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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION
R 625

DETERMINATION OF CARBON AND HYDROGEN IN COAL AND COKE BY THE LIEBIG METHOD

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BRIEF HISTORY

The ISO Recommendation R 625, *Determination of Carbon and Hydrogen in Coal and Coke by the Liebig Method*, 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 by the Technical Committee began in 1952 and led, in 1958, to the adoption of a Draft ISO Recommendation.

This first Draft ISO Recommendation (No. 236) was circulated in May 1958 to all the ISO Member Bodies for enquiry. As the results of this consultation were not considered satisfactory the Technical Committee presented a Second Draft ISO Recommendation, which was circulated to all the Member Bodies in October 1963 and which was approved, subject to a few modifications of an editorial nature, by the following Member Bodies:

Argentina
Australia
Austria
Belgium
Bulgaria
Canada
Chile
Czechoslovakia
Denmark
Germany
Greece
India
Italy
Korea, Rep. of
Netherlands
New Zealand
Poland
Portugal
Republic of South Africa
Romania
Spain
Switzerland
Turkey
United Kingdom
U.S.A.
U.S.S.R.
Yugoslavia

One Member Body opposed the approval of the Draft:

France

This Second Draft ISO Recommendation was then submitted by correspondence to the ISO Council which decided, in October 1967, to accept it as an ISO RECOMMENDATION.

UDC 662.6/.7 : 620.1

Ref. No. : ISO/R 625-1967/A1-1971 (E)

Amendment 1 – November 1971 – to ISO Recommendation R 625-1967

Amendment 1
to ISO Recommendation R 625-1967

DETERMINATION OF CARBON AND HYDROGEN IN COAL AND COKE BY THE LIEBIG METHOD

Section 3, REAGENTS

Delete the 3rd line of clause 3.1.
Delete clause 3.2.
Delete the 1st sentence of the Note.
Delete the 2nd line of clause 3.3.
Delete clause 3.4.

Accordingly renumber clauses 3.3 to 3.10.

Section 4, APPARATUS

Clause 4.1

Delete "*or* calcium chloride (3.2)", "*or* potassium hydroxide (3.4)" and "*or* calcium chloride (3.2)" in the 3rd, 5th and 6th lines.
Replace "3.3" by "3.2" in the 5th line.

Clause 4.3

Delete "*or* calcium chloride (3.2)" in the 3rd, 6th and 9th lines, and "*or* potassium hydroxide (3.4)" in the 8th line.
Replace "3.5" by "3.3" and "3.3" by "3.2" in the 5th and 8th lines respectively.

Section 5, PREPARATION OF THE APPARATUS AND BLANK DETERMINATION

Replace all the reference numbers 3.6 to 3.9 by 3.4 to 3.7 respectively.

BRIEF HISTORY

Amendment 1 to ISO Recommendation R 625-1967, *Determination of carbon and hydrogen in coal and coke by the Liebig method*, was drawn up by Technical Committee ISO/TC 27, *Solid mineral fuels*, the Secretariat of which is held by the British Standards Institution (BSI).

Draft ISO Recommendation No. 1937 was drawn up on this subject, and was circulated to all the ISO Member Bodies for enquiry in April 1970. It was approved by the following Member Bodies :

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

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 AMENDMENT 1 to ISO Recommendation R 625-1967.

ISO Recommendation R 625 October 1967

DETERMINATION OF CARBON AND HYDROGEN IN COAL AND COKE BY THE LIEBIG METHOD

1. SCOPE

This ISO Recommendation describes the Liebig method of determining the total carbon and the total hydrogen in hard coal, brown coal and lignite, and coke; the results include the carbon in the carbonates and the hydrogen combined in the moisture and in the water of hydration of silicates. A determination of moisture is carried out at the same time and the appropriate correction is applied to the hydrogen value obtained by combustion. A determination of carbon dioxide may also be made and the total carbon value corrected for the presence of mineral carbonates.

2. PRINCIPLE

The sample is burned in a current of oxygen, the products of the incomplete combustion being burned over copper oxide; all the hydrogen is converted to water and all the carbon to carbon dioxide. These products are absorbed by suitable reagents and determined gravimetrically. Oxides of sulphur are retained by lead chromate, chlorine by silver gauze and oxides of nitrogen by granular manganese dioxide.

