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Steel — Determination of low carbon contents — Part II : Titrimetric method after combustion

Acier — Dosage du carbone en faibles teneurs — Partie II : Méthode titrimétrique après combustion

FOREWORD

Technical Report 4830 was drawn up by Technical Committee ISO/TC 17, *Steel*, and approved by a majority of its members. The reasons which led to the publication of this document in the form of a Technical Report are given in the Introduction.

In January 1978, this document was submitted to the ISO Council, which approved its publication as a Technical Report.

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0 INTRODUCTION

Four methods for the determination of low carbon contents in steels have been examined by ISO/TC 17, namely :

- manometric (low-pressure);
- titrimetric (titration in non-aqueous medium);
- conductimetric;
- coulometric.

The results of experiments carried out in relation to these four methods have not allowed a decision to be taken on the adoption of any one of them as a standard method at the international level.

Consequently, it has been generally agreed, as a preliminary measure, to make all four methods available in the form of parts of a Technical Report, i.e. ISO/TR 4830.

1 SCOPE AND FIELD OF APPLICATION

This part of this Technical Report describes a titrimetric method for the determination of the total carbon content in pure iron and in steels after combustion in an electric resistance furnace.

The method is applicable to carbon contents between 0,005 and 0,1 %.

2 REFERENCE

ISO/R 377, *Selection and preparation of samples and test pieces for wrought steel.*

3 PRINCIPLE

Combustion of a test portion in an electric resistance furnace in a current of oxygen, in the presence of a fluxing agent which encourages the combustion (see note 9.10), converting the carbon to carbon dioxide, which is absorbed in a mixture of pyridine and 2-aminoethanol or of formdimethylamide and 2-aminoethanol, and which is at the same time titrated using thymol blue as indicator.

Calculation of the carbon content from the consumption of the standard volumetric solution. This solution is standardized against calcium carbonate (primary standard), which is heated to a temperature between 1 250 and 1 400 °C in the same furnace.

4 REAGENTS

During the analysis, use only reagents of recognized analytical quality, and only distilled water or water of equivalent purity.

4.1 Oxygen, purified.

Pass the current of oxygen through a combustion tube, filled with platinized asbestos (4.2.1) and placed in a heated furnace so that a 25 cm portion of the tube has a temperature of 600 to 625 °C. Pass the oxygen leaving the tube through absorption columns, filled respectively with soda lime (4.2.3) and soda asbestos (4.2.2).

4.2 Oxygen-purifying agents :

4.2.1 Platinized asbestos, with 10 % platinum.

4.2.2 Soda asbestos, grain size about 2 to 4 mm.

4.2.3 Soda lime, grain size about 2 to 4 mm.

4.3 Agents for absorbing sulphur oxides :

4.3.1 Manganese(IV) oxide, grain size about 0,7 to 1,5 mm; or

4.3.2 Hydrogen peroxide fixed on urea, grain size about 4 mm.

4.4 Fluxing agents : tin, iron or steel, having the lowest possible carbon content determined in accordance with 7.4.2.

4.5 Iron having a low carbon content.

4.6 Active charcoal.

4.7 Pyridine, dried if necessary by means of an activated molecular sieve (water content of pyridine less than 0,25 %).

4.8 Formdimethylamide, dried if necessary.

4.9 2-Aminoethanol (ethanolamine).

Avoid contact with air.

1 ml of ethanolamine should consume not more than 1,25 ml of the standard volumetric solution (4.11).

4.10 Absorption mixture.

Add to 150 ml of the pyridine (4.7) or formdimethylamide (4.8), 2,5 ml of the ethanolamine (4.9) and 2 ml of the thymol blue solution (4.12).

This mixture should be freshly prepared each day (see note 9.13).

4.11 Standard volumetric solution.

4.11.1 *Preparation*

Prepare either of the two following solutions :

4.11.1.1 **Sodium methanolate,** about 0,02 M solution.

Dissolve 2,3 g of white sodium in 1 litre of methanol free from carbon dioxide (water content less than 0,02 %).

