



# Standard Test Method for Spectrographic Analysis of Thermionic Nickel Alloys by the Powder Technique<sup>1</sup>

This standard is issued under the fixed designation E 129; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Section 17 was added editorially in December 1993.

## 1. Scope

1.1 This test method covers the determination of the following elements in thermionic nickel alloys in the concentration ranges shown:

Element	Concentration Range, %
Cobalt	0.01 to 1.0
Copper	0.001 to 0.50
Iron	0.005 to 0.30
Magnesium	0.005 to 0.30
Manganese	0.005 to 0.30
Aluminum	0.003 to 0.30
Chromium	0.003 to 0.10
Silicon	0.003 to 0.10
Titanium	0.003 to 0.10

1.2 The test method has been designed for inspection testing of nickel alloy thermionic cathodes. It is equally applicable to the determination of the elements listed in 1.1 in any nickel alloy where the nickel content is greater than 98.0 %, provided the total sample available exceeds 50 mg.

NOTE 1—The concentration ranges of the elements listed in 1.1 have been established through cooperative testing of secondary standards and by preparation of synthetic standards provided in the method. The scope is underwritten by three primary spectrochemical standards.<sup>2</sup> Cooperative testing of the first two of these standards has provided supporting data for this method.<sup>3</sup>

1.3 The values stated in inch-pound units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety problems, 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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals<sup>4</sup>

<sup>1</sup> This test method 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 Ni and Co and High Temperature Alloys.

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<sup>2</sup> National Institute of Standards and Technology nickel oxide standards Nos. 671, 672, and 673.

<sup>3</sup> Appendix I to 1957 Report of Committee E-2, *Proceedings*, ASTEA, Am. Soc. Testing Mats., Vol 57, 1957.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 03.05.

E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis<sup>4</sup>

E 116 Practice for Photographic Photometry in Spectrochemical Analysis<sup>4</sup>

E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes<sup>4</sup>

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials<sup>4</sup>

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E 135.

## 4. Summary of Test Method

4.1 The sample is dissolved in dilute nitric acid and evaporated to dryness and baked. The oxide powder is then mixed with graphite powder which acts as a buffer and diluent. This mixture is packed into the crater of a graphite cup. Direct-current arc excitation is employed. The spectra are recorded photographically. Intensity ratios of selected pairs of analytical lines and internal standard nickel lines are determined photometrically. The concentration of each element is read from an analytical curve relating the log intensity ratio to log concentration.

## 5. Apparatus

5.1 *Sample Preparation Equipment*—A mortar and pestle made of material that will not contaminate the sample with any of the elements to be determined, or a dental amalgamator<sup>5</sup> utilizing a plastic vial and a plastic ball. If a mortar and pestle are used, highly polished agate may be employed for all determinations except silicon, highly polished sapphire for all determinations except aluminum, or high polished tool steel for all determinations except iron.

5.2 *Excitation Source*—A d-c arc source capable of providing a current of 8.0 to 12.0 A.

5.3 *Spectrograph*, having sufficient resolving power and linear dispersion to separate clearly the analytical lines from other lines in the spectrum of the sample in the spectral region 2400 to 4500 Å. These conditions are satisfied by instruments having a reciprocal linear dispersion of 5 to 7 Å/mm at 2800 Å.

5.4 *Photographic Processing Equipment*, providing developing, fixing, washing, and drying operations and con-

<sup>5</sup> A dental amalgamator suitable for this purpose is sold under the trade name "Wig-L-Bug."

forming to the requirements of Practice E 115.

5.5 *Microphotometer*, having a precision of  $\pm 1.0\%$  for transmittances between 5 and 90 %.

5.6 *Calculating Equipment*—The use of a calculating board shall be optional.

## 6. Reagents and Materials

6.1 *Purity and Concentration of Reagents*—The purity and concentration of chemical reagents shall conform to the requirements prescribed in Practices E 50.

6.2 *Graphite Powder*, highest purity obtainable, passing a No. 100 (150- $\mu\text{m}$ ) sieve.

6.3 *Electrodes*, high-purity graphite. The sample electrode shall be high-purity Type S-4 or S-15 and the counter electrode high-purity Type C-6 or C-9 as described in Practice E 130. The electrode pair shall be standardized within the laboratory.

6.4 *Metals or Metal Salts*—Nickel, cobalt, copper, iron, magnesium, manganese, aluminum, chromium, and titanium as pure metals or as pure metal salts soluble in  $\text{HNO}_3$  (1+1).