NOTE. — Oxides of nitrogen formed in the combustion would in the absence of precautions, be absorbed by the soda asbestos and considered as carbon dioxide. The error in the carbon determination thus caused, of the order of 0.2 % of carbon, is substantially avoided by the use of a guard-tube (see Fig. 1, page 9) in which the gases pass through an annular space to allow oxidation of nitric oxide to nitrogen peroxide, which is absorbed by the manganese dioxide.

If water is condensed in the first absorber, some nitrogen peroxide may dissolve in it and be considered as water. Because of the conversion factor from water to hydrogen, the error in the hydrogen determination thus caused is small, of the order of 0.05 % of hydrogen. This can be avoided only by heating the absorption tube to a sufficient temperature to prevent condensation of water.

3. REAGENTS

All reagents should be of analytical reagent quality. Distilled water should be used throughout.

3.1 **Magnesium perchlorate, anhydrous (anhydrone).** Free from dust and within the size range 2.4 to 0.4 mm; preferably within the size range 1.2 to 0.7 mm (see Note below)

or, if magnesium perchlorate is not readily available,

3.2 **Calcium chloride, anhydrous.** Freshly prepared and of size range 1.2 to 0.7 mm.

NOTE. — Calcium chloride should be saturated with carbon dioxide before use; many varieties of anhydrone do not need this conditioning treatment, but a new source should be checked in this respect before use. Regeneration of magnesium perchlorate should not be attempted, owing to the risk of explosion. When exhausted the magnesium perchlorate should be washed down the sink with a current of water.

3.3 **Soda asbestos.** Size range 1.2 to 0.7 mm;

or, if soda asbestos is not readily available:

3.4 **Potassium hydroxide.** Pellet or stick form.

3.5 **Manganese dioxide, granular.** Dissolve manganese sulphate in water and boil the solution. Make alkaline with dilute ammonia and add solid ammonium persulphate, in small portions, to the boiling solution until precipitation is complete. Filter through a fast, hardened paper, wash with water by decantation, then with dilute sulphuric acid and finally with water until acid-free. Transfer the moist precipitate to a mortar and place in an oven until most of the water has evaporated, but the powder is still damp. Press the mass into a cake with a pestle, using firm pressure. Complete the drying, break up the cake cautiously and sieve to separate the 1.2 to 0.7 mm size.

3.6 **Copper gauze.**

3.7 **Copper oxide.** Wire form.

3.8 **Lead chromate.** Fused, size range 2.4 to 1.2 mm.

3.9 **Pure silver gauze.** Approximately 10 meshes per centimetre, made of wire approximately 0.3 mm in diameter.

3.10 **Oxygen, hydrogen-free.** The oxygen should preferably be prepared from liquid air and not by electrolysis. Electrolytically prepared oxygen should be passed over red hot copper oxide before use to remove any trace of hydrogen.

4. APPARATUS

4.1 **A purification train,** for absorbing water vapour and carbon dioxide present in the oxygen. Assemble the train using the following reagents in the order stated:

(1) Magnesium perchlorate (3.1) *or* calcium chloride (3.2) for absorbing water (see Note below).

(2) Soda asbestos (3.3) *or* potassium hydroxide (3.4) for absorbing carbon dioxide.

(3) Magnesium perchlorate (3.1) *or* calcium chloride (3.2) for absorbing the water evolved in the reaction between carbon dioxide and soda asbestos (see Note below).

The purification train should be large enough to render frequent recharging unnecessary even with continuous use.

4.2 Combustion device

4.2.1 *Furnaces.* The combustion tube is heated by three furnaces, the lengths of which should be specified by the standardizing authority in each country. For the 127 cm combustion tube described in section 5, the following lengths are appropriate:

Furnace No. 1 to heat the boat and its contents to 925 °C — 24 cm.
Furnace No. 2 to keep the copper oxide section of the tube heated throughout to 800 °C — 47 cm.

Furnace No. 3 to cover the lead chromate and the roll of pure silver gauze and to heat the former to about 500 °C — 21.5 cm.

