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Hard coal -- Determination of oxygen content

Houille -- Dosage de l'oxygène

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INTERNATIONAL STANDARD 1994

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Hard coal — Determination of oxygen content

Houille — Dosage de l'oxygène

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Descriptors : coal, chemical analysis, determination of content, oxygen, volumetric analysis, gravimetric analysis.

FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

Prior to 1972, the results of the work of the technical committees were published as ISO Recommendations; these documents are in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 27, *Solid mineral fuels*, has reviewed ISO Recommendation R 1994-1971 and found it technically suitable for transformation. International Standard ISO 1994 therefore replaces ISO Recommendation R 1994-1971, to which it is technically identical.

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ISO Recommendation R 1994 had been approved by the member bodies of the following countries :

Australia	Greece	Spain
Belgium	India	Sweden
Canada	Italy	Switzerland
Chile	Japan	Thailand
Czechoslovakia	Netherlands	Turkey
Denmark	New Zealand	United Kingdom
Egypt, Arab Rep. of	Poland	U.S.A.
France	Portugal	Yugoslavia
Germany	South Africa, Rep. of	

No member body had expressed disapproval of the Recommendation.

No member body disapproved the transformation of the Recommendation into an International Standard.

Hard coal – Determination of oxygen content

0 INTRODUCTION

This International Standard follows methods developed by Schützel[1], Unterzaucher[2], and Oita and Conway[3] for the direct determination of the oxygen content of organic compounds. Modifications have been incorporated to avoid errors due to the presence of moisture in coal. Oxygen is evolved (as water and carbon dioxide) from the mineral matter associated with the coal when the sample is pyrolysed and, to reduce errors from this source, coals containing more than 5 % of ash and all samples of unknown characteristics should be demineralized before analysis (see ISO 602).

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies semi-micro methods for the direct determination of the oxygen content of hard coal.

2 REFERENCES

ISO 331, *Coal – Determination of moisture in the analysis sample – Direct gravimetric method.*

ISO 348, *Hard coal – Determination of moisture in the analysis sample – Direct volumetric method.*

ISO 602, *Coal – Determination of mineral matter.*

3 PRINCIPLE

The sample is dried at 105 to 110 °C in a stream of nitrogen and then pyrolysed under conditions in which the organic matter leaves an oxygen-free char. The volatile products, containing the organically bound oxygen and also water and carbon dioxide from any mineral matter, are decomposed with either pure carbon or platinized carbon to convert the oxygen to carbon monoxide. The carbon monoxide is oxidized to carbon dioxide and determined by a titrimetric^[4] or a gravimetric procedure.

4 REAGENTS

4.1 Nitrogen.

The nitrogen used for the pyrolysis shall not contain more than 10 ppm of oxygen. If nitrogen of this purity is available commercially, further purification is not necessary if the total "blank" is within the limits specified in clause 7.

4.2 Alternative reagents for converting the volatile pyrolysis products to carbon monoxide

4.2.1 Pure carbon, particle size 0,7 to 2,0 mm¹⁾, ash content not exceeding 0,01 %.

The carbon shall be ignited to dull red heat in an inert atmosphere to remove any oil before being placed in the pyrolysis tube.

Carbon containing up to 0,05 % ash can usually be purified as follows :

To remove any residual oil, heat to dull red, in an inert atmosphere, enough carbon to pack the pyrolysis tube and to provide a sample for the determination of ash. Allow to cool and digest the residue with hydrochloric acid, ρ 1,18 g/ml, at incipient boiling for 1 h. Allow the carbon to settle and decant the liquid through a hardened filter paper in a Buchner funnel. Wash the carbon several times by decantation, then transfer it to the filter and continue until the washings are free from chloride. Dry the cake first by suction, then in an oven at 120 °C.

Crush and sieve the dried cake carefully to obtain the maximum yield of 0,7 to 2,0 mm material. Determine the ash content of the granules.

or

4.2.2 Platinized carbon, particle size 0,7 to 2,0 mm¹⁾, containing about 50 % of platinum.

A suitable method of preparation is as follows :

Dissolve 5 g of platinum in aqua regia and evaporate the solution to near dryness. Add 5 ml of hydrochloric acid, ρ 1,18 g/ml, and again evaporate to near dryness. Continue

1) To avoid too great a resistance to gas flow, it is important that material with particle size below 0,7 mm should be removed by sieving. Excessive resistance to gas flow may necessitate increasing the maximum size to 3 mm.

