INTERNATIONAL STANDARD

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Steel and iron — Determination of nitrogen content — Titrimetric method after distillation

Acier et fonte — Dosage de l'azote — Méthode titrimétrique après distillation

Reference number
ISO 10702:1993(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 10702 was prepared by Technical Committee ISO/TC 17, *Steel*, Sub-Committee SC 1, *Methods of determination of chemical composition.*

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

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Steel and iron — Determination of nitrogen content — Titrimetric method after distillation

1 Scope

This International Standard specifies a method for the determination of nitrogen in steel and iron, finishing with a titration.

The method is applicable to nitrogen contents from 0,002 % (*m/m*) to 0,5 % (*m/m*). However, the method is not applicable to samples containing silicon nitride.

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 377-2:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 2: Samples for the determination of the chemical composition.*

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 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 hydrochloric acid followed by oxidation with hydrogen peroxide.

Fuming of the acid-insoluble residue in sulfuric acid with potassium sulfate and copper(II) sulfate.

Distillation of the solution made alkaline with sodium hydroxide, and collection of ammonia in a receiver containing orthoboric acid solution.

Titration of the ammonium ion with amidosulfuric acid.

4 Reagents

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

4.1 Potassium sulfate.

4.2 Copper(II) sulfate pentahydrate, $CuSO_4.5H_2O$.

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

4.4 Sulfuric acid, ρ about 1,84 g/ml.

4.5 Orthoboric acid, 1 g/l solution.

Dissolve 1 g of orthoboric acid (H_3BO_3) in water and dilute to 1 litre.

4.6 Orthoboric acid, 5 g/l solution.

Dissolve 5 g of orthoboric acid (H_3BO_3) in water and dilute to 1 litre.

4.7 Sodium hydroxide, 500 g/l solution.

Dissolve 500 g of sodium hydroxide pellets in water. Cool and dilute to 1 litre.

4.8 Hydrogen peroxide, 300 g/l solution.

4.9 Amidosulfuric acid, standard volumetric solution A.

Keep amidosulfuric acid ($HOSO_2NH_2$), of primary standard substance grade for volumetric analysis, in an evacuated desiccator containing sulfuric acid for 48 h.

Dissolve 3,466 g of predried amidosulfuric acid in water, transfer the solution to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution corresponds to 0,500 mg of nitrogen.

4.10 Amidosulfuric acid, standard volumetric solution B.

Transfer 200,0 ml of the amidosulfuric acid, standard volumetric solution A (4.9) to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution corresponds to 0,100 mg of nitrogen.

4.11 Mixed indicator.

Dissolve 0,125 g of 4′-dimethylaminoazobenzene-2-carboxylic acid (methyl red, $C_{15}H_{15}N_3O_2$) and 0,083 g of methylene blue n-hydrate ($C_{16}H_{18}ClN_3S.nH_2O$, $n = 2$, 3 or 4) in 100 ml of ethanol [99,5 % (V/V)].

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Volumetric glassware, of grade A, in accordance with ISO 385-1, ISO 648 or ISO 1042, as appropriate.

Reserve glassware exclusively for this work. Clean it with chromic acid/sulfuric acid solution and wash thoroughly with water before use.

5.2 Steam distillation apparatus (see annex A). Suitable forms of apparatus are illustrated in figures A.1 and A.2.

5.3 Burette, of capacity 10 ml, with 0,02 ml graduations.

6 Sampling

Carry out sampling in accordance with ISO 377-2 or appropriate national standards for steel and iron.

7 Procedure

CAUTION — Carry out operations in a well-ventilated room away from all sources of nitrogen compounds.

7.1 Test portion

Weigh, to the nearest 1 mg, the mass given below as a function of the expected nitrogen content:

a) nitrogen contents from 0,002 % (m/m) to 0,015 % (m/m), mass of test portion approximately 5,0 g;

b) nitrogen contents from 0,015 % (m/m) to 0,03 % (m/m), mass of test portion approximately 2,5 g;

c) nitrogen contents from 0,03 % (m/m) to 0,5 % (m/m), mass of test portion approximately 1,0 g.

7.2 Blank test

In parallel with the determination and following the same procedure, carry out duplicate blank tests using the same quantities of all the reagents in the determination, as specified in 7.4, but replacing the test portion with 2,5 g and 5,0 g respectively of a steel of low nitrogen content [about 0,002 % (m/m)].