4.2.2 *A combustion tube* of fused silica or suitable hard glass. The diameter of the tube and the lengths of the various packings can be varied and should be specified by the standardizing authority in each country (see section 5).

4.2.3 *A combustion boat* of platinum, porcelain or fused silica, approximately 7 cm long.

4.3 **An absorption train,** for absorbing the water and carbon dioxide evolved by the combustion of the sample. Assemble the train using the following reagents in the order stated:

(1) Magnesium perchlorate (3.1) *or* calcium chloride (3.2) for absorbing the water evolved during the combustion (see Note below).

(2) Granular manganese dioxide (3.5) for absorbing oxides of nitrogen.

(3) Magnesium perchlorate (3.1) *or* calcium chloride (3.2) for absorbing the water evolved from the manganese dioxide.

(4) Soda asbestos (3.3) *or* potassium hydroxide (3.4) for absorbing carbon dioxide.

(5) Magnesium perchlorate (3.1) *or* calcium chloride (3.2) for absorbing the water produced in the reaction between carbon dioxide and soda asbestos (see Note below).

A typical absorption train, with details of the packing, is shown in Figure 2, page 10. *A* is the absorber for water, *B* is the absorber for oxides of nitrogen, and *C* absorbs any water evolved from the manganese dioxide. Carbon dioxide is absorbed in *D*, the magnesium perchlorate in the upper portion serving to absorb any water produced in the reaction between carbon dioxide and soda asbestos.

Stoppered U-tubes may be used, if preferred, in place of the Midvale tubes (illustrated in Fig. 3).

4.4 **Control of oxygen flow rate.** A reducing valve on the oxygen cylinder together with a small needle valve immediately before the purification train is generally adequate. A bubbler device (see Note below) may usefully be attached at the exit end of the assembled apparatus to give a visual indication of the rate of flow.

4.5 **Balance,** sensitive to 0,1 mg.

NOTE. — It is permissible to use sulphuric acid, $d = 1.84$, in place of the solid reagent in the water absorbing units, in which case a separate bubbler is unnecessary, but particular care is required to ensure that the acid is not carried or drawn into any other part of the train during a determination.

5. PREPARATION OF THE APPARATUS AND BLANK DETERMINATION

For a combustion tube 127 cm long and 12 to 15 mm diameter, the following arrangement of the packing is suitable:

- 1 cm space for a rubber stopper,
- 30 cm space to allow the furnace to be removed behind and away from the boat,
- 8 cm occupied by a spiral of the copper gauze* (3.6), through which passes a stout copper wire provided with a loop for convenience in withdrawal,
- 7 cm space for the boat,

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* The copper gauze spiral and rolls are oxidized during the preliminary heating in a current of oxygen.

- 5 cm space to prevent the front of the boat being heated too soon,
- 1 cm occupied by a plug roll of the copper gauze* (3.6),
- 47 cm occupied by the copper oxide (3.7),
- 1 cm occupied by a plug roll of the copper gauze* (3.6),
- 10 cm occupied by the lead chromate (3.8),
- 1 cm occupied by a plug roll of the copper gauze* (3.6),
- 10 cm occupied by a roll of the pure silver gauze (3.9),
- 5 cm space,
- 1 cm space for a rubber stopper.

In setting up the assembly, and in order to avoid leakage of gas, there should be a minimum of rubber connections and all joints should be made glass to glass. Grease used for lubricating stoppers should have a low vapour pressure.

Before starting a determination with a newly-packed combustion tube, heat the tube throughout its length, while passing a current of oxygen at a rate of about 12 ml** per minute. Heating should be continued for 3 hours, with furnace No. 1 at a temperature of 925 °C, furnace No. 2 at a temperature of 800 °C and furnace No. 3, containing that portion of the tube packed with lead chromate and pure silver gauze, at a temperature of about 500 °C. The empty space adjacent to the exit end of the tube should be heated in such a manner that, without charring the rubber stopper, condensation of steam is avoided.

