INTERNATIONAL STANDARD

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Determination of carbon content in uranium dioxide powder and sintered pellets — High-frequency induction furnace combustion — Titrimetric/coulometric/infrared absorption methods

Détermination de la teneur en carbone dans la poudre et les pastilles frittées de dioxyde d'uranium — Combustion dans un four électrique à induction — Méthodes par titrimétrie/coulométrie/absorptiométrie infrarouge

Reference number
ISO 9891:1994(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.

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Determination of carbon content in uranium dioxide powder and sintered pellets — High-frequency induction furnace combustion — Titrimetric/coulometric/infrared absorption methods

1 Scope

This International Standard specifies titrimetric/calometric/infrared absorption methods for determining the carbon content in uranium dioxide powder and sintered pellets, the test sample being heated in an induction furnace.

It is applicable to the determination of 5 µg to 500 µg of carbon in uranium dioxide powder and pellets. Interference from sulfur and halogens is prevented by the use of appropriate traps.

2 Principle

A portion of the test sample is heated at a temperature of at least 1 100 °C to 1 200 °C in a quartz-encapsulated tungsten crucible or in a platinum crucible, in an oxygen atmosphere. The evolved oxidation products are passed over a purification trap, filled with manganese dioxide and silver permanganate catalyst. Manganese dioxide absorbs nitrogen oxides. Silver permanganate catalyst will oxidise carbon monoxide to carbon dioxide and absorb sulfur oxides and halogens.

The carbon dioxide is trapped in an absorption solution of barium perchlorate, adjusted to pH = 10,0. Absorption of carbon dioxide causes a decrease of the pH. The initial pH is restored continuously by the addition of hydroxyl ions either by potentiostatic titrimetry or by coulometry.

Alternatively, the carbon dioxide may be determined by absorption of infrared radiation and integration of the signal obtained.

3 Reaction

$$CO_2 + H_2O + Ba(ClO_4)_2 \rightarrow BaCO_3 + 2H^+ + 2ClO_4^-$$

4 Reagents and materials

During the analyses, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Oxygen, of commercial grade, better than 99,9 % (*V/V*) purity.

4.2 Carbon dioxide, commercial grade, better than 99,9 % (*V/V*) purity.

4.3 Copper oxide, 1 mm to 2 mm granules.

4.4 Soda lime, of the self indicating type, 1 mm to 2 mm granules.

4.5 Molecular sieve 4A, 1,6 mm (1/16 in) pellets, preheated at 300 °C.

4.6 Silver permanganate catalyst (in Europe available as Korbl's combustion catalyst), for element analysis.

4.7 Manganese dioxide, activated, combustion analysis grade, 0,5 mm to 1,5 mm granules.

4.8 Accelerators, tin metal, powder form, low in carbon, or tungsten granules.

4.9 Moist hydrogen reduced iron, chips, containing less than 5 ppm of carbon.

4.10 SRM steels[1], of certified reference material grade, chips, certified for carbon, containing 15 ppm to 500 ppm carbon.

4.11 Barium perchlorate [$Ba(ClO_4)_2$].

4.12 2-Propanol ($CH_3CHOHCH_3$).

4.13 Absorption solution

Dissolve 200 g of barium perchlorate (4.11) in water. Add 1,0 ml of 2-propanol (4.12), dilute to 1,0 l and mix.

4.14 Sodium hydroxide, solution [c(NaOH) = 0,10 mol/l], free from carbon dioxide, standardized against potassium hydrogen phthalate.

4.15 Sodium hydroxide, solution [c(NaOH) = 0,02 mol/l], free from carbon dioxide. Prepare fresh daily by accurate dilution of the sodium hydroxide solution 4.14.

NOTE 1 Use this sodium hydroxide solution (4.15) for the titration of less than 50 µg of carbon, otherwise use the 0,10 mol/l solution (4.14).

5 Apparatus

Typical dimensions are given for the apparatus; an alternative system giving similar performances may however be used.

5.1 High-frequency induction furnace, 1,5 kVA to 2,5 kVA, 1 MHz to 20 MHz, with silica combustion tube of inner diameter 30 mm (see figure 1). The induction coil surrounding the combustion tube should be 40 mm to 60 mm high and have 4 to 5 turns.

The crucible containing the test portion and, if necessary, an accelerator is supported on an alumina pedestal and positioned within the induction coil to ensure effective coupling.

