



# Standard Test Method for Determination of Lead in Nickel Alloys by Electrothermal Atomic Absorption Spectrometric Method<sup>1</sup>

This standard is issued under the fixed designation E 1834; 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.

## 1. Scope

1.1 This test method covers the determination of lead in nickel and nickel alloys in the concentration range of 0.00005 % to 0.001 % by electrothermal atomic absorption spectrometry.

NOTE 1—If this test method is used to test materials having contents less than 0.0001 % lead, users in different laboratories will experience more than the usual 5 % risk that their results will differ by more than 50 % relative error.

1.2 *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.

## 2. Referenced Documents

### 2.1 ASTM Standards:

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals, Ores, and Related Materials<sup>2</sup>

E 1184 Practice for Electrothermal (Graphite Furnace) Atomic Absorption Analysis<sup>2</sup>

E 1452 Practice for Preparation of Calibration Solutions for Spectrophotometric and Spectroscopic Atomic Analysis<sup>2</sup>

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method<sup>2</sup>

E 1770 Practice for Optimization of Electrothermal Atomic Absorption Spectrometric Equipment<sup>3</sup>

### 2.2 ISO Standards:

ISO Standard 11437—Nickel Alloys—Determination of Trace-Element Content—Electrothermal Atomic Absorption Spectrometric Method—Part 2: Determination of Lead Content<sup>4</sup>

ISO Guide 5725—Accuracy, Trueness, and Precision of

## Measurements, Methods and Results<sup>4</sup>

## 3. Summary of Test Method

3.1 The sample is dissolved in a mixture of nitric acid, hydrofluoric acid, and water. The sample and a nickel-ammonium phosphate matrix modifier are injected into the electrothermal atomizer of an atomic absorption spectrometer, which is provided with a background corrector. Measurement of the absorbance is made at a wavelength of 283.3 nm. The lead concentration is determined from a calibration curve established with nickel solutions containing a known amount of lead.

## 4. Significance and Use

4.1 This test method is intended to be used for the determination of trace levels of lead in nickel and nickel alloys. It is assumed that the procedure will be performed by trained analysts capable of performing common laboratory practices skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory and proper waste disposal procedures will be followed.

## 5. Apparatus

5.1 *Atomic Absorption Spectrometer*, with electrothermal atomizer, equipped with an appropriate background corrector, a signal output device, such as a video display screen, a digital computer, a printer or strip chart recorder, and an autosampler.

5.2 *Pyrolytically Coated Graphite Tubes*, grooved, conforming to the instrument manufacturer's specifications.

5.3 *Pyrolytic Graphite Platforms*, L'vov design, fitted to the tubes specified in 5.2.

5.4 *Radiation Source*, lead hollow cathode lamp, or electrodeless discharge lamp with an appropriate power supply.

## 6. Instrument Parameters and Criteria

6.1 The atomic absorption spectrometer and electrothermal atomizer are satisfactory if after adjustment of the instruments and optimization of the furnace heating program as described in Practice E 1770, they meet the criteria given in 6.4-6.7.

6.2 Calibration solutions  $S_0$  through  $S_3$  prepared in accordance with 7.9 and summarized in Table 1 shall be used for testing criteria.

6.3 The parameters for the determination of lead and the

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 03.06.

<sup>4</sup> Available from American National Standards Institute, 25 W. 43rd St., 4th Floor, New York, NY 10036.

**TABLE 1 Lead Concentration of Calibration Solutions**

Calibration Solution	Concentration of Pb in Calibration Solution		Pb Concentration in Calibration Solution Corresponds to Concentration of Pb in Sample <sup>A</sup>
	µg/L	ng/mL	ppm (g/metric ton)
S <sub>0</sub>	0	0	0
S <sub>1</sub>	10	10	2
S <sub>2</sub>	20	20	4
S <sub>3</sub>	30	30	6
S <sub>4</sub>	40	40	8
S <sub>5</sub>	60	60	12

<sup>A</sup> Based 0.500 g sample/100 mL sample solution (9.1).

establishing of the instrument criteria are as follows:

6.3.1 The injection volume is 20 µL.

6.3.2 The peak area absorbance integration measurements shall be at a wavelength of 283.3 nm.

6.4 *Characteristic Mass*—The characteristic mass determined in accordance with Practice E 1770 shall be within 20 % of that given in the manufacturer's literature.