For a blank determination, connect the absorption train to the apparatus and purge with oxygen for 20 minutes, with the furnaces at their working temperatures. Disconnect absorbers *A* and *D* from the absorption train, stopper the side-arms and close the taps, and allow them to cool to the balance room temperature. Wipe each absorber with a clean cloth, remove the stoppers from the side-arms and weigh each absorber. Re-connect the absorption train to the combustion tube and reopen the taps. Particular care should be taken to ensure that the inlet of the water-absorption tube of the absorption train is flush with the inner end of the rubber stopper in the combustion tube and that all joints between the component parts of the absorption train are made by bringing the ends of tubes close together, using the rubber tubing merely as a seal. After the absorption train has remained attached to the apparatus for a period of 2 hours, remove and weigh absorbers *A* and *D* as before, observing the same precautions as in the initial weighing. If each of these absorbers is within 0.0005 g of its previous mass, the apparatus is considered to be in a proper condition for use.

NOTE. — Absorbers *A* and *D* should be weighed full of oxygen before and after a determination, purging with air being unnecessary; absorbers *B* and *C* are not weighed. A second carbon dioxide absorber may be added as a precautionary measure, if desired.

6. PROCEDURE

When starting the first determination of each day, raise the temperatures of the furnaces to 925 °C, 800 °C and 500 °C respectively, whilst passing oxygen at the rate of 12 ml** per minute. Connect the absorption train and purge for 20 minutes. Disconnect the train and weigh absorbers A and D as described above. Switch off furnace No. 1 and allow it to cool.

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* The copper gauze spiral and rolls are oxidized during the preliminary heating in a current of oxygen.

** The volume of 12 ml per minute relates to a combustion tube of 12 to 15 mm diameter. The standardizing authority in a country specifying a tube of a different diameter should also specify an appropriate oxygen flow rate.

Before commencing the determination, mix the air-dried sample of coal or coke, ground to pass a sieve of 0.2 mm aperture, thoroughly for at least 1 minute, preferably by mechanical means. A small portion of the sample should be re-exposed to the air for a few hours and again mixed before weighing out the quantity required for the determination.

A determination of moisture should be made immediately on the remainder of this small sample.

Weigh accurately between 0.2 and 0.3 g of the sample and spread evenly over the bottom of a previously ignited boat. Connect the weighed absorption train to the combustion tube as described above. Place the boat and the oxidized copper roll in the combustion tube, insert the rubber stopper connecting the purification train and pass oxygen through the apparatus at a rate of about 12 ml* per minute. Switch on furnace No. 1 and start the combustion by heating the copper roll; when this is at 800 °C, gradually draw the furnace forward to cover the boat and its contents, keeping a steady stream of oxygen through the whole system while the sample is being burned. Continue until all visible carbon has disappeared and until the portion of the combustion tube containing the sample has been raised to 925 °C.

After combustion is complete, switch off furnace No. 1, allow the exit end of the combustion tube to cool and disconnect the absorption train. Wipe absorbers *A* and *D*, allow them to cool as before, and weigh.

NOTE. — Two hours are usually sufficient to complete the combustion of coal samples and 1 hour may be sufficient for most coke samples.

Carefully inspect the ash in the boat for unburnt carbon; if present, this invalidates the determination, which should then be repeated.

7. CALCULATION AND EXPRESSION OF RESULTS

If

m_1 = mass of sample taken, expressed in grammes,

m_2 = increase in mass of soda asbestos tube, expressed in grammes,

m_3 = increase in mass of anhydrone tube, expressed in grammes,

M = moisture in the sample as analysed, expressed as a percentage,

CO_2 = carbon dioxide in the sample as analysed**, expressed as a percentage,

C = total carbon in the sample as analysed, expressed as a percentage,

C_1 = total carbon less that present as carbon dioxide,

H = total hydrogen in the sample as analysed, expressed as a percentage,

and

H_1 = total hydrogen less that present as moisture, expressed as a percentage,

then

$$C = 27.29 \frac{m_2}{m_1}$$

$$C_1 = C - 0.273\ CO_2$$

$$H = 11.19 \frac{m_3}{m_1}$$

and

$$H_1 = H - 0.1119\ M$$

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* The volume of 12 ml per minute relates to a combustion tube of 12 to 15 mm diameter. The standardizing authority in a country specifying a tube of a different diameter should also specify an appropriate oxygen flow rate.