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adding 5 ml portions of hydrochloric acid and evaporating to near dryness until nitrous fumes are no longer evolved and then evaporate the solution to dryness. Moisten the residue with 2 ml of hydrochloric acid and add sufficient water to dissolve the platinic chloride. Add 5 g of ignited carbon that contains not more than 0,01 % of ash (see 4.2.1) and more water, if necessary, to form a paste. Mix thoroughly and evaporate to dryness on a water bath, mixing frequently with a glass spatula or rod to ensure a homogeneous product. Dry the resulting cake at 150 °C.

Break the cake into pieces and insert them into a 10 to 12 mm internal diameter silica tube. Pass dry nitrogen (4.1) through the tube and heat the tube slowly to red heat, in stages, using a Bunsen burner. Begin heating the tube at the inlet end and when this is hot, move the burner very slowly along the tube until all the contents have been ignited. Replace the nitrogen with hydrogen and heat again in a similar manner in a stream of hydrogen. Repeat heating in hydrogen in this way until the effluent gas is free from hydrogen chloride as shown by its neutrality to litmus. Replace the hydrogen with nitrogen and allow the contents of the tube to cool to room temperature in a stream of nitrogen.

Remove the platinized carbon, and crush and sieve the product carefully to obtain the maximum yield of 0,7 to 2,0 mm material.

4.3 Copper gauze.

4.4 Mixture of lithium hydroxide, particle size 0,7 to 2,0 mm¹⁾ (9 parts by volume) and **soda asbestos**, particle size 0,7 to 2,0 mm¹⁾ (1 part by volume).

4.5 Dry magnesium perchlorate, particle size 0,7 to 2,0 mm¹⁾²⁾.

4.6 Potassium iodide/cotton wool.

Dissolve 160 g of potassium iodide in water and dilute to 250 ml. Impregnate 100 g of cotton wool with this solution and dry at 80 °C in a stream of nitrogen. Store in a dark bottle.

4.7 Alternative reagents for converting carbon monoxide to carbon dioxide

4.7.1 Schütze reagent.

Dry 30 g of pure granular silica gel (particle size 1 to 2 mm) at 200 °C for 1 h and transfer it to a 250 ml round bottom flask fitted with a ground glass cone having an aperture of approximately 25 mm³⁾. Add slowly, with

frequent shaking, 25 ml of sulphuric acid, ρ 1,84 g/ml. Then add, in about 1 g portions, 30 g of finely ground iodine pentoxide; after the addition of each portion of iodine pentoxide, thoroughly mix the contents of the flask by shaking. Close the flask with a socket that has a tube through which the flask can be evacuated. Immerse the flask to the ground joint in an oil bath at 200 °C and evacuate to a pressure less than 5 kPa⁴⁾ for 2 h. Allow the flask to cool under vacuum and transfer the reagent to a dry glass bottle that has a well ground glass stopper. Store the bottle in a desiccator to prevent the reagent from absorbing moisture.

or

4.7.2 Anhydro-iodic acid (HI₃O₈).

If anhydro-iodic acid suitable for the determination of carbon monoxide cannot be obtained commercially, it may be prepared by the following method :

Add an excess of iodic acid or iodine pentoxide to a boiling mixture of 3 volumes of nitric acid, ρ 1,4 g/ml, and 2 volumes of water. Boil the solution with the undissolved excess for 1 h to obtain a saturated solution. Filter the hot solution immediately by suction through a sintered glass filter (pore size 15 to 40 μ m). Leave the filtrate to crystallize for a day. Transfer the crystals to a sintered glass Buchner funnel and wash them with cold nitric acid, ρ 1,4 g/ml. Dry the crystals at room temperature, first by aspirating clean air over them for 1 h and then in a desiccator containing dishes of sodium hydroxide and phosphorus(V) oxide.

or

4.7.3 Red mercury(II) oxide, pellets about 2 mm diameter and 1 mm thick prepared from good quality commercial material.

Mercury(II) oxide having the following specification has been found suitable :

Assay :	not less than 99,3 % (dry)
Loss on drying :	not more than 0,3 % at 150 °C
Mercury(I) salts :	not more than a trace
Chloride :	not more than 0,25 %
Nitrate :	no reaction
Non-volatile residue :	not more than 0,1 %

1) To avoid too great a resistance to gas flow, it is important that material with particle size below 0,7 mm should be removed by sieving. Excessive resistance to gas flow may necessitate increasing the maximum size to 3 mm.

2) The regeneration of magnesium perchlorate should not be attempted owing to the risk of explosion. When exhausted, it should be washed down the sink in a stream of water.