6.5 *Precision*—The variability obtained from calibration solution S<sub>3</sub> shall not exceed 10 % of the mean absorbance of the same solution, and the variability of calibration solution S<sub>1</sub> shall not exceed 4 % of the mean absorbance of solution S<sub>3</sub> when determined in accordance with Practice E 1770.

6.6 *Limit of Detection*—The limit of detection of lead as described in Practice E 1770 shall be less than 20 pg (equivalent to 1.0 µg/L in the test solution or 0.2 ppm in the original sample).

6.7 *Linearity*—The linearity of the calibration as determined in Practice E 1770 shall not be less than 0.7.

## 7. Reagents

7.1 *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 minimal amounts (<0.01 µg/g) of lead.

7.2 *Dissolution Acid Mixture*—To 150 mL water carefully add 150 mL nitric acid and 150 mL hydrofluoric acid. Mix and store in plastic bottle.

7.3 *Pure Nickel Metal*—99.9 % minimum purity nickel, and shall contain less than 0.1 ppm lead.

7.4 *Nickel, Stock Solution (50 g/L)*—Dissolve 25 ± 0.1 g of the pure nickel in 200 mL of nitric acid (1:1) in a 600 mL beaker. Cool the solution and transfer to a 500 mL volumetric flask. Dilute to the mark and mix.

NOTE 2—If large nickel turnings or chunks are used, gentle heating may be required to complete the dissolution. When using carbonyl nickel powder, the solution must be filtered to remove undissolved carbon.

7.5 *Nickel, Solution (5.0 g/L)*—Transfer 10.0 mL of the Nickel Stock Solution to a 100 mL volumetric flask. Dilute to the mark with water and mix.

7.6 *Nickel Nitrate-Ammonium Phosphate Matrix Modifier Solution*—Dissolve 6.0 ± 0.1 g high purity ammonium dihydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) in 50 mL water. Transfer to 100 mL volumetric flask and add 20 mL of nickel solution (7.5). Dilute with water and mix. This solution shall be freshly prepared.

7.7 *Lead Reference Solution (100 mg/L)*—Dissolve 0.100 ± 0.001 g of lead metal (99 % minimum purity) in 20 mL nitric acid (1:1) in a 250-mL beaker. Heat to assist dissolution. Cool and transfer to 1-L volumetric flask, dilute to mark with water and mix. Store in polypropylene or high density polyethylene bottle.

7.8 *Lead Standard Solution (1.0 mg/L)*—Pipette 10.0 mL of the lead reference solution (7.7) into a 1-L volumetric flask. Add 20 mL nitric acid and dilute to volume with water and mix. This solution shall be freshly prepared.

7.9 *Calibration Solutions*—Transfer 10.0 mL nickel solution (50 g/L) to each of six 100 mL volumetric flasks. Add respectively 0, 1.0, 2.0, 3.0, 4.0, and 6.0 mL of lead standard solution (7.8). Dilute with water and mix. These calibration solutions contain 0, 10.0, 20.0, 30.0, 40.0 and 60.0 µg Pb/L. These calibration solutions shall be identified as calibration solutions S<sub>0</sub> through S<sub>5</sub>, respectively (see Table 1).

## 8. Sampling and Sample Preparation

8.1 Sampling and sample preparation are to be performed by procedures agreed upon between buyer and seller.

8.2 The sampling procedure shall not involve any steps or procedures that can result in the loss or pick up of lead in the sample.

NOTE 3—Sometimes a heterogeneous scrap composite is homogenized by melting, then milling a laboratory sample from the solid. Arc melting of the sample or induction melting of the sample under vacuum can result in significant loss of several elements, including lead, that have a low vapor pressure. Arc melting of the sample should be avoided and induction melting should be performed only with at least a partial inert atmosphere.