Let x ml and y ml be the titration values of the 2,5 g and 5,0 g portions respectively. The blank value V_2 is given by $(2x - y)$ ml.

It is essential that blank values be controlled at consistently low and reproducible levels. It is recommended that duplicate blanks be run with each batch of tests and that the mean value be used as the basis for calculation. High or divergent blank values are unacceptable and steps should be taken to trace the source of contamination by checking the cleanliness of the atmospheric air in the test room, the glassware and the steam distillation apparatus and the quality of the water and individual reagents before proceeding further. In particular, hydrogen peroxide requires careful selection.

It is recommended that the mean value of duplicate blank values and the difference between them do not exceed 1,3 ml and 0,2 ml, which are equivalent to 0,13 mg and 0,02 mg of nitrogen, respectively.

7.3 Preparation of steam distillation apparatus (see figure A.1 or A.2)

Place 2 litres of water in the steam generator (a). Add 120 ml of sodium hydroxide solution (4.7) to the distillation flask (b) through funnel (f) and rinse with water. With taps 1 and 3 open and tap 2 closed, heat the water in the steam generator (a) to boiling and allow steam to escape through the inlet (e). Close tap 1 and allow steam to escape from the open drainage tube of a trap (g) for about 1 min.

Place a 300 ml conical beaker containing 20 ml of orthoboric acid solution (4.6) under the condenser (c) and raise it until the condenser tip is immersed in the orthoboric acid solution. Close taps 1, 2 and 3, and allow steam to pass through a distillation flask (b) and the condenser (c) until about 100 ml of the distillate has been collected.

Lower the beaker until the condenser tip is uncovered, then collect a further 10 ml of distillate. Rinse the condenser tip with water and titrate with amidosulfuric acid standard solution B (4.10) in the presence of 3 drops of mixed indicator (4.11). If the titration value is greater than that recommended in 7.2, distill and titrate a further 110 ml of the distillate. If this titration value is still above that recommended in 7.2, a source of contamination is probable and determinations should not be carried out until this has been ascertained and eliminated.

Switch off the heat source to the steam generator (a). When the solution in the distillation flask (b) has siphoned into the trap (g), open tap 3 and discharge into the waste receiver.

7.4 Determination

7.4.1 Dissolution of the test portion

Place the test portion (7.1) in a 500 ml conical flask. Add 70 ml of hydrochloric acid (4.3), cover with a funnel and heat until solvent action has apparently ceased. Carefully add 5 ml of hydrogen peroxide solution (4.8) and continue heating until solvent action has ceased.

Filter the solution through a filter paper (see note 1) and collect the filtrate in a 300 ml beaker. Rinse the flask with water, remove adherent particles with a rubber-tipped rod, and filter the rinsings through the same filter paper. Wash the filter paper with a minimum quantity of water. Keep the filtrate and the washings in the beaker. (This is test solution S_1.)

NOTE 1 A medium-texture filter paper is suitable for samples which do not contain fine nitrides. However, a close-texture filter paper is recommended if the sizes of nitrides are unknown. Vacuum filtration, using a nuclepore filter with pore size less than 0,2 µm, is necessary for samples which are known to contain fine nitrides such as boron nitride.

7.4.2 Treatment of the insoluble residue

Transfer the filter paper and the insoluble residue to the original 500 ml conical flask and add 10 g of potassium sulfate (4.1), 1 g of copper(II) sulfate pentahydrate (4.2) and 20 ml of sulfuric acid (4.4).

Heat gently until the water in the flask has evaporated, cover the flask with a funnel and continue fuming (at 335 °C to 350 °C) for 60 min to decompose the residue. Cool to room temperature, add 50 ml of water and boil thoroughly for 5 min to remove sulfur dioxide from the solution. (This is test solution S_2.)

7.4.3 Steam distillation (see figure A.1 or A.2)

With tap 2 open, add 120 ml of sodium hydroxide solution (4.7) to the distillation flask (b) through the funnel (f) and rinse with a minimum quantity of water. Transfer 20 ml of orthoboric acid solution (4.5 or 4.6), depending on the expected nitrogen content of the test sample as shown in table 1, to a 300 ml conical beaker.

Table 1

Nitrogen contents % (*m/m*)	**Orthoboric acid solution used**	**Amidosulfuric acid standard volumetric solution used**
0,002 to 0,1	1 g/l solution (4.5)	Solution B (4.10)
0,1 to 0,5	5 g/l solution (4.6)	Solution A (4.9)

Place the beaker under the condenser (c) and raise it until the condenser tip is immersed in orthoboric acid solution. Add test solutions S_1 and S_2 (see 7.4.1 and 7.4.2) to the distillation flask (b) through the funnel (f) and rinse the flask with a minimum quantity of water.

