INTERNATIONAL
STANDARD

ISO
11437

First edition
2018-01

Nickel alloys — Determination of lead — Electrothermal atomic absorption spectrometric method

Alliages de nickel — Détermination du plomb — Méthode par spectrométrie d'absorption atomique électrothermique

Reference number
ISO 11437:2018(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*.

This first edition cancels and replaces ISO 11437-1:1994 and ISO 11437-2:1994, which have been merged and technically revised.

INTERNATIONAL STANDARD **ISO 11437:2018(E)**

Nickel alloys — Determination of lead — Electrothermal atomic absorption spectrometric method

1 Scope

This document specifies an electrothermal atomic absorption spectrometric method for the determination of lead in the range of 1 µg/g to 10 µg/g in nickel alloys.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

Dissolution of a test portion in a mixture of nitric acid and hydrofluoric acid, dilution of the test solution to a known volume, and transfer of an aliquot to a plastic vial.

Addition of a modifier to the aliquot of the test solution, and injection of a small volume of this solution into the electrothermal atomizer of an atomic absorption spectrometer.

Measurement of the atomic absorption of the 283,3 nm spectral line energy emitted by a lead hollow-cathode lamp and comparison with those of the calibration solutions.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1 **Pure nickel**, containing less than 1 µg/g of lead.

5.2 **Nickel**, base-solution 50 g/l.

Weigh, to the nearest 0,1 g, 25,0 g of pure nickel (5.1). Transfer to a 600 ml tall-form beaker and add 100 ml of water. Cautiously add 100 ml of nitric acid (ρ_{20} = 1,41 g/ml) in small portions, in such a manner that the dissolution remains under control. Cool the solution and transfer it to a 500 ml one-mark volumetric flask. Make up to the mark with water and mix.

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

5.3 Nickel, base solution 5 g/l.

Transfer 10,0 ml of the nickel base solution (5.2) to a 100 ml one-mark volumetric flask. Make up to the mark with water and mix.

5.4 Nitric acid, ρ_{20} = 1,41 g/ml, diluted 1 + 1.

5.5 Hydrofluoric acid, ρ_{20} = 1,13 g/ml.

WARNING — Hydrofluoric acid is extremely irritating and corrosive to skin and mucous membranes producing severe skin burns which are slow to heal. In case of contact with skin, wash well with water, apply a topical gel containing 2,5 % (mass fraction) calcium gluconate and seek immediate medical treatment.

5.6 Nitric/hydrofluoric acids, mixture.

Carefully add 150 ml of nitric acid (ρ_{20} = 1,41 g/ml) and 150 ml of hydrofluoric acid (5.5) to 150 ml of water. Mix and store in a plastic bottle.

5.7 Modifier, nickel nitrate-ammonium phosphate solution.

Weigh, to the nearest 0,1 g, 6,0 g of ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) and dissolve it in 50 ml of water. Transfer the solution to a 100 ml one-mark volumetric flask. Add 20,0 ml of the nickel base solution (5.2), make up to the mark with water and mix.

This solution shall be freshly prepared.

5.8 Lead, standard solution, 100 mg/l.

Weigh, to the nearest 0,001 g, 0,100 g of lead of a mass fraction of 99,9 % minimum purity and transfer to a 250 ml beaker. Add 40 ml of nitric acid (5.6) and heat to assist dissolution. Cool the solution and transfer it to a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

Store in a polyethylene bottle.

1 ml of this solution contains 0,1 mg of lead.

5.9 Lead, standard solution, 1 mg/l.

Transfer 10,0 ml of the lead standard solution (5.8) into a 1 000 ml one-mark volumetric flask. Add 20 ml of nitric acid (ρ_{20} = 1,41 g/ml). Make up to the mark with water and mix.

1 ml of this solution contains 1 µg of lead.

This solution shall be freshly prepared.

6 Apparatus

All volumetric glassware shall be class A and calibrated, in accordance with ISO 648 or ISO 1042 as appropriate.

Before use, all glassware shall be cleaned by boiling with hydrochloric acid to remove any chemical contamination.

