

BUREAU OF INDIAN STANDARDS

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भारतीय मानक मसौदा

कोयला और कोक के परीक्षण के तरीके

भाग 4 अंतिम विश्लेषण

अनुभाग 2 नाइट्रोजन का निर्धारण

[आईएस 1350 (भाग 4/ अनुभाग 2) का दूसरा पुनरीक्षण]

Draft Indian Standard

COAL AND COKE — METHODS OF TEST

PART 4 ULTIMATE ANALYSIS

Section 2 Determination of Nitrogen

[*Second Revision of IS 1350 (Part 4/Sec 2)*]

(ICS 73.040)

Solid Mineral Fuels and Solid Biofuels
Sectional Committee, PCD 07

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FOREWORD

This standard was originally published as IS 1351 : 1959 'Methods of test for coal and coke - ultimate analysis'. In the light of the experience gained in the country and the ISO standard published on this subject, the Committee responsible for the preparation of this standard, decided to revise IS 1351 and issue it as Part 4/Sec 1 and Part 4/Sec 2 of IS 1350, during the first revision, taken up in the year 1975. This section (Part 4/Sec 2) covers the determination of nitrogen content in coal and coke, while section 1 (Part 4/ Sec 1) covers determination of carbon and hydrogen content in coal and coke. In this standard two methods of determination of nitrogen have been prescribed. The first is the conventional Kjeldahl method, which was standardized at the Central Fuel Research Institute (CSIR), Dhanbad and the second is the semi-micro Kjeldahl method. Assistance was derived from the following publication issued by the International Organization for Standardization (ISO) during the first revision:

ISO/R 332 Determination of nitrogen in coal by the Kjeldahl method, and

ISO/R 333 Determination of nitrogen in coal by the semi-micro Kjeldahl method

In this (second) revision, considerable assistance has been drawn from ISO 11261 : 1995 Determination of total nitrogen by the modified Kjeldahl method. Further, preparation of sample

for coke has been referred by IS 16143 (Part 5) and IS 16143 (Part 6) as the erstwhile referred standard IS 436 (Part 2) has been withdrawn.

The other parts in this series are:

- Part 1 Proximate analysis
- Part 2 Determination of gross calorific value
- Part 3 Determination of total sulphur eschka method
- Part 4 Ultimate analysis;
Section 1 Determination of carbon and hydrogen

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off it shall be done in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'.

1 SCOPE

1.1 This standard (Part 4/ Sec 2) prescribes the methods for determination of nitrogen content in coal.

NOTE — The method prescribed in **6.2** is also applicable to brown coals, lignites and coke except for the fact that a longer period of digestion (*see 6.2.4*) is required in the case of high rank coal, anthracite and coke.

2 REFERENCES

The following standards contain provisions, which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibilities of applying the most recent editions of the standards indicated below:

<i>IS No.</i>	<i>Title</i>
IS 266:1993	Sulphuric acid — Specification (<i>third revision</i>)
IS 1070 : 1992	Reagent grade water — Specification (<i>third revision</i>)
IS 16143 (Part 5) : 2021/ISO 13909-5 : 2016	Hard Coal and Coke — Mechanical sampling: Part 5 Coke Sampling from moving streams (<i>first revision</i>)
IS 16143 (Part 6) : 2021/ISO 13909-6 : 2016	Hard Coal and Coke — Mechanical sampling: Part 6 Coke Preparation of test samples (<i>first revision</i>)
Doc No.: PCD 07 (19732)	Methods for sampling of Coal and Coke: Part 1 Sampling of Coal Section 1 Manual sampling

3 TERMINOLOGY

3.1 For the purpose of this standard, the following term shall apply:

3.1.1 *Ultimate Analysis*

The analysis of coal in terms of its carbon, hydrogen, nitrogen, sulphur and oxygen contents. But for the basis of ultimate analysis or any part thereof, moisture and ash content shall also have to be determined concurrently.

4 QUALITY OF REAGENTS

4.1 Unless specified otherwise, 'pure chemicals' and distilled water (*see* IS 1070) shall be employed in tests.

NOTE - 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

5 SAMPLE

5.1 The method of preparing samples for carrying out tests shall be as prescribed in 7 of Doc No.: PCD 07 (19732) and IS 16143 (Part 5) and IS 16143 (Part 6) for Coke.

