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Nickel alloys — Determination of trace-element content by electrothermal atomic absorption spectrometric method —

Part 1:
General requirements and sample dissolution

Alliages de nickel — Dosage des éléments-traces — Méthode par spectrométrie d'absorption atomique à excitation électrothermique —
Partie 1: Caractéristiques générales et mise en solution de l'échantillon

Reference number
ISO 11437-1:1994(E)

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11437-1 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*, Subcommittee SC 4, *Analysis of nickel alloys*.

ISO 11437 consists of the following parts, under the general title *Nickel alloys — Determination of trace-element content by electrothermal atomic absorption spectrometric method*:

- *Part 1: General requirements and sample dissolution*
- *Part 2: Determination of lead content*
- *Part 3: Determination of bismuth content*
- *Part 4: Determination of silver content*

Annex A forms an integral part of this part of ISO 11437. Annex B is for information only.

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Introduction

This part of ISO 11437 is to be used in conjunction with the other parts which specify methods for the determination of individual trace elements in nickel alloys by electrothermal atomic absorption spectrometry.

Although the analytical methods are specified in independent International Standards, it is possible to determine more than one element on a single test solution.

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Nickel alloys — Determination of trace-element content by electrothermal atomic absorption spectrometric method —

Part 1:
General requirements and sample dissolution

1 Scope

1.1 ISO 11437 specifies electrothermal atomic absorption methods for the determination of trace elements in nickel alloys, in the concentration ranges given in clause 1 of other parts of ISO 11437. Other elements may be added in subsequent parts of ISO 11437. Typical compositions of some nickel alloys are given in annex B.

1.2 This part of ISO 11437 specifies the general requirements for analysis by electrothermal atomic absorption spectrometry, preparation and dissolution of the test sample, method of calculation and the procedures used for the evaluation of the repeatability and reproducibility of the individual methods specified in other parts of ISO 11437.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 11437. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 11437 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Principle

Dissolution of a test portion in a mixture of dilute nitric acid and hydrofluoric acid.

Dilution of the test solution to a known volume and transfer of an aliquot to a plastics vial.

Addition of a modifier and/or diluent, where necessary, and injection of a small volume of the test solution into an electrothermal atomizer.

Measurement of the absorption of the resonance line energy from the spectrum of the element being determined and comparison with that of calibration solutions containing the same element.

4 Reagents

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

4.1 High purity metals, 99,9 % (*m/m*) minimum, as specified in the relevant part of ISO 11437.

4.2 Nitric acid, $\rho_{20} = 1{,}41$ g/ml, diluted 1+1.

4.3 Hydrofluoric acid, $\rho_{20} = 1{,}13$ 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 the case of contact with skin, wash well with water and seek medical advice.

4.4 Acid mixture for dissolution.

Carefully add 150 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml) and 150 ml of the hydrofluoric acid (4.3) to 150 ml of water. Mix and store in a plastics bottle.

4.5 Modifiers.

Prepare separately for each metal as specified in the appropriate part of ISO 11437.

4.6 Standard reference solutions, 100 mg/l of metal.

Prepare separately for each metal as specified in the relevant part of ISO 11437.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Atomic absorption spectrometer.

5.1.1 The atomic absorption spectrometer used in this method shall be fitted with an electrothermal atomizer and shall meet the performance criteria given in annex A.

5.1.2 The spectrometer shall be equipped with a background corrector and a rapid 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 as specified in the relevant part of ISO 11437.

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

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

5.3 Plastics vials, of capacity 5 ml.

5.4 Plastics volumetric flasks, of capacities 50 ml and 100 ml.

5.5 Glass volumetric flasks, of capacities 100 ml, 500 ml and 1 000 ml, in accordance with ISO 1042, Class A.

5.6 Burettes, of capacities 10 ml (graduated in divisions of 0,02 ml) and 25 ml (graduated in divisions of 0,1 ml), in accordance with ISO 385-1, Class A.

5.7 Pipettes, in accordance with ISO 648, Class A.

5.8 Mechanical micropipettes, of capacities 10 µl to 100 µl.

5.9 Variable mechanical pipette, of capacity 2,0 µl to 10,0 µl, fitted with plastics positive displacement tips.

6 Sampling and sample preparation

6.1 Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in case of dispute, by the relevant International Standard.

