



Designation: E 1917 – 97

Standard Test Method for Determination of Phosphorus in Nickel, Ferronickel, and Nickel Alloys by Phosphovanadomolybdate Molecular Absorption Spectrometric Method¹

This standard is issued under the fixed designation E 1917; 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.

1. Scope

1.1 This test method covers the determination of phosphorus in nickel, ferronickel, and nickel alloys in the 0.0007 % through 0.05 % range.

1.2 Arsenic, chromium, hafnium, niobium, silicon, tantalum, titanium, and tungsten interfere, but the interference can be avoided by complexation or volatilization (for Cr). The lowest phosphorus content (0.0007 %) can be reached only in samples with low contents of interfering elements.

1.3 *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 hazards associated with the use of this practice see Practices E 50. Refer to specific warning notes given throughout this test method.

2. Referenced Documents

2.1 ASTM Standards:

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals²

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory³

E 1452 Practice for Preparation of Calibration Solutions for Spectrophotometric and for Spectroscopic Atomic Analysis³

E 1601 Practice for Conducting Interlaboratory Study to Evaluate the Performance of an Analytical Method³

2.2 ISO Standards:

ISO 5725:1986 Precision of Test Methods—Determination of Repeatability and Reproducibility for a Standard Test Method by Inter-laboratory Tests⁴

ISO 11400:1992(E) Nickel, Ferronickel and Nickel Alloys—Determination of Phosphorus Content—Phosphovanadomolybdate Molecular Absorption Spectrometric Method⁴

3. Summary of Test Method

3.1 The sample is dissolved in a mixture of hydrochloric acid and nitric acid. The solution is evaporated to perchloric acid fumes and chromium is removed as volatile chromyl chloride. Silicon and refractory elements are complexed with fluoride ions. The phosphorus is converted to phosphovanadomolybdic acid in a perchloric and nitric acid solution. The phosphovanadomolybdic acid is extracted with 2-methyl-2-pentanone in the presence of citric acid to complex arsenic. Absorbance is measured at 355 nm.

4. Significance and Use

4.1 This test method is used for the analysis of nickel, ferronickel, and nickel base alloy samples by molecular absorption spectrometry to check compliance with compositional specifications. It is assumed that all who use the procedure will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory and that proper waste disposal procedures will be followed. Appropriate quality control practices must be followed, such as those described in Guide E 882.

5. Apparatus

5.1 *Spectrophotometer*—Capable of measuring absorbance at a wavelength of 355 nm.

5.2 *Cells*—To fit spectrophotometer, having an optical path of 1 cm.

NOTE 1—Cells having other dimensions can be used, provided suitable adjustments can be made in the amount of sample and reagents used.

6. Reagents

6.1 *Purity and Concentration of Reagents*—The purity and concentration of common chemical reagents shall conform to Practices E 50. The reagents should be free of or contain only

¹ This practice is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry of Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.08 on Nickel, Cobalt and High Temperature Alloys.

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² *Annual Book of ASTM Standards*, Vol 03.05.

³ *Annual Book of ASTM Standards*, Vol 03.06.

⁴ Available from American National Standards Institute, 11 West 42nd Street, New York, NY 10036.

minimal amounts (<0.1 µg/g) of phosphorus. Calibration solutions shall be prepared in accordance with Practice E 1452.

6.1.1 Verify the absence of phosphorus in the reagents using the blank test (9.6.1). Reagents giving high blank values are unsuitable and should not be used. The blank value for all reagents should be below 0.0005 % *P* calculated for a 1 g sample.

6.2 *Ammonium Metavanadate Solution*—Dissolve 2.5 g of ammonium metavanadate (NH₄VO₃) in water and dilute to 1 L.

6.3 *Citric Acid Solution*—Dissolve 500 g citric acid monohydrate (C₆H₈O₇·H₂O) in water and dilute to 1 L.

6.4 *Fluoroboric Acid Solution*—Disperse 75 g of boric acid (H₃BO₃) in 600 mL of hot water in a plastic beaker. Add 50 mL HF (40 %) and dilute to 1 L. Digest over medium heat until the boric acid is dissolved. Store in plastic bottle. The solution should be gently heated if the boric acid forms crystals.

NOTE 2—Warning: HF and fluoroboric acid are extremely irritating and corrosive to skin and mucous membranes, producing severe skin burns that are slow to heal. In case of contact with skin, wash well with water and seek medical advice. When using HF and fluoroboric acid, always wear appropriate safety gear, such as goggles and gloves.

6.5 *Hexaammonium Heptamolybdate Solution*—Dissolve 15 g of hexaammonium heptamolybdate tetrahydrate [(NH₄)₆Mo₇O₂₄·4H₂O] in warm water and dilute to 100 mL. Prepare fresh solution each day. If high and unstable blank values appear, there might be a problem with the salt used. In such a case, switch to another lot.

6.6 *4-methyl-2-pentanone*—methylisobutyl ketone.