6 DETERMINATIONS OF NITROGEN

6.1 General

For the determination of nitrogen, two methods have been prescribed, namely, conventional Kjeldahl method and semi-micro Kjeldahl method. The conventional method shall be employed for routine determinations and the semi-micro method, only as a referee method, or when the amount of sample available is less than 1 g.

6.2 Conventional Kjeldahl Method

6.2.1 Principle

A known mass of the sample is heated with concentrated sulphuric acid in the presence of a catalyst to destroy the organic material and to convert the nitrogen into ammonium sulphate, from which ammonia released by steam distillation in alkaline solution, is absorbed in boric acid solution and titrated directly with 0.05 N sulphuric acid.

6.2.2 Apparatus

6.2.2.1 Digestion flask

A Kjeldahl flask of hard glass having a pear shaped bulb of 200 to 500 ml effective capacity, a neck about 20 cm long and 2.3 cm in internal diameter and provided with a suitable device for closing the mouth of the flask, such as a light blown glass stopper which fits loosely into the mouth of the flask.

6.2.2.2 Heating arrangement

To heat one or more flasks inclined at about 35° from the vertical. The heating unit may be a gas burner or an electrical heater.

6.2.3 *Reagents*

6.2.3.1 *Concentrated sulphuric acid*, preferably nitrogen-free (*see* IS 266).

6.2.3.2 *Potassium sulphate*, anhydrous, nitrogen-free or containing not more than 0.001 percent nitrogen.

6.2.3.3 *Selenium powder*

OR

Potassium sulphate catalyst mixture

Grind and thoroughly mix 200 g of potassium sulphate, 6g of copper (II) sulphate pentahydrate and 6 g of titanium oxide, with the crystal structure of anatase.

NOTE — Potassium sulphate catalyst mixture containing titanium oxide may also be used as catalyst in place of selenium, as titanium oxide is ecotoxicologically less harmful than selenium.

6.2.3.4 *Sucrose*, pure, free from nitrogenous substances.

6.2.3.5 *Standard sulphuric acid*, approximately 0.05 N.

6.2.3.6 *Sodium hydroxide solution*, 40 percent (m/v).

6.2.3.7 *Saturated boric acid solution*

Dissolve 60 g of boric acid in 1 litre of hot water. Allow to stand for 3 days, decant and use the clear solution.

6.2.3.8 *Methyl red and Methylene Blue Mixed Indicator*

Prepare and use as follows:

- a) Dissolve 0.125 g of methyl red in 100 ml of rectified spirit, and
- b) Dissolve 0.083 g of methylene blue in 100 ml of rectified spirit.

Mix equal volumes of (a) and (b) immediately before use.

NOTE - Bromocresol green may also be used in place of methylene blue. A mixture of bromocresol green and methyl red gives a red colour in acidic conditions and green colour in basic conditions with a sharp transition through grey colour at pH 5.1.

6.2.4 *Procedure*

6.2.4.1 Mix the air-dried sample of coal (ground to pass 212 micron IS Sieve) in the bottle by a long spatula for at least 1 min. Weigh about 1 g of the sample to the nearest 0.1 mg and transfer

to the dry digestion flask. Add 10 g of potassium sulphate followed by 0.2 g of the selenium powder and 30 ml of concentrated sulphuric acid.

NOTE — When titanium oxide catalyst is used instead of selenium powder, for 1 g sample, 20 ml of concentrated sulphuric acid and 10 g of the potassium sulphate catalyst mixture are used for the digestion process.

6.2.4.2 Place the digestion flask on the heating arrangement, close the open end of the neck by means of the loosely fitting glass stopper, to minimize loss of sulphuric acid and to prevent intrusion of dust. Heat the flask gently until the initial frothing has ceased. Heat the liquid to the boiling point, continue boiling freely until the solution becomes almost colourless, and then boil for a further period of 3 h.

NOTE — The period of digestion required to obtain an almost colourless or a pale yellow solution usually varies from 30 to 60 min or even more depending on the rank of coal from lignite to anthracite. The higher the rank of coal, the greater is the time for the clearing period. The period after clearing, called the after-boil period, is very important for complete conversion of nitrogen into ammonium sulphate and depends on the rank of coal and rate of heating. Usually an after-boil period of 3 h is sufficient for low rank high volatile coal (carbon less than 84 percent dmf) but this should be at least 4 to 6 h for higher rank coal, anthracite and coke. It is appropriate to specify after-boil-period on the basis of critical rate of heating. Critical rate of heating is that rate of heating for which the clearing time of digest is the minimum.

