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Steel — Determination of high cobalt content — Potentiometric titration method after separation by ion exchange

Aciers — Dosage du cobalt en fortes teneurs — Méthode par titrage potentiométrique après séparation par échange d'ions

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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 11653 was prepared by Technical Committee ISO/TC 17, *Steel,* Subcommittee SC 1, *Methods of determination of chemical composition.*

Annexes A and B of this International Standard are for information only.

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Steel — Determination of high cobalt content — Potentiometric titration method after separation by ion exchange

1 Scope

This International Standard specifies a method for the determination of cobalt in steel using a potentiometric titration method after separation by ion exchange.

The method is applicable to a cobalt content of between 5,0 % (*m/m*) and 17,0 % (*m/m*).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard 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:— [1], *Laboratory glassware — One-mark volumetric flasks.*

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

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions.*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method.*

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 nitric and hydrochloric acids.

Separation of cobalt from interfering elements by selective elusion from an anion exchange column using hydrochloric acid.

1) To be published. (Revision of ISO 1042:1983)

Oxidation with perchloric acid. Removal of dissolved chlorine and oxygen with a stream of nitrogen.

Addition of the test solution to a solution containing ammonium citrate, ammonium hydroxide and an excess of potassium hexacyanoferrate (III) standard solution and titration of the excess with a standard cobalt solution using potentiometric end-point detection.

4 Reagents

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

4.1 Hydrochloric acid, ρ about 1,19 g/ml.

4.2 Hydrochloric acid, ρ about 1,19 g/ml, diluted 7+5.

4.3 Hydrochloric acid, ρ about 1,19 g/ml, diluted 2+3.

4.4 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1+2.

4.5 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1+19.

4.6 Nitric acid, ρ about 1,40 g/ml.

4.7 Perchloric acid, ρ about 1,67 g/ml (see note 1).

NOTE 1 Perchloric acid (ρ about 1,54 g/ml) may also be used. 100 ml of perchloric acid (ρ about 1,67 g/ml) is equivalent to 127 ml of perchloric acid (ρ about 1,54 g/ml).

4.8 Ammonium hydroxide, ρ about 0,89 g/ml.

4.9 Ammonium citrate, solution, corresponding to 200 g per litre. Dissolve 100 g of citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) in approximately 250 ml of water. Cautiously, and with constant stirring, add 170 ml of ammonium hydroxide (4.8). After cooling, dilute to 500 ml with water and mix.

4.10 Cobalt, standard solution, corresponding to 2,00 g of cobalt per litre.

Weigh, to the nearest 0,001 g, 2,000 g of cobalt metal [minimum purity 99,95 % (*m*/*m*)] (see note 2). Transfer to a 600 ml beaker and dissolve in 40 ml of nitric acid (ρ about 1,40, diluted 1+1). Heat to complete dissolution, boil gently to expel oxides of nitrogen, cool and transfer to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix. Store in a polyethylene bottle.

1 ml of this solution contains 2,00 mg of Co.

NOTE 2 High purity cobalt powder should not be used because surface oxygen adversely affects accuracy. For example rod, shot or wire should be used.

4.11 Potassium hexacyanoferrate (III), standard volumetric solution.

4.11.1 Preparation of the standard volumetric solution.

Dissolve 5,6 g of potassium hexacyanoferrate(III) [$K_3Fe(CN)_6$] in 250 ml of water. Filter the solution through a pulp pad and wash thoroughly with water. Transfer to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix. Refilter and standardize this solution as specified in 4.11.2 immediately prior to use.

4.11.2 Standardization of the standard volumetric solution.

Transfer two portions of 20,0 ml of the cobalt standard solution (4.10) to two beakers. Treat the solution according to 7.2.3 and 7.2.4.

Calculate the standardization factor T for each sample according to the equation

$$T = \frac{V_1 + V_2}{V_3}$$

where

V_1 is the volume, in millilitres, of the cobalt standard solution (4.10) taken in 4.11.2 (= 20,0 ml);

V_2 is the volume, in millilitres, of the cobalt standard solution (4.10) used in the factor titration ;

V_3 is the volume, in millilitres, of the potassium hexacyanoferrate (III) solution used in the titration ;

T is the required factor, which will be less than 1 if the solution is below theoretical strength etc. Calculate the average of the two determined T values.