Transfer 200 ml of this solution to a 1 000 ml volumetric flask. Add 10 ml of the thymol blue solution (4.12), make up to volume with the pyridine (4.7) and mix.

NOTE – Prepare and store this solution in such a way as to exclude carbon dioxide.

4.11.1.2 **Tetra-*n*-butylammonium hydroxide (TBAH),** about 0,02 M solution.

Place 200 ml of a 0,1 M TBAH solution in a 1 000 ml volumetric flask. Add 10 ml of the thymol blue solution (4.12), make up to volume with the pyridine (4.7) and mix.

NOTE – Prepare and store this solution in such a way as to exclude carbon dioxide.

4.11.2 *Standardization*

Weigh 0,020 g of calcium carbonate (primary standard), previously dried for 2 h at 400 °C and kept on calcium sulphate free from water. Place in a calcined boat and treat as specified in 7.3.

4.11.3 *Blank test*

Carry out a blank test using an empty calcined boat and treating it as specified in 7.3.

4.11.4 *Calculation of the concentration*

The concentration T, expressed as a molarity, of the standard volumetric solution is given by the formula

$$T = \frac{m_1}{100{,}08\ (V_1 - V_2)}$$

where

m_1 is the mass, in milligrams, of calcium carbonate taken for the standardization (4.11.2);

V_1 is the volume, in millilitres, of the standard volumetric solution consumed for the standardization (4.11.2);

V_2 is the volume, in millilitres, of the standard volumetric solution consumed for the blank test (4.11.3).

4.12 Thymol blue, 50 mg/25 ml solution in pyridine (4.7).

5 APPARATUS

The apparatus is divided into two parts :

— the first part includes a flowmeter, an electric resistance furnace with combustion tube, and an absorption tube, filled with absorbing agents (4.3) to retain the sulphur oxides;

— the second part is the apparatus for the titration of the carbon dioxide formed.

The two parts are connected by tubes and bungs to form an airtight unit.

A diagram of the complete apparatus is shown in figure 1. The titration vessel is shown in figure 2 (see also note 9.14), and details of the tuyere fitted to the combustion tube are given in figure 3.

The tuyere, which slides on to the combustion tube (see figure 3), may be considered as a T-connection : the oxygen on entering divides in two directions. One part is drawn into the combustion tube by means of a pump, at the end of the system, combined with a high-precision regulating valve and a flowmeter; the remaining part leaves the combustion tube at the point marked G. By adjusting the current of oxygen leaving at G to a sufficient rate, the penetration of air into the tube is prevented. Moreover, the combustion boat may be easily introduced into and withdrawn from the furnace.

The combustion gases leave the combustion tube together with the remaining oxygen via the tube for absorbing sulphur oxides, and are introduced into the titration vessel, where the carbon dioxide is absorbed. The residual gas leaves the titration vessel via two columns, filled with active charcoal (4.6), and is evacuated through a three-way tap and the high-precision regulating valve by means of the pump. The rate of flow of the gas passing through the titration vessel is controlled by the regulating valve. The three-way tap is used to put the current of gas "in" or "out" of the circuit. Account should be taken of the fact that the three-way tap has two incorrect positions.

Tap T_1 has no basic importance here but serves as a possible safety device in cases of emergency.

See also notes 9.4, 9.5, 9.6, 9.7 and 9.13.

6 SAMPLING

Sampling shall be carried out in accordance with ISO/R 377.

7 PROCEDURE

7.1 Preparation of the test portion

Degrease the test sample by washing (for example with freon or ether). Evaporate the last traces of the washing liquid by heating.

Weigh 1 g of the test sample to the nearest 0,001 g and transfer to a calcined boat (see note 9.6). Add 1,0 g of fluxing agent (4.4).

7.2 Preparation of apparatus

Heat the furnace to a temperature between 1 250 and 1 400 °C (see note 9.10). Adjust the current of oxygen (4.1) to at least 180 l/h, as shown by the flowmeter C. Set the three-way tap T_3 in the "out" position and set the pump working. Adjust the regulating valve for a very limited aspiration of air.