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

6.3 The laboratory sample shall be cleaned by washing with pure acetone and drying in air.

6.4 If brazed alloy tools are used in the preparation of the laboratory 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 distilled water followed by several washings with acetone, and air dried.

7 Procedure

7.1 Preparation of test solution — General method

7.1.1 Weigh, to the nearest 0,001 g, 0,500 g of the laboratory sample and transfer to the 100 ml PTFE beaker (5.2). Add 20 ml of the acid mixture for dissolution (4.4). Apply sufficient heat to initiate and maintain the reaction until dissolution is complete.

7.1.2 Cool the solution and proceed as directed in the relevant part of ISO 11437.

NOTE 1 It may be difficult to dissolve certain alloys in the nitric acid-hydrofluoric acid mixture. In such cases, the proportions of the dissolving mixture may be adjusted, but a corresponding blank test is necessary.

7.2 Blank test

Carry out a blank test in parallel with the determination, following the same procedure and using the same quantities of all the reagents.

7.3 Preparation of calibration solutions

Proceed as directed in the relevant part of ISO 11437.

7.4 Calibration and determination

7.4.1 Atomic absorption measurements

7.4.1.1 The spectral lines for each element, the type of graphite tube and the measurement mode (peak height or peak area integration) to be used in the analysis are specified in the relevant part of ISO 11437. Condition new graphite tubes as instructed by the manufacturer.

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

7.4.1.3 The volume injected into the furnace shall be between 10 µl and 50 µl, depending on the sensitivity of the analyte.

7.4.1.4 Starting with the calibration solutions, atomize the preselected volume (10 µl to 50 µl). Record three absorbance measurements for each of the calibration solutions.

7.4.1.5 Atomize the preselected volume (10 µl to 50 µl) for the blank solution. Record three absorbance measurements.

7.4.1.6 Check the calibration slope by atomizing the preselected volume (10 µl to 50 µl) of the zero and highest calibration solutions. Record three measurements for each of the solutions.

7.4.1.7 Atomize the preselected volume (10 µl to 50 µl) for two of the test solutions. Record three absorbance measurements.

7.4.1.8 Repeat the instructions in 7.4.1.6 and 7.4.1.7 until all of the test solutions are measured.

7.4.1.9 Calculate the means of the three absorbance measurements obtained in 7.4.1.4 to 7.4.1.8.

7.4.2 Preparation of calibration graphs

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

7.4.2.2 Construct a graph relating the mean absorbance values obtained for the calibration solutions (7.4.2.1) to their analyte concentrations (in micrograms per litre).

8 Expression of results

8.1 Calculation

8.1.1 Using the mean absorbance obtained for the blank test solution (7.4.1.5), determine the analyte concentration of the blank test solution from the calibration curve (7.4.2.2).

8.1.2 If the calibration check measurement obtained in 7.4.1.6 shows that the calibration curve has drifted significantly, adjust the calibration curve accordingly.

8.1.3 Using the mean absorbance values obtained in 7.4.1.7, determine the analyte concentration of two of the test solutions.

8.1.4 Repeat the instructions given in 8.1.2 and 8.1.3 until the analyte concentrations of the remaining test solutions are obtained.

8.1.5 Subtract the analyte concentration of the blank test solution (8.1.1) from the analyte concentration of the test solutions found in 8.1.3 and 8.1.4.

8.1.6 Calculate the analyte content w of the test sample, in grams per tonne, using the formula

$$\frac{\rho \times F}{20 \times m}$$

where

ρ is the analyte concentration, in micrograms per litre, in the test solution, as calculated in 8.1.5;

F is a dilution factor given in the relevant part of ISO 11437;

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

8.2 Precision

8.2.1 Laboratory tests

The methods in the subsequent parts of ISO 11437 have been subjected to interlaboratory testing.

8.2.2 Statistical analysis

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

8.2.2.2 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 tests 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.

8.2.2.3 Repeatability and reproducibility were calculated according to ISO 5725 at the 95 % confidence level. Results of the statistical analysis, including the within-laboratory and between-laboratory standard deviations are given for each element in the relevant part of ISO 11437.