3) See ISO 383, *Laboratory glassware — Interchangeable conical ground joints* : 29/32 or 34/35.

4) 1 kPa = 1 kN/m²

Alternatively, red mercury(II) oxide may be prepared as follows :

Dissolve 140 g of mercury in about 100 ml of nitric acid, ρ 1,4 g/ml. Evaporate the solution to dryness in a porcelain dish. Heat the dish at about 400 °C in an efficient fume cupboard until no yellow crystals of mercury(II) nitrate [Hg(NO₃)₂] remain.

4.8 Silver wire, 0,1 to 0,2 mm diameter.

4.9 Pyridine.

Pyridine having the following specification has been found suitable :

C₅H₅N : not less than 99,0 %

Density at 20 °C : 0,981 to 0,983 g/ml

n_D^{20} : 1,509 0 to 1,510 0

Not less than 95 % distils at 114 to 117 °C

Maximum limits of impurities :

– water-insoluble matter :

nil

– non-volatile matter : 0,002 %

– chloride : 0,000 5 %

– copper : 0,000 2 %

– ammonia : 0,002 %

– oxygen absorbed from permanganate : 0,000 8 %

– water : 0,1 %

If sufficiently pure pyridine is not available, re-distil with a column of 15 to 20 theoretical plates. Using a reflux ratio of 100, distil and reject the first 10 %. Reduce the reflux ratio to 10 and distil and collect the next 75 % for use.

4.10 Ethanolamine.

4.11 Thymol blue indicator, 0,4 % solution in pyridine (4.9).

4.12 Sodium methoxide, 0,05 N standard volumetric solution.

4.12.1 Preparation of the solution

Dissolve 1,15 g of sodium in 500 ml of methanol and dilute with pure pyridine to 1 l. Store the solution so as to exclude carbon dioxide.

4.12.2 Standardization of the solution

Weigh, to the nearest 0,1 mg, about 50 mg of benzoic acid. Place 15 ml of the pyridine (4.9) in a 100 ml conical flask and add 2 drops of the thymol blue indicator (4.11). With nitrogen passing through the flask to exclude air, neutralize

the contents with the sodium methoxide solution, dissolve the weighed benzoic acid in the contents of the flask and titrate with the sodium methoxide solution to a blue end-point.

The normality T of the sodium methoxide solution is given by the formula

$$T = \frac{m}{122,1 V}$$

where

m is the mass, in milligrams, of benzoic acid taken;

V is the volume, in millilitres, of sodium methoxide solution used in the titration.

5 APPARATUS

The general arrangement of the apparatus is shown in figure 1. The components shall be constructed with ground glass joints for connecting one to the other, except for the tube or vessel in which the carbon dioxide produced from the oxygen is absorbed.

5.1 Nitrogen purification train.

A typical purifying train (see figure 2) consists of the following items :

5.1.1 Pressure regulator, containing heavy (medicinal quality) paraffin; a cylinder 300 mm high and 50 mm in diameter is suitable.

5.1.2 Vertical tube, about 120 mm high and 30 mm internal diameter containing dry magnesium perchlorate (4.5).

5.1.3 Vertical quartz tube, about 300 mm long and 15 mm internal diameter containing porous copper heated to approximately 500 °C. Porous copper is produced by reducing copper oxide in wire form with hydrogen diluted with nitrogen at the lowest temperature at which reduction occurs, usually between 200 and 250 °C.

5.1.4 Bubbler, containing heavy (medicinal quality) paraffin, to provide a visual indication of the flow rate of the nitrogen.

5.1.5 U-tube, about 150 mm high and 15 mm internal diameter, the first one-third of which contains a mixture of lithium hydroxide and soda asbestos (4.4), the next one-third magnesium perchlorate (4.5) and the final one-third a mixture of 2 parts by volume of phosphorus(V) oxide powder and 1 part by volume of 0,7 to 2,0 mm glass chips.

5.2 Pyrolysis tube assembly.

The pyrolysis tube shall be of 10 ± 1 mm internal diameter and made from the purest available clear quartz, free from striae and other visible defects.

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Two typical designs for the inlet end of the pyrolysis tube are shown. The design shown in figure 3a) incorporates an auxiliary tube with which it is possible to exclude air while the sample is being inserted. The sample is both dried and pyrolysed between the nitrogen inlet tube and the carbonaceous packing and this section shall be sufficiently long to accommodate any heater used for drying the sample and also for pyrolysing the sample. A suitable removable heater for drying the sample is shown in figure 4.