6.5 *Photographic Emulsions*—Eastman Process, SA No. 1, SA No. 2, or equivalent. Either films or plates may be used.

6.6 *Photographic Processing Solutions*—The formulas for processing solutions are given in Practice E 115.

6.7 *Sodium Metasilicate* ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ).

## 7. Standards

7.1 Three primary standards<sup>2</sup> are available for use with this method. Additional standards can be prepared in the laboratory to supplement the scope of the method, if desired.

## 8. Preparation of Standards

8.1 *Primary Standards*—Dissolve 0.3 g or more of the primary standards in  $\text{HNO}_3$  (1+1). Evaporate the solutions to dryness in a platinum evaporating dish and bake at 400°C for 20 min. Grind and mix thoroughly with a suitable mortar and pestle. Mix the dry powder with three parts by weight of graphite powder.

8.2 *Synthetic Standards*:

8.2.1 Prepare all synthetic standards except those for silicon and titanium in the following manner: To nickel nitrate ( $\text{Ni}(\text{NO}_3)_2$ ) solution (1 mL = 100 mg Ni), add aliquots of solutions made from the metal reagents listed in 6.4. Prepare a series of standards to cover the concentration ranges desired.

8.2.2 *Silicon Stock Solution* (1 mL = 0.1 mg Si)—Dissolve 1.012 g of sodium metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) in 500 mL of water in a 1000-ml volumetric flask and dilute to volume.

8.2.3 *Titanium Stock Solution* (1 mL = 0.1 mg Ti)—Dissolve 0.1 g of titanium metal (99.9 %) in 10 mL of hydrofluoric acid (49 %). Add 5 mL of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and heat to expel all HF. Dilute to 1000 mL with water.

8.2.4 To a nickel nitrate solution (1 mL = 100 mg Ni) containing the other added elements, add aliquots from the silicon and titanium standard solutions to cover the concentration ranges desired. Evaporate the solutions to dryness in a platinum evaporating dish, bake at 400°C for 20 min., grind, and mix thoroughly with a suitable mortar and pestle. Mix three parts of pure graphite powder with one part of dry nickel oxide powder.

## 9. Preparations of Samples

9.1 Dissolve samples in  $\text{HNO}_3$  (1+1). Approximately 0.5 g of representative sample shall be used if available, but a complete analysis can be made on 50 mg if the sample is limited. Evaporate the solution to dryness in a platinum evaporating dish and bake at 400°C for 20 min. Grind and mix thoroughly with a suitable mortar and pestle. Mix a portion of this powder with three parts by weight of graphite powder.

## 10. Electrode System

10.1 Place the sample electrode, filled level-full with standard or sample, in the lower electrode holder (anode). If the S-4 electrode is used, hold it in a water-cooled clamp, if possible, for best results. Position the external optics, including the gap, in such a manner that the resulting spectral lines represent radiant energy from the entire arc column, except that both electrode tips shall be screened out. These conditions should be satisfied with an analytical gap of 3.0 mm.

## 11. Excitation and Exposure

11.1 Produce and record the spectrum in accordance with the following conditions:

### 11.1.1 Electrical Parameters:

Voltage, V	250
Current, A	8.0 to 12.0

### 11.1.2 Exposure Conditions:

Spectral region, Å	2400 to 4300
Slit width, mm	0.025 to 0.070
Slit length, mm	1.0 to 6.0
Filter	three-step spectral filter or equivalent sector wheel, placed at stigmatic focal point, transmitting approximately 100, 20, and 4 %
Preburn period, s	none
Exposure period, s	60

11.1.3 *Replicate Exposures*—Expose samples in quadruplicate.

## 12. Photographic Processing

12.1 Process the emulsion in accordance with the Practices E 115.

## 13. Photometry

13.1 Measure the transmittance of the spectrum line pairs listed in Table 1 and convert to relative intensities using an emulsion calibration curve obtained in accordance with 14.1.

## 14. Calibration

14.1 *Emulsion Calibration*—Calibrate emulsions in accordance with Practice E 116.

14.2 *Preparation of Analytical Curves*—Make sufficient exposures of the standards to establish analytical curves. Convert the percent transmittances of the analytical and internal standard lines to log intensity ratios, using the emulsion calibration curve. Prepare analytical curves by plotting the log intensity ratio versus the log concentration for each of the respective elements in the standard samples.

## 15. Calculation

15.1 Frequently check the analytical curve by exposing a high and a low standard with any series of samples. Compen-