9 Test report

The test report shall include the following information:

a) a reference to the method used;

b) the results of the analysis;

c) the number of independent replications;

d) any unusual features noted during the analysis;

e) any operation not included in this part of ISO 11437 or regarded as optional.

Annex A
(normative)

Optimization and checking of spectrometer performance criteria

A.1 Introduction

To obtain the best results when using the graphite furnace technique, the instrument settings, particularly the furnace programme, shall be optimized. Once the instrument settings are optimized, it is essential that the instrument meets certain performance requirements before it is used in the method specified in the relevant part of ISO 11437.

A.2 Initial instrument checks and adjustments

A.2.1 Switch on the power, cooling water, gas supplies and fume extraction system.

A.2.2 Open the furnace and inspect the tube and contacts. Replace the graphite components if wear or contamination is evident. Inspect the windows and clean if necessary.

If a new tube or graphite contacts are fitted, condition these using the heating programme recommended by the manufacturer.

NOTE 2 In the absence of the manufacturer's recommendations, the conditioning furnace programme shown in table A.1 should be used.

A.3 Radiation source

Both single-element hollow cathode lamps or electrodeless discharge lamps are suitable. These should be installed and operated as recommended by the manufacturer.

After the warm-up time specified by the manufacturer, the signal from each radiation source should not deviate by more than 0,5 % from the maximum value (i.e. by not more than 0,002 absorbance units) over a period of 15 min. Significantly greater fluctuations are usually indicative of a faulty lamp.

NOTE 3 The use of multi-element lamps is not generally recommended.

Table A.1 — Programme for graphite tube conditioning

Step	Temperature °C	Increase time s	Hold time s	Gas flow ml/min
1	1 500	60	20	300
2	20	1	10	300
3	2 000	60	20	300
4	20	1	10	300
5	2 600	60	10	300
6	20	1	10	300
7	2 650	2	5	0

A.4 Spectrometer parameters

A.4.1 Wavelength

Select the wavelength specified in the relevant part of ISO 11437.

A.4.2 Slit

Select the slit width recommended by the manufacturer. Where two slit settings are available, ensure that the type provided for use with the graphite furnace is selected.

A.4.3 Background correction

A.4.3.1 Deuterium background correction systems.

Select the background correction option and allow the lamps to stabilize for 30 min. Check that the energies of the analyte radiation source and the deuterium radiation source are balanced within the tolerances recommended by the manufacturer.

A.4.3.2 Zeeman background correction systems.

Ensure that the poles of the magnet are clean.

A.4.3.3 Test of background correction system.

Measure the atomic and background absorbances of 20 µl of a 0,2 % (*m*/*V*) magnesium nitrate solution at a wavelength between 200 nm and 250 nm (e.g. Bi 223,1 nm) using a charring temperature of 950 °C and an atomization temperature of 1 800 °C. A large background signal should be observed, with no over or under correction of the atomic signal.

NOTE 4 In general, the deuterium correction system should be able to correct for broad band background absorbances of up to 0,5 to 0,6 absorbance units. Zeeman systems should cope with levels as high as 1,0 to 1,5 absorbance units.

A.5 Autosampler

The operation of the autosampler should be checked. Particular attention should be paid to the condition of the pipette tip and the position of the tip during sample deposition. The manufacturer's instructions regarding the adjustment of the autosampler should be followed.

A.6 Optimization of the furnace heating programme

Optimization of the furnace heating programme is essential if good results are to be obtained using this technique. Furnace programmes recommended by manufacturers are often concerned with samples completely unrelated to nickel alloys. Consequently, the analyst shall optimize the furnace programme for use with the nickel alloy matrix in the manner described in A.6.1 to A.6.4.

The furnace programme for the nickel alloy matrix being considered here consists of four basic steps: drying, charring, atomization and cleaning.

A.6.1 Drying

A.6.1.1 For most samples a drying temperature of 120 °C is satisfactory. To avoid spattering, the temperature should be increased to 120 °C in 20 s and then held at that temperature for a time depending on the volume of sample introduced. The following hold times are typical.

Injected volume, µl	**Hold time,** s
10	15
40	30

A.6.1.2 When samples are deposited on the L'vov platform, a two-stage drying process is beneficial in preventing spattering.

