



Designation: D 6501 – 99

An American National Standard

Standard Test Method for Phosphonate in Brines¹

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1. Scope

1.1 This test method covers the colorimetric determination of phosphonate (PNA) in brines from gas and oil production operations in the range from 0.1 to 5 mg/L.

1.2 This phosphonate method is intended for use to analyze low concentration of phosphonate in brine containing interfering elements. This test method is most useful for analyzing phosphonate at 0.1 to 1 mg/L range in brines with interfering elements; however, it requires personnel with good analytical skill.

1.3 This test method has been used successfully with reagent water and both field and synthetic brine. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 *This standard does not purport to address all of the safety concerns, if any, 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 specific hazard statements, see 9.1.3.

2. Referenced Documents

2.1 ASTM Standards:

- D 1129 Terminology Relating to Water²
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits²
- D 1193 Specification for Reagent Water²
- D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water²
- D 3370 Practices for Sampling Water from Closed Conduits²
- D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water²
- D 4375 Terminology for Basic Statistics in Committee D-19 on Water²
- D 5810 Guide for Spiking into Aqueous Samples²
- D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis³

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 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 11.02.

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers⁴

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *phosphonate, n*—a group of organophosphorus compounds typically used for mineral scale and corrosion control, as cleaning agents, dispersants, and chelants. Typical phosphonate compounds include, but are not limited to, the following phosphonic acid and their neutralized salts: Aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetra (methylenephosphonic acid), hexamethylenediaminetetra (methylenephosphonic acid), and diethylenetriaminepenta (methylenephosphonic acid).

4. Summary of Test Method

4.1 Phosphonate materials are converted to orthophosphate by potassium persulfate digestion. The orthophosphate is then reacted with ammonium molybdate to form a phosphomolybdate complex. The complex is extracted with a methyl isobutyl ketone/cyclohexane mixture and measured colorimetrically.

5. Significance and Use

5.1 This test method is useful for the determination of trace level phosphonate residues in brines. Chemical treatment which contain phosphonates are used as mineral scale and corrosion inhibitors in gas and oil drilling and production operations; and other industrial applications. Often, the decision for treatment is based on the ability to measure low phosphonate concentration and not upon performance criteria. Phosphonate concentrations as low as 0.16 mg/L have been shown effective in carbonate scale treatment. This test method enables the measurement of sub-mg/L phosphonate concentration in brines containing interfering elements.

5.2 The procedure includes measuring total (see 12.3.8) and free orthophosphate (see 12.4.3) ions and the difference in concentration is the phosphonate concentration. The sample could contain orthophosphate naturally, or from decomposition

⁴ Annual Book of ASTM Standards, Vol 03.06.



of the phosphonate during processing or well treatment or from treating compounds containing molecular dehydrated phosphates.

6. Interferences

6.1 Sulfide interferes in this test method, but techniques described in the procedure (see 9.1.2) eliminate this interference. Concentrations less than 1000 mg/L copper (Cu^{+2}) and silica ($\text{SiO}_2/\text{SiO}_3^{-2}/\text{Si}^{+4}$); and less than 200 mg/L of iron ($\text{Fe}^{+2}/\text{Fe}^{+3}$) can be tolerated.

6.2 Produced brines can contain high concentrations of dissolved solids. Some of these dissolved solids tend to precipitate when produced brines reach new equilibria at atmospheric temperature and pressure. Phosphonate will coprecipitate or adsorb onto these newly formed solids and become unavailable for analysis. This problem can be minimized by acidifying the brine sample on-site with hydrochloric acid to pH below 2.

6.3 Glassware must be cleaned with phosphate free detergent and rinsed with 0.1 N hydrochloric acid to remove all residual phosphate or phosphonate.

6.4 The standard addition method in 12.6 is recommended for brine with high matrix interference.

7. Apparatus

7.1 *Pressure Cooker or Sterilizer (Autoclave)*⁵.

7.2 *Spectrophotometer*⁶, for measurement above 650 nm with 4-cm light path cells. A longer light path will yield a corresponding higher sensitivity (see 12.5.1). Spectrophotometer practices prescribed in this test method shall conform to Practice E 275.

7.3 *Bottle Top Liquid Dispenser*⁷, 20-mL capacity, <1 % accuracy, and <0.1 % precision.

7.4 *Pipetter*, automated⁸, 10-mL capacity with 0.2 to 0.5 % accuracy.

7.5 *Glass Bottles*⁹, 60 mL and 240 mL with Teflon[®]¹⁰ lined screw cap closure.

8. Reagents and Materials

8.1 *Purity of Reagents*—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 Society¹¹.

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.