This furnace gives a temperature of 1 100 °C; an alternative giving a higher temperature may be used.

5.2 Oxygen purification and flow control system (see figure 2)

5.2.1 Oxygen purification system (see figure 3), consisting of a stainless steel tube, of inner diameter 30 mm and length 200 mm, filled with copper oxide (4.3) and heated at 650 °C. The stainless steel tube is connected to a glass tube, of inner diameter 30 mm and length 300 mm, filled with approximately 100 mm of soda lime (4.4) and approximately 200 mm of molecular sieve (4.5). The layers are separated by layers of quartz wool.

5.2.2 Pressure regulators 0 kPa to 200 kPa, manometers 0 kPa to 200 kPa, flow regulators and flow meters 0 ml/min to 100 ml/min

All connections of the gas delivery system should be made using stainless steel tubing of inner diameter 3 mm. The connections between the furnace and the measuring system should preferably be made of stainless steel of inner diameter approximately 1 mm, except for a short piece of PTFE tubing of inner diameter approximately 0,4 mm which is used as the gas inlet to the absorption vessel.

5.2.3 Two-litre buffer vessel, to supply additional oxygen during the combustion of steels.

5.2.4 Six-way valve, to supply an oxygen backflush to the combustion tube when it is open. This flush prevents absorption of carbon dioxide from the air in the combustion tube.

1) Standard Reference Steels are available from:

NBS (National Bureau of Standards), Washington, D.C., USA;

BCR (Bureau communautaire de référence), Brussels, Belgium;

BAS (Bureau of Analysed Samples), Middlesbrough, United Kingdom;

BAM (Bundesanstalt für Materialprüfung), Berlin, Germany;

IRSID (Institut de recherches de la sidérurgie française), Saint-Germain-en-Laye, France.