The first stage involves heating the sample rapidly to 80 °C in 1 s and then holding the temperature at 80 °C for a short time. The time during which the temperature is maintained at 80 °C depends on the volume of solution injected. The following hold times are typical.

Injected volume, µl	**Hold time,** s
10	15
40	30

The temperature is then increased over a period of 20 s to 30 s, to a value 20 °C to 40 °C above the boiling point of the solvent. This higher temperature is held for 15 s to 40 s depending on the volume of sample injected. The following hold times are typical.

Injected volume, µl	**Hold time,** s
10	15
40	40

A.6.1.3 In A.6.1.1 and A.6.1.2, once suitable drying conditions have been selected, the drying process can be monitored visually with the aid of a dental mirror to ensure that it proceeds smoothly without spattering.

WARNING — Do not view the tube directly during the charring, atomization or cleaning steps.

A.6.2 Charring

During this step, volatile components of the matrix are driven off and precursor reactions occur, for example reduction of the analyte oxide to the elemental state and the formation of matrix refractory oxides and carbides.

NOTE 5 Because of the low volatility of the nickel alloy matrix, most of it will remain in the furnace after charring.

The analyst shall first select the combination of graphite tube, normal or L'vov platform, and measuring mode, peak height or peak area to be used.

The analyst shall then determine the optimum charring temperature experimentally as described in A.6.2.1 to A.6.2.10.

A.6.2.1 Use the optimum drying conditions as determined in A.6.1.

NOTE 6 At this stage, both the optimum charring and atomization settings are unknown. Estimates for suitable atomization settings should be made and the charring conditions optimized first.

A.6.2.2 Consult the manufacturer's literature and set the atomization temperature accordingly. Select the GAS STOP option. Select an atomization integration time of 10 s. This ensures that the whole of the analyte peak will be measured.

A.6.2.3 Select a charring time comprising a 30 s increase and a 30 s hold.

A.6.2.4 Select a calibration solution which will give an absorbance reading of 0,2 to 0,4.

A.6.2.5 Vary the charring temperature, in steps of 100 °C, throughout the range 500 °C to 1 400 °C taking three measurements for the calibration solution (A.6.2.4) at each step.

A.6.2.6 Calculate the mean of the three measurements attained for each temperature step. Plot a graph relating the charring temperature to the mean absorbance. Note the temperature at which the absorbance starts to decline. Subtract 50 °C from this value to obtain the optimum charring temperature.

NOTE 7 The 50 °C allowance is to accommodate any day-to-day variations in the working of the temperature measuring system.

A.6.2.7 Use the optimum charring temperature found in A.6.2.6 and vary the hold time over the range 15 s to 60 s in steps of 15 s. Take three measurements for the calibration solution (A.6.2.4) during each step. Monitor the background signal during this process. Note the time at which the background signal returns to the baseline.

A.6.2.8 Calculate the mean of the three absorbance measurements. There shall be no evidence of analyte loss (indicated by lower absorbances for the longer hold times).

A.6.2.9 Provided the condition in A.6.2.8 is satisfied, select the shortest time in which the background signal returns to the baseline (A.6.2.7). Add 10 s to this value to obtain the optimum hold time.

A.6.2.10 If the condition in A.6.2.8 is not satisfied, repeat actions A.6.2.7 to A.6.2.9 using a charring temperature which is 50 °C less than that originally selected in A.6.2.6.

NOTE 8 A slow time of 30 s and a hold time of 30 s is usually sufficient for all pretreatment reactions to occur. Short increase times may provoke loss of sample from the tube caused by explosive splatter.

A.6.3 Atomization

This step involves the production of gaseous analyte atoms inside the graphite tube. As far as is possible, matrix atoms should be absent to minimize interference.

The analyst shall determine the optimum atomization temperature and integration time experimentally using the same GAS STOP, graphite tube and measuring mode combination selected before the optimization of the charring step.

NOTE 9 Although it is possible to optimize the L'vov platform using the peak height measurement mode to achieve its full potential, the analyst should optimize the atomization step in such a manner that the conditions required for the Stabilized Temperature Platform Furnace (STPF) operation are satisfied. In addition to the use of GAS STOP and matrix modification (inherent in the procedure), the following additional conditions should be satisfied.

a) The temperature difference between the charring step and the atomization step should be as small as possible (less than 1 000 °C). This allows the furnace to approach conditions which are nearly isothermal more quickly, and reduces the amount of matrix volatilized.

b) The peak area integration measurement mode should be used.

c) There shall be zero time increase between the charring and atomization steps.