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

8.3 *Alcoholic Sulfuric Acid Solution*—Cautiously add 20 mL concentrated H_2SO_4 (sp. gr. 1.89) to 900 mL methyl alcohol and dilute to 1 L with methyl alcohol. It is recommended to dispense the liquid with a bottle top liquid dispenser, which dispenses a 10-mL volume.

8.4 *Ammonium Molybdate Solution*—Dissolve 39.1 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 200 mL water. Cautiously add 210 mL concentrated HCl (sp. gr. 1.19) to 400 mL water. Cool, add molybdate solution, and dilute to 1 L. It is recommended to dispense the liquid with a liquid dispenser, which dispenses a 10-mL volume.

8.5 *Glycerol*—Reagent grade, 99 % or greater.

8.6 *Hydrochloric Acid (6N)*—Add 500 mL of concentrated HCl (sp. gr. 1.19) to 500 mL of water.

8.7 *Methyl Alcohol*—Reagent grade, 99 % or greater.

8.8 *Methyl Isobutyl Ketone/Cyclohexane Solvent*—Mix equal volumes of methyl isobutyl ketone (MIBK) and cyclohexane.

NOTE 1—**Warning:** This solvent is highly flammable.

It is recommended to dispense the liquid with a bottle top liquid dispenser, which dispenses a 20-mL volume.

8.9 *Phosphate Solution*, standard (1.00 mL = 0.05 mg PO_4). Dissolve 71.6 mg anhydrous KH_2PO_4 in water and dilute to 1 L.

8.10 *Phosphonate Solution*, (50-mg/L phosphonate)—If the standard addition procedure (see 12.6) is to be used, a stock solution of 50 mg/L, as phosphonate, should be prepared. To prepare this solution, a concentrated sample of the phosphonate to be measured along with the wt/wt percent phosphonate concentration must be obtained from the manufacturer. The wt/wt percent phosphonate concentration also can be calibrated by this procedure as described in 12.2 and 12.3.

8.11 *Potassium Persulfate*, $\text{K}_2\text{S}_2\text{O}_8$.

8.12 *Sodium Chloride Solution (1.0 M, Synthetic Brine)*—Dissolve 58.44 g. NaCl in 800 mL water and dilute to 1 L. This solution is used as a synthetic brine.

8.13 *Sodium Hypochlorite*, (5.65–6 %).

8.14 *Stannous Chloride Solution*—Mix 0.4 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 mL glycerol. This reagent is stable for at least six months. The solution is stored in a dropper bottle.

9. Hazards

9.1 Precautions:

⁵ Fisher Scientific No. 14-141-S has been satisfactory for this purpose, or equivalent, should be used.

⁶ Varian DMS-100 has been satisfactory for this purpose, or equivalent, should be used.

⁷ Fisher Scientific No. 13-687-21 REPIPET has been satisfactory for this purpose, or equivalent, should be used.

⁸ Fisher Scientific No. 21-279-25 Eppendorf Maxipipetter has been satisfactory for this purpose.

⁹ Fisher Scientific No. 03-326-3C and 03-326-3G have been satisfactory for this purpose.

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¹¹ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of Reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.





9.1.1 Most phosphonate inhibitors are strongly adsorbed to glass or metal; therefore, polyethylene beakers, flasks, pipets, etc., should be used to contain and transfer brine solutions from the field.

9.1.2 A glass bottle is recommended for use in the color development steps (see 12.2 and 12.3) for better visualization of the reaction. Since the reaction media is acidic, phosphonate will not adsorb to the glass surface.

9.1.3 Personnel performing this test must be familiar with all precautions for handling strong sulfuric acid, hydrochloric acid and sulfide-containing brine. Personnel should consult the material safety data sheet for handling strong acids. Protective clothing and latex gloves should be worn. The sulfide brine should be handled in the hood with good ventilation. Sulfide containing brine can be treated with sodium hypochlorite prior to analysis to oxidize the hydrogen sulfide.

10. Sampling

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

10.2 Preserve the samples immediately at the time of collection by adding 4 mL of 6 N hydrochloric acid per 100-mL brine.

11. Calibration and Standardization

11.1 Prepare standards by adding 2.0, 4.0, 6.0, 8.0, 10.0 mL each of phosphate standard solution (1.00 mL = 0.05 mg PO_4) to separate 100-mL volumetric flasks. Dilute to 100 mL with 1 M sodium chloride solution. These solutions will contain 1.0, 2.0, 3.0, 4.0, 5.0 mg/L phosphate as PO_4 . If the procedure in 12.5 is used for samples with low phosphonate concentrations, then solutions containing 0.2, 0.4, 0.6, 0.8, 1.0 mg/L phosphate as PO_4 should be used.

