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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION
R 601

DETERMINATION OF ARSENIC IN COAL AND COKE

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BRIEF HISTORY

The ISO Recommendation R 601, *Determination of Arsenic in Coal and Coke,* 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 1951 and led, in 1963, to the adoption of a Draft ISO Recommendation.

In March 1964, this Draft ISO Recommendation (No. 678) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies:

Australia	Germany	Switzerland
Austria	Italy	Turkey
Belgium	Japan	U.A.R.
Brazil	Korea, Rep. of	United Kingdom
Canada	Netherlands	U.S.A.
Chile	New Zealand	U.S.S.R.
Colombia	Poland	
Czechoslovakia	Republic	
Denmark	of South Africa	
France	Romania	

One Member Body opposed the approval of the Draft:

India

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, wich decided, in July 1967, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 601 July 1967

DETERMINATION OF ARSENIC IN COAL AND COKE

1. SCOPE

This ISO Recommendation describes a photometric method of determining the amount of arsenic in hard coal, brown coal and lignite, and coke.

The method is applicable to samples containing not more than 0.0016 % of arsenic (or 0.0021 % of arsenious oxide). For samples containing more arsenic, the procedure requires modification (see Note 1).

2. PRINCIPLE

The sample is oxidized by means of nitric and sulphuric acids or by the use of Eschka mixture. The arsenic is reduced to the trivalent state and evolved as arsine by the action of zinc in sulphuric acid or hydrochloric acid medium. The arsine evolved is absorbed and oxidized to arsenic acid by a dilute iodine solution. Treatment with ammonium molybdate solution and reduction with hydrazine sulphate produces a molybdenum-blue coloration. The optical density of the coloured solution is proportional to the arsenic present in the sample*.

3. REAGENTS

All reagents should be of arsenic-free analytical reagent quality, except in the case of arsenious oxide, which should be of the highest purity obtainable. Distilled water should be used throughout.

3.1 **Zinc,** granulated, containing less than 0.000002 % of arsenic.

3.2 **Sulphuric acid,** *d* 1.84.

3.3 **Nitric acid,** *d* 1.42.

3.4 **Hydrochloric acid,** *d* 1.18.

3.5 **Hydrazine sulphate solution,** 0.15 % (m/v). Dissolve 0.15 g of hydrazine sulphate in 100 ml of water.

3.6 **Stannous chloride solution,** 33.5 % (m/v). Dissolve 40 g of stannous chloride, $SnCl_2.2H_2O$, in hydrochloric acid (*d* 1.18) and dilute to 100 ml with the hydrochloric acid.

3.7 **Potassium iodide solution,** 15 % (m/v). Dissolve 15 g of potassium iodide in 100 ml of water. Prepare fresh before using.

3.8 **Lead acetate solution,** saturated. Prepare fresh before using.

3.9 **Sulphuric acid solution,** approximately 7 N. Add 200 ml of the sulphuric acid (3.2) cautiously to about 700 ml of water, cool and dilute to 1 litre.

3.10 **Ammonium molybdate solution,** 1 % (m/v) in 5 N sulphuric acid. Dissolve 5 g of ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$, in about 400 ml of sulphuric acid (3.14) and dilute to 500 ml with the sulphuric acid (3.14).

3.11 **Stock iodine solution,** approximately 0.02 N. Dissolve 2.54 g of iodine in 25 ml of water containing 8 g of potassium iodine. Dilute to 1000 ml and store in a dark glass bottle.

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* See *The determination of arsenic in microgram quantities in coal and coke,* A. Crawford, J.G. Palmer, J.H. Wood, 1958/2, 227–294, Mikrochim. Acta.

3.12 **Working iodine solution,** approximately 0.002 N. Dilute 10 ml of the stock iodine solution (3.11) to 100 ml. Prepare fresh before using.

3.13 **Working iodine solution,** approximately 0.001 N. Dilute 5 ml of the stock iodine solution (3.11) to 100 ml. Prepare fresh before using.

3.14 **Sulphuric acid solution,** 5.0 N. Add 140 ml of the sulphuric acid (3.2) cautiously to about 500 ml of water, cool and dilute to 1000 ml. Standardize against sodium carbonate, using methyl orange as indicator and adjust to 5.0 N.

3.15 **Standard arsenic solution** (1 ml = 1 mg As). Weigh 0.1320 g of arsenious oxide, previously dried at 110 °C for 2 hours, and dissolve in 50 ml of water containing 0.5 ml of 70 % (m/v) sodium hydroxide solution. Add 2 ml of the sulphuric acid (3.14) and dilute to 100 ml.