6.1 Polytetrafluoroethylene (PTFE) beakers, of capacity 100 ml.

6.2 Plastic vials, of capacity 5 ml.

6.3 Plastic volumetric flasks, of capacities 50 ml and 100 ml.

6.4 Micropipettes, of capacities from 2,0 µl to 100 µl.

6.5 Atomic absorption spectrometer.

The atomic absorption spectrometer to be used shall be fitted with an electrothermal atomizer and shall meet the performance criteria given in Annex A.

The atomic absorption spectrometer and electrothermal atomiser are satisfactory if, after optimization according to Annex A (A.3 to A.6), they meet the criteria specified in 7.1.

The spectrometer shall be equipped with a background corrector and a fast recording system capable of measuring peak heights and peak areas. The electrothermal atomizer shall be fitted with a pyrolytic graphite tube and L'vov platform, or a normal graphite tube.

The spectrometer should be capable of using single-element hollow cathode lamps or electrodeless discharge lamps operated at currents recommended by the manufacturer.

7 Instrument criteria

7.1 Preparation of solutions required for testing criteria

Follow the instructions given for the preparation of lead calibration solutions in 9.3 and 9.4.2.3. The composition of these calibration solutions is given in Table 1.

Table 1 — Lead concentration of calibration solutions

Calibration solution	Lead concentration		
	µg/litre	ng/ml	µg/g
S1	0	0	0
S2	10	10	2
S3	20	20	4
S4	30	30	6

7.2 Characteristic mass

The characteristic mass determined as described in A.7.1, shall be within 20 % of that given in the manufacturer's instructions.

7.3 Minimum precision

The minimum precision of calibration solution S4 shall not exceed 10 % of the mean absorbance of the same solution, and the minimum precision of calibration solution S2 shall not exceed 4 % of the mean absorbance of solution S4 when determined as described in A.7.2.

7.4 Limit of detection

The limit of detection of lead, determined as described in A.7.3, shall be less than 20 pg (equivalent to 1,0 µg/l or 0,2 µg/g).

7.5 Linearity

The linearity of the calibration, determined as described in A.7.4, shall not be less than 0,7.

8 Sampling and sample preparation

Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in case of dispute, by appropriate national standards.

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

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

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

9 Procedure

9.1 Preparation of the test solution

Weigh, to the nearest 0,001 g, 0,500 g of the sample and transfer into a 100 ml PTFE beaker (6.1). Add 20 ml of the acid mixture (5.6). Apply sufficient heat to initiate and maintain the reaction until dissolution is complete.

Cool the solution and then transfer it into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Dissolving certain alloys in the nitric acid-hydrofluoric acid mixture is sometimes difficult. In such cases, the proportions of the dissolving mixture should be adjusted, but a corresponding blank test is necessary.

9.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all reagents as used for the determination.

9.3 Preparation of the calibration solutions

Transfer 10,0 ml of the nickel base solution (5.2) into each of a series of 100 ml one-mark volumetric flasks. Add 0 ml; 0,5 ml;1,0 ml; 2,0 ml; 3,0 ml; 4,0 ml; 5,0 ml and 6,0 ml of the lead standard solution (5.9). Make up to the mark with water and mix.

These calibration solutions contain 0 µg; 5,0 µg; 10,0 µg; 20,0 µg; 30,0 µg; 40,0 µg; 50 µg and 60,0 µg of lead per litre.

9.4 Calibration and determination

9.4.1 Adjustment of the atomic absorption spectrometer

Equip the atomic absorption spectrometer with a pyrolytic graphite tube fitted with a L'vov platform. Condition new graphite tubes as instructed by the manufacturer.

Set up the instrument conditions for

— measuring peak area integration absorbance at a wavelength of 283,3 nm, and

— using an injection volume of 20 µl.

NOTE The volume injected into the furnace may be different, depending on the sensitivity of the instrument.

Establish the optimum furnace temperature programme in accordance with the instructions given in Annex A.

9.4.2 Atomic absorption measurements

9.4.2.1 General

The procedures described in this subclause shall be carried out immediately prior to the measurement.