11.2 Follow the procedure in 12.2 and 12.3 to develop color, and determine the absorbance at 725 nm.

11.3 Prepare a calibration curve showing phosphate ion concentration in mg/L on the X axis with the corresponding absorbance (A) reading of the spectrophotometer on the Y axis of linear graph paper.

12. Procedure

12.1 The procedures in 12.2 and 12.3 are applicable to samples containing 0.5 to 5 mg/L phosphonate. For samples containing less than 0.5 mg/L phosphonate, a larger sample volume or a different light path cell can be used (see 12.5).

12.2 Persulfate Digestion Procedure:

12.2.1 Pipet 20 mL of the following samples (a, b, c) into separate 60-mL glass bottles, each containing 200 mg of potassium persulfate. Multiple samples can be digested at the same time.

12.2.1.1 Blank, 1-M sodium chloride (see 8.12).

12.2.1.2 Phosphate standards (see 11.1).

12.2.1.3 Samples of acidified brine.

12.2.2 Close the sample bottles loosely with Teflon[®]-lined caps.

12.2.3 Heat the samples for 30 minutes in a pressure cooker or sterilizer at 100–120°C (15–20 psig).

12.2.4 Make sure the samples are cooled to room temperature before proceeding to color development. The temperature

of solution is critical in procedure 12.2.3. At this point in the procedure, all of the phosphonate has been oxidized to phosphate.

12.3 Color development and extraction procedure:

12.3.1 The timings specified in procedures 12.3.3, 12.3.4, and 12.3.7 are critical to the test. It is recommended to run small numbers of samples at a time in order to manage the timing.

12.3.2 Standard addition method (see 12.6) should be used for data quality control.

12.3.3 Add 20 mL MIBK/Cyclohexane solvent and 10 mL ammonium molybdate solution to the sample bottles, and immediately, vigorously shake each bottle for 15 s. At this point, the clear, and electrically-neutral phosphomolybdate complex has been formed and extracted into the organic solvent phase.

12.3.4 Wait exactly five minutes to allow the aqueous and organic solvent phases to be separated, and withdraw 10.0 mL of liquid from the organic solvent layer into a clean 60-mL glass bottle using an automatic pipetter. Care should be taken not to disturb the solvent/water interface or accidentally withdraw some aqueous solution, since the excess molybdenum in the aqueous phase can also be reduced by stannous chloride to form a deep blue color.

12.3.5 Add 10 mL alcoholic H_2SO_4 solution to the samples, and swirl to mix.

12.3.6 Add four drops stannous chloride solution to each sample, and mix thoroughly.

12.3.7 After 10 minutes, but before 20 minutes, pour each sample into a 4-cm cell and read the absorbance against the blank at 725 nm. Absorbance readings also can be taken at 650 or 700 nm, but with reduced sensitivity. Use the sample blank as reference solution in measuring the sample.

12.3.8 Read the total phosphate concentration ($C_{T-\text{PO}_4}$) from a calibration curve prepared by analyzing known phosphate standards, as described in Section 11.

12.4 Procedure for Analyzing Orthophosphate Concentration in the Brine:

12.4.1 Pipet 20 mL of the acidified brine sample to a separate 60-mL glass bottle.

12.4.2 Follow the procedure in 12.3.3-12.3.7 to develop phosphomolybdate complex and to extract the complex to the organic liquid phase.

12.4.3 Read the orthophosphate concentration ($C_{F-\text{PO}_4}$) from a calibration curve prepared in Section 11.

12.5 Procedure for brines containing phosphonate concentrations outside the range(s) specified.

12.5.1 The above concentration range is specified for using a 4-cm light path cell. Longer light path cells are suitable for analyzing phosphonate at low concentrations (see the following):

Approximate Phosphonate Range (mg/L)	Light Path (cm)
0.1–2.0	10

12.5.2 Alternatively, the sample size can be adjusted to analyze brines containing low phosphonate concentration other than that specified in 12.1. An example of 100-mL sample size is given below.





12.5.2.1 Pipet 100 mL instead of 20 mL into a 240-mL bottle. The organic solvent phase in the 240-mL bottle will be a thin layer. Care should be taken not to disturb the solvent/water interface or accidentally withdraw aqueous solution when removing the phosphomolybdate complex from the organic solvent phase.

12.5.2.2 Add 1 g potassium persulfate to the sample bottle.

12.5.2.3 Follow 12.2.2-12.3.8 to analyze for phosphate ion.

12.6 Standard Additions Procedure:

12.6.1 This procedure is recommended to determine the concentration of phosphonate in brine containing interfering components.