3.16 **Eschka mixture.** Mix two parts by weight of light calcined magnesium oxide with one part of anhydrous sodium (or potassium) carbonate. The mixture should entirely pass a test sieve of 0.2 mm nominal aperture.

4. APPARATUS

All glass apparatus should be constructed from borosilicate glass and should be of the best analytical quality obtainable. Ground glass joints, when used, should comply with the relevant ISO Recommendation*. The balance used should be accurate to 0.1 mg.

4.1 Wet oxidation apparatus

A suitable apparatus is illustrated in Figure 1, page 7. It consists of the following parts:

4.1.1 *Kjeldahl flasks,* of 300 ml capacity fitted with a ground glass socket of joint size 24/29.

4.1.2 *Fume ducts,* each fitted with a dropping funnel and, at one end, a ground glass cone of joint size 24/29. The ducts may be of one-piece construction or assembled from separate units by means of ground glass joints.

4.1.3 *Fume extractor,* consisting of a glass tube, of diameter approximately 38 mm, sealed at one end and drawn out at the other to form a connection point for the pump. The tube is fitted with a series of lipped holes, to accommodate several fume ducts, and with a drain cock.

4.1.4 *Glass water pump*

4.1.5 *Digestion rack,* fitted with several positions, each of which will accommodate a Kjeldahl flask held at an angle of 45°, with a holder for the fume extractor.

4.2 Dry oxidation apparatus

4.2.1 *Electrically heated muffle furnace,* with a zone of substantially uniform temperature at 800 ± 25 °C and a ventilation rate of about 5 air changes per minute.

4.2.2 *Crucibles* of porcelain or silica, of approximately 25 ml capacity.

4.2.3 *Flat plate* 6 mm thick, of silica or other suitable insulating material which fits easily in the muffle.

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* ISO Recommendation R 383, *Interchangeable Conical Ground Glass Joints,* which provides for a size designation for each of the standard joints based on the large-end diameter and nominal length in millimetres.

4.3 Evolution apparatus

This apparatus has been designed to ensure the efficient generation and absorption of arsine; the dimensions given should be adhered to. It consists of the following parts (see Figure 2, page 8):

4.3.1 *Evolution flask (A)*, a 50 ml conical flask fitted with a ground glass socket of joint size 19/26.

4.3.2 *Delivery tube (B)*, consisting of thick-walled glass tubing of internal diameter 4 mm, fitted at one end with a ground glass cone of joint size 19/26 and at the other end with a ground glass cone of joint size 7/16. Glass hooks are fitted just above the smaller cone.

4.3.3 *Extension delivery tube (C)*, consisting of thick-walled glass tubing of internal diameter 4 mm fitted at one end with a ground glass socket of joint size 7/16, with glass hooks beneath, and drawn out at the other end to a portion 80 mm long of internal diameter 2 mm.

4.3.4 *Absorption tube (D)*, of length approximately 150 mm and fitted at one end with a ground glass stopper of joint size 14/15. The internal diameter of the tube is 15 mm at the stopper end, but at the other end a portion about 80 mm long has an internal diameter of 11 mm.

4.3.5 *Helix (E)*, of glass rod or inert plastics material such as unplasticized polyvinyl chloride, of circular section and of length 80 mm and 5 mm pitch. The helix has an outside diameter such that it fits the lower half of the absorption tube freely but not loosely and an internal diameter slightly larger than the external diameter of the narrow end of delivery tube *C*. A correctly fitted helix causes gas bubbles to follow a spiral course freely and without by-pass.

4.3.6 *Springs*. Small springs of suitable metal to ensure a gas-tight joint between the delivery tube *B* and its extension *C*.

4.4 **Spectrophotometer,** of a suitable type, with accessories.

4.5 **5 ml pipette** and three *5 ml burettes* graduated to 0.01 ml.