8.3 In most cases the laboratory sample is in the form of homogeneous turnings, millings or drillings and no further mechanical preparation of the sample is necessary.

8.4 The laboratory sample shall be cleaned by first washing in pure acetone and drying in air.

8.5 If brazed alloy tools are used in the preparation of the sample, the sample shall be further cleaned by pickling in dilute nitric acid for a few minutes. The sample shall then be washed several times with water followed by several washes with acetone and air dried.

## 9. Procedure

9.1 *Preparation of Test Solution*—Transfer 0.50 g sample, weighed to the nearest mg, to a 100 mL PTFE beaker. Add 20 mL of the dissolution acid mixture (7.2). Apply sufficient heat to initiate and maintain the reaction until dissolution is complete. Transfer solution to a 100 mL volumetric flask, cool, and dilute to volume with water.

NOTE 4—It may be desirable to reduce the sample solution to wet salts (approximately 5 mL). This will reduce the presence of excess fluoride ions (a known interference for a number of elements determined by electrothermal atomic absorption spectrometry).

NOTE 5—Certain nickel alloys may be difficult to dissolve in the nitric acid-hydrofluoric acid mixture. In such cases, the proportions of the dissolution acid mixture may be adjusted, but a corresponding blank test is necessary.

9.2 A reagent blank shall be carried along during the entire procedure.

**TABLE 2 Nominal Composition of Test Samples, %**

Sample	Pb	Co	Cr	Mo	Ta	Ti	Al	Hf	W	V	Ni
1	0.0001	15	15	5	...	2.5	2.5	...	...	...	Balance
2	0.001	15	15	5	...	2.5	2.5	...	...	...	Balance
3	<0.0001	10	8	...	2.5	1.5	5	1.5	10	...	Balance
4	0.0004	10	8	...	2.5	1.5	5	1.5	10	...	Balance
5	0.001	10	8	...	2.5	1.5	5	1.5	10	...	Balance
6	<0.00005	14	10	3	...	4.5	6	...	...	1	Balance

### 9.3 Dilution for samples containing up to 5 ppm lead:

9.3.1 Transfer 1.0 mL of each test solution containing up to 25 µg/L lead, the reagent blank, and each of the calibration solutions from S<sub>0</sub> through S<sub>3</sub> into a 5 mL plastic vial using a micropipette. Add 100 µL of the matrix modifier (7.6) using a micropipette and mix.

### 9.4 Dilution for samples containing from 5 to 10 ppm lead:

9.4.1 Transfer 0.50 mL of each test solution containing between 25 µg/L and 50 µg/L of lead, the reagent blank, and of the calibration solutions from S<sub>0</sub> through S<sub>5</sub> into 5 mL plastic vials using a micropipet. Add 0.50 mL nickel solution (7.5) and 100 µL of the matrix modifier solution (7.6) to each using a micropipet and mix.

NOTE 6—If the electrothermal atomizer is fitted with an autosampler, the modifier addition, dilution, and mixing can be done in the autosampler cups.

NOTE 7—The mixing can be done by repeatedly charging and discharging the contents of the plastic vial using a larger micropipette.

9.5 Analyze several replicates of the S<sub>0</sub> solution to establish a stable instrument response. Set the last replicate to zero.

9.6 Starting with the appropriately diluted calibration solutions (9.3 or 9.4), inject 20 µL into the electrothermal atomizer and atomize the sample. Record the absorbance. Run each calibration solution in triplicate.

9.7 Inject 20 µL of the appropriately diluted reagent blank (9.3 or 9.4) into the electrothermal atomizer and atomize the sample. Record the absorbance. Run at least in duplicate.

9.8 Check calibration slope by injecting and atomizing 20 µL of S<sub>0</sub> and the highest calibration solution used. Run in triplicate and record absorbance values.