9.4.2.2 Lead contents of up to 5,0 µg/g

With a micropipette (6.4) transfer 1,0 ml of each test solution containing up to 25 µg/l of lead and of each calibration solution containing up to 30 µg/l of lead into 5 ml plastic vials (6.2). With a micropipette (6.4), add 100 µl of the modifier solution (5.4) and mix.

9.4.2.3 Lead contents between 5,0 µg/g to 10,0 µg/g

With a micropipette (6.4) transfer 0,50 ml of each test solution containing between 25 µg and 50 µg of lead per litre, and of the calibration solutions containing 0 µg; 20,0 µg; 40,0 µg; 50 µg and 60,0 µg of lead per litre, into 5 ml plastic vials (6.2). With micropipettes (6.4), add 0,50 ml of the nickel base solution (5.3) and 100 µl of the modifier solution (5.4) and mix.

NOTE 1 If the electrothermal atomizer is fitted with an autosampler, the addition of modifier, dilution and mixing can be done in the autosampler cups.

NOTE 2 Mixing can be carried out by repeated charging and discharging of the contents of the plastics vial using the largest micropipette.

9.4.2.4 Preparation of the calibration curves

Atomize the preselected volume of each calibration solution and record three absorbance measurements for each of them.

Subtract the mean absorbance value obtained for the 0 µg/l calibration solution from the mean absorbance values obtained for the other calibration solutions.

Establish a graph relating the mean absorbance values obtained for the calibration solutions to their analyte concentrations (in micrograms per litre).

9.4.2.5 Determination

Check the calibration slope by atomizing the preselected volume of the zero and highest calibration solutions and record three measurements for each solution.

Atomize the preselected volume of the blank test solution. Record three absorbance measurements.

Atomize the preselected volume of two of the test solutions. Record three absorbance measurements for each.

Repeat the measurement instructions above until all of the test solutions are measured.

Calculate the mean of the three absorbance measurements obtained in each case.

9.5 Number of determinations

Carry out the determination at least in duplicate.

10 Expression of results

10.1 Calculation

Using the mean absorbance obtained for the blank test solution (9.2), determine the lead concentration in the blank test solution from the calibration curve (9.4.2.4).

If the calibration check measurement as described in 9.4.2.5 shows that the calibration curve has drifted significantly, adjust the calibration curve accordingly.

Using the mean absorbance values obtained in 9.4.2.5, determine the lead concentration in two of the test solutions.

Repeat the procedure above until the lead concentrations of the remaining test solutions are obtained.

Subtract the lead concentration in the blank test solution (9.2) from the lead concentration in the test solutions.

Calculate the lead content *w* of the test sample, in micrograms per gram, using Formula (1):

$$w = \rho/(10^{*}\ m) \tag{1}$$

where

ρ is the lead concentration, expressed in micrograms per litre, in the test solutions;

m is the mass, in grams, of the test portion.

10.2 Precision

10.2.1 Interlaboratory tests

Nine laboratories in four countries participated in the testing of this procedure using six samples having the nominal composition given in Table 2.

Table 2 — Nominal composition of test samples (% in mass fraction)

Sample label	Pb	Co	Cr	Mo	Ta	Ti	Al	Hf	W	Ni
1	0,000 1	15	15	5	—	2,5	2,5	—	—	Remainder
2	0,001	15	15	5	—	2,5	2,5	—	—	Remainder
3	< 0,001	10	8	—	2,5	1,5	5	1,5	10	Remainder
4	0,000 4	10	8	—	2,5	1,5	5	1,5	10	Remainder
5	0,001	10	8	—	2,5	1,5	5	1,5	10	Remainder
6	< 0,000 05	14	10	3	—	4,5	6	Vanadium:1		Remainder

10.2.2 Precision data

Results from the interlaboratory test programme were evaluated according to ISO 5725:1986. The data were tested for statistical outliers by the Cochran and Dixon tests described in ISO 5725:1986.

The principle of the Cochran test is that a set of results is an outlier if the within-laboratory variance is too large in relation to the others. Dixon's test is to determine if the mean from a laboratory is too far from the other laboratory means. Both tests were applied at the 95 % confidence level.

Repeatability and reproducibility were also calculated according to ISO 5725:1986 at the 95 % confidence level.