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Standard Test Methods for Phosphorus in Water[1]

This standard is issued under the fixed designation D 515; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope*

1.1 These test methods cover the determination of phosphorus in water and wastewater. The following two methods are included:

	Sections
Method A—Colorimetric Ascorbic Acid Reduction	8 to 16
Method B—Semiautomated Digestion/Colorimetric Ascorbic Acid Reduction	17 to 25

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific caution statement, see 19.1.

1.3 Former Test Methods B (Colorimetric Amino Reduction) and C (Colorimetric Molybdovanadophosphate) have been discontinued. Refer to Appendix X1 for historical information.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[2]
D 1129 Definitions of Terms Relating to Water[2]
D 1192 Specification for Equipment for Sampling Water and Steam[2]
D 1193 Specification for Reagent Water[2]
D 2777 Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water[2]
D 3370 Practices for Sampling Water[2]
E 60 Practice for Photometric Methods for Chemical Analysis of Metals[3]
E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[4]

3. Summary of Test Methods

3.1 Both test methods are based on reactions that are specific for the orthophosphate ion. With Test Method A the analytical scheme shown in Fig. 1 is used to measure various forms of phosphorus in the water sample. The separations into various forms are largely analytically defined, but the differentiations have been selected for interpretive purposes.

3.1.1 Separation into dissolved and total recoverable forms depends on filtration of the water sample through a 0.45-μm membrane filter. A reproducible, gross separation of dissolved from particulate forms of phosphorus is made with the uniform pore size membrane filter, but no claim can be made that separation is complete. The sample should be filtered as soon as possible after it is drawn if dissolved forms are to be measured, since the ratio of dissolved to particulate phosphorus may change when analysis is delayed. Total recoverable phosphorus includes all phosphorus forms when the unfiltered, shaken sample is heated in the presence of sulfuric acid and ammonium persulfate.

3.1.2 *Orthophosphate (A)*—Only orthophosphate and a negligible amount of hydrolyzable phosphorus is measured when the test is run on the undigested sample. An insignificant fraction of the hydrolyzable phosphorus may be converted to orthophosphate on addition of the acidic reagent during the test, particularly if completion of the test is delayed after the addition of acid.

3.1.3 *Hydrolyzable Phosphorus + Orthophosphate (B)*—By boiling the sample in the presence of acid such hydrolyzable phosphorus materials as meta-, pyro-, and tripolyphosphates are converted to orthophosphate. The measurement will include these forms of phosphorus plus the orthophosphate present in the unboiled sample and a reaction of a few organic phosphorus forms.

3.1.4 *Total Phosphorus (C)*—The acid-persulfate digestion of the sample converts all forms of phosphorus including organic forms to orthophosphate, and hence measures all forms except possibly certain heavy metallic phosphates present in sediments.

3.1.5 The following calculations can be made for specific phosphorus forms:

Organic phosphorus = $C - B$
Hydrolyzable phosphorus = $B - A$
Particulate phosphorus = (total recoverable phosphorus) − (total dissolved phosphorus)

3.2 Selection of the test method to use for a specific water depends primarily on its expected phosphorus content. All phosphorus forms are measured with the Colorimetric Ascorbic Acid Test Method. Lower concentrations are measured with the

[1] These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D 19.05 on Inorganic Constituents in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.
[3] *Annual Book of ASTM Standards*, Vol 03.05.
[4] *Annual Book of ASTM Standards*, Vol 14.01.

