INTERNATIONAL STANDARD

# ISO 11438-1

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# Ferronickel — Determination of trace-element content by electrothermal atomic absorption spectrometric method —

## Part 1:
## General requirements and sample dissolution

*Ferro-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 11438-1:1993(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 11438-1 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*, Sub-Committee SC 3, *Analysis of nickel and ferronickel*.

ISO 11438 consists of the following parts, under the general title *Ferronickel — 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 antimony content*
- *Part 4: Determination of tin content*
- *Part 5: Determination of tellurium content*
- *Part 6: Determination of thallium content*
- *Part 7: Determination of silver content*
- *Part 8: Determination of indium content*

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## Introduction

This part of ISO 11438 is to be used in conjunction with the other parts which specify methods for the determination of individual trace elements in ferronickel by electrothermal atomic absorption spectrometry, according to the principle of standard additions.

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

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# Ferronickel — Determination of trace-element content by electrothermal atomic absorption spectrometric method —

## Part 1:
General requirements and sample dissolution

## 1 Scope

**1.1** ISO 11438 specifies electrothermal atomic absorption methods for the determination of trace elements in ferronickel, in the specific concentration ranges shown in clause 1 of parts 2 to 8. For each element, the range of contents, in grams per tonne (g/t), corresponds to the linear part of the calibration graph of the standard additions for which the procedure may be used.

**1.2** This part of ISO 11438 specifies the general requirements for analysis by electrothermal atomic absorption spectrometry, preparation and dissolution of the test sample, general procedure, method of calculation and the procedures used for the evaluation of the repeatability and reproducibility of the individual methods specified in the other parts of ISO 11438.

## 2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 11438. 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 11438 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 648:1977, *Laboratory glassware — One-mark pipettes.*

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

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

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

ISO 8050:1988, *Ferronickel ingots or pieces — Sampling for analysis.*

## 3 Principle

Dissolution of a test portion in dilute nitric acid.

Dilution of the test solution to a known volume and injection of a small aliquot into an electrothermal atomizer.

Atomization and measurement of the absorption of the resonance line energy from the spectrum of the element being determined.

Calibration by the standard additions method:

- an initial semi-quantitative determination is carried out using a single incremental addition;
- a second quantitative determination is carried out using two incremental additions to the diluted test solution, to obtain the optimum concentration range for sensitivity and linearity.

NOTE 1 For this determination, it is necessary to use a corrector of non-specific absorption. The procedure using standard additions was selected to enable the method to be applied to ferronickel samples with widely variable iron and nickel content ratios. It also eliminates the need to find and use very pure iron for matching the test sample matrix in calibrations solutions.

## 4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696.

**4.1 High purity metals or compounds,** 99,9 % ($m/m$) minimum, as specified in the relevant part of ISO 11438.

**4.2 Nitric acid** ($HNO_3$), $\rho_{20} = 1{,}41$ g/ml.

The same bottle of acid shall be used for the entire analysis.

**4.3 Nitric acid** ($HNO_3$), $\rho_{20} = 1{,}41$ g/ml, diluted 1 + 1.

Carefully mix together a known volume of the nitric acid (4.2) with the same volume of water.

**4.4 Standard solutions.**

Prepare separately for each metal as specified in the relevant part of ISO 11438.

**4.4.1 Standard reference solution,** 1 000 mg/l of analyte.

**4.4.2 Standard solution,** 10,0 mg/l of analyte.

**4.4.3 Working standard solution,** 1,0 mg/l of analyte.

## 5 Apparatus

Glass and plastics bottles used to store all solutions shall be suitably cleaned by soaking for several hours in the dilute nitric acid (4.3) and thoroughly rinsed with water.

Ordinary laboratory apparatus, and

### 5.1 Volumetric glassware

**5.1.1 One-mark volumetric flasks,** of capacities 25 ml, 100 ml and 1000 ml, in accordance with ISO 1042, class A.

**5.1.2 Pipettes,** in accordance with ISO 648, class A.

**5.1.3 Mechanical micropipettes,** of capacities 10 µl to 30 µl.

**5.2 Atomic absorption spectrometer,** fitted with an electrothermal atomizer.

**5.2.1** The spectrometer shall be equipped with a background corrector and a rapid-recording system capable of measuring peak heights and peak areas.

**5.2.2** The electrothermal atomizer shall be fitted with a pyrolytic graphite tube. Use of a L'vov platform is recommended.

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

## 6 Sampling and sample preparation

**6.1** Sampling and preparation of the laboratory sample shall be carried out in accordance with ISO 8050.

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

**6.3** The laboratory sample shall be cleaned by washing with high purity acetone and dried in air, to eliminate any risk of contamination with oil or grease.

## 7 Procedure

### 7.1 Preparation of the test solution

**7.1.1** Weigh, to the nearest 0,001 g, 5,000 g of the laboratory sample and transfer this test portion to a 250 ml beaker. Add 50 ml of the dilute nitric acid (4.3). Cover with a watch glass and heat until effervescence ceases.

NOTE 2 Depending on the ferronickel composition, the dissolution of the test portion may not be total (carbon, silica, etc.).