6.2.4.3 Transfer the contents of the digestion flask, with about 200 ml of cold water, into a round-bottom flask fitted with a tap or thistle funnel and an efficient splash head and connect it through a condenser, if desired, to a bulbed tube dipping into about 20 ml of saturated boric acid solution contained in a conical flask to which 6 drops of mixed indicator solution is added.

6.2.4.4 Add through the thistle funnel 125 ml of sodium hydroxide solution and distil 150 to 200 ml of the liquid into the conical flask. Rinse the end of the condenser tube with water. Titrate the ammonia present in the distillate with standard sulphuric acid until grass-green colour changes to steel grey, a further drop then giving the purple acid colour.

NOTE — In case of bromocresol green, a green colour changes into grey and then to a red colour at end point.

6.2.4.5 Carry out a blank determination in exactly the same manner as above, but using 1.0 g of sucrose in place of the coal sample.

6.2.5 Calculation

Calculate the percentage of nitrogen percent by mass, as follows:

$$\text{Nitrogen, percent by mass} = \frac{1.4 \times N \times (V_1 - V_2)}{m}$$

where

N = normality of standard sulphuric acid;

V_1 = volume of standard sulphuric acid used in the test, in ml;

V_2 = volume of standard sulphuric acid used in blank, in ml; and

m = mass of the sample taken for the test, in g.

6.3 Semi-micro Kjeldahl Method

6.3.1 Principle

A known mass of coal sample is heated with concentrated sulphuric acid in the presence of a mixed catalyst to destroy the organic matter and to convert the evolved nitrogen into ammonium sulphate, from which ammonia, released by steam distillation with alkaline solution, is absorbed in boric acid solution and determined by titration with standard sulphuric acid.

6.3.2 Apparatus

6.3.2.1 Digestion flask

A flask of hard glass, of bulb capacity 50 ml, preferably pistol-shaped, with a light blown-glass stopper fitting loosely in the neck of the flask, to prevent loss of acid.

6.3.2.2 Distillation apparatus

A suitable distillation apparatus of hard glass fitted with a splash head to arrest the passage of any entrained sodium hydroxide solution from the distillation flask, is illustrated in Fig. 1.