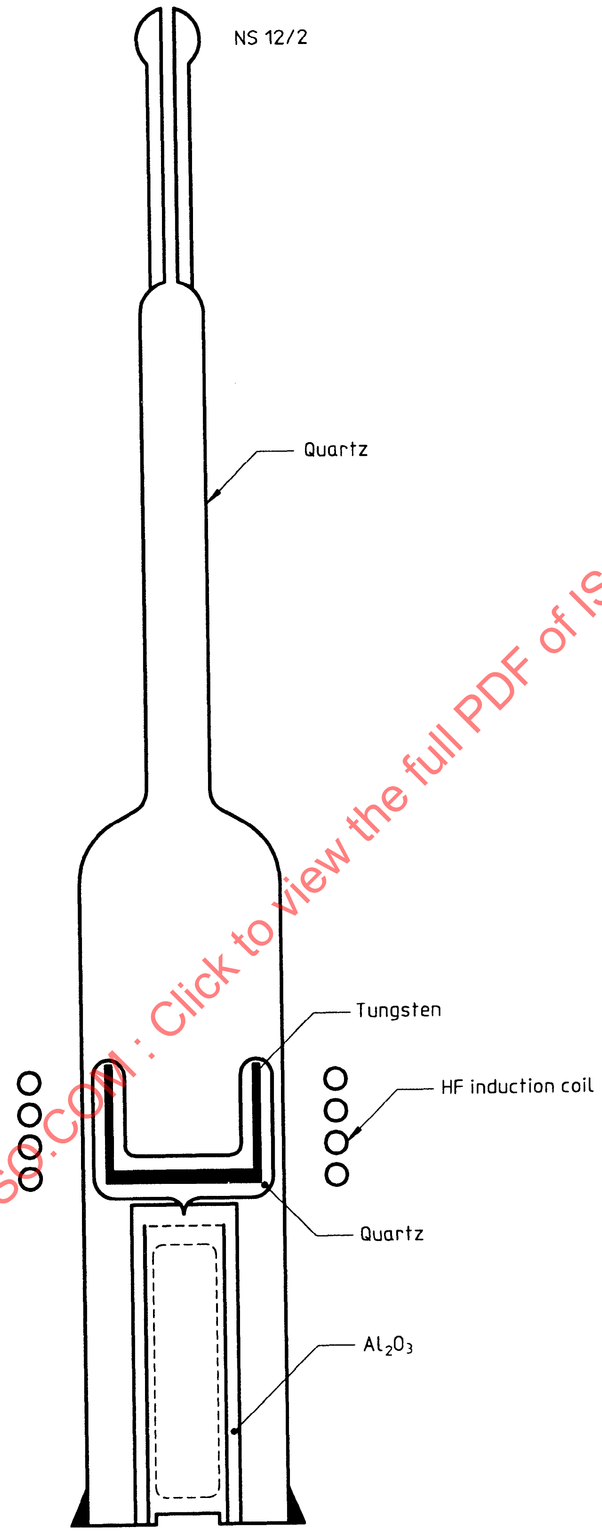
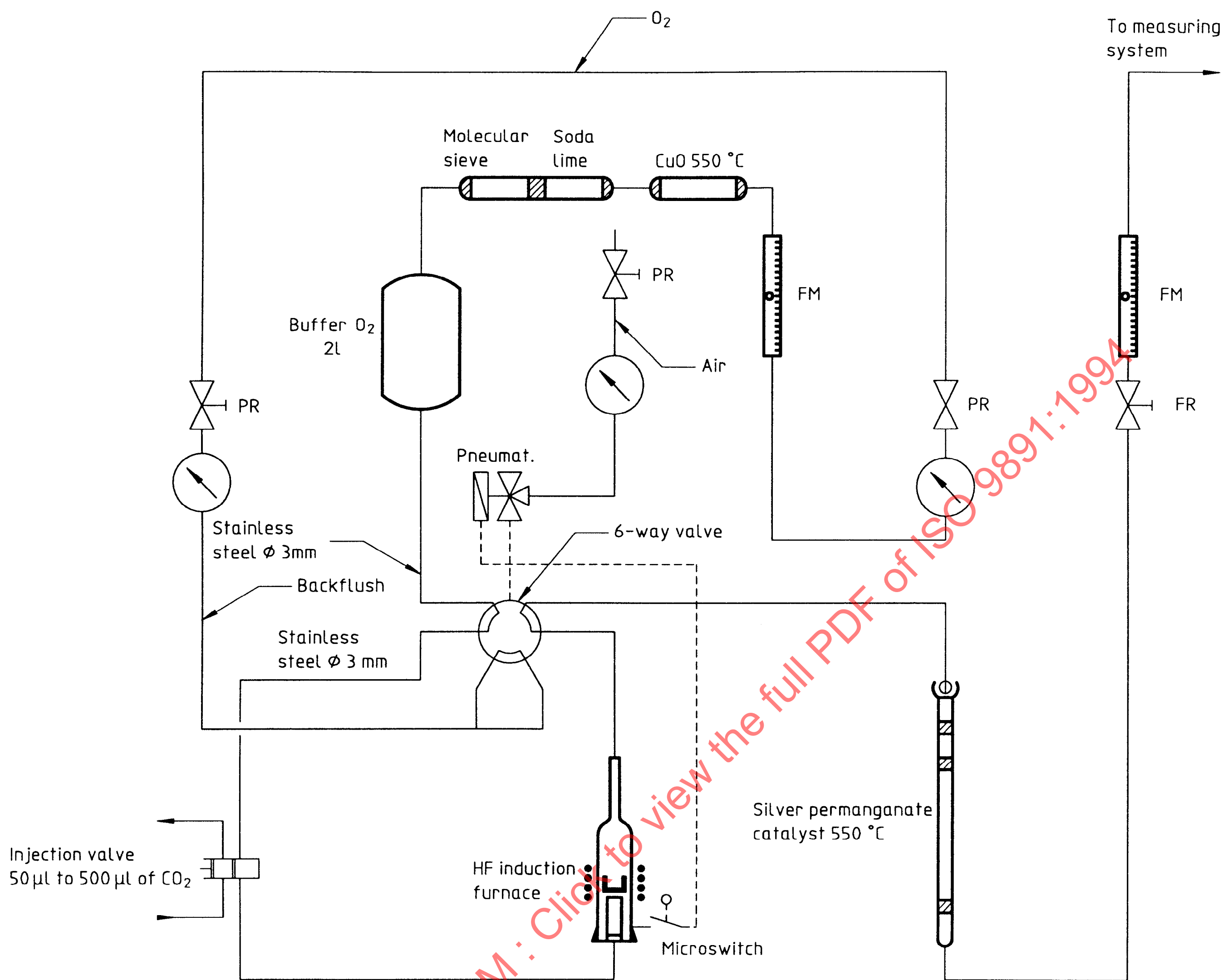


Figure 1 — Combustion tube



FR = Flow regulator

PR = Pressure regulator

FM = Flow meter

Figure 2 — Oxygen purification and flow control system

5.3 Combustion gas purification tower (see figure 4), comprising a quartz tube 200 mm long, of inner diameter 8 mm, filled with 40 mm of manganese dioxide (4.7) and 100 mm of silver permanganate catalyst (4.6), the layers separated by layers of quartz wool.