6.7 *Phosphorus Stock Calibration Solution (1.000 g/L)*—Transfer 4.3942 g of potassium dihydrogenorthophosphate (KH₂PO₄) (which has been previously dried at 110°C to constant weight and cooled in a desiccator) to a 1 L volumetric flask. Dissolve in water, dilute to the mark and mix.

6.8 *Phosphorus Calibration Solution (10 mg/L)*—Transfer 10.0 mL of the phosphorus stock calibration solution to a 1 L volumetric flask. Dilute to the mark with water and mix.

6.9 *Sodium Nitrite Solution (50 g/L)*—Dissolve 50 g of sodium nitrite (NaNO₂) in water and dilute to 1 L.

7. Interlaboratory Studies (ILS)

7.1 This test method was evaluated by a subcommittee within ISO Technical Committee 155 (ISO/TC 155/SC 4) on analysis of nickel alloys, in accordance with ISO Standard 5725. It was published as ISO Standard 11400. ILS test data were not available for recalculation.

8. Sampling and Sample Preparation

8.1 The sampling shall be carried out by normal procedures agreed upon between the parties, or in the event of a dispute, in accordance with the relevant standard, if one is available.

8.2 The laboratory sample is normally in the form of millings or drillings and no further preparation of the sample is necessary.

8.3 If it is suspected that the laboratory sample is contaminated with oil or grease from the milling or drilling operation, it shall be cleaned by washing it with high purity acetone and dried in air.

8.4 If the sample contains particles or pieces of widely varying sizes, the test sample should be obtained by riffing.

9. Procedure

9.1 Test Portion and Preparation of Test Solution:

9.1.1 Weigh to the nearest 0.1 mg a test portion of the sample in accordance with Table 1.

9.1.2 Transfer the test portion to a polytetrafluoroethylene (PTFE) beaker and add 5 mL of HNO₃ and then 5 mL of HCl. For samples with high contents of Nb, Si, Ta, or Hf, also add 7 mL of HF. Cover the beaker with a PTFE cover and heat gently until the reaction ceases. Use a sandbath or other means to avoid direct contact of the PTFE beaker with a metal hotplate surface. Add 10 mL of HClO₄ and, leaving a small opening to release the vapors, evaporate to dense HClO₄ fumes.

NOTE 3—Nickel and some copper bearing nickel alloys, such as monel, will dissolve more readily in HNO₃ (1+1).

NOTE 4—Warning: Fuming HClO₄ is a powerful oxidant and can cause explosions when in contact with organic materials. All evaporations must be carried out in the presence of HNO₃ and in a fume hood suitable for use with HClO₄.

9.1.3 For samples containing less than 0.1 % chromium, omit the next step and proceed directly to 9.3.

9.2 Removal of Chromium:

9.2.1 Continue fuming for 3 min. Cautiously begin adding HCl drop by drop to the fuming solution in the partly covered beaker until colored fumes are no longer liberated. Then resume fuming to re-oxidize the remaining chromium. Repeat the treatment until no brown fumes appear when the HCl is added. Cool to room temperature.

9.3 Complexation:

9.3.1 Add 25 mL HNO₃ (1+4) and 4 mL HF to the solution and heat for 8 to 10 minutes until the precipitate is dissolved.

NOTE 5—It is important that the precipitated refractory oxides dissolve completely. If this does not happen, add another 2 mL HF and repeat the boiling. If the precipitate still remains undissolved, a new test sample of a smaller weight must be taken for the analysis.

9.3.2 Add 10 mL of sodium nitrite solution and boil the solution for 10 minutes to reduce the residual dichromate and expel all nitrous fumes. Cautiously wash the beaker walls a few times with water during boiling.

9.3.3 Add 40 mL of fluoroboric acid solution and rapidly cool the solution to between 20 and 30°C, and proceed immediately with the color development.

NOTE 6—The oxides might precipitate again if it required more than 10 min to cool the solution.

9.4 Color Development and Extraction:

9.4.1 Add 10 mL of the ammonium metavanadate solution and 15 mL of the hexaammonium heptamolybdate solution to the cooled clear solution. Allow to stand at a temperature between 18 and 25°C for a minimum of 7 min, but not longer than 15 min.

TABLE 1 Weight of Test Portion of the Sample

Expected Phosphorus Content, %	Weight of Test Portion, g	Maximum concentration of the interfering elements, %					
		As	Hf	Nb	Ta	Ti	W
0.0005 to 0.010	1.0	0.05	0.1	1	0.1	2	2
0.002 to 0.04	0.25	0.2	0.5	5	0.5	10	8
0.005 to 0.050	0.10	0.5	1.5	10	1	25	25

9.4.2 Transfer the solution to a 250 mL separatory funnel that has been marked at the 100 mL level and, if necessary, make up to the mark with water. Add 10 mL of citric acid solution and immediately follow with 40 mL of 4-methyl-2-pentanone. Shake the funnel for 30 s. Allow the two layers to separate and discard the lower (aqueous) phase. Dry the inside of the stem of the separatory funnel with a small piece of filter paper. Filter the organic layer through a dry filter paper into a small dry beaker. Proceed immediately with the spectrometric measurement.