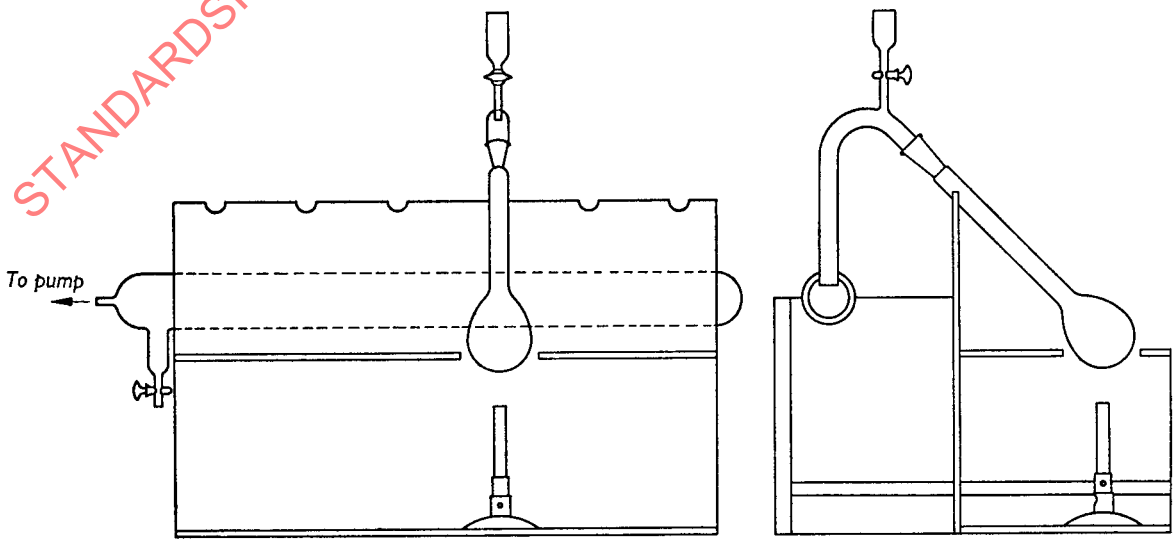

FIG. 1. — **Wet oxidation apparatus**

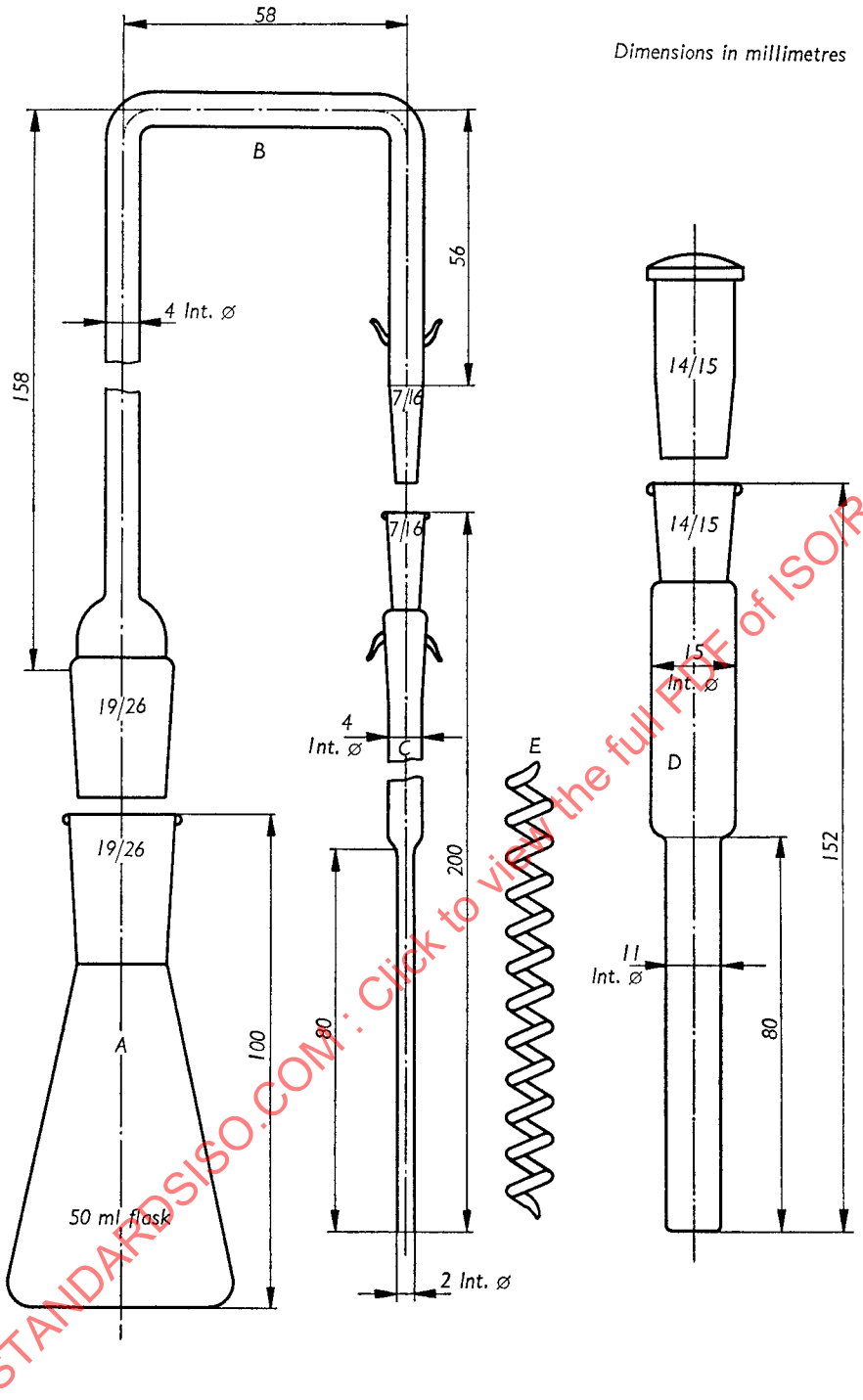

FIG. 2. — **Evolution apparatus**

Joint size designations in accordance with ISO Recommendation R 383,
Interchangeable conical ground glass joints.

5. PROCEDURE

5.1 Wet oxidation procedure

Before commencing the determination, mix the air-dried sample, ground to pass a sieve of 0.2 mm aperture, thoroughly for at least one minute, preferably by mechanical means.

Accurately weigh about 1 g of the sample and transfer to a clean, dry Kjeldahl flask, tapping the neck of the flask gently to remove any adhering material. Assemble the wet oxidation apparatus and fit it to the digestion rack (Figure 1, page 7). Add 7.0 ml of the sulphuric acid (3.2) and 3.5 ml of the nitric acid (3.3) to the flask by means of the dropping funnel, rotating the flask so as to wash down any remaining material.

After the initial reaction has subsided (see Note 2), commence heating the flask, using the tip of a non-luminous gas flame about 5 cm long (see Note 3). No further adjustment of the burner is required until the final stages of the oxidation. When only white fumes of sulphuric acid are being evolved add 0.2 to 0.4 ml of the nitric acid (3.3) to the dropping funnel and run the acid drop by drop into the flask. Dense brown fumes will immediately appear and continue to be evolved. Continue these additions of the nitric acid (3.3) until all visible carbonaceous matter has been oxidized, rotating the flask periodically to wash down into the reaction mixture any carbonaceous matter adhering to the sides of the flask. After about 1½ hours the reaction mixture should be a pale greenish yellow colour (see Note 4), with no visible carbonaceous matter present.