The section containing the silver permanganate catalyst should be heated at 550 °C.

5.4 Gas dosing valves, calibrated volumes of 50 µl and 500 µl for the admission of carbon dioxide.

5.5 Detection system

5.5.1 For titrimetry: titration vessel (see figure 5) or equivalent, temperature controlled at 25,0 °C ± 0,2 °C, filled with absorption solution (4.13), glass (NaCl, AgCl) Ag electrode combination and a potentiostatic control circuit to drive a 1 ml plunger-type burette. Intimate contact between the gas and liquid phase should be provided by efficient stirring with a stirring disc.

5.5.2 For coulometry: commercially available cell (see figure 6). Efficient stirring with a stirrer basket and temperature control at 35,0 °C ± 0,2 °C should be provided.

5.5.3 For infrared absorption: instrument capable of measuring the amount of specific infrared absorption by carbon dioxide. It consists of an infrared emitter, a sample, a reference cell and a detector. The measured absorption is usually amplified, integrated and converted to give a digital display of the amount of carbon.

WARNING — Fluoride in more than trace amounts can damage the infrared detector.

5.6 Crucibles, ceramic, platinum or quartz encapsulated tungsten.

6 Test sample

6.1 Uranium dioxide powder: no preparation is necessary.

6.2 Uranium dioxide pellets: crush or break the laboratory sample without producing excessive amounts of fine particles and pass it through a 1 mm sieve until about 5 g has passed.

Retain this portion for use as the test sample.

NOTE 2 Uranium dioxide powder absorbs carbon dioxide; this inteferes with the determination. It is removed prior to analyses (see note 6 in 7.4.3).

7 Procedure

7.1 Setting-up of the apparatus

7.1.1 Adjust the pressure within the oxygen supply system to about 125 kPa and the oxygen outlet flow to 100 ml/min. After equilibration check both flow meters; the inlet flow and the, adjusted, outlet flow must be equal. If not, trace and repair leaks.

7.1.2 Place a quartz encapsulated tungsten or a platinum crucible (5.6) on the pedestal, close the combustion tube.

7.1.3 Fill the absorption vessel with the absorption solution (4.13), stir vigorously and adjust the pH to 10,0. Titrate over 4 min periods until the titrant consumption, in millilitres or coulombs, becomes stable or, in the case of infrared detection, until the integrator output is constant.

NOTE 3 In case of very low carbon contents, it will be advantageous to use pH = 9,5 as the preset potential; at this pH the absorption capacity is less but sensitivity is enhanced.

7.2 Functional check

7.2.1 Heat the crucible at 1 100 °C to 1 200 °C for 4 min periods until the volume of titrant (V_0) or number of coulombs (C_0) is constant. In case of infrared detection, compensate the output to zero until stable.

NOTES

4 V_0, C_0 or the compensated signal should be equivalent to not more than 5 µg of carbon.

5 Quartz encapsulated tungsten or platinum crucibles can be used only if the powder of the HF generator can be controlled and if a proper temperature measuring device is available. Too much power will of course cause melting of these materials.

