

INTERNATIONAL STANDARD

**ISO
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Determination of carbon content in uranium dioxide powder and sintered pellets — Resistance furnace combustion — Titrimetric/coulometric/infrared absorption method

*Détermination de la teneur en carbone dans la poudre et les pastilles
frittées de dioxyde d'uranium — Combustion dans un four à
résistance — Méthode par titrimétrie|coulométrie|absorptiométrie
infrarouge*



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Foreword

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Determination of carbon content in uranium dioxide powder and sintered pellets — Resistance furnace combustion — Titrimetric/coulometric/infrared absorption method

1 Scope

This International Standard specifies a titrimetric/coulometric/infrared absorption method for determining the carbon content in uranium dioxide powder and sintered pellets.

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.

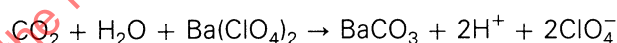
2 Principle

A portion of the test sample is heated at a temperature of 1 200 °C to 1 300 °C in a resistance furnace in an oxygen atmosphere. The oxidation products evolved 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



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

4.3 Argon, of commercial grade, better than 99,9 % (V/V) purity.

4.4 Copper oxide, 1 mm to 2 mm granules.

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

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

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

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

4.9 Tin metal, in powder form, low in carbon.

4.10 SRM steels¹⁾, of certified reference material grade, chips, certified for carbon, containing 15 ppm to 500 ppm carbon.

4.11 Barium perchlorate [$\text{Ba}(\text{ClO}_4)_2$].

4.12 2-Propanol ($\text{CH}_3\text{CHOHCH}_3$).

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
[$c(\text{NaOH}) = 0,10 \text{ mol/l}$], free from carbon dioxide, standardized against potassium hydrogen phthalate.

4.15 Sodium hydroxide, solution
[$c(\text{NaOH}) = 0,02 \text{ mol/l}$], 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 solution 4.14.

5 Apparatus

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

5.1 Combustion furnace (see figure 1), suitable for operation at 1 300 °C, with a hot zone of 200 mm to 250 mm.

5.2 Combustion tubes, suitable for operation at 1 300 °C, of internal diameter 17 mm, external diameter 22 mm and length 600 mm.

5.3 Oxygen purification system (see figure 2), consisting of a stainless steel tube, of inner diameter 30 mm and length 200 mm, filled with copper oxide (4.4) and heated at 650 °C. The tube is connected to a second tube, of inner diameter 30 mm and length 300 mm, filled with approximately 100 mm of soda lime (4.5) and approximately 200 mm of molecular sieve (4.6). The layers are separated by layers of quartz wool.

Alternatively, one of the tubes of the double furnace may be used for oxygen purification.

5.4 Pressure regulators 0 kPa to 200 kPa, manometers 0 kPa to 200 kPa, flow regulators and flow meters 0 ml/min to 2 000 ml/min and 0 ml/min to 500 ml/min

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

5.5 Needle valves, to control the flow of oxygen, argon and carbon dioxide.

5.6 Combustion gas purification tower (see figure 3), consisting of a quartz tube of length 200 mm and inner diameter 8 mm, filled with 40 mm of manganese dioxide (4.8) and 100 mm of silver permanganate catalyst (4.7), the layers separated by layers of quartz wool. The section containing the silver permanganate catalyst should be heated at 550 °C.

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 recherche de la sidérurgie française), Saint-Germain-en-Laye, France.