With taps 1, 2 and 3 closed, allow steam to pass through the distillation flask (b) and condenser (c) until about 120 ml of the distillate has collected.

Lower the beaker until the condenser tip is uncovered, then collect a further 10 ml of the distillate. Rinse the condenser tip with water.

Switch off the heat source to the steam generator (a). When the solution in the distillation flask (b) has siphoned into the trap (g), open tap 3 and discharge into the waste receiver. The apparatus is now ready for the next determination.

7.4.4 Titration

Add 3 drops of mixed indicator (4.11) to the beaker containing the distillate. Titrate with amidosulfuric acid solution A or B (4.9 or 4.10), depending on the expected nitrogen content of the test sample as shown in table 1, to a red-purple end point of the mixed indicator.

8 Expression of results

8.1 Method of calculation

The nitrogen content, w_N, expressed as a percentage by mass, is given by the equation

$$w_N = \frac{(e_{N,1} \times V_1) - (e_{N,2} \times V_2)}{m \times 10^3} \times 100$$

$$= \frac{(e_{N,1} \times V_1) - (e_{N,2} \times V_2)}{10m}$$

where

$e_{N,1}$ is the nitrogen equivalent, in milligrams per millilitre, of the amidosulfuric acid standard volumetric solution used in the titration;

$e_{N,2}$ is the nitrogen equivalent, in milligrams per millilitre, of the amidosulfuric acid standard volumetric solution used in the blank test (7.2);

V_1 is the volume, in millilitres, of the amidosulfuric acid standard volumetric solution consumed in the titration;

V_2 is the volume, in millilitres, of the amidosulfuric acid standard volumetric solution consumed in the blank test;

m is the mass, in grams, of the test portion (7.1).

8.2 Precision

A planned trial of this method was carried out by ten laboratories in five countries, at eight levels of nitrogen, each laboratory making three determinations (see notes 2 and 3) of nitrogen content at each level.

The test samples used are listed in table B.1, and the results obtained are listed in table B.2.

The results obtained were treated statistically in accordance with ISO 5725, using the data obtained from the samples containing eight levels of nitrogen.

The data obtained showed a logarithmic relationship between nitrogen content and repeatability (r) and reproducibility (R and R_w) of the test results (see note 4), as summarized in table 2. The graphical representation of the data is shown in figure C.1.

NOTES

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

3 The third determination was carried out at a different time (on a different day) by the same operator as in note 2, using the same apparatus with a new calibration.

4 From the results obtained on day 1, the repeatability (r) and the reproducibility (R) were calculated using the procedure specified in ISO 5725. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_w) was calculated.

Table 2

Nitrogen content % (m/m)	**Repeatability** r	**Reproducibility** R	R_w
0,002 0	0,000 2	0,000 7	0,000 5
0,005 0	0,000 4	0,001 2	0,000 8
0,010 0	0,000 6	0,001 9	0,001 2
0,020 0	0,000 9	0,002 9	0,001 7
0,050 0	0,001 6	0,005 1	0,002 9
0,100	0,002 4	0,007 8	0,004 2
0,200	0,003 5	0,012 0	0,006 0
0,500	0,006 0	0,021 2	0,009 9

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 International Standard;

