dihydrogenphosphate to constant mass at 105°C . Dissolve 0,219 7 g KH_2PO_4 in about 800 ml water in a 1 000 ml volumetric flask. Add 10 ml of 4,5 mol/l sulfuric acid (3.2) and make up to the mark with water.

The solution is stable for at least 1 week if stored in a well-stoppered glass bottle. Refrigeration is recommended.

3.11 Orthophosphate, standard solution corresponding to 2 mg of P per litre.

Pipette 20 ml of orthophosphate stock standard solution (3.10) into a 500 ml volumetric flask. Make up to the mark with water.

Prepare this solution each day it is required.

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

4 Apparatus

Ordinary laboratory apparatus, and

4.1 Spectrometer, prism or grating type, or filter type, capable of accepting optical cells of thickness 10 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 is acceptable, absorbance can be measured at 700 nm.

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

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

NOTE ON THE PREPARATION OF GLASSWARE

Before use all glassware should be washed with hot 2 mol/l hydrochloric acid and rinsed thoroughly with water. Do not use detergents containing phosphate.

Preferably the glassware should be used only for the determination of phosphorus. After use it should be cleaned as above and kept covered until needed again.

Glassware used for the colour development stage should be rinsed occasionally with sodium hydroxide solution (3.4) to remove deposits of the coloured complex which has a tendency to stick as a thin film on the walls of glassware.

5 Sampling and samples

5.1 Sampling

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

5.2 Preparation of the test sample

Filter the laboratory sample (5.1) within 4 h after sampling. If the sample has been kept cool in the meantime, bring to room temperature before filtration.

Filter the sample through a membrane filter of pore size 0,45 µm (see notes 1 and 2) that has been washed free of phosphates by passing through it approximately 200 ml water warmed to 30 to 40 °C. Discard these washings. Reject the first 10 ml of sample filtrate and collect the remainder in a clean dry glass bottle for the immediate determination of orthophosphate as specified in clause 6.

If the filtrate is not within the range of pH 3 to 10, adjust it with sodium hydroxide solution (3.4) or 2 mol/l sulfuric acid (3.3).

NOTES

- 1 The filtration time should not exceed 10 min. If necessary, choose a larger diameter filter.
- 2 The membrane filter must be checked for phosphorus content. Membrane filters free from phosphorus are commercially available.

6 Procedure

6.1 Test portion

The maximum volume of test portion to be used is 40,0 ml. This is suitable for the determination of orthophosphate concentrations of up to $\rho_P = 0,8$ mg/l when using an optical cell of thickness 10 mm to measure the absorbance of the coloured complex formed by reaction with acid molybdate reagent. Smaller test portions may be used as appropriate in order to accommodate higher phosphate concentrations as shown in table 1. Phosphate concentrations at the lower end of the calibration ranges are best determined by measuring absorbance in an optical cell of thickness 40 or 50 mm.

Table 1

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

6.2 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.

6.3 Calibration

6.3.1 Preparation of the set of calibration solutions

Transfer, by means of a pipette, 1,0; 2,0; 3,0; 4,0; 5,0; 6,0; 7,0; 8,0; 9,0; and 10,0 ml of the orthophosphate standard solution (3.11) to a series of 50 ml volumetric flasks. Dilute with water to about 40 ml. Proceed accordingly for other ranges of phosphate concentration.

6.3.2 Colour development

Add to each flask, while swirling, 1 ml of ascorbic acid (3.5) followed by 2 ml of acid molybdate solution I (3.6). Make up to the mark with water and mix well.

6.3.3 Spectrometric measurements

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

6.3.4 Plotting the calibration graph

Plot a graph of absorbance against the phosphorus content, in milligrams per litre, of the calibration solutions. The relationship between absorbance and concentration is linear. Determine the reciprocal of the slope of the graph.