In the design shown in figure 3b), air admitted when the sample is inserted is removed, together with the moisture, before the sample is pyrolysed. The distance between the nitrogen inlet and the cap of the pyrolysis tube shall be sufficient to accommodate the heater used to dry the sample and the distance between the nitrogen inlet and the carbonaceous packing sufficient for pyrolysing the sample.

The sample may be pyrolysed using either gas or electric heating, but electric furnaces are preferable for heating reagents.

Conversion of the oxygen in the volatile pyrolysis products to carbon monoxide may be achieved either with pure carbon (4.2.1) or with platinized carbon (4.2.2). If pure carbon is used, the packed length shall be 190 to 200 mm. Rolled platinum gauze plugs 5 mm long shall be used to retain the packing in position. A furnace shall be provided to heat the carbon to $1\ 125 \pm 25$ °C.

If platinized carbon is used, the packing shall consist of two 45 to 50 mm sections separated and retained by 5 mm long platinum gauze plugs. A furnace shall be provided to heat the platinized carbon to 940 °C, but the normal operating temperature is 910 ± 10 °C.

Either reducing agent shall be followed by a roll of copper gauze (4.3), 50 to 60 mm long, heated by a suitable furnace to 900 °C.

5.3 Carbon monoxide purification tube.

The tube shall have an internal diameter of 10 to 15 mm and a length of 190 to 210 mm. A length of 130 to 140 mm is packed with a mixture of lithium hydroxide and soda asbestos (4.4) to remove acidic gases (HCl, H₂S, etc.), followed by about 60 to 70 mm packed with dry magnesium perchlorate (4.5) to remove water produced by reaction of the acidic gases with the soda asbestos.

5.4 Carbon monoxide oxidation tube.

The tube shall have an internal diameter of 10 ± 1 mm and a length of 220 to 250 mm (depending on which of the alternative reagents is used). The tube is packed with one of the following series of reagents in the order given in each case :

- a) 1) 15 to 20 mm packed with potassium iodide/cotton wool (4.6);
- 2) 100 to 110 mm packed with the Schütze reagent (4.7.1);

3) 35 to 40 mm packed with potassium iodide/cotton wool (4.6);

4) 45 to 50 mm packed with dry magnesium perchlorate (4.5).

Adjacent reagents shall be separated and retained by plugs of glass wool 5 mm long.

or

b) 1) 130 to 140 mm packed with anhydro-iodic acid (4.7.2), heated to 120 °C;

2) 35 to 40 mm packed with potassium iodide/cotton wool (4.6);

3) 45 to 50 mm packed with dry magnesium perchlorate (4.5).

Adjacent reagents shall be separated and retained by plugs of glass wool 5 mm long.

or

c) 1) 140 to 150 mm packed with red mercury(II) oxide (4.7.3), retained by 5 mm plugs of glass wool and heated to 200 °C;

2) 45 to 50 mm empty (and at room temperature) to allow mercury to condense;

3) 35 to 40 mm packed with a plug of silver wire (4.8) to absorb mercury vapour.

5.5 Apparatus for determining the carbon dioxide produced in the oxidation tube (5.4)

5.5.1 Titrimetric finish

Suitable apparatus for absorbing and titrating the carbon dioxide is shown in figure 5.

5.5.2 Gravimetric finish

A convenient design of absorption tube is shown in figure 6. The absorption tube is followed by a guard tube containing dry magnesium perchlorate (4.5) and a mixture of lithium hydroxide and soda asbestos (4.4).

A balance accurate to 0,01 mg is necessary for weighing the absorption tube.

5.6 Platinum boat, about 15 mm long, 4 mm wide and 4 mm deep, which has a lug pierced with a hole attached at one of its upper ends to facilitate removal from the apparatus.

6 SAMPLE

The coal used for the determination is the analysis sample, ground to pass a sieve of 200 µm aperture. Before commencing a determination, thoroughly mix the air-dried sample of coal for at least 1 min, preferably by mechanical means.

7 PREPARATION OF THE APPARATUS

Assemble the components of the apparatus, charged with the appropriate reagents as indicated in clauses 4 and 5, in the order shown in figure 11¹⁾. Use low vapour pressure grease and wax that are impervious to atmospheric oxygen, carbon dioxide and water vapour to seal the ground joints. Use tubing impervious to water vapour and carbon dioxide²⁾ to connect the absorption vessel or tube to the oxidation tube; the ends of the glass tubes inside the sleeve shall touch.