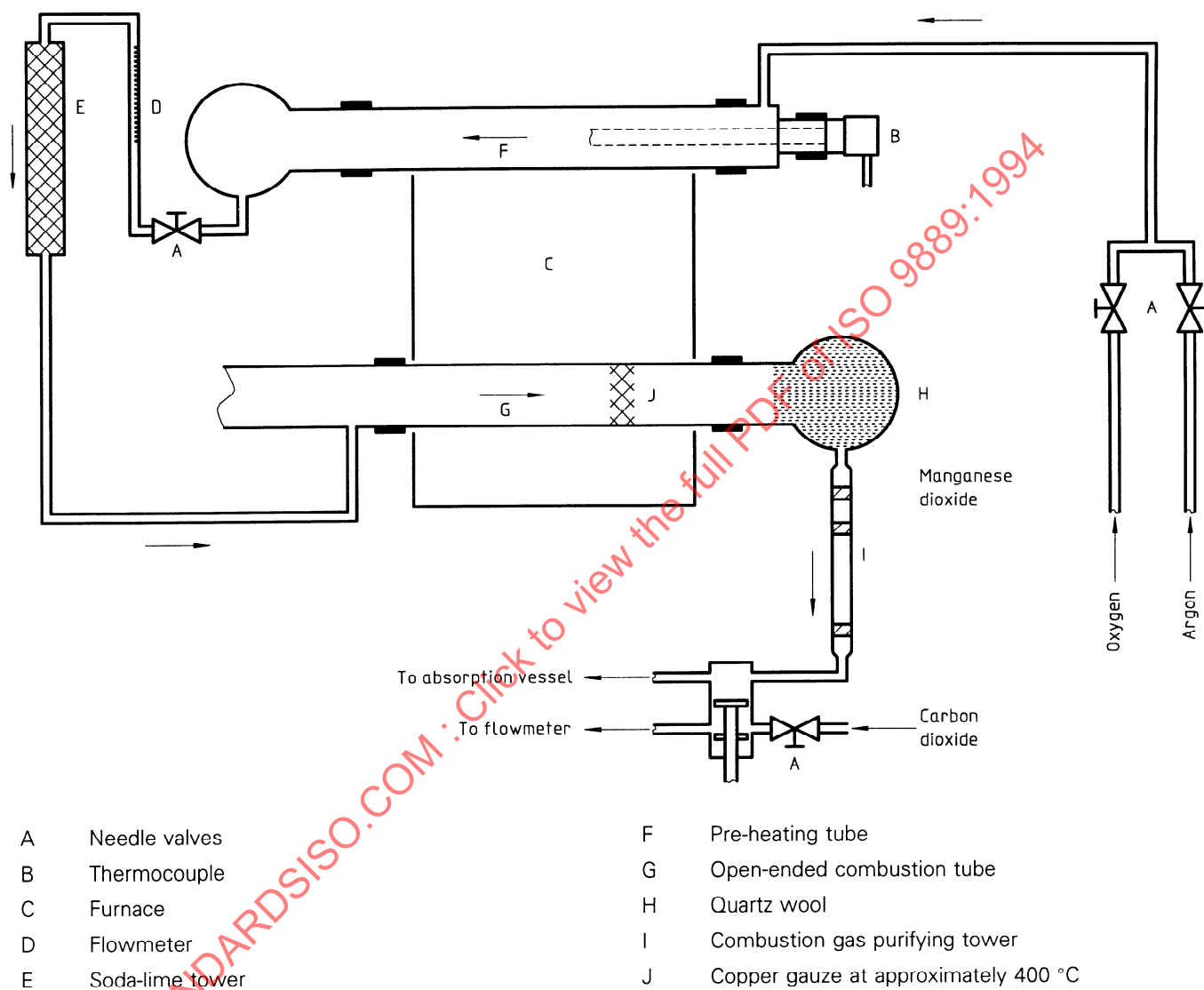


Figure 1 — Combustion furnace

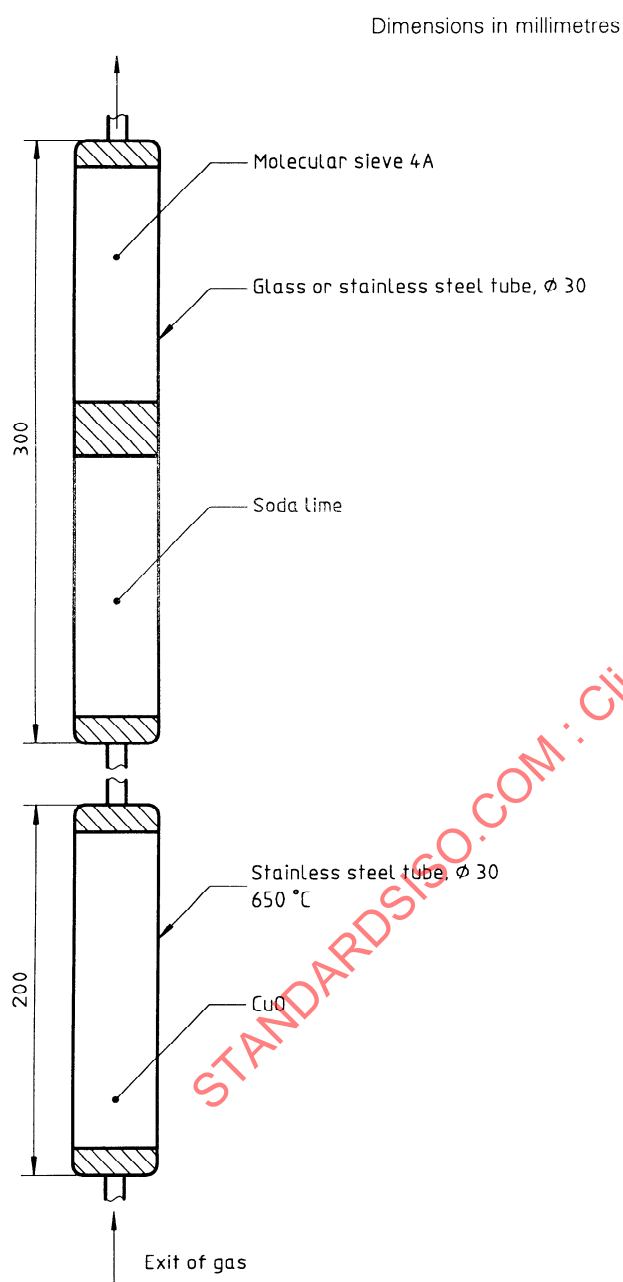


Figure 2 — Oxygen purification system

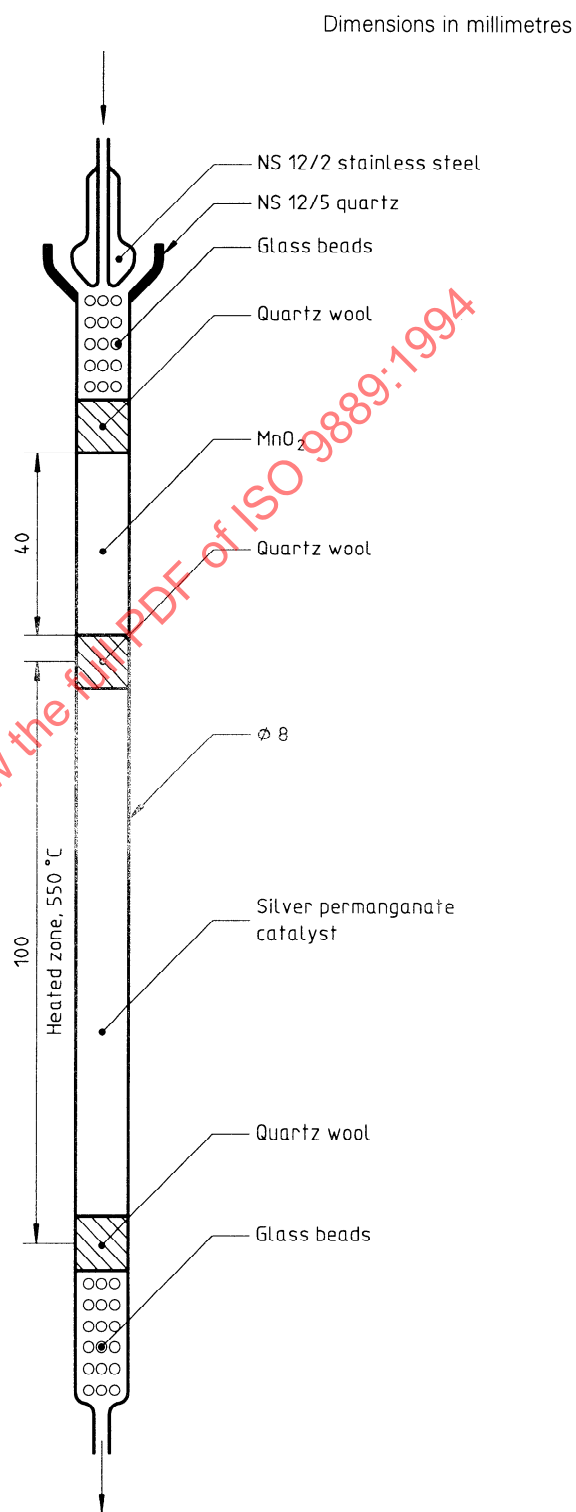


Figure 3 — Combustion gas purification system

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

5.8 Detection system

5.8.1 For titrimetry: titration vessel (see figure 4) or equivalent, temperature controlled at $25\text{ °C} \pm 0,2\text{ °C}$, 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.

5.8.2 For coulometry: commercially available cell (see figure 5).

Efficient stirring with a stirrer basket and temperature control at $35\text{ °C} \pm 0,2\text{ °C}$ should be provided.

5.8.3 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.

5.9 Combustion boats, open form, porcelain, capable of being pre-ignited at 1 000 °C without fracturing on re-igniting at 1 300 °C, and of approximate size 90 mm × 9 mm × 12 mm.

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 the 1 mm sieve.

Retain this fraction for use as the test sample.