4.12 Ion exchange resin

Use an anion exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a nominal crosslinkage of 8 %, and 200 to 400 nominal mesh size. To remove those beads greater than about 180 µm in diameter, as well as the excessively fine beads, treat the resin as follows.

Transfer a supply of the resin to a beaker, cover with water, and allow sufficient time (at least 30 min) for the beads to undergo maximum swelling. Place a 180 µm sieve, 150 mm in diameter, over a 2 litre beaker. Prepare a thin slurry of the resin and pour it onto the sieve. Wash the fine beads through the sieve using a small stream of water. Discard the beads retained on the sieve periodically, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 ml of resin to a 400 ml beaker. Add 200 ml of hydrochloric acid (4.5), stir vigorously, allow the resin to settle for 4 min to 6 min, decant 150 ml to 175 ml of the suspension, and discard it. Repeat the treatment with hydrochloric acid (4.5) twice more and reserve the coarser resin for the column preparation.

Prepare the column as follows.

Place a 10 mm to 30 mm layer of glass wool or poly (vinyl chloride) plastic fibre in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately 140 mm. Place a 20 mm layer of glass wool or poly (vinyl chloride) plastic fibre at the top of the resin bed to protect it from being carried into suspension when the solutions are added. While passing a minimum of 35 ml of hydrochloric acid (4.2) through the column, with the hydrostatic head 100 mm above the top of the resin bed, adjust the flow rate to not more than 3,0 ml per min. Drain to 10 mm to 20 mm above the top of the resin bed and then close the lower stopcock.

5 Apparatus

During the analysis, unless otherwise stated, use only ordinary laboratory apparatus.

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

5.1 Potentiometric titration apparatus

5.1.1 Indicator electrode, of bright platinum, which shall be kept in a clean, highly polished condition. It shall be cleaned by dipping in the nitric acid (4.6) and rinsed with water prior to use.

5.1.2 Reference electrode, of silver/silver chloride, calomel or mercury(I) sulfate. The manufacturer's instructions on the care and maintenance of these electrodes shall be followed.

5.1.3 Titration assembly, consisting of a 400 ml beaker, two 50 ml burettes complying with the requirements of ISO 385-1, class A, and a magnetic stirrer.

5.1.4 High-impedance electronic voltmeter: Normally a pH-meter can be used as a voltmeter. Commercial automatic titrators or potentiographs have an advantage over manual systems in that the titration curve is plotted and the end-point can be evaluated by interpolation of the curve rather than by calculation from the first or second derivative (see clause 9).

5.2 Ion exchange column

Approximately 25 mm in diameter and 300 mm long, tapered at one end, and provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. A reservoir for the eluants may be added at the top of the column.

6 Sampling

Carry out sampling in accordance with ISO 14284.

7 Procedure

WARNING – Fuming perchloric acid is a powerful oxidant and can cause an explosive mixture when in contact with ammonia, nitrous fumes or organic matter. All evaporation must be carried out in fume cupboards suitable for use with perchloric acid.

7.1 Test portion

Weigh, to the nearest 0,000 1 g, 0.5 g of the test sample.

7.2 Determination

7.2.1 Preparation of the test solution

Place the test portion (7.1) in a 150 ml beaker. Add 20 ml of a mixture of five parts of hydrochloric acid (4.1) and one part of nitric acid (4.6) (see note 3). Cover the beaker and digest at 60 °C to 70 °C until the test portion is decomposed. Rinse and remove the cover. Place a ribbed cover glass on the beaker, and evaporate the solution nearly to dryness, but do not bake. Cool, add 20 ml of hydrochloric acid (4.2), and digest at 60 °C to 70 °C until the salts are dissolved (approximately 10 min) (see note 4).

NOTES

3 Other ratios and concentrations of acids, with or without the addition of hydrofluoric acid, are used for the decomposition of special grades of alloys.