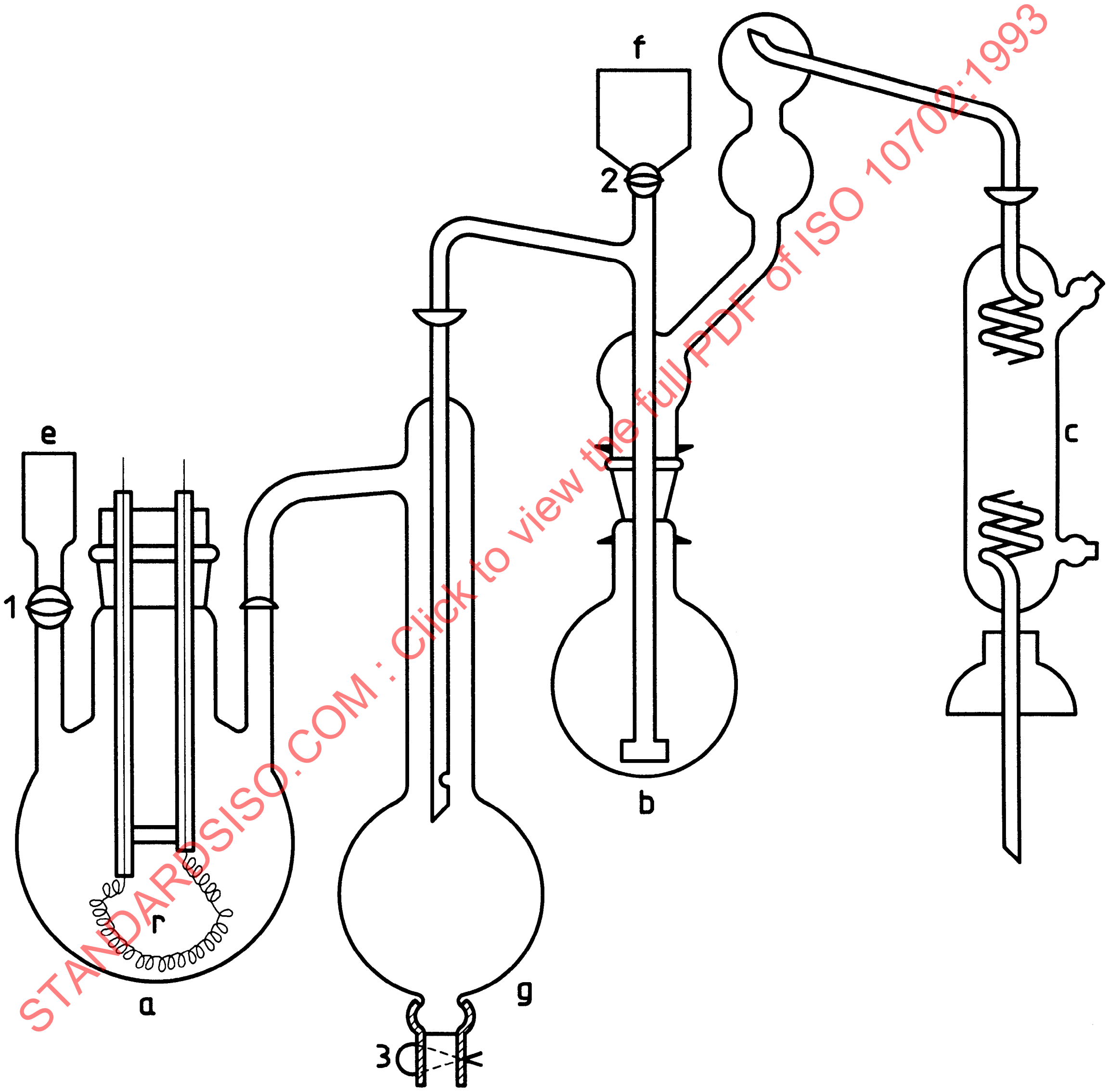
c) the results, and the form in which they are expressed;

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.

Annex A
(normative)