*** A Summary of Changes section appears at the end of these test methods.**

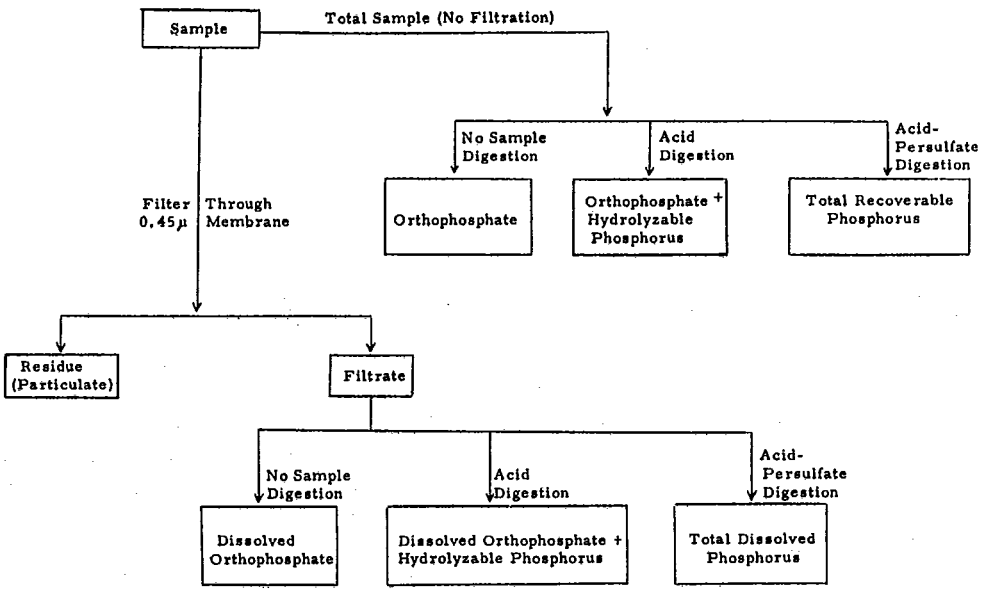

FIG. 1 Analytical Scheme for Differentiation of Phosphorus Forms—Test Method A

Absorbic Acid Reduction Test Method.

4. Significance and Use

4.1 Phosphorus is widely distributed in the environment as both inorganic and organically bound phosphates. Sources of phosphates include surface-applied fertilizers, cleaning and laundering products, boiler water conditioners, and drinking water treatment aids. Because phosphorus is a nutrient for photosynthetic organisms, it may be important to monitor and control discharge into the environment.

5. Terminology

5.1 *Definitions*—For definitions of terms used in these test methods, refer to Definitions D 1129.

6. Purity of Reagents

6.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II.

7. Sampling

7.1 Collect the sample in accordance with Practices D 3370, Practice D 1066, or Specification D 1192, as applicable.

7.2 When determining only dissolved phosphorus, filter the sample through a 0.45-μm membrane filter as soon as possible after sampling. Delay in the filtration may alter the relationship between the dissolved and particulate forms of phosphorus. Since membrane filters may contain significant amounts of phosphorus, they should be washed prior to use. Soak them in at least 1 L of water for a day or in three changes of water for 1 h each.

7.3 Analysis is best performed immediately after collecting the sample to minimize possible change. If analysis cannot be performed the same day the sample is collected, preserve the sample by adding 40 mg of mercuric chloride per litre of sample and refrigerating it at 4°C. To prevent precipitation of the mercury, previously add sufficient sodium chloride to the sample, if necessary, so that it will have a chloride content of at least 50 mg/L. No sample preservation is needed if only total recoverable phosphorus is to be determined. Sample storage in glass bottles is suggested.

7.4 Usually, the concentration of particulate phosphorus in a surface water is several times higher than the dissolved phosphorus. When samples are collected from rivers and lakes, the analytical values for total recoverable phosphorus may vary with depth, stream flow, and distance from shore. A grab sample should be taken in the middle of the stream and at mid-depth. A composite sample from top to bottom may be taken at mid-stream if proper equipment is available.

[5] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

TEST METHOD A—COLORIMETRIC ASCORBIC ACID REDUCTION

8. Scope

8.1 This test method[6,7,8,9,10] covers the determination of specified forms of phosphorus compounds in waters and in wastewaters. This test method is usable in the range from 0.01 to 0.5 mg/L of phosphorus. The range is for photometric measurements made at 880 nm in a 20 to 25-mm cell. Higher concentrations can also be determined by either taking a diluted sample or measuring the color at 625 to 650 nm.