** See ISO R . . ., *Determination of carbon dioxide in coal*, at present at the stage of draft proposal.

The results (preferably the mean of duplicate determinations, see section 8 below) should be reported to the nearest 0.1% for the carbon determination and to the nearest 0.01% for the hydrogen determination.

Calculation of the results to other bases is being studied* and will be the subject of a separate ISO Recommendation.

8. ACCURACY OF DETERMINATION

	Maximum acceptable differences between results obtained	
	in the same laboratory	in different laboratories
Carbon	0.25% absolute	0.5% absolute
Hydrogen	0.12% absolute	0.25% absolute

8.1 In the same laboratory.

The results of duplicate determinations carried out at different times in the same laboratory by the same operator with the same apparatus, on representative portions taken from the same sample after the last stage of the reduction process, should not differ by more than the above values.

8.2 In different laboratories.

The means of the results of duplicate determinations carried out in each of two different laboratories on representative portions taken from the same sample after the last stage of the reduction process should not differ by more than the above values.

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* By Technical Committee ISO/TC 27, *Solid Mineral Fuels.*

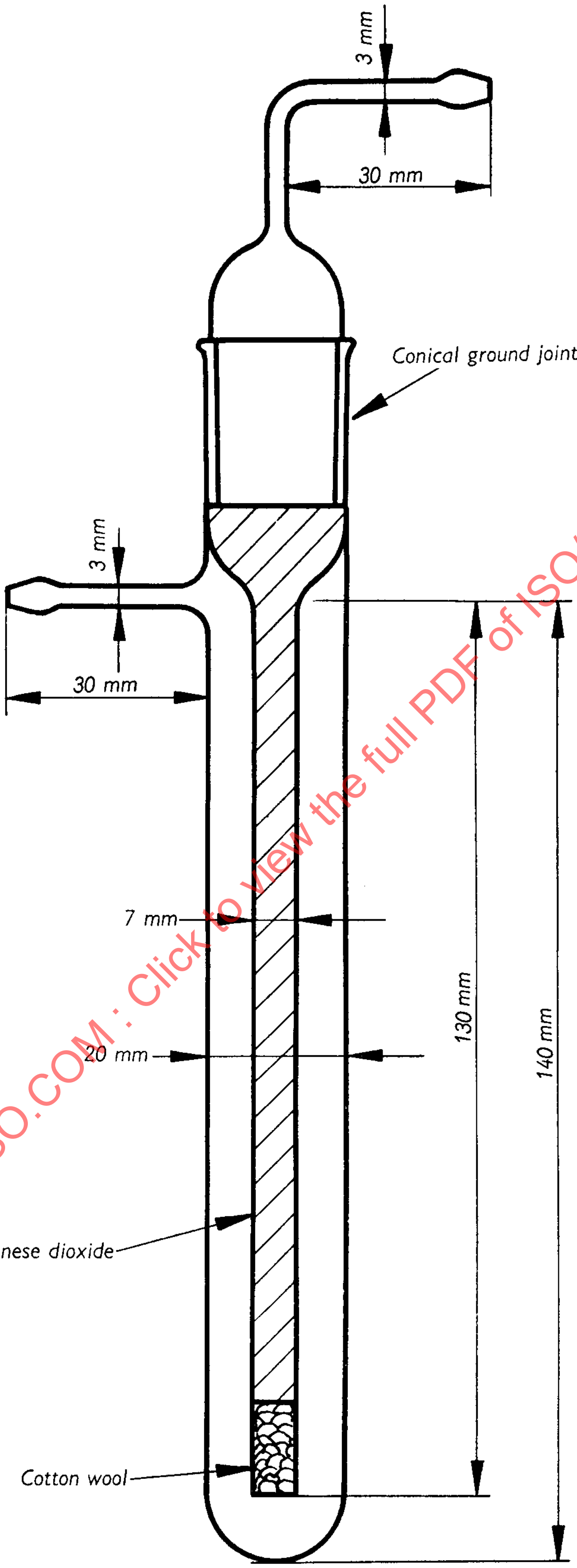

FIG. 1. — **Guard-tube**

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* Conforming to ISO Recommendation R 383, *Interchangeable Conical Ground Glass Joints* (joint 14/22 is suitable).