Open tap T_1 and set the three-way tap in the "in" position (see note 9.3). Now adjust the gas flow to about 18 l/h by means of the regulating valve. Introduce a suitable amount (see notes 9.1 and 9.14) of the absorption mixture (4.10) into the titration vessel (see figure 1 and note 9.8).

Owing to the carbon dioxide present in the apparatus, the absorption mixture turns yellow; add the standard volumetric solution (4.11) until a permanent blue colour is obtained (see note 9.11).

7.3 Determination

Place the boat containing the test portion at the entrance to tube G and leave it for several minutes. During this time, the absorption mixture should not change colour. Take the reading of the burette. Introduce the boat rapidly into the combustion zone of the tube and during combustion titrate (see note 9.5) the carbon dioxide with the standard volumetric solution (see note 9.2).

Do not stop the current of oxygen after combustion until there is no further consumption of the standard volumetric solution (see note 9.10); then take the reading of the burette.

Carry out a total blank test in accordance with 7.4.1 or carry out a blank test in accordance with 4.11.3.

7.4 Blank test

The value of the blank consists of the carbon content of the boat used, of the fluxing agent and of the oxygen (see note 9.12).

7.4.1 *Total blank test*

Weigh out, to the nearest 0,001 g, several quantities of the iron (4.5), for example 0,3 g; 0,6 g; 0,9 g and 1,2 g. In each case add 1,0 g of the same fluxing agent as used in the determination. Burn each in accordance with the procedure described in 7.3. Titrate the solutions as described in 7.3.

Plot the volumes of the standard volumetric solution consumed against the masses of iron on a graph; the graph will be a straight line and generally will not pass through the origin. The consumption indicated by the graph for a mass of 0,000 g gives the total blank consumption.

7.4.2 *Determination of the carbon content of the fluxing agent* (4.4)

Weigh out, to the nearest 0,001 g, several quantities of the fluxing agent (4.4), for example 0,3 g; 0,6 g; 0,9 g and 1,2 g. In each case add 1,0 g of the iron (4.5). Burn each in accordance with the procedure described in 7.3. Titrate the solutions as described in 7.3.

Plot the volumes of the standard volumetric solution consumed against the masses of fluxing agent on a graph; the graph will be a straight line. From the slope of this straight line determine the consumption of standard volumetric solution for 1 g of the fluxing agent.

8 EXPRESSION OF RESULTS

8.1 Blank value of boat, fluxing agent and oxygen : Total blank

The total blank value, m_2, expressed in milligrams of carbon, is given by the formula

$$m_2 = 12{,}01\ V_3 T$$

where

V_3 is the volume, in millilitres, representing the total blank consumption of standard volumetric solution (4.11) read from the graph in accordance with 7.4.1;

T is the concentration, expressed as a molarity, of the standard volumetric solution, calculated in accordance with 4.11.4.

8.2 Carbon content of fluxing agent (4.4)

The carbon content of the fluxing agent (4.4), expressed as a percentage by mass, is given by the formula

$$\frac{12{,}01\ V_4 T}{10}$$

where

V_4 is the volume, in millilitres, of standard volumetric solution (4.11) consumed for 1 g of the fluxing agent, calculated from the slope of the straight line in accordance with 7.4.2;

T is as defined in 8.1.

8.3 Carbon content of the test sample

The carbon content of the test sample, expressed as a percentage by mass, is given by the formula

$$\frac{12{,}01\ V_5 T - m_2}{10\ m_5}$$

where

V_5 is the volume, in millilitres, of standard volumetric solution (4.11) consumed during the determination;

m_2 is the total blank value, in milligrams of carbon, calculated in accordance with 8.1;

m_5 is the mass, in grams, of the test portion;

T is as defined in 8.1.