Adjust the nitrogen flow rate to 25 ml/min. Check that the apparatus is gas-tight, for example by pressurizing the apparatus to the pressure provided by the regulator in the nitrogen purification train (5.1) and observing that the flow of nitrogen through the bubbler (5.1.4) ceases. Heat the reagents to their working temperatures and heat the section of the pyrolysis tube in which the sample will be pyrolysed to a minimum temperature of 900 °C. Sweep out the apparatus with nitrogen for at least 15 h.

Carry out a blank determination as specified in clause 8, but omitting the sample. If the blank is equivalent to more than 0,12 mg of oxygen, i.e. more than 0,15 ml of 0,05 N sodium methoxide solution (titrimetric finish) or more than 0,33 mg of carbon dioxide (gravimetric finish), sweep out the apparatus with nitrogen for a further period and then re-check the blank³⁾. When satisfactory blanks are obtained, check the performance of the apparatus using a pure organic compound⁴⁾⁵⁾. If the result is within 0,2 % of the theoretical oxygen content, the apparatus is ready for use⁶⁾.

8 PROCEDURE

Heat the platinum boat (5.6) in nitrogen to the pyrolysis temperature and allow it to cool in nitrogen. Weigh, to the nearest 0,1 mg, 20 to 50 mg⁵⁾ of the sample into the boat.

8.1 Pyrolysis tube of the form shown in figure 3a)

8.1.1 Titrimetric finish

With nitrogen passing through the apparatus at about 25 ml/min, allow about 12 ml of the pyridine (4.9) to flow slowly from the reservoir to the absorption vessel so that pyridine does not enter the jet. Add about 100 mg of the ethanolamine (4.10) and 2 drops of the thymol blue indicator solution (4.11). Wait 2 to 3 min for the contents of the vessel to mix and then neutralize the solution with the 0,05 N sodium methoxide solution (4.12) to the blue end-point. Close stopcock S₂ (figure 5) at the entrance to the absorption vessel⁷⁾.

Pass nitrogen into the auxiliary tube at about 50 ml/min. Remove the stopper from the pyrolysis tube and fit the auxiliary tube. Using the magnet, slide the boat holder into the auxiliary tube. Insert the boat containing the sample into the holder and immediately slide it into the pyrolysis tube, remove the auxiliary tube and replace the stopper in the pyrolysis tube.

Pressurize the apparatus to the pressure provided by the regulator in the nitrogen purification train (figure 2a). Open stopcock S₂ (figure 5). Heat the boat to 105 to 110 °C in about 10 min. Titrate the carbon dioxide produced from the moisture in the sample continuously, to the blue end-point. Maintain the boat at 105 to 110 °C until the production of carbon dioxide ceases (about 20 min), thus showing that the sample is dry⁸⁾. Read the burette, pyrolyse the sample at a minimum temperature of 900 °C for 20 min and titrate the carbon dioxide continuously to the blue end-point. Sweep out the apparatus for a further 10 min and complete the titration⁹⁾.

- 1) The reagents used in the titrimetric procedure contain pyridine, which necessitates housing the apparatus in well ventilated surroundings.
- 2) Polyethylene or polytetrafluorethylene tubing is suitable for connecting the absorption vessel when the titrimetric finish is used, and butyl rubber or natural rubber impregnated with wax for the absorption tube in the gravimetric finish.
- 3) It may be necessary to sweep with nitrogen for a few days before a satisfactory blank is obtained.
- 4) Acetanilide, anthraquinone, benzoic acid, 2-naphthol, octadecanol, sucrose or vanillin is suitable.
- 5) The mass of sample taken shall be such that the blank is equivalent to an oxygen content not exceeding 0,25 %.
- 6) Some batches of platinized carbon need a higher temperature than 920 °C. If the values are only slightly low, raise the operating temperature to 940 °C and again check the performance of the apparatus.
- 7) This stopcock must be closed when the pyrolysis tube is opened to insert the sample, to prevent the reagent in the absorption vessel flowing into the jet, where carbon dioxide would be absorbed but not titrated.
- 8) The moisture content of the sample may be calculated from the volume of sodium methoxide used. 1 ml of N sodium methoxide is equivalent to 18,02 mg of water.
- 9) Alternatively, the pre-drying may be omitted and the total oxygen in the air-dried sample, including that present as moisture, determined by heating for 10 min at 105 to 110 °C and 20 min at a minimum temperature of 900 °C, followed by 10 min sweeping out. The moisture is determined separately (see ISO 331 or ISO 348) and the oxygen present as moisture deducted from the total oxygen (water contains 88,81 % of oxygen).