9.5 Spectrometric Measurement:

9.5.1 Ensure that the temperature of the solutions is constant to $\pm 1^\circ\text{C}$. Measure the absorbance of the solution with a spectrophotometer at a wavelength of 355 nm. Use 4-methyl-2-pentanone as the reference and cells with a 1 cm optical path length.

9.6 Blank Test:

9.6.1 Carry out a blank test in parallel with the determination following the same procedure and using the same quantities of reagents as in the determination, but omitting the test portion.

9.7 Calibration:

9.7.1 Transfer 0 mL, 2.5 mL, 5.0 mL, and 10.0 mL, respectively, of the phosphorus calibration solution to four plastic beakers. The additions correspond to 0 mg, 0.025 mg, 0.050 mg, and 0.100 mg of phosphorus. Proceed as directed in 9.1.2-9.6, but do not add any test portions.

9.7.2 Subtract the absorbance of the “zero” solution from that of each solution containing phosphorus, and plot the absorbance against the weight, in milligrams, of phosphorus added.

9.8 Number of Determinations:

9.8.1 Carry out the determinations at least in duplicate.

10. Calculation

10.1 Correct the absorbance reading of the test solution by subtracting the absorbance reading in the blank test. Convert

TABLE 2 Nominal Composition of Nickel and Ferro-nickel Samples, %

Test Material	P	As	Cr	Fe	Si	Ni
Ni #1	0.00005	-	-	<0.01	-	balance
Ni #2	0.0008	-	-	balance	-	balance
Fe-Ni #1	0.01	<0.001	0.5	balance	0.5	25
Fe-Ni #2	0.01	0.1	4.5	balance	5	25
Fe-Ni #3	0.045	0.001	0.5	balance	0.6	25
Fe-Ni #4	0.045	0.1	4.5	balance	5	25

TABLE 3 Nominal Composition of Nickel Alloy Samples, %

Sample	P	Co	Cr	Cu	Fe	Mo	Ni	Nb	W
4D-7	0.01	-	-	32	1	-	65	-	-
4D-8	0.01	-	21	-	4	9	62	3	-
4D-9	0.02	-	19	-	19	3	53	5	-
4D-10	0.02	-	20	-	46	-	31	-	-
4D-11	0.01	-	21	-	20	8	47	-	-
4D-12 ^A	0.005	42	21	-	2	4	20	4	4

^A Standard Reference alloy BAM 328-1, certified at 0.005 % P was used as sample 4D-12.

the net absorbance of the test solution into mg of phosphorus by means of the calibration graph.

10.2 Calculate the percentage by weight of phosphorus in the test sample using the formula:

$$\% P = A/10B \quad (1)$$

where:

A = the weight, in mg, of phosphorus found in the test portion, and

B = the weight, on g, of the test portion.

11. Test Reports

11.1 Report the following information:

11.1.1 The reference to the method used.

11.1.2 The results of the analysis.

11.1.3 The number of independent replications.

11.1.4 Any unusual feature noted during the analysis.

11.1.5 Any omission, addition, or deviation from this test method.

12. Precision and Bias ⁵

12.1 *Precision*—Eight laboratories cooperated in the testing of this test method using samples described in Table 2 and Table 3 and obtained statistical information summarized in Table 4.

12.2 *Bias*—No information on the accuracy of this test method is known because only one accepted reference standard was used in the ILS. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this test method as it applies in a specific laboratory.

13. Keywords

13.1 colorimetric; molecular absorption; nickel; phosphorus content; spectrophotometric

⁵ Supporting data are available from ASTM Headquarters. Request RR:E01-1021.

TABLE 4 Results of Statistical Analysis

Test Material ^A	Mean, %	Repeatability SD (S _r , ISO 5725) ^B	Reproducibility SD (S _R , ISO 5725) ^C	Reproducibility (R, ISO 5725) ^D	R _{rel} %
Ni #2	0.00091	0.00007	0.00012	0.0004	44
4D-12 ^E	0.0054	0.0001	0.0008	0.0022	40
4D-8	0.0089	0.0009	0.0015	0.0050	56
FeNi #1	0.0100	0.0004	0.0002	0.0014	14
FeNi #2	0.0100	0.0004	-	0.0012	12
4D-7	0.0120	0.0007	0.0007	0.0026	21
4D-11	0.0135	0.0006	0.0008	0.0027	20
4D-9	0.0148	0.0008	0.0006	0.0028	18
4D-10	0.0185	0.0003	0.0007	0.0022	11
FeNi #4	0.0425	0.0010	0.0010	0.0038	8.9
FeNi #3	0.0437	0.0014	0.0021	0.0068	15

^A Material Compositions are summarized in Table 2 and Table 3.

^B Equivalent to minimum standard deviation, s_M, (Practice E 1601).

^C Equivalent to reproducibility standard deviation, s_R, (Practice E 1601).

^D Equivalent to reproducibility index, R, (Practice E 1601).

^E Standard Reference alloy BAM 328-1, certified at 0.005 % P was used as sample 4D-12.

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