Dimensions in millimetres

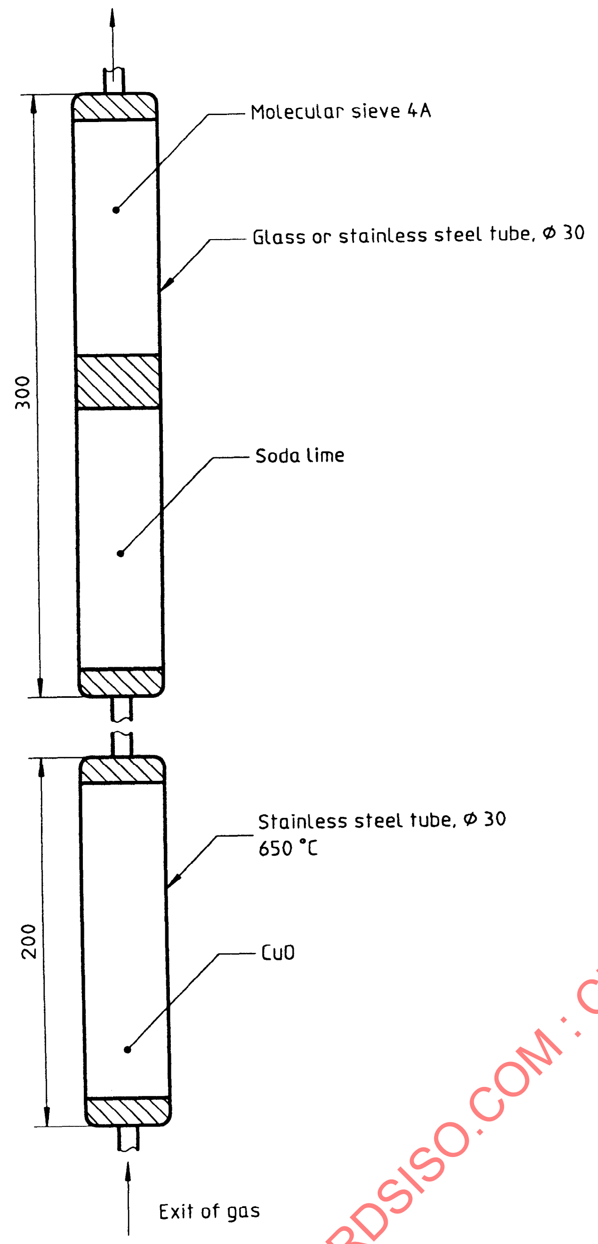


Figure 3 — Oxygen purification system

Dimensions in millimetres

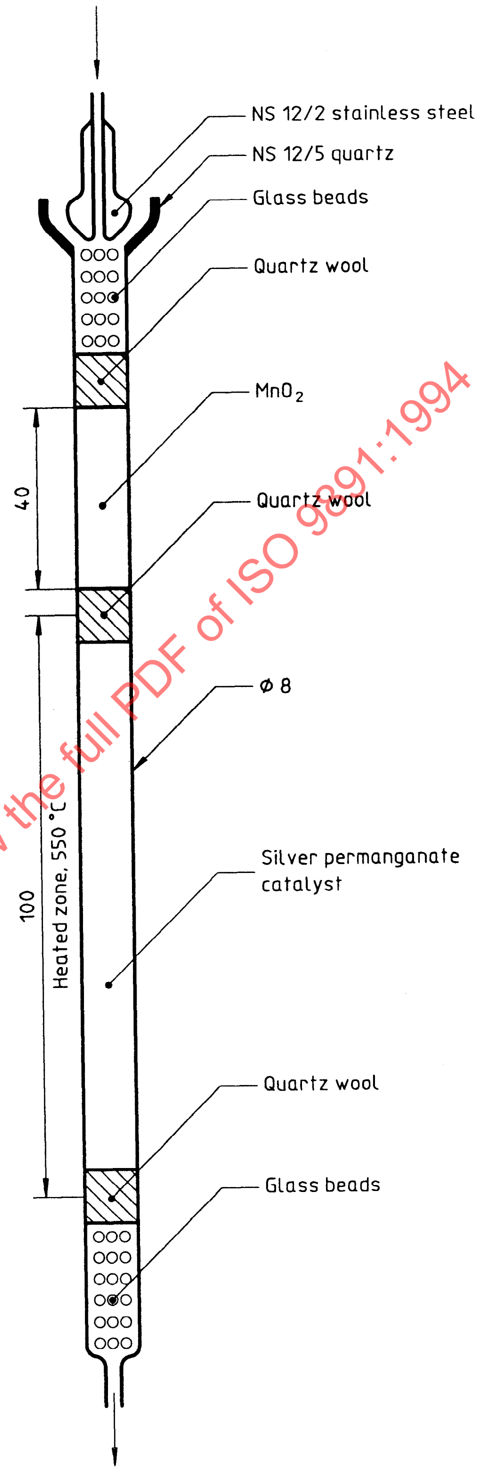


Figure 4 — Combustion gas purification system

Dimensions in millimetres

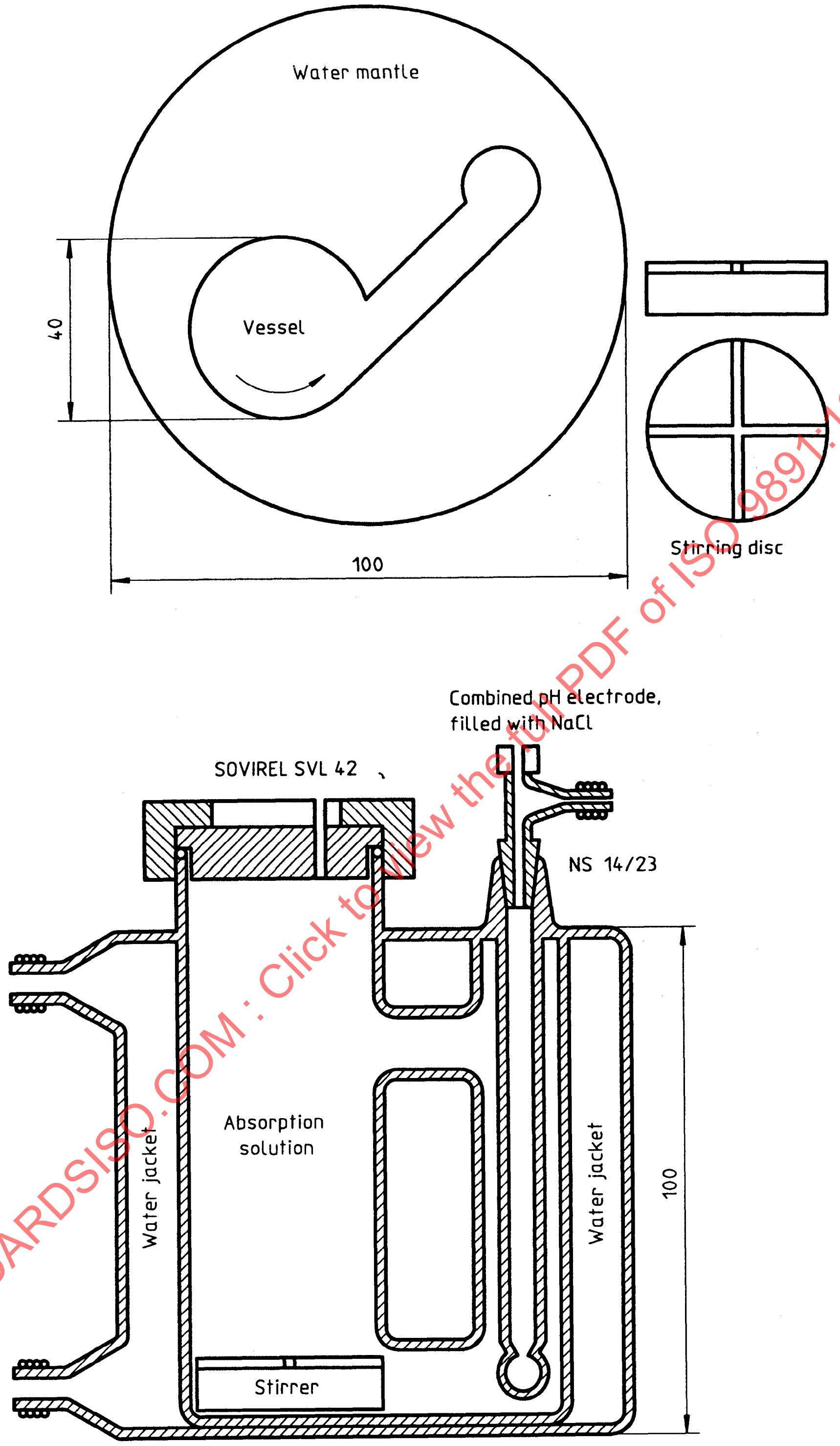


Figure 5 — Titration vessel

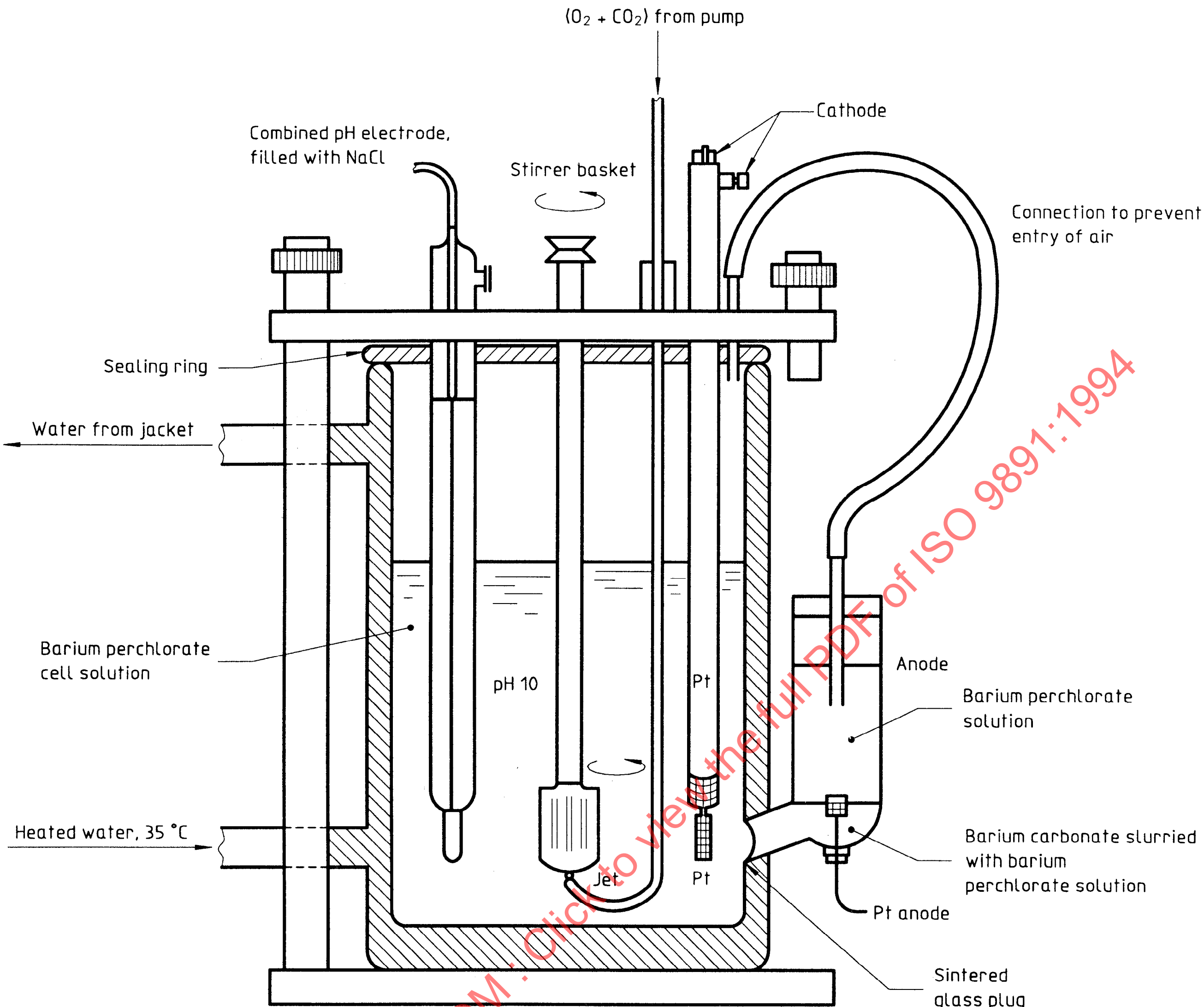


Figure 6 — Coulometric cell

7.2.2 Check the absorption efficiency, or the integrator output, by introducing 50 µl and 500 µl of carbon dioxide from the calibrated injection valves. Heat for 4 min and read the detector output, the titrant consumption (V_x) or the coulombs used (C_x).

7.2.3 Calculate the absorption efficiency, A_{eff}, as a percentage, as follows:

$$A_{eff} = \frac{(V_x - V_0)N \times 0,5 \times 22,4 \times 10^3 \times 100 \times 273 \times p_x}{A_x \times 101,3 \times T_x}$$

or

$$A_{eff} = \frac{(C_x - C_0) \times 0,5 \times 22,4 \times 10^6 \times 100 \times 273 \times p_x}{A_x \times 96\,500 \times 101,3 \times T_x}$$

where

V_x is the volume of titrant used in the determination, in millilitres (see 7.2.2);

V_0 is the volume of titrant used in the blank test, in millilitres (see 7.2.1);

N is the concentration of the titrant, in millimoles per millilitre;

p_x is the pressure of the injected carbon dioxide gas, in kilopascals;

A_x is the volume of the injection valve at NTP, in microlitres;

T_x is the temperature of the injected carbon dioxide gas, in kelvins;

C_x is the number of coulombs used in the determination (see 7.2.2);

C_0 is the number of coulombs used during the blank test (see 7.2.1);

96 500 is the Faraday constant, in coulombs per mole.

