

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION R 1994

HARD COAL

DETERMINATION OF OXYGEN

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BRIEF HISTORY

The ISO Recommendation R 1994, *Hard coal – Determination of oxygen*, was drawn up by Technical Committee ISO/TC 27, *Solid mineral fuels*, the Secretariat of which is held by the British Standards Institution (BSI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1994, which was circulated to all the ISO Member Bodies for enquiry in June 1970.

The Draft was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

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

No Member Body opposed the approval of the Draft.

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided to accept it as an ISO RECOMMENDATION.

HARD COAL

DETERMINATION OF OXYGEN

INTRODUCTION

This ISO Recommendation follows methods developed by Schütze ⁽¹⁾, Unterzaucher ⁽²⁾, and Oita and Conway ⁽³⁾ for the direct determination of oxygen in 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 ⁽⁴⁾ before analysis.

1. SCOPE

This ISO Recommendation describes semi-micro methods for the direct determination of oxygen in hard coal.

2. 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 ⁽⁵⁾ or a gravimetric procedure.

3. REAGENTS

3.1 *Nitrogen.* The nitrogen used for the pyrolysis should contain not 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 section 6.

3.2 *Alternative reagents for converting the volatile pyrolysis products to carbon monoxide*

(a) *Pure carbon*, 0.7 to 2.0 mm ⁽⁶⁾, ash content not exceeding 0.01 %.

The carbon should 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 :

Heat enough carbon to pack the pyrolysis tube and to provide a sample for the determination of ash to dull red heat in an inert atmosphere to remove any residual oil. Allow to cool and digest the residue with hydrochloric acid ($d = 1.18$) at incipient boiling for 1 hour. 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.

(1) Schütze, M.Z., Anal. Chem., 1939, 118, 258.

(2) Unterzaucher, J., Analyst, 1952, 77, 584.

(3) Oita, I.J. and Conway, H.S., Anal. Chem., 1954, 26, 600.

(4) See ISO Recommendation R 602, *Determination of mineral matter in coal*.

(5) Blom, L., Zeit. Anal. Chem., 1962, 189, 91.

(6) To avoid too great a resistance to gas flow, it is important that material < 0.7 mm should be removed by sieving. Excessive resistance to gas flow may necessitate increasing the maximum size to 3 mm.

or

- (b) *Platinized carbon* 0.7 to 2.0 mm ⁽¹⁾, 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 ($d = 1.18$) and again evaporate to near dryness. Continue 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 clause 3.2(a)) 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 quartz tube. Pass dry nitrogen (3.1) 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.

3.3 *Copper gauze*

3.4 *Soda asbestos*, 0.7 to 2.0 mm ⁽¹⁾.

3.5 *Dry magnesium perchlorate*, 0.7 to 2.0 mm ⁽¹⁾ ⁽²⁾.

3.6 *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.

3.7 *Alternative reagents for converting carbon monoxide to carbon dioxide*

- (a) *Schütze reagent*. Dry 30 g of pure granular silica gel (1 to 2 mm) at 200 °C for 1 hour and transfer it to a 250 ml round-bottomed flask fitted with a ground glass cone having an aperture of approximately 25 mm ⁽³⁾. Add slowly, with frequent shaking, 25 ml of sulphuric acid ($d = 1.84$). 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 0.05 bar for 2 hours. 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.

(1) To avoid too great a resistance to gas flow, it is important that material < 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 Recommendation R 383, *Interchangeable conical ground glass joints* : 29/32 or 34/35.

or

(b) *Anhydro-iodic acid* (HI_3O_8).

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 ($d = 1.4$) and 2 volumes of water. Boil the solution with the undissolved excess for 1 hour to obtain a saturated solution. Filter the hot solution immediately, by suction, through a sintered glass filter (pore size 15 to 40 μm). Leave the filtrate to crystallize for a day. Transfer the crystals to a sintered glass Buchner funnel and wash them with cold nitric acid ($d = 1.4$). Dry the crystals at room temperature, first by aspirating clean air over them for 1 hour and then in a desiccator containing dishes of sodium hydroxide and phosphorus pentoxide.

or

(c) *Red mercuric oxide*, pellets about 2 mm diameter and 1 mm thick prepared from good quality commercial material.

Mercuric 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
Mercurous salts :	not more than a trace
Chloride :	not more than 0.25 %
Nitrate :	no reaction
Non-volatile residue :	not more than 0.1 %

Alternatively, red mercuric oxide may be prepared as follows :

Dissolve 140 g of mercury in about 100 ml of nitric acid ($d = 1.4$). 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 mercuric nitrate [$\text{Hg}(\text{NO}_3)_2$] remain.

3.8 *Silver wire*, 0.1 to 0.2 mm diameter.

3.9 *Pyridine*

Pyridine having the following specification has been found suitable :

$\text{C}_5\text{H}_5\text{N}$:	not less than 99.0 %
Density at 20 °C :	0.981 to 0.983 g/ml
n_D^{20} :	1.5090 to 1.5100

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

Maximum limits of impurities :

– water-insoluble matter :	nil
– non-volatile matter :	0.002 %
– chloride :	0.0005 %
– copper :	0.0002 %
– ammonia :	0.002 %
– oxygen absorbed from permanganate :	0.0008 %
– 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.