Designation: E1917 – 13

Standard Test Method for Determination of Phosphorus in Nickel, Ferronickel, and Nickel Alloys by Phosphovanadomolybdate Spectrophotometry[1]

This standard is issued under the fixed designation E1917; 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 range 0.0007 % to 0.05 %.

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

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 hazards associated with the use of this test method see Practices E50. Refer to specific warning notes given throughout this test method.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

2.2 *ISO Standards:*[3]

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

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

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 The sample is dissolved in a mixture of HCl and HNO_3. $HClO_4$ is added and the solution is evaporated to fumes of $HClO_4$ to remove chromium as volatile chromyl chloride. Silicon and refractory elements are complexed with fluoride ions through the addition of HF. Phosphorus is converted to phosphovanadomolybdic acid in an $HClO_4$ and HNO_3 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.

5. Significance and Use

5.1 This test method is used for the determination of phosphorus in nickel, ferronickel, and nickel 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 E882.

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[1] This practice is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.08 on Ni and Co and High Temperature Alloys.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

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

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.

TABLE 4 Results of Statistical Analysis

Test Material[A]	Mean, %	Repeatability Index (Practice E1601)	Reproducibility Index (Practice E1601)
Ni #2	0.00091	0.0002	0.0004
4D-12[B]	0.0054	0.0004	0.0022
4D-8	0.0089	0.0024	0.0050
FeNi #1	0.0100	0.0012	0.0014
FeNi #2	0.0100	0.0012	0.0012
4D-7	0.0120	0.0016	0.0026
4D-11	0.0135	0.0016	0.0027
4D-9	0.0148	0.0023	0.0028
4D-10	0.0185	0.0010	0.0022
FeNi #4	0.0425	0.0027	0.0038
FeNi #3	0.0437	0.0021	0.0068

[A] Material compositions are summarized in Table 2 and Table 3.

[B] Standard Reference alloy BAM 328-1, certified at 0.005 % *P* was used as sample 4D-12.

6. Apparatus

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

6.2 *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.

6.3 Plastic separatory funnels, 250-mL capacity.

7. Reagents

7.1 *Purity and Concentration of Reagents*—The purity and concentration of common chemical reagents and water shall conform to Practices E50. The reagents should be free of or contain only minimal amounts (< 0.1 µg/g) of phosphorus.

7.1.1 Verify the absence of phosphorus in the reagents using the blank test. 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.

7.2 *Ammonium Metavanadate Solution*—Dissolve 2.5 g of ammonium metavanadate (NH_4VO_3) in water, dilute to 1 L, and mix.

7.3 *Citric Acid Solution*—Dissolve 500 g citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) in water, dilute to 1 L, and mix. Warm the solution if necessary to facilitate dissolution.

7.4 *Fluoroboric Acid Solution*—Disperse 75 g of boric acid (H_3BO_3) in 600 mL of hot water in a plastic beaker. Add 50 mL of HF (40 %) and dilute to 1 L. Digest over medium heat until the boric acid is dissolved. Store in a plastic bottle. The solution should be heated gently if the boric acid forms crystals. (**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.)

7.5 *Hexaammonium Heptamolybdate Solution*—Dissolve 15 g of hexaammonium heptamolybdate tetrahydrate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ 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.

7.6 *4-Methyl-2-pentanone*—Methylisobutyl ketone.

7.7 *Phosphorus Stock Calibration Solution (1.000 g/L)*—Transfer 4.3942 g of potassium dihydrogenorthophosphate (KH_2PO_4) (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.

7.8 *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 and mix.

7.9 *Sodium Nitrite Solution (50 g/L)*—Dissolve 50 g of sodium nitrite ($NaNO_2$) in water and dilute to 1 L.

8. Sampling and Sample Preparation

8.1 The sampling shall be performed 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, or other appropriate solvent, and dried in air.

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

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 HNO_3 and then 5 mL of HCl. For samples with high contents of niobium, silicon, tantalum, or hafnium, 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 $HClO_4$ and, leaving a small opening to release the vapors, evaporate to dense $HClO_4$ fumes. (**Warning—**Fuming $HClO_4$ is a powerful oxidant and can cause explosions when in contact with organic materials. All evaporations must be performed in the presence of HNO_3 and in a fume hood specifically designed for use with $HClO_4$.)

NOTE 2—Nickel and some copper bearing nickel alloys, such as Monel, will dissolve more readily in HNO_3 (1 + 1).

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 of HNO_3 (1 + 4) and 4 mL of HF to the solution and heat for 8 min to 10 min until the precipitate is dissolved.

NOTE 3—It is important that the precipitated refractory oxides dissolve completely. If this does not happen, add another 2 mL of 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 min 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 °C and 30 °C, and proceed immediately with the color development.

NOTE 4—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 °C and 25 °C for a minimum of 7 min, but not longer than 15 min.

9.4.2 Transfer the solution to a 250-mL plastic 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 ± 1 °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 Perform 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, 2.5, 5.0, and 10.0) mL, respectively, of the phosphorus calibration solution to four plastic beakers. The additions correspond to (0, 0.025, 0.050, and 0.100) mg of phosphorus. Proceed as directed in 9.1.2 – 9.5.1, 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 Perform 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 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:

$$\% P = A/10B \tag{1}$$

where:

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

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

11. Precision and Bias[4]

11.1 *Precision*—Eight laboratories in six countries cooperated in the testing of this test method under the auspices of ISO/TC155/SC4 in the late 1980s and published as ISO 11400:1992(E). Two samples of nickel metal, four samples of ferronickel, and six samples of nickel based alloys as described in Table 2 and Table 3 were used to obtain the statistical information, as evaluated by ISO 5725:1986 and equivalent to Practice E1601, summarized in Table 4.

11.2 *Bias*—No information on the accuracy of this test method is known because only one accepted reference standard

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1021.

was used in the interlaboratory study. 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.

12. Keywords

12.1 ferronickel; molecular absorption spectrometry; nickel; nickel alloy; phosphorus content; spectrophotometric

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