INTERNATIONAL STANDARD

ISO 13898-1

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Steel and iron — Determination of nickel, copper and cobalt contents — Inductively coupled plasma atomic emission spectrometric method —

Part 1:
General requirements and sample dissolution

Aciers et fontes — Dosage du nickel, du cuivre et du cobalt — Méthode par spectrométrie d'émission atomique avec plasma induit par haute fréquence —

Partie 1: Prescriptions générales et mise en solution de l'échantillon

Reference number
ISO 13898-1:1997(E)

Foreword

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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 13898-1 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition.*

ISO 13898 consists of the following parts, under the general title *Steel and iron — Determination of nickel, copper and cobalt contents — Inductively coupled plasma atomic emission spectrometric method.*

- *Part 1: General requirements and sample dissolution*
- *Part 2: Determination of nickel content*
- *Part 3: Determination of copper content*
- *Part 4: Determination of cobalt content*

Annex A forms an integral part of this part of ISO 13898. Annexes B and C are for information only.

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Introduction

This part of ISO 13898 is to be used in conjunction with subsequent parts which specify methods for the determination of individual elements in steel and iron by inductively coupled plasma atomic emission spectrometric method (ICP-AES).

Although the analytical methods are specified as independent standards, more than one element in a single test solution can be determined.

ISO 13898 is optimized to give the highest accuracy for each individual element, which implies that the multi-element capability of the ICP technique is not utilized.

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Steel and iron — Determination of nickel, copper and cobalt contents — Inductively coupled plasma atomic emission spectrometric method —

Part 1:
General requirements and sample dissolution

1 Scope

1.1 This part of ISO 13898 specifies a method for determination of nickel, copper and cobalt contents in unalloyed steel and unalloyed iron within the ranges specified in table 1 by means of inductively coupled plasma atomic emission spectrometric method.

Table 1 - Application ranges of the elements to be determined

Element	**Application range** %(m/m)
Nickel	0,001 to 0,30
Copper	0,001 to 0,40
Cobalt	0,001 to 0,10

1.2 This part of ISO 13898 specifies the general requirements for analyses by ICP-AES, preparation and dissolution of the test portion and method of calculation and the procedures used for the evaluation of the precision data of the individual methods specified in the subsequent parts.

1.3 The International Standard specifies two alternative methods of evaluating concentrations in test solutions. One is with, the other is without the use of an internal standard.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 13898. 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 13898 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 3696:1987, *Water for analytical laboratory use - Specification and test methods.*

ISO 13898-2:1997, *Steel and iron - Determination of nickel, cobalt and copper contents - Inductively coupled plasma atomic emission spectrometric method - Part 2: Determination of nickel content.*

ISO 13898-3:1997, *Steel and iron - Determination of nickel, cobalt and copper contents - Inductively coupled plasma atomic emission spectrometric method - Part 3: Determination of copper content.*

ISO 13898-4:1997, *Steel and iron - Determination of nickel, cobalt and copper contents - Inductively coupled plasma atomic emission spectrometric method -Part 4: Determination of cobalt content.*

ISO 14284:1996, *Steel and iron - Sampling and preparation of samples for the determination of chemical composition.*

3 Principle

Dissolution of a test portion in a mixture of hydrochloric and nitric acids and dilution of the solution to known volume. If necessary, addition of scandium or yttrium as internal standard. Nebulization of the solution into an inductively coupled plasma atomic emission spectrometer and measurement of the intensity of the emitted light from each element, or with emitted light from scandium or yttrium, simultaneously. Examples of the analytical lines are given in table 2.

Table 2 - Examples of analytical lines of the elements to be determined

Element	Analytical lines nm
Nickel	231,60
Copper	324,75 or 327,40
Cobalt	228,62
Scandium	361,38 or 424,68 (internal standard)
Yttrium	371,03 (internal standard)

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 Pure iron, containing less than 0,000 1 %(*m*/*m*) of each element.

4.2 Hydrochloric acid, ρ approximately 1,19 g/ml, diluted 1+1.

4.3 Nitric acid, ρ approximately 1,40 g/ml, diluted 1+1.

4.4 Scandium internal standard solution, corresponding to 1 g of scandium per litre.

Weigh, to the nearest 1 mg, 1,534 g of scandium oxide [purity >99,98 %(*m*/*m*)]. Transfer to a 500 ml beaker and dissolve in 40 ml of nitric acid (**4.3**). Transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this internal standard solution contains 1 mg Sc.

4.5 Yttrium internal standard solution, corresponding to 1 g of yttrium per litre.

Weigh, to the nearest 1 mg, 1,270 g of yttrium oxide [purity >99,98 %(m/m)]. Transfer to a 500 ml beaker and dissolve in 50 ml of hydrochloric acid (**4.2**). Transfer into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix .

1 ml of this internal standard solution contains 1 mg Y.

4.6 Standard solutions of each element to be determined

Prepare separately for each element as specified in the appropriate part of ISO 13898.