**7.1.2** Heat to boiling and maintain boiling to expel nitrogen oxide vapours, then allow to cool.

**7.1.3** Filter in a 100 ml one-mark volumetric flask and wash the filter thoroughly. Make up to the mark with water and mix carefully.

**7.1.4** Proceed as directed in the relevant part of ISO 11438.

### 7.2 Blank test

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

NOTE 3 Two blank tests should be performed in parallel as a precaution if the first blank, used to plot the standard additions graph, became contaminated.

## 7.3 Determination by the standard additions method

### 7.3.1 Atomic absorption measurements

**7.3.1.1** The spectral lines for each element to be used in the analysis are specified in the relevant part of ISO 11438.

**7.3.1.2** Condition new graphite tubes as instructed by the manufacturer.

**7.3.1.3** Check the zero stability and the absence of spectral interference in the atomization device by running the preset heating programme to heat the graphite tube until it is white hot.

**7.3.1.4** Establish the optimum furnace temperature programme in accordance with the manufacturer's instructions.

**7.3.1.5** The volume injected into the atomizer shall be 10 µl to 30 µl, depending on the analyte sensitivity.

### 7.3.2 Semi-quantitative estimation of the analyte content

**7.3.2.1** Add 0 ml and 0,5 ml of the working standard solution (4.4.3) to two 25 ml one-mark volumetric flasks, each containing 10,0 ml of the test solution (7.1). Make up to the mark with water and mix thoroughly to obtain the solutions "zero" and 1, respectively.

**7.3.2.2** Atomize a preselected volume (10 µl to 30 µl) of each of these two solutions. Record the absorbance measurements $A_0$ and $A_1$ for the solution "zero" and 1, respectively.

**7.3.2.3** Calculate the semi-quantitative estimate $b$ of the analyte content in the solution "zero", as directed in 8.1.1 .

### 7.3.3 Quantitative determination of the analyte content

**7.3.3.1** Add increments of the analyte working standard solution (4.4.3) to a set of three 25 ml one-mark volumetric flasks, each containing 10,0 ml of the test solution (7.1), to obtain, after making up to the mark with water and mixing, final solutions whose analyte contents correspond to concentration $\rho_{\mathrm{Me}}$ of the solution "zero" (see 7.3.2.1) in the first flask, to concentration $\rho_{\mathrm{Me}} + b$ in the second, and concentration $\rho_{\mathrm{Me}} + 2b$ in the third.

**7.3.3.2** Add the same increments of the analyte working standard solution (4.4.3) as were used in 7.3.3.1 to another set of three 25 ml one-mark volumetric flasks, each containing 10,0 ml of the blank test solution (7.2). Make up to the mark and mix thoroughly.

**7.3.3.3** Atomize the preselected volume (10 µl to 30 µl) of the solutions resulting from the blank test (see 7.3.3.2). Record three absorbance measurements for each of the solutions.

**7.3.3.4** Atomize the preselected volume (10 µl to 30 µl) of the three solutions obtained in 7.3.3.1. Record three absorbance measurements for each of the solutions.

**7.3.3.5** Calculate the mean of the three absorbance measurements of each solution, as recorded in 7.3.3.3 and 7.3.3.4 .

### 7.3.4 Plotting of standard additions

**7.3.4.1** For the test solutions obtained in 7.3.3.1, plot the mean absorbance values as a function of the concentrations. The intercept on the x-axis corresponds to the test solution whose analyte content is unknown.

Plot the same type of graph for the blank solutions obtained in 7.3.3.2 .

NOTE 4 This procedure is applicable to the linear part of the graphs.

**7.3.4.2** Calculate the concentration $\rho_{\mathrm{Me}}$, in micrograms per litre, of the analyte in the test solution as directed in 8.1.2.

## 7.4 Number of determinations

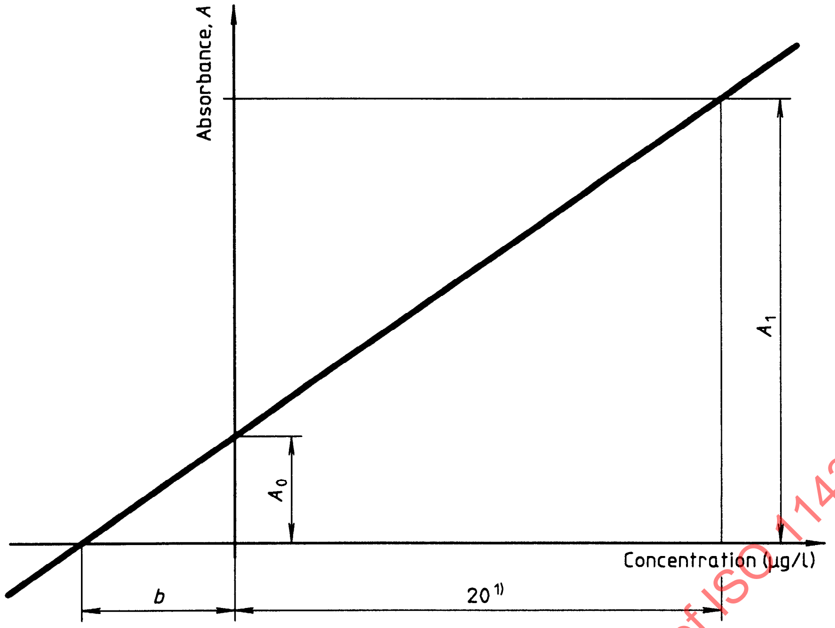
Carry out the determination at least in duplicate.