Proceed only if A_{eff} is greater than 95 %; if it is not, trace and cure the cause of the discrepancy.

7.3 Calibration

7.3.1 Pre-ignite a stock of ceramic crucibles (5.6) at 1 000 °C to 1 100 °C for at least 4 h. Store at 250 °C to prevent absorption of carbon dioxide from the air.

7.3.2 Weigh, to the nearest 0,1 g, approximately 0,5 g of moist hydrogen reduced iron (4.9) and 1,0 g of tin flux (4.8) onto a piece of aluminium foil. Pour it into a still hot ceramic crucible, place it on the pedestal and quickly close the furnace.

7.3.3 Wait 2 min for equilibration and burn the sample smoothly for 4 min.

7.3.4 Read the volume (V_b) or coulombs (C_b) used or, in case of infrared detection, compensate to zero.

7.3.5 Weigh, to the nearest 0,001 g, 0,5 g to 1,5 g (M_x) of SRM steel (4.10) onto a piece of aluminium foil. Add 0,5 g of moist hydrogen reduced iron (4.9) and 1,0 g of tin (4.8), pour into a still hot ceramic crucible, place it on the pedestal and quickly close the furnace. Repeat the operation given in 7.3.3.

7.3.6 Read the volume (V_x) or coulombs (C_x) used or, in case of infrared detection, the amount of carbon.

7.3.7 Repeat 7.3.5 and 7.3.6 with at least four 0,5 g to 1,5 g portions of SRM steels, covering the range of carbon to be measured in the uranium oxide.

7.3.8 Calculate the carbon content of the steel, following the formula given in 7.5, with $(V_x - V_0) = (V_x - V_b)$ and $(C_x - C_0) = (C_x - C_b)$. Proceed only if there is agreement with the certified values within the given limits.

7.4 Determination

7.4.1 Place a quartz encapsulated tungsten or platinum crucible on the pedestal. Close the oven and allow 2 min for equilibration.

7.4.2 Heat for 4 min at at least 1 100 °C to 1 200 °C. Read the volume (V_0) or coulombs (C_0) used; in case of infrared detection compensate to zero.

7.4.3 Weigh, to the nearest 0,001 g, approximately 2 g of the test sample (M_x) into a pre-ignited quartz encapsulated tungsten or platinum crucible. Place the crucible on the pedestal, close the oven and allow 2 min for equilibration.

NOTES

6 If the carbon content is expected to be less than 50 µg/g, the sample and crucible should be heated at 250 °C for 1 h. After this treatment, place the crucible on the pedestal and quickly close the oven.

Heating the sample at 250 °C will remove the absorbed carbon dioxide which otherwise will be measured as carbon.

7 Alternatively ceramic crucibles may be used. In that case, use 2 g of tungsten flux (4.8) for the blank determination and 1 g of sample plus 2 g of tungsten flux for the determination.

7.4.4 Heat for 4 min at at least 1 100 °C to 1 200 °C, note the volume (V_x) or coulombs (C_x) of titrant used.

In case of infrared detection, read the carbon content directly from the integrator. Verify whether the correct sample mass was entered.

7.5 Calculation

Calculated the carbon content in the test sample, C, in micrograms, as follows.

For the titrimetric method:

$$C = \frac{(V_x - V_0)N \times 6 \times 1\,000}{M_x}$$

For the coulometric method:

$$C = \frac{(C_x - C_0) \times 6 \times 10^6}{96\,500 M_x} = \frac{(C_x - C_0) \times 6 \times 1\,000}{96{,}5 M_x}$$

where

V_x is the volume of titrant used in the determination, in millilitres (see 7.4.4);

V_0 is the volume of titrant used in the blank test, in millilitres (see 7.4.2);

M_x is the mass of the test sample, in grams;

C_x is the number of coulombs used in the determination (see 7.4.4);

C_0 is the number of coulombs used during the blank test (see 7.4.2);

96 500 is the Faraday constant, in coulombs per mole.

8 Precision

The difference between two independent results, found on identical test materials, by one analyst using the same apparatus within a short time interval should not exceed 2 µg/g of carbon or 5 % of the carbon content, whichever is the greater.

9 Test report

The test report shall include the following information:

a) the method used, with reference to this International Standard;

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

c) any unusual features noted during the determination;

d) any operation not specified in this International Standard which may have influenced the results.