4 Some tungsten and/or molybdenum oxides can remain undissolved. They are eliminated later by filtration.

7.2.2 Separation by ion exchange resin

Cool to room temperature and filter the solution through a close-texture filter paper and wash thoroughly with water. Transfer the solution to the ion exchange column. Place a beaker under the column and open the lower stopcock. When the solution reaches a level 10 mm to 20 mm above the resin bed, rinse the original beaker with 5 ml to 6 ml of hydrochloric acid (4.2) and transfer the rinsings to the column. Repeat this at 2 min intervals until the beaker has been rinsed four times. Wash the upper part of the column with hydrochloric acid (4.2) 2 or 3 times and allow the level to drop to 10 mm to 20 mm above the resin bed each time. Maintain the flow rate at not more than 3,0 ml/min and add hydrochloric acid (4.2) to the column until a total of 175 ml to 185 ml of solution (test solution and

washings) containing mainly chromium, manganese and nickel is collected (see note 4). When the solution in the column reaches a level 10 mm to 20 mm above the resin bed, discard the eluate and then use a 400 ml beaker for the collection of the cobalt eluate.

To prevent any loss of cobalt, it is essential that the leading edge of the cobalt band is not allowed to proceed any further than 25 mm from the bottom of the resin. Normally, when the cobalt has reached this point in the column, chromium, manganese and nickel have been removed. Elution can be stopped at this point, although the total volume collected may be less than 175 ml.

Add hydrochloric acid (4.4) to the column and collect 165 ml to 175 ml of the solution while maintaining the 3,0 ml/min flow rate. Keep this solution. If the test solution does not contain more than 0,200 g of iron, precondition the column for the next samples as follows. Drain the remaining solution in the column to 10 mm to 20 mm above the resin bed, pass 35 ml to 50 ml of hydrochloric acid (4.2) through the column until 10 mm to 20 mm of the solution remains above the resin bed, then close the lower stopcock. If the test solution contains more than 0,200 g of iron, the ion exchange columns have, after each elution, to be regenerated with approximately 500 ml of hydrochloric acid (4.3) in order to wash out iron(II) and thereafter with approximately 200 ml of hydrochloric acid (4.5) to wash out iron(III).

7.2.3 Treatment of the eluated solution

Add 30 ml of nitric acid (4.6) and 15 ml of perchloric acid (4.7) to the solution from the previous paragraph and evaporate, producing fumes of perchloric acid until almost completely dry (1 ml to 2 ml remaining) (see note 5). Cool, add 25 ml to 35 ml of water, boil for 1 min to 2 min, cool and add 10 ml of ammonium citrate solution (4.9).

NOTE 5 Insufficient dryness leads to precipitation after adding potassium hexacyanoferrate(III) solution (4.11).

Cool the solution and pass a rapid stream of nitrogen through it for 10 min to 15 min to remove dissolved chlorine and oxygen. Cool to room temperature.

7.2.4 Titration

Using a 50 ml burette, transfer to a 400 ml beaker, a sufficient volume of potassium hexacyanoferrate(III) solution (4.11) to oxidize the cobalt plus an excess of about 5 ml. Record the total volume of potassium hexacyanoferrate(III) solution (4.11) added (V_4). The volume V_4 of potassium hexacynoferrate(III) solution (4.11) can be estimated by the following empirical equation:

$$V_4 = \frac{x \cdot w \times 0{,}055\ 8}{11{,}2} \times 1\ 000 + \text{excess}$$

where

x is the expected content of cobalt, expressed as a percentage by mass, in the sample ;

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

0,005 8 is a recalculation factor to $K_3Fe(CN)_6$;

11,2 is the concentration, in grams per litre, of $K_3Fe(CN)_6$ (see 4.11.1) ;

1 000 is a recalculation factor to millilitres.

Add 50 ml of ammonium hydroxide solution (4.8) and cool. Place the beaker on the magnetic stirrer of the titration assembly (5.1.3) and start the stirrer.