A.6.3.1 Use the optimum drying and charring conditions determined in A.6.1 and A.6.2, respectively.

A.6.3.2 Select an atomization temperature of 1 200 °C and an integration time of 20 s.

A.6.3.3 Using the same calibration solution (A.6.2.4), obtain three absorbance measurements at this atomization temperature.

A.6.3.4 Vary the atomization temperature by increasing it up to 2 000 °C in 100 °C steps. Measure the absorbance of the calibration solution during each step as directed in A.6.3.3.

A.6.3.5 Plot the mean of the three measurements obtained for each step against the atomization temperature.

A.6.3.6 Examine the graph and determine the lowest atomization temperature where maximum absorbance is obtained. Add 200 °C to this value to obtain the optimum atomization temperature.

NOTES

10 At the lowest atomization temperature giving maximum absorbance when using the peak area integration measurement mode, the peaks are broad with considerable tailing. The extra 200 °C will overcome these problems.

11 If the L'vov platform is to be used under STPF conditions, check that the difference between the optimum charring temperature and optimized atomization temperature does not exceed 1 000 °C.

A.6.3.7 Duration of the atomization step

Use the optimum temperature found in A.6.3.6 and a hold time of 10 s.

A.6.3.7.1 Instruments equipped with a VDU or fast recorder

Measure the calibration solution (A.6.2.4) and observe the atomic signal during the atomization stage. Determine the optimum hold time by adding 1 s to the time taken for the trace to return to the zero-axis of the absorbance scale.

A.6.3.7.2 Instruments without a VDU or fast recorder

Make three measurements of the calibration solution used in A.6.2.4. Calculate the mean absorbance. Repeat these measurements using progressively shorter hold times (1 s intervals) until the mean of the three measurements starts to decrease. Add 1 s to the hold time at this point to obtain the optimum hold time.

A.6.4 Cleaning step

Heat the furnace at 2 650 °C for 5 s to remove as much of the residual matrix as possible.

NOTE 12 In practice, the matrix elements that form refractory oxides and carbides cannot be completely removed, even at high temperatures.

A.7 Instrument performance criteria

The following tests shall be performed after optimization of the instruments described in A.2 to A.6, using the calibration solutions identified in 5.1, table 1 of the relevant part of ISO 11437.

A.7.1 Determination of characteristic mass, m_c

A.7.1.1 Measure the absorbance of calibration solution S1 three times, using the injection volume recommended in the procedure. Calculate the mean absorbance $\bar{A}_{S1}$.

A.7.1.2 Measure the absorbance of calibration solution S2 three times, using the injection volume recommended in the procedure. Calculate the mean absorbance $\bar{A}_{S2}$.

A.7.1.3 The characteristic mass, m_c is given by the equation:

$$m_c = \frac{\rho \times V \times 0{,}004\ 4}{\bar{A}_{S2} - \bar{A}_{S1}}$$

where

ρ is the concentration of the analyte in calibration solution S2, expressed in nanograms per millilitre;

V is the volume of the solution injected, expressed in microlitres.

A.7.2 Determination of minimum precision

A.7.2.1 Measure the absorbance of calibration solution S2 ten times, using the injection volume recommended in the relevant procedure. Record the individual absorbance readings A_{S2} and calculate the mean value $\bar{A}_{S2}$.

A.7.2.2 Calculate the standard deviation s_B for calibration solution S2 using the equation

$$s_B = \sqrt{\frac{\Sigma(A_{S2} - \bar{A}_{S2})^2}{9}}$$

A.7.2.3 Calculate the minimum precision for calibration solution S2 using the formula

$$\frac{s_B \times 100}{\bar{A}_{S2}}$$

A.7.2.4 Measure the absorbance of the most concentrated calibration solution ten times, using the injection volume recommended in the procedure. Record the individual absorbance readings A_c and calculate the mean value $\bar{A}_c$.

A.7.2.5 Calculate the standard deviation for the most concentrated calibration solution using the equation