Heat the flask more strongly until white fumes appear and allow to fume for 5 minutes (see Note 5). Allow to cool somewhat, remove the dropping funnel and fume duct assembly and add a few glass beads to the contents of the flask.

Add cautiously 10 ml of water, heat until white fumes appear and then fume gently for 10 minutes. Cool slightly, add 0.2 ml of the nitric acid (3.3) and fume again for 10 minutes.

Repeat the procedure described in the previous paragraph (see Note 6).

Cool, add 10 ml of water, heat to fuming and fume for 20 minutes. Cool again, add 10 ml of water, heat to fuming and fume for 10 minutes. Cool, add 10 ml of water and transfer quantitatively to the evolution flask *A*, so that the final volume is approximately 35 ml.

5.2 Dry oxidation procedure

Before commencing the determination, mix the air-dried sample, ground to pass a sieve of 0.2 mm aperture, thoroughly for at least one minute, preferably by mechanical means.

Accurately weigh about 1 g of the sample in a scoop and transfer to a crucible (4.2.2) containing 2 g of the Eschka mixture (3.16). Mix thoroughly, using a small spatula, and cover with a further 1 g of the Eschka mixture (3.16).

Place the crucible on the plate (4.2.3), insert both into the muffle at 800 ± 25 °C and maintain this temperature for 5 hours. Withdraw the crucible and allow it to cool.

Transfer the incinerated mixture to the evolution flask *A*, wash the crucible with 10 ml of hot water and dissolve with 20 ml of the hydrochloric acid (3.4), so that the final volume is approximately 35 ml.

5.3 Evolution procedure

To the 35 ml of solution in the evolution flask *A* (see Note 1), obtained in accordance with either clause 5.1 or clause 5.2, add 2.0 ml of the potassium iodide solution (3.7) and 0.5 ml of the stannous chloride solution (3.6), mixing well after each addition. Allow to stand for 15 minutes at room temperature.