9.9 Inject 20 µL of the test solution and atomize. Record absorbance values. Run each sample at least in duplicate.

9.9.1 Repeat step 9.9 with the next test solution.

9.10 Repeat steps 9.8, 9.9, and 9.9.1 until all the test solutions are measured.

9.11 Calculate the means of the absorbance measurements obtained in steps 9.6-9.10.

## 10. Calibration Graphs and Calculation

10.1 Most electrothermal atomizers controlled by a computer will calculate the means, establish the calibration curves and calculate and display the results. If using instruments not having this capability, prepare the calibration graph and perform the calculation in accordance with 10.2-10.9.

10.2 Subtract the mean absorbance value obtained for the S<sub>0</sub> calibration solution, the reagent blank, from the mean absorbance values obtained for each of the remaining calibration solutions.

10.3 Construct a graph relating the mean absorbance values obtained for the calibration solutions (10.2) to their lead content in µg/L.

10.4 Using the mean absorbance obtained for the reagent blank solution (9.7) determine the lead concentration of the reagent blank solution from the calibration curve (10.3).

10.5 If the calibration check measurement obtained in 9.8 shows that the calibration curve has drifted slightly, adjust the calibration curve accordingly.

10.6 Using the mean adjusted absorbance values obtained in 9.9 determine the lead content of the two test solutions.

10.7 Repeat instructions given in 10.5 and 10.6 until the lead content of the remaining test solutions are obtained.

10.8 Subtract the lead content of the reagent blank solution (10.4) from the lead content of the test solutions found in 10.6 and 10.7.

10.9 Calculate the lead content of the test sample, in ppm (g/metric ton), using the formula:

$$\text{Pb in ppm} = c/10 m \text{ (for dilutions made in accordance with 9.3)} \quad (1)$$

$$\text{Pb in ppm} = c/20 m \text{ (for dilutions made in accordance with 9.4)}$$

where:

$c$  = the lead concentration, in µg/L in the test solution, as calculated in 10.8.

$m$  = the mass, in g, of the test portion (9.1).

## 11. Test Reports

11.1 Report the following information:

11.1.1 The reference to this test method;

11.1.2 The results of the analysis;

11.1.3 The number of independent replications;

11.1.4 Any unusual features noted during the analysis; and

11.1.5 Any operations not included in this test method or regarded as optional.

## 12. Precision and Bias<sup>5</sup>

12.1 *Interlaboratory Studies (ILS)*—This test method was evaluated by a subcommittee within ISO Technical Committee 155 on analysis of nickel alloys (ISO/TC 155/SC 4) in accordance with ISO Standard 5725. It was published as ISO Standard 11437, Part 2. The ILS test data was not available for recalculation. The published ISO statistics are summarized.

12.2 *Precision*—Nine laboratories cooperated in testing this method and obtained the statistical information summarized in Table 3.

12.3 *Bias*—No information on the bias of this test method is known. The user of the method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this method as applied in a specific laboratory.

<sup>5</sup> Supporting data are available from ASTM International Headquarters. Request RR:E01-1017.

**TABLE 3 Results of the Statistical Analysis, Lead in Nickel Alloys**

Test Material	Average Pb Found, ppm	Repeatability ( $s_r$ , ISO 5725) <sup>A</sup>	Reproducibility ( $S_R$ , ISO 5725) <sup>B</sup>	$R_{rel}$ %
6	0.04	0.27	0.26	650
3	0.14	0.33	0.42	300
1	1.6	0.26	0.45	28
4	4.0	0.59	0.86	21
2	9.6	1.31	2.13	22
5	10.7	1.42	2.06	19

<sup>A</sup> Equivalent to  $2.8 \times S_M$  where  $S_M$  is minimum standard deviation (see Practice E 1601).

<sup>B</sup> Equivalent to  $R$ , reproducibility index (see Practice E 1601).

### 13. Keywords

13.1 atomic absorption spectrometry; flameless atomic absorption spectrometry; graphite furnace analysis; lead content; nickel alloys; trace element determination

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