# 8 Expression of results

## 8.1 Calculation

### 8.1.1 Semi-quantitative estimation

Plot absorbances $A_0$ and $A_1$ versus concentrations of the solutions "zero" and 1, respectively, to obtain the graph shown in figure 1.



1) 20 µg/L is the value by which the analyte concentration was increased in solution 1 in comparison to solution "zero".

**Figure 1 — Graph of semi-quantitative standard additions**

Calculate $b$, the semi-quantitative estimate of the analyte concentration, in micrograms per litre, in the solution "zero", using equation (1) as follows:

$$\frac{A_1}{A_0} = \frac{b+20}{b} \qquad \ldots (1)$$

Thus

$$b = \frac{20A_0}{A_1 - A_0} \qquad \ldots (2)$$

### 8.1.2 Quantitative determination

The standard additions plots for the blank and test solutions, as obtained in 7.3.4.1, are shown in figure 2.

Calculate the concentration $\rho_{\text{Me}}$, in micrograms per litre, of the analyte in the first solution in 7.3.3.1 ("zero" solution) as follows:

$$\rho_{\text{Me}} = \frac{2b(d-d')}{D}$$

### 8.1.3 Calculation of the analyte content

Calculate the analyte content $w_{\text{Me}}$ of the test sample, in grams per tonne, using the formula

$$w_{\text{Me}} = \frac{F\rho_{\text{Me}}}{10m}$$

where

$\rho_{\text{Me}}$ is the analyte concentration, in micrograms per litre, found in the "zero" test solution, as described in 8.1.2;

$m$ is the mass, in grams, of the test portion;

$F$ is a dilution factor given in the relevant part of ISO 11438.

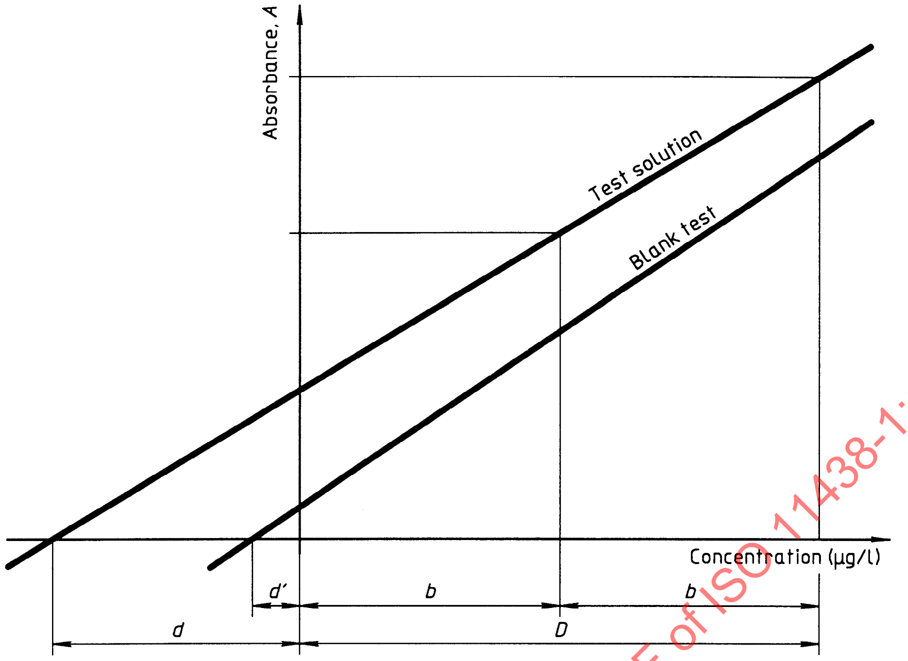
## 8.2 Precision

### 8.2.1 Laboratory tests

The methods in the subsequent parts of ISO 11438 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.



| | |
|---|---|
| $d$ | Distance between the origin and the intersection of the "test solution" line with the x-axis |
| $d'$ | Distance between the origin and the intersection of the "blank test" line with the x-axis |
| $D$ | Distance corresponding to the value of the increment $2b$, in micrograms per litre. |

**Figure 2 — Quantitative standard additions plot**

**8.2.2.2** The principle of the Cochran test is that a set of results in an outlier if the within-laboratory variance is too large in relation to 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.

**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 11438.

## 9 Note on procedure

Because of the high sensitivity of electrothermal atomic absorption, stringent precautions must be taken to clean all glassware and avoid contamination of the sample and standard and calibration solutions by foreign material and dust in the laboratory atmosphere.

## 10 Test report

The test report shall include the following information:

a) the reference to the method used;

b) the results of the analysis;

c) the number of independent replicates;

d) any unusual features noted during the analysis;

e) any operation not included in this part of ISO 11438 or regarded as optional.