Transfer the alloy solution quantitatively to the 400 ml beaker while stirring continuously. Immerse the indicator and reference electrodes (5.1.1 and 5.1.2) in the solution. Titrate slowly with the cobalt standard solution (4.10) until the end-point is approached. Continue the titration in 0,1 ml or one drop increments and record the burette and potential

readings when equilibrium is reached after each incremental addition. Continue the titration through the end-point. Determine the end-point by interpolation of the titration curve. Determine the volume (V_5) corresponding to the end-point (see clause 9).

8 Expression of results

8.1 Method of calculation

The cobalt content, w_{Co}, expressed as a percentage by mass, is given by the equation

$$w_{Co} = \frac{(V_4 \times T - V_5) \times \rho_{Co}}{m \times 10^3} \times 100$$

$$= \frac{(V_4 \times T - V_5) \times \rho_{Co}}{m} \times 0{,}1$$

where

V_4 is the volume, in millilitres, of the potassium hexacyanoferrate(III) solution (4.11) used in the determination ;

V_5 is the volume, in millilitres, of the cobalt standard solution (4.10) indicated by the calculated end-point (see 7.2.4) ;

T is the standardization factor of the potassium hexacyanoferrate(III) solution as calculated in 4.11.2. ;

ρ_{Co} is the concentration, in milligrams per millilitre, of the cobalt standard solution (4.10) ;

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

8.2 Precision

A planned trial of this method was carried out by eight laboratories in four countries, at eight levels of cobalt content, each laboratory making three determinations (see notes 6 and 7) of cobalt content on each level.

NOTES

6 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725-1; i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

7 The third determination was carried out at a different time (on a different day) by the same operator as in note 6, using the same apparatus with a new calibration.

The test samples used and mean/precision results obtained are listed in table A.1.

The results obtained were treated statistically in accordance with ISO 5725, Parts 1, 2 and 3.

The data obtained showed a logarithmic relationship between cobalt content and repeatability limit (r) and reproducibility limits (R and R_w) of the test results (see note 8) as summarized in table 1. The graphical representation of the data is shown in annex B.

Table 1 — Results for repeatability limit and reproducibility limits

Cobalt content	Repeatability limit	Reproducibility limits	
% (*m*/*m*)	*r*	*R*	R_w
5,0	0,051	0,202	0,061
10,0	0,067	0,285	0,079
15,0	0,079	0,348	0,093
17,0	0,084	0,365	0,098

NOTE 8 From the two values obtained on day 1, the repeatability limit (r) and reproducibility limit (R) were calculated using the procedure specified in ISO 5725-2. From the first value obtained on day 1 and the value obtained on day 2, the within -laboratory reproducibility limit (R_w) was calculated using the procedure given in ISO 5725-3.

9 Note on determination of the end-point

The accurate and reproducible evaluation of the potentiometric end-point differs from the normal visual end-point detection in that the titration is normally carried out well past the equivalence point. The classical S-shaped titration curve shows a steep rise of the potential in the vicinity of the equivalence point. The mid-point of the steep portion of the curve is usually the inflection point and as such coincides with the equivalence point for a symmetrical titration curve. For an asymmetrical titration curve where the true equivalence point does not coincide with the mid-point, the change in potential is usually large enough to make the titration error negligible.

Manual potentiometric titrations are slow as the equilibrium potential must be established and recorded after each addition of titrant. In the vicinity of the equivalence point, the titrant must be added in small increments and at least three measurements must be taken after a large change in potential has been observed. About six drops of ethylene-diamine can be added to the titration to improve the sharpness of the end-point and speed up the manual titration. From the data recorded, the end-point can be determined by plotting the titration curve and interpolating the end-point from the steep part of the curve. However, it is more desirable to calculate the first derivative (dE/dV), which has a maximum at the equivalent point. The exact value of the end-point volume can be determined by calculation of the second derivative of the potential, with respect to volume, which must be numerically equal to zero. If equal increments of titrant are added just before and after the large potential change, it is easy to see that the second derivative function changes sign between two additions. Thus, it must have passed through zero at some point which is determined by interpolation.

There is a great advantage in using automatic titrates which record the titration curve directly or process the data in a digital form. Such instrumentation is recommended for this International Standard.

10 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 the analysis ;

b) the method used, by reference to this International Standard ;

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 International Standard, or any optional operation which may have influenced the results.