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042 as appropriate.

Ordinary laboratory equipment and

5.1 Atomic emission spectrometer, equipped with inductively coupled plasma (ICP-AES).

The ICP-AES used will be satisfactory if after optimization according to 7.4.1 it meets the performance criteria given in 5.1.1 to 5.1.3.

The spectrometer can be either the simultaneous or the sequential type. If a sequential spectrometer can be equipped with an extra arrangement for simultaneous measurement of the internal standard line (scandium or yttrium), it can be used with the internal standard technique. If the sequential spectrometer is not equipped with this arrangement, an internal standard cannot be used and an alternative technique without internal standard can be applied.

5.1.1 Short term stability

See A.1.3.

The standard deviation of ten measurements of the absolute intensity or ratioed intensity of the emitted light of the most concentrated calibration solution is calculated for each element to be determined.

The relative standard deviation shall not exceed (0,4 %) of the mean absolute or ratioed intensities.

5.1.2 Background equivalent concentration and detection limit

See A.1.1 and A.1.2.

The background equivalent concentration (BEC) and detection limit (DL) is calculated for the analytical line in a solution containing only the analyte element.

The value shall be below the values indicated in table 3.

5.1.3 Graph linearity

See A.2.

The linearity of the calibration graph is checked by calculating the correlation coefficient.

This coefficient shall be more than 0,999.

Table 3 - Background equivalent concentration and detection limit

Analytical line nm	BEC mg/l	DL mg/l
Ni 231,60	1,5	0,04
Cu 324,75	0,8	0,02
Co 228,62	0,8	0,04

6 Sampling

Carry out sampling in accordance with ISO 14284.

7 Procedure

7.1 Test portion

Weigh, to the nearest 1 mg, 1,000 g of the test sample.

7.2 Blank test (corresponding to the zero member)

In parallel with the determination of the content and following the same procedure, carry out a blank test using the same quantities of all the reagents including the pure iron (**4.1**).

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (7.1) in a 200 ml beaker. Add 10 ml of nitric acid (**4.3**),cover the beaker with a watch-glass and heat gently until the effervescence ceases. Add 10 ml of hydrochloric acid (**4.2**) and continue the heating until complete dissolution occurs.

Cool to ambient temperature and transfer the solution quantitatively to a 200 ml one-mark volumetric flask. If the internal standard technique is used, using a pipette, add 2 ml of the scandium internal standard solution (**4.4**) or 10 ml of yttrium internal standard solution (**4.5**). Dilute to the mark with water and mix.

7.3.2 Preparation of the calibration solutions

Proceed as directed in the relevant part of ISO 13898.

7.4 Spectrometric measurements

7.4.1 Optimization of the instrument

Start the ICP-AES and let it run for at least one hour before taking any measurements.

Adjust all instrumental parameters, each gas flow-rate (outer, intermediate or central), torch position, entrance slits, exit slits, photomultiplier tube voltage, wavelength of the analytical line specified in table 2, pre-spraying time and integrating time according to the instrument manufacturer's recommended operating practices and guidelines (see annex A) while aspirating the highest concentration of calibration solution.

Prepare the software to measure the intensity, mean value and relative standard deviation of the analytical line.

Set an appropriate observation time and high voltage on the attenuators and measure the high standard to give optimum intensity reading according to the manufacturer's recommendation.

If an internal standard is used prepare the software to use the scandium line (361,38 nm) or the yttrium line (371,03 nm) as an internal standard and to calculate the ratio between the intensity of each element and scandium or yttrium intensity.

The intensity of the internal standard shall be measured simultaneously with the analyte intensity.

Check the instrument performance requirements given in 5.1.1 to 5.1.3.

7.4.2 Measurements of the emitted intensities

If the absolute intensities are to be measured, the temperatures of all solutions shall be within 1 °C of each other. Filter all solutions through a medium texture filter paper. Discharge the first 2 ml to 3 ml.

Measure the absolute intensity or intensity ratio of the analytical line beginning with the lowest calibration solution (zero member).

Continue with two or three unknown test solutions, then the next lowest calibration solution, two or more unknown solutions and so on. In this way all unknown test solutions are measured with the same time period as the calibration solutions, minimising any possible drift between calibration and unknown test solutions.

For each solution make five integrations and check that the short term stability is the same as specified in 5.1.1 and calculate the mean intensity or the mean ratioed intensity for each solution.

Subtract the mean absolute intensity or the mean ratioed intensity (I_0) of the zero member from the mean absolute intensity or the mean ratioed intensity (I_i) of each solution giving the net absolute intensity or the net ratioed intensity (I_N):

$$I_N = I_i - I_0$$

7.4.3 Preparation of the calibration graph

U Use an electronic calculator to make a linear regression through the points with the net intensities or the net intensity ratios on the Y-axis and the concentration, expressed as micrograms per millilitre, of each element to be determined in the calibration solution on the X-axis.