9 NOTES

9.1 After the addition of about 5 ml of the standard volumetric sodium methanolate solution (4.11.1.1) or 10 ml of the standard volumetric TBAH solution (4.11.1.2) to 10 ml of the absorption mixture (4.10), the contents of the titration vessel shall be renewed.

For low consumptions of standard volumetric solution, the liquid in the absorption vessel may therefore be used several times.

9.2 It is advisable to ensure in advance that the absorption mixture is alkaline by adding a quantity of the standard volumetric solution (4.11).

9.3 Before beginning the first analysis of the day, the combustion tube shall be thoroughly purged at combustion temperature with oxygen, as otherwise the results obtained would be too high.

9.4 Pyridine and formdimethylamide vapours are toxic. For this reason the gases which have passed through the titration vessel are passed through a tube filled with active charcoal (4.6). The odour of pyridine may help to detect leaks in the system.

9.5 The use of a piston burette is preferable.

9.6 The porcelain boat shall be calcined in a combustion tube for at least 3 min directly prior to use. If necessary, precalcination for a longer period (several hours) in a separate furnace at at least 900 °C is possible.

9.7 In order to obtain a negligible blank value for the apparatus, the pure oxygen should be passed only through glass connections to the combustion tube. With the T-connection used as an inlet, the influence of the apparatus is also reduced.

9.8 Care should be taken to avoid the solution returning into the supply tube, as it is possible that the carbon dioxide absorbed may not be titrated.

9.9 After the end point has been reached, the consumption of standard volumetric solution should not exceed 0,01 ml for every 5 min.

9.10 It is not possible to indicate the correct combustion temperature and the correct fluxing agent for all grades of steel. The particle size, as well as the composition of the material, greatly affects the speed and completeness of combustion.

9.11 Check whether at this moment the gas circuit is free from carbon dioxide; if it is, the blue colour of the indicator will not change for several minutes.

9.12 Determination of the total blank value (7.4.1) and of the carbon content of the fluxing agent (7.4.2), and the blank determination (4.11.3), depend on the fact that by using boats from the same producer and in the same apparatus the blank values appear to be constant within the limits of analysis.

9.13 Adapt the volume of the absorption mixture storage vessel to the daily consumption, as the reagent should be freshly prepared each day.

9.14 A suitable titration vessel may have the following dimensions :

- internal diameter 18 mm;
- height 200 to 250 mm.

For a quantity of 15 ml of absorption mixture, the solution then reaches a height of about 50 mm.

10 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this part of this Technical Report, or in the document to which reference is made, or regarded as optional.