9. Summary of Test Method

9.1 Ammonium molybdate and antimony potassium tartrate react with orthophosphate to form an antimony-phosphate-molybdate complex. The complex is reduced with ascorbic acid to form a deep-colored, blue molybdenum complex. The color intensity is proportional to the phosphorus concentration.

9.2 Although the test is specific to orthophosphate only, other phosphorus compounds can be converted to this reactive form by various sample pretreatments prescribed in this test method.

10. Interferences

10.1 As much as 50 mg/L of ferric iron, 10 mg/L of copper, and 10 mg/L of silica do not interfere in the test. Higher silica concentrations cause positive interferences over the range of the test, as follows: results are high by 0.005 mg/L of phosphorus for 20 mg/L of SiO_2, 0.015 mg/L of phosphorus for 50 mg/L, and 0.025 mg/L of phosphorus for 100 mg/L. Salt concentrations as high as 20 % cause an error of less than 1 %.

10.2 Arsenic is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. Interference from nitrite or sulfide can be eliminated by adding to the sample an excess of bromide water or a saturated potassium permanganate solution.

11. Apparatus

11.1 *Photometer*—A spectrophotometer suitable for measurements at 880 nm and capable of holding cells with a light path of 20 mm or more should be used. The color can also be measured at 625 to 650 nm with either a spectro- or filter photometer, but with about one-third loss in sensitivity. Filter photometers and photometric practices prescribed in this test method shall conform to Practice E 60, and spectrophotometers to Practice E 275.

11.2 *Acid-Washed Glassware*—All glassware used in the determinations should be washed with hot HCl (1+3) and rinsed with water. Commercial detergents should never be used to clean glassware.

12. Reagents

12.1 *Ammonium Persulfate*—Crystalline ammonium persulfate ($(NH_4)_2S_2O_8$).

12.2 *Combined Reagent*—Dissolve 0.50 g of ascorbic acid in 100 mL of solution mixture (see 12.2.1). The reagent is stable for a week if stored at 4°C; otherwise, prepare the solution fresh daily as needed.

12.2.1 *Solution Mixture*—Dissolve 0.13 g of antimony potassium tartrate [$K(SbO)C_4H_4O_6 \cdot ½\ H_2O$] in a 1-L volumetric flask containing about 700 mL of water. Add 5.6 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$] and shake flask until dissolved. Cautiously add 70 mL of concentrated sulfuric acid (sp gr 1.84) while swirling the contents of the flask. Cool the solution and dilute to the 1-L mark with water. The solution is stable for at least a year if stored in a polyethylene bottle away from heat.

12.3 *Phenolphthalein Indicator Solution* (5 g/L)—Dissolve 0.5 g of phenolphthalein in a mixture of 50 mL ethyl or isopropyl alcohol and 50 mL of water.

12.4 *Phosphorus, Standard Solution* (1.00 mL = 0.0025 mg P)—First prepare a stock solution (1.0 mL = 0.05 mg of phosphorus) by dissolving 0.2197 g of potassium dihydrogen phosphate (KH_2PO_4), that has been dried for 1 h in an oven at 105°C, in water and diluting the solution to exactly 1 L with water. Prepare the standard solution by diluting 50.0 mL of the stock solution to exactly 1 L with water. Each mL of the standard solution contains 0.0025 mg of phosphorus.

12.5 *Sodium Hydroxide Solution* (40 g/L)—Dissolve 20 g of sodium hydroxide (NaOH) in about 400 mL of water. Cool the solution to room temperature and dilute to 500 mL with water.

12.6 *Sulfuric Acid* (31+69)—Slowly add 310 mL of concentrated H_2SO_4 (sp gr 1.84) to about 600 mL of water. Cool the solution and dilute to 1 L with water.