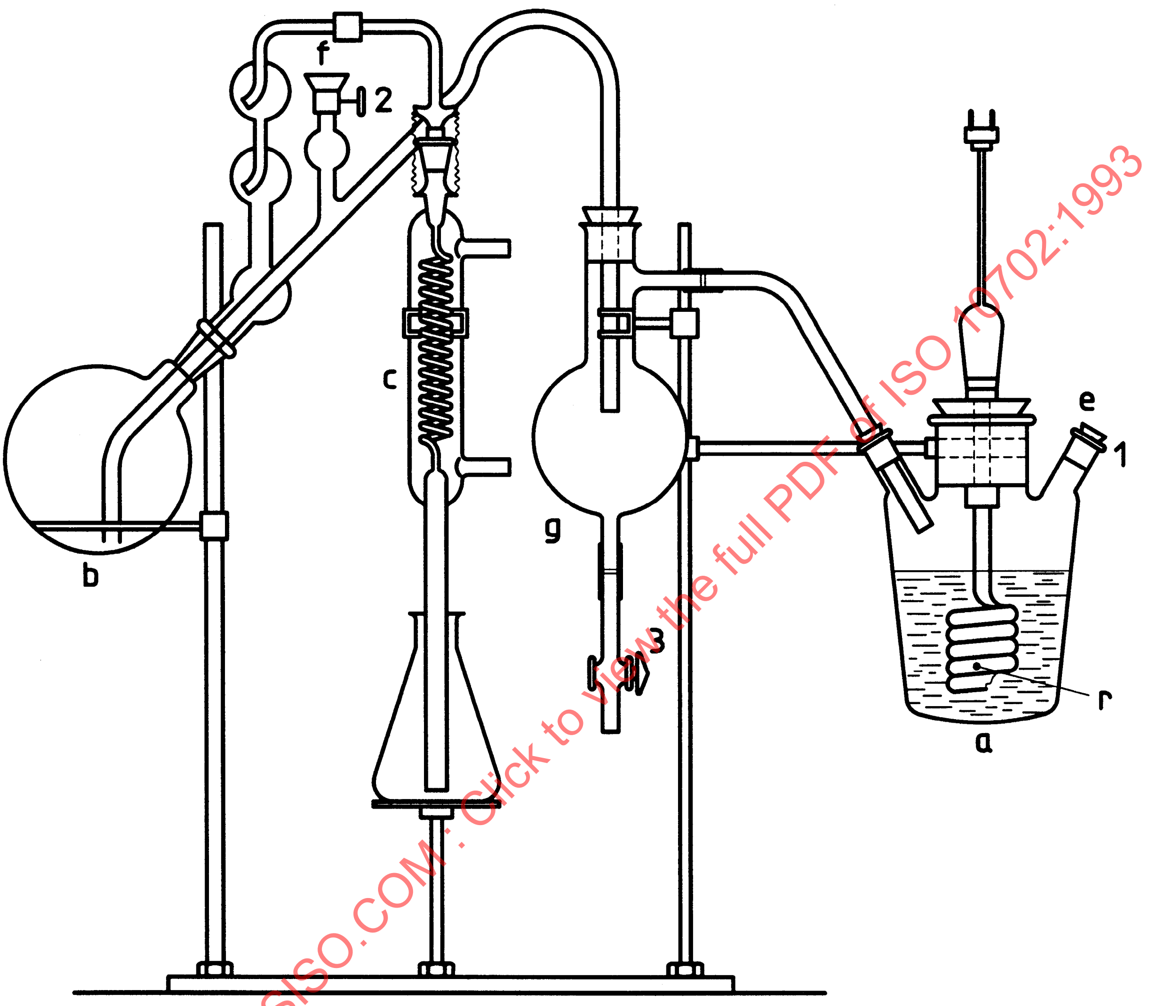
Examples of distillation apparatus



Key

a	Steam generator, of capacity 2 litres
b	Distillation flask
c	Condenser
e	Inlet for steam generator
f	Funnel
g	Trap
r	Resistance heater
1, 2, 3	Taps

Figure A.1 — First example of a distillation apparatus



Key

a	Steam generator, of capacity 2 litres
b	Distillation flask
c	Condenser
e	Inlet for steam generator
f	Funnel
g	Trap
r	Resistance heater, 220 V 600 W
1, 2, 3	Taps

Figure A.2 — Second example of a distillation apparatus

Annex B
(informative)

Additional information on the international cooperative tests

Table 2 was derived from the results of international analytical trials carried out in 1989 on seven steel samples and one pig iron sample in five countries, involving ten laboratories.

The results of the trials were reported in document ISO/TC 17/SC 1 N 841, March 1990. The precision data are presented in graphical form in annex C.

The test samples used are listed in table B.1, and the results obtained are listed in table B.2.

Table B.1

Sample (CRM or other No.)	**Chemical composition,** % (*m/m*)							
	N	C	Si	Mn	Ni	Cr	Ti	Others
High purity iron (ECRM 088-1)	0,000 9	0,002	0,002	0,02	—	—	—	—
Unalloyed steel (ECRM 083-1)	0,002 2	0,03	—	0,29	0,01	—	—	—
Unalloyed steel (JSS 030-6)	0,004 0	0,18	0,26	0,72	—	—	—	—
Pig iron for casting (JSS 110-8)	0,006 3	4,1	1,7	0,58	0,01	0,02	0,05	—
Unalloyed steel (ECRM 057-1)	0,016	0,07	0,06	0,52	—	—	—	—
High speed steel (JSS 611-8)	0,054 8	0,86	0,37	0,30	0,13	4,0	—	Mo: 4,9 W: 6,3 V: 1,9 Co: 0,4
Heat-resisting steel (None)	(0,23)1)	0,2	0,1	1	11	21	0,01	—
Heat-resisting steel (None)	(0,45)1)	0,5	0,1	9	4	21	0,01	—

1) Non-certified value