Calculate the correlation coefficient. The coefficient shall meet the specification given in 5.1.3.

8 Expression of results

8.1 Method of calculation

Using the electronic calculator convert the absolute intensity or ratioed intensity into the concentration, ρ_e, expressed as micrograms per millilitre, of the element in the test solution, by using the calibration graph (see 7.4.3).

The content of the element, w_e, expressed as a percentage by mass, is given by the formula:

$$w_e = \frac{(\rho_{e,1} - \rho_{e,0}) \times 200}{10^6} \times \frac{100}{m} + w_{e,0} = \frac{(\rho_{e,1} - \rho_{e,0})}{50m} + w_{e,0}$$

where

$\rho_{e,1}$ is the concentration, expressed in micrograms per millilitre, of the element in the test solution;

$\rho_{e,0}$ is the concentration, expressed in micrograms per millilitre, of the element in the blank test;

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

$w_{e,0}$ is the content, expressed as a percentage by mass, of the element in the pure iron used.

8.2 Precision

A planned trial of these methods was carried out. The test samples used are listed in annex B.

The precision shall be as specified in the relevant part of ISO 13898.

9 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis;

b) the method used by reference to this part of ISO 13898;

c) the results and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this part of ISO 13898, or any optional operation which may have influenced the results.

Annex A
(normative)

Procedures for the determination of instrumental criteria

A.1 Determination of detection limit (DL), background equivalent concentration (BEC) and short term stability

For the preparation of standard methods of analysis using ICP-AES, these criteria shall be decided by the working group in charge of the inter-laboratory test results.

Switch on the apparatus (plasma and electronics) and allow to stabilize. Stabilization time may vary from instrument to instrument and therefore cannot be exactly specified here. As a guideline, modern instrumentation should be stable within fifteen minutes under ordinary laboratory conditions. It may be verified by a further measurement of short term stability on completion of the tests given below.

Prepare three solutions containing the analyte elements of interest at concentration levels of zero, 10 x detection limit and 1 000 x detection limit. These solutions should also contain concentrations of acids, fusion agents and matrix elements similar to those in the samples to be analysed. Detection limits for these reference solutions may be laboratory estimates or the specified values in the method.

Spray the 1 000 x DL solution and wait about ten seconds after the solution arrives in the plasma to ensure stable nebulization.

Set operating and instrumental conditions for the element in question.

Position carefully on the maximum peak at the selected wavelength and select an appropriate photomultiplier gain (if not automatic) to ensure that the measured intensity is to four significant digits. Set an integration time of 3 s.

A.1.1 Determination of detection limit

Detection limits may be determined by different methods depending on the type of instrument. Normally the following procedure can be used.

Spray the blank solution for approximately 10 s.

Take ten readings at the pre-set integration time.

Spray the 10 x DL solution for about 60 s.

Take ten readings at the pre-set integration time.

From the intensity readings obtained for the blank and the 10 x DL solutions, calculate the mean intensities X_1 and X_b and the standard deviation of the blank S_b.

Calculate the net mean intensity for the 10 x DL solution

$$X_{n1} = X_1 - X_b$$

Calculate the detection limit for the element considered according to the following expression:

$$\mathrm{DL} = 3S_b(C_1 / X_{n1})$$

where C_1 is the concentration, expressed as micrograms per millilitre, of the 10 x DL solution.

A.1.2 Determination of background equivalent concentration

Calculate the background equivalent concentration (BEC) according to the expression:

$$\text{BEC} = \left(X_b / X_{n1}\right)C_1$$

A.1.3 Determination of short term stability

Spray the 1 000 x DL solution for about ten seconds. Take ten readings at the predetermined integration time.

From these and measurements taken previously on the 10 x DL solution calculate respectively the mean net intensities X_{n1} and X_{n2} and also the corresponding standard deviations S_1 and S_2.

Calculate the short term stability of the emission signal for the two concentration levels.

$$\text{RSD}_1 = \left(S_1 / X_{n1}\right) 100\ \%$$

$$\text{RSD}_2 = \left(S_2 / X_{n2}\right) 100\ \%$$

If several sets of readings are available, calculate the mean RSD for each set.

$$\text{Mean RSD} = \text{total RSD}/n$$

A.2 Calculation of calibration curves

Fitting the best straight line to a set of points (linear regression) simply involves finding values for a and b in the equation

$$I = a + bC$$

where

I is the measured absolute or ratioed intensities;

C is the concentration of the calibration solutions.

The mathematical operation is known as the method of least squares. The slope of the curve (b) and the intercept (a) are given by.

$$b = S_{CI}/S_{CC}$$

$$a = \overline{I} - b\overline{C}$$

in which

$$S_{CI} = S\left(C - \overline{C}\right)\left(I - \overline{I}\right)$$

$$S_{CC} = S\left(C - \overline{C}\right)^2$$

where

$\overline{C}$ is the mean of the concentrations C;

$\overline{I}$ is the mean of the intensities I.