12.6.2 Prepare a blank and three samples, as in 12.2.1. Add 100 µL of 50 mg/L phosphonate standard solution to one of the sample bottles. Add 200 µL of 50 mg/L phosphonate Standard solution to a second sample bottle.

12.6.3 Complete the procedures in 12.2.2-12.3.7 to digest phosphonate and to analyze for phosphate ion concentration.

12.6.4 Plot the absorbance versus concentration of added phosphonate. Draw a straight line through these three data points. Extend this line to intersect the X axis at a negative value of phosphonate concentration. The absolute value of this intersection is the concentration of phosphonate in the sample of interest.

13. Calculation

13.1 Calculate the phosphonate concentration in the sample (as mg/L PO_4) as follows:

$$\text{mg/L } PO_4 = [(C_T - PO_4) - (C_F - PO_4)] \left[\frac{\text{Volume of Standard}}{\text{Volume of Sample}} \right] (\text{Field Dilution}) \quad (1)$$

where:

C_{T-PO_4} = Concentration of total phosphate (mg/L) read from calibration curve (see 12.3.8);

C_{F-PO_4} = Concentration of orthophosphate (mg/L) read from calibration curve (see 12.4.3);

Volume of Standard = Volume (mL) of standard used (see 12.2.1); and,

Volume of Sample = Volume (mL) of sample used (see 12.2.1, 12.5.2.1).

13.1.1 See 10.2 and as follows:

$$\text{Field Dilution} = \left(\frac{\text{Field Sample Volume(mL)} + \text{Acid Volume(mL)}}{\text{Field Sample Volume(mL)}} \right) \quad (2)$$

13.2 Use the following conversion factor to convert the mg/L PO_4 in Eq 2, to phosphonate:

$$\text{mg/L Phosphonate} = \frac{\text{mg/L } PO_4}{95 \text{ g/mol}} \times \frac{\text{Molecular Wt. of Phosphonate}}{\text{No. of phosphorus atoms phosphonate}} \quad (3)$$

13.2.1 For example, see Table 1.

14. Report

14.1 Report mg/L as phosphonate.

14.2 Report to one significant figure.

TABLE 1

Common Names ^A	Formula	Molecular Weight (g/mol)	No. of P-atoms/mole
ATMP, Dequest 2000®	(H ₂ O ₃ PCH ₂) ₃ N	299 g/mol	3
DTPMP, Dequest 2060®	{(H ₂ O ₃ PCH ₂) ₂ NCH ₂ CH ₂)} ₂ N-	573 g/mol	5
HEPP, Dequest 2110®	(H ₂ OO ₃ P) ₂ CCH ₃ OH	206 g/mol	2

^ADequest® is a registered trade name of the Monsanto Company, St. Louis, MO 63167.

15. Quality Control

15.1 The concentration specified in the following quality control is for the procedure in 12.1-12.4. If low range procedure is used (see 12.5), reduce the specified concentration by a factor of 3.3.

15.2 In order to be certain that analytical values obtained from using this test method are valid and accurate within the confidence limits of the test, the following quality control procedures must be followed when performing the test:

15.2.1 Analyst Performance Check:

15.2.1.1 If the analyst has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate the laboratory capability. Analyze seven replicates of a standard solution, Initial Demonstration of Performance (IDP) solution, prepared from a reference material (the matrix and chemistry of the solution should be equivalent to the solutions used in the collaborative study) containing 2 mg/L of phosphonate (PNA) for the procedure described in 12.1-12.4. If the low-range procedure, described in 12.5, is used, the reference material should contain 0.6 mg/L PNA. Each replicate must be taken through the complete analytical test method including any sample preservation steps. Calculate the mean and standard deviation of these values as described in Terminology D 4375. The criteria for evaluating the mean of seven replicates is listed as follows:

Phosphonate, mg/L	Mean(interval), mg/L
2.0	1.2 to 2.3
0.6	0.3 to 0.6

The mean and standard deviation of the seven values should be calculated and compared, according to Practice D 5847, to the single operator precision established for this test method, as detailed below:

Analyte	IDP Solution Concentration	Method S_o	Acceptable IDP Precision, $n = 7$
Phosphonate	2 mg/L	0.0735	≤ 0.15 mg/L
Phosphonate	0.6 mg/L	0.01472 mg/L	≤ 0.07 mg/L

15.3 Calibration Verification:

15.3.1 When using this test method, an Instrumentation Verification Standard (IVS) should be used to verify the calibration standard and acceptable instrument performance. Analyze at least duplicate IVS containing 2 mg/L PNA prior to the analysis of samples to check the instrument. If low range procedure is used, see 12.5, then at least duplicate IVS should contain 0.6 mg/L PNA. If the determined IVS concentrations are not within ±15 % of known values, the analyst should