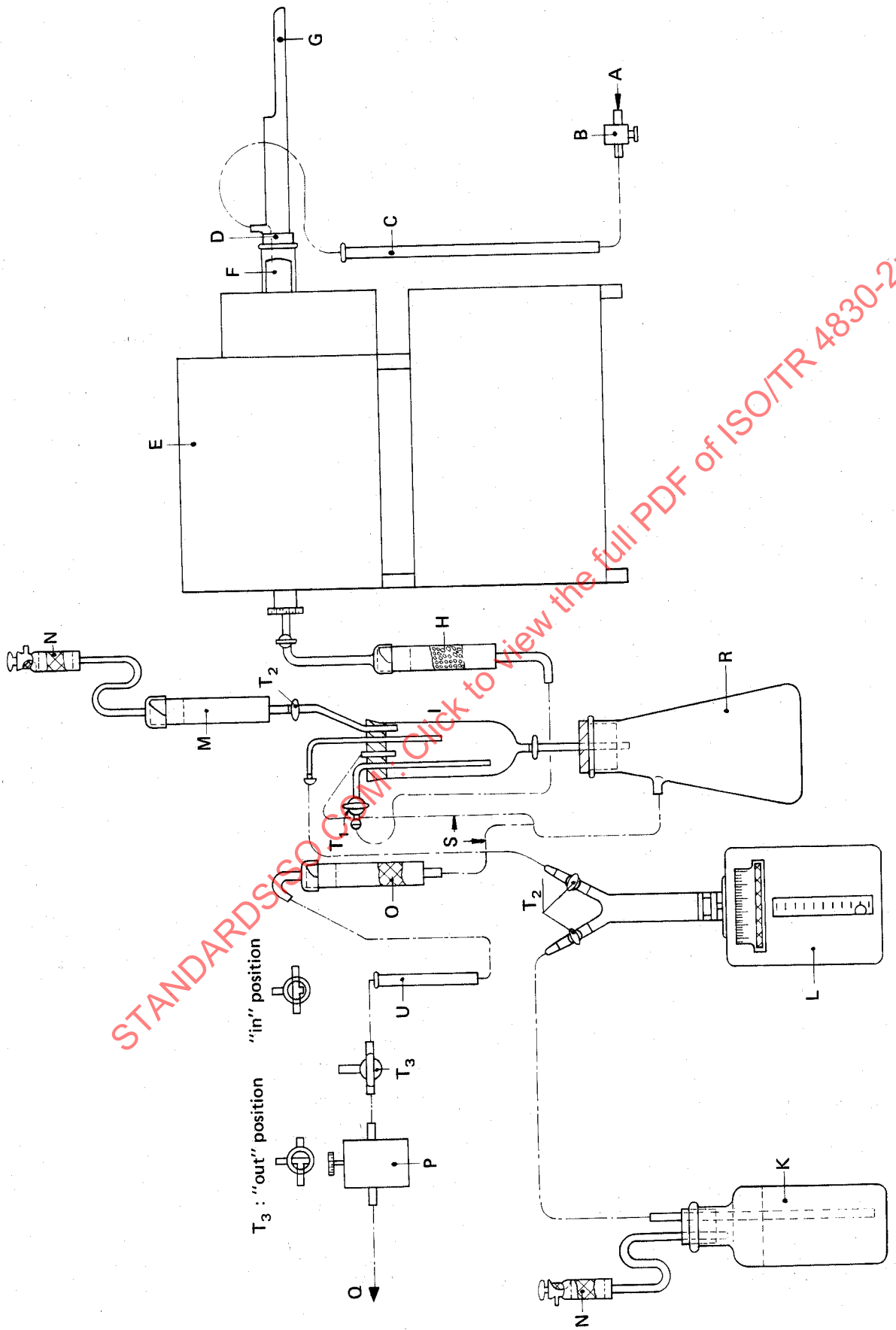

FIGURE 1 – Diagram of complete apparatus

KEY TO FIGURE 1

A : inlet for purified oxygen (4.1)

B : valve (regulator)

C : flowmeter, capable of measuring an oxygen flow of 180 l/h

D : metal supply tuyere; see detailed drawing in figure 3

E : resistance furnace capable of being heated to 1 400 °C (see note 9.10)

F : airtight ceramic combustion tube, length 500 to 700 mm, internal diameter 17 mm, external diameter 23 mm (based on the diameter of the supply tuyere)

G : aperture

H : glass tube containing agents (4.3) for absorbing sulphur oxides

I : titration vessel; see diagram in figure 2

K : storage vessel for standard volumetric solution (4.11)

L : (piston) burette (see note 9.5)

M : storage vessel for absorption mixture (4.10) (see note 9.13)

N : absorption vessel filled, from bottom to top, with glass wool — soda asbestos (4.2.2) — glass wool

O : tube filled with active charcoal (4.6)

P : high-precision regulating valve

Q : pump

R : conical vacuum-filtering flask

S : polyethylene tubing

T_1 : tap (for emergencies)

T_2 : tap, preferably of polytetrafluorethylene

T_3 : three-way tap

U : flowmeter capable of measuring an oxygen flow of 18 l/h

All the tubes from the combustion tube to the titration vessel are capillary in connection, with as small a volume as possible. The tubes between the pump and the titration vessel are plastic; the rest are glass with spherical lappings as connections. The standard volumetric solution is added to the titration vessel through a capillary tube with a drawn point discharging into the absorption mixture.