13. Calibration

13.1 Pipet 0, 1, 2, 4, 7, and 10 mL of standard phosphorus solution into a series of 125-mL Erlenmeyer flasks and dilute each to 50.0 mL with water to prepare standards containing 0, 0.05, 0.1, 0.2, 0.35, and 0.5 mg/L of phosphorus.

13.2 Add 10 mL of combined reagent to each standard and swirl each flask to mix.

13.3 After a minimum of 10 min, but no longer than 30 min, measure the color absorbance of each solution at 880 nm in a 20 to 25-mm cell with a spectrophotometer, using the zero standard as reference solution for the initial instrument setting at zero absorbance.

13.4 Plot milligrams per litre (parts per million) of phosphorus on the abscissa and absorbance on the ordinate of linear graph paper. A straight line should be obtained passing through the point of origin.

NOTE 1—A separate calibration curve must be made for each photometer. Each curve must be checked periodically to ensure reproducibility.

[6] Murphy, J., and Riley, J. P., "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters," *Analytica Chimica Acta*, Vol 27, 1962, pp. 31–36.

[7] Gales, M. E., Jr., Julain, E. G., and Kroner, R. C., "Method for Quantitative Determination of Total Phosphorus in Water," *Journal of the American Water Works Assn.*, Vol 58, No. 10, 1966, p. 1363.

[8] Fishman, M. J., and Skougstad, M. W., *Rapid Field and Laboratory Determination of Phosphate in Natural Water*, U. S. Geol. Survey, Prof. Paper 525-B, 1965, p. B 167.

[9] *FWPCA Methods for Chemical Analysis of Water and Waste*, 1971, Environmental Protection Agency, Cincinnati, Ohio.

[10] Jenkins, D., "The Differentiation, Analysis, and Preservation of Nitrogen and Phosphorus in Natural Water," *Advances in Chemistry Series 73*, 1967, p. 265–280.

14. Procedure

14.1 *Orthophosphate:*

14.1.1 Pipet a volume of sample no greater than 50 mL, estimated to contain less than 0.25 mg of orthophosphate phosphorus, into a 125-mL Erlenmeyer flask (See Note 2). Dilute the sample to 50 mL with water, if necessary.

NOTE 2—Frequently, when the sample contains such ions as ferric iron and aluminum, some of the phosphorus compounds may be lost in adherent hydroxide films on the walls of the sample container if analysis is not carried out soon after sampling. If these films are suspected, add sufficient H_2SO_4 (31+69) solution (see 12.6) to the water in the sample container *just prior* to analysis to drop the pH to about 2 to dissolve the film and avoid the possible loss of phosphorus. Shake the sample well for mixing. Neutralize the portion of sample taken for analysis by dropwise addition of NaOH solution in the presence of phenolphthalein. Discharge the pink color with H_2SO_4 (31+69) in accordance with 14.1.2. Correct for sample dilution in the calculations if significant volumes of H_2SO_4 and NaOH solution are used.

14.1.2 Add a drop of phenolphthalein indicator solution. If a red color develops, add H_2SO_4 (31+69) (see 12.6) dropwise to just discharge the color.

14.1.3 Add 10 mL of combined reagent to the sample and mix thoroughly by swirling the flask.

NOTE 3—Color may develop slowly and incompletely if the temperature of the test solution at this point is less than 20°C. The temperature, however, may be as high as 50°C without affecting the results.

14.1.4 After a minimum of 10 min, but no longer than 30 min, measure the absorbance of the blue color at 880 nm with a photometer, using a reagent blank as the reference solution. The reagent blank is 50 mL of water treated similarly to the sample in the procedure.

14.1.5 Determine the milligrams per litre of phosphorus by referring absorbance value to the reference curve.

14.2 *Hydrolyzable Phosphorus (Polyphosphate) + Orthophosphate:*

14.2.1 Pipet a volume of sample, estimated to contain no more than 25 µg of hydrolyzable phosphorus plus orthophosphate phosphorus, into a 125-mL Erlenmeyer flask (see Note 2).