NOTE 2 Uranium dioxide powder absorbs carbon dioxide; this interferes with the determination. It is removed prior to analyses (see note 5 in 7.4.5).

7 Procedure

7.1 Setting-up of the apparatus

7.1.1 Pre-ignite a stock of combustion boats (5.9) for at least 4 h at 1 000 °C. Store at 250 °C to avoid absorption of carbon dioxide from the air.

7.1.2 Adjust the temperature of the combustion furnace (5.1) to 1 300 °C, adjust the oxygen flow to 1,5 l/min and set the pump system to deliver 0,5 l/min to the absorption vessel. The remaining 1 l/min leaves the combustion tube at its open end and serves to prevent carbon dioxide from entering the tube by providing an oxygen curtain.

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 Titrate for 4 min periods until the volume of titrant (V_0) or the number of coulombs (C_0) is constant.

In case of infrared detection, compensate the output to zero until stable.

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

7.2.2 Check the absorption efficiency by introducing 50 µl and 500 µl of carbon dioxide from the calibrated injection valves. After 4 min read the volume (V_x) or coulombs (C_x) consumed.

Dimensions in millimetres

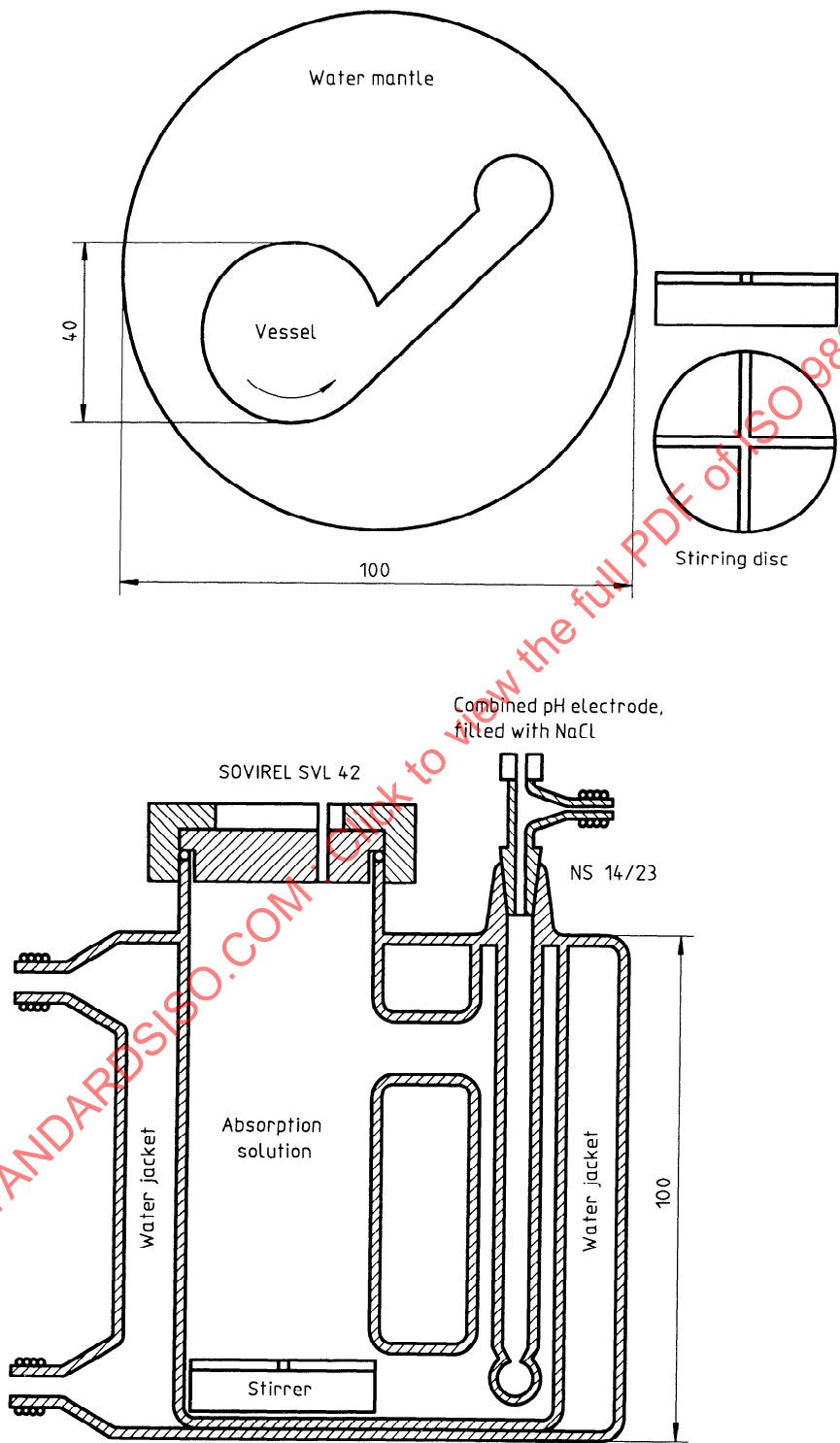


Figure 4 — Titration vessel

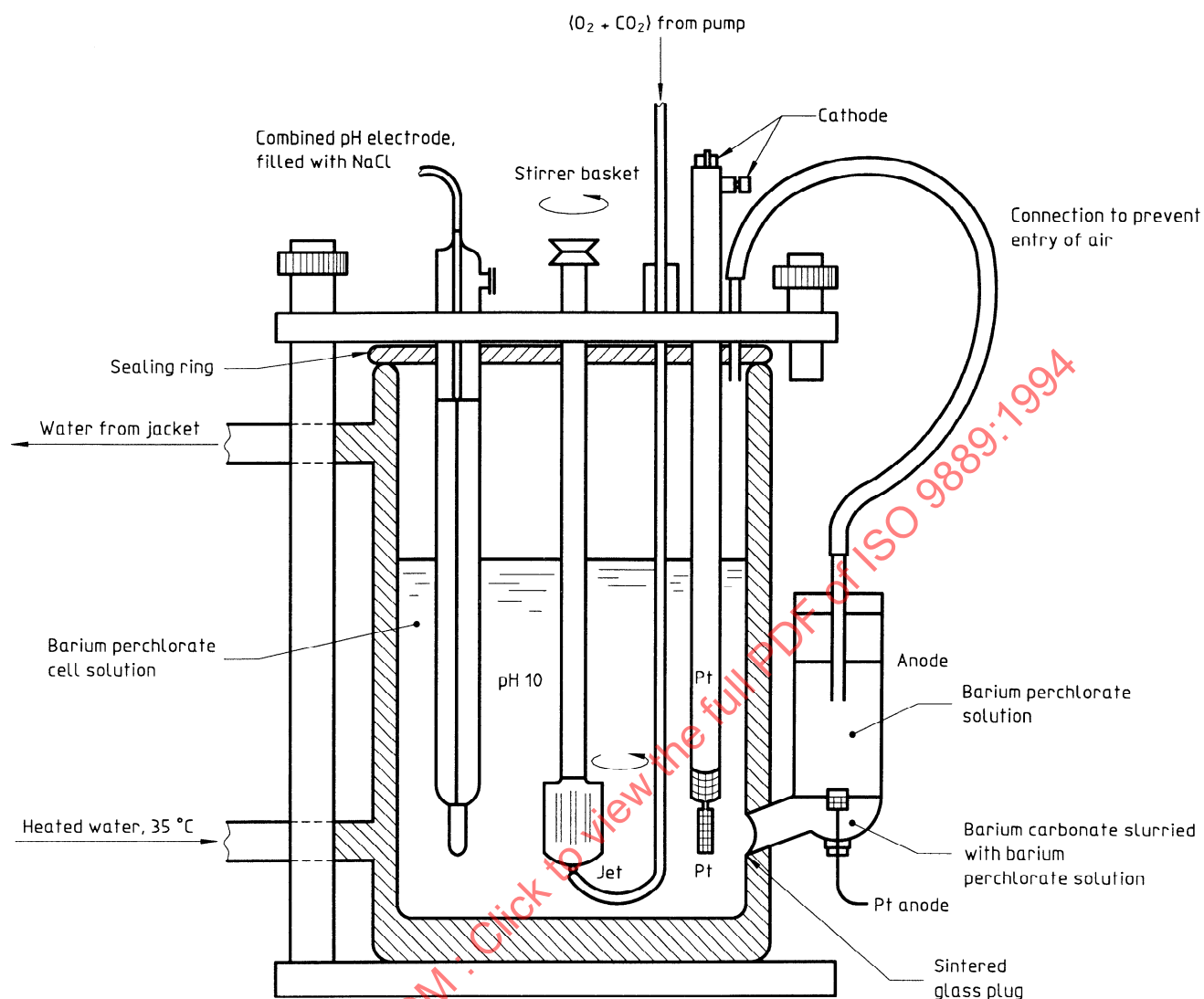


Figure 5 — Coulometric cell

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

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

or

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

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, 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.