14.2.2 Add 1 mL of H_2SO_4 (31+69) and a few boiling beads to the sample and boil gently on a hot plate for at least 30 min. Add water to the sample during the boiling step to maintain a volume between 10 to 50 mL. Permit the volume to decrease to 10 mL at the end of the boiling step, but do not allow the sample to go to dryness or to dense, white sulfur trioxide fumes. Alternatively, carry out the complete digestion step in an autoclave for 30 min at 121°C, 103 to 138 kPa (15 to 20 psi).

14.2.3 Add a drop of phenolphthalein indicator solution to the cooled sample and adjust it to a faint pink by the addition of NaOH solution. A volume of 11.2 mL is usually required. Bring it back to colorless with a drop of H_2SO_4 (31+69).

14.2.4 Cool the sample to a temperature of about 30°C, quantitatively transfer the sample to a 50-mL volumetric flask, and dilute it to exact volume with water. Continue in accordance with 14.1.3 to 14.1.5.

14.3 *Total Phosphorus:*

14.3.1 Analyze the sample in accordance with 14.2, but add 0.4 g of ammonium persulfate to the sample in 14.2.1.

15. Calculation

15.1 Calculate the concentration of the various forms of phosphorus in milligrams per litre (parts per million) of phosphorus by applying Eq 1 for the orthophosphate determined in 14.1, 14.2, and 14.3:

$$\text{Orthophosphate, mg/L of phosphorus} = (A \times 50)/B \quad (1)$$

where:

A = phosphorus indicated by the calibration curve, mg/L, and

B = sample analyzed mL.

Hydrolyzable phosphorus = (hydrolyzable phosphorus + orthophosphate phosphorus) − (orthophosphate phosphorus)

Organic phosphorus = (total recoverable phosphorus) − (hydrolyzable phosphorus + orthophosphate phosphorus)

Particulate phosphorus = (total recoverable phosphorus) − (total dissolved phosphorus)

16. Precision and Bias[11]

16.1 The precision of this test method within the designated range varies with the determined concentration as shown in Table 1.

16.2 This data may not apply to waters of untested matrices.

TABLE 1 Precision of Ascorbic Acid Reduction Method

Orthophosphate Phosphorus		Total Phosphorus	
$\bar{X}^A$ mg of phosphorus/litre	S_T^B	$\bar{X}^A$, mg of phosphorus/litre	S_T^B
0.027	0.010	0.121	0.033
0.036	0.008	0.155	0.051
0.374	0.023	0.890	0.129
0.326	0.018	0.813	0.130

[A] $\bar{X}$ = average concentration of phosphorus, mg/L.

[B] S_T = overall percision, mg/L of phosphorus.

TEST METHOD B—SEMIAUTOMATED DIGESTION/COLORIMETRIC ASCORBIC ACID REDUCTION

17. Scope

17.1 This test method covers the determination of total phosphorus in water and wastewater.

17.2 This test method is a semiautomated procedure applicable to drinking water, surface water, domestic and industrial wastes in the range from 0.1 to 5.0 mg/L P.

17.3 This test method has been used successfully with reagent water, natural surface water, lake water, estuary water, and a nonspecified wastewater. The information on bias and accuracy may not apply to other waters.

18. Summary of Test Method

18.1 This test method consists of digesting the sample in a block digestor in the presence of sulfuric acid, potassium sulfate, and mercuric sulfate at approximately 200°C for 1 h and then at 380°C for 1½ h. (The block digestor is an electrically heated-metal block designed to hold 40 reaction tubes). During the digestion, organic phosphorus is converted to orthophosphate. After digestion, the residue is

[11] Supporting data for this test method has been filed at ASTM Headquarters. Request RR:D-19-144.