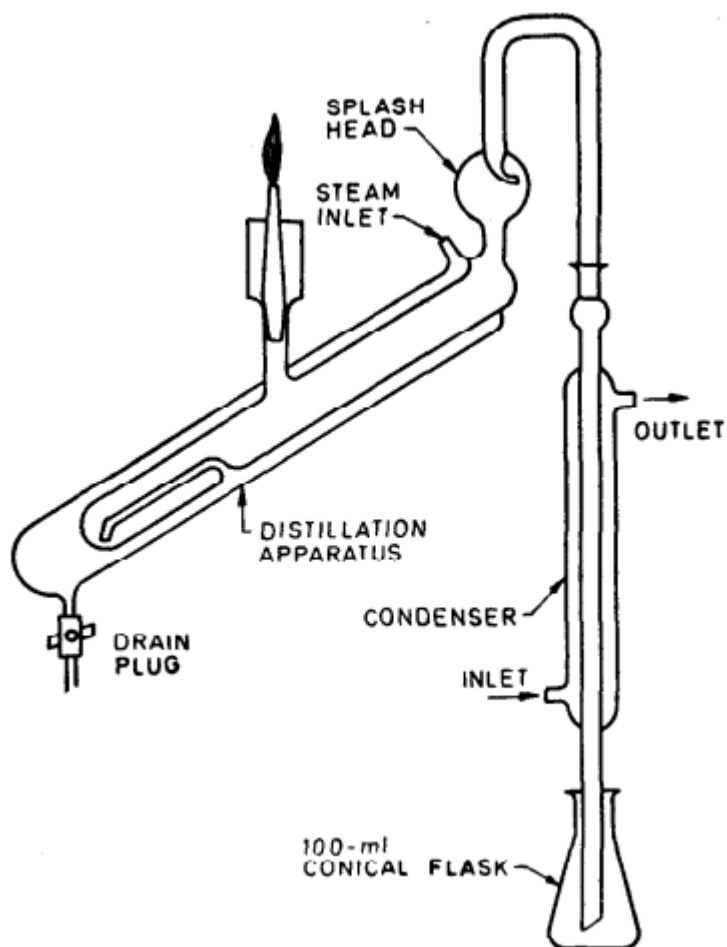


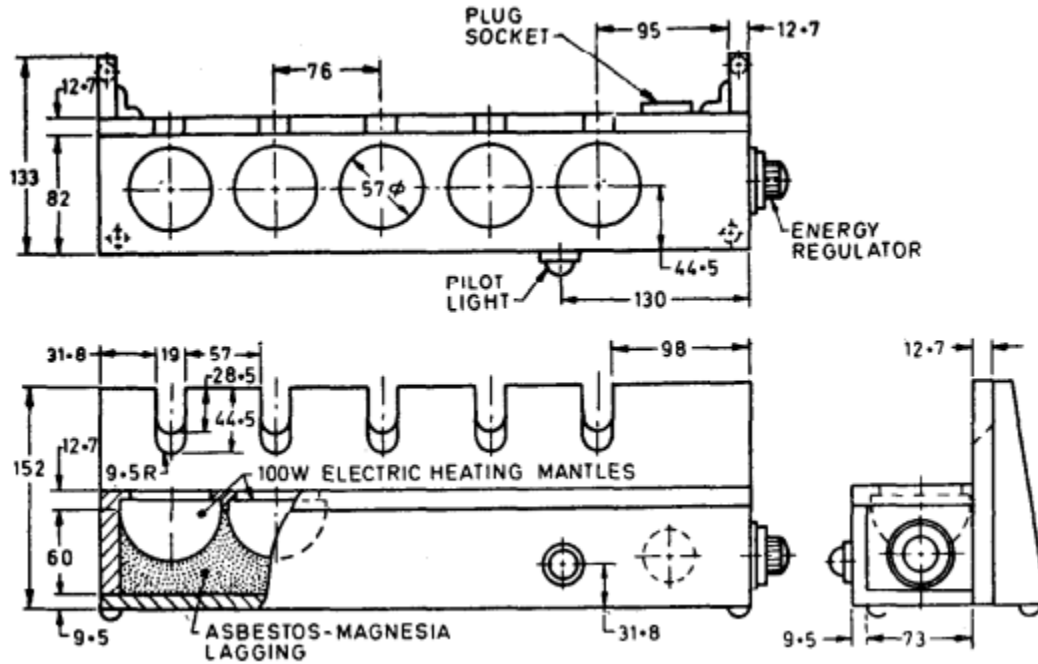
FIG. 1 DISTILLATION APPARATUS FOR SEMI-MICRO KJELDAHL METHOD

6.3.2.3 Receiver

A wide necked, flat-bottomed conical flask of 100 ml capacity.

6.3.2.4 Burette, 25 ml capacity.

6.3.2.5 Heating arrangement, to heat simultaneously one or more flasks inclined at about 35° from the vertical. A suitable arrangement is illustrated in Fig. 2.



All dimensions in millimeter

NOTE — Unit constructed of 10 or 12 mm asbestos board on angle-iron framework. Asbestos-magnesia lagging is packed around electric-heating mantles.

FIG. 2 ELECTRIC DIGESTION UNIT SUITABLE FOR SEMI MICRO KJELDHAL METHOD

6.3.3 Reagents

6.3.3.1 Concentrated sulphuric acid, same as in 6.2.3.1

6.3.3.2 Mixed catalyst

a) Containing by mass 90 parts of potassium sulphate, 2 part of selenium powder and 5 parts of vanadium pentoxide.

OR

b) Grind and thoroughly mix 200 g of potassium sulphate, 6 g of copper(II) sulphate pentahydrate and 6 g of titanium oxide, with the crystal structure of anatase.

NOTE — Titanium oxide may also be used in the mixed catalyst in place of selenium, as titanium oxide is ecotoxicologically less harmful than selenium.

6.3.3.3 Alkaline sodium sulphide solution

Dissolve 20 g of sodium sulphide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) in water, dilute to 50 ml, and add 600 ml of sodium hydroxide solution (see 6.2.3.6).

6.3.3.4 *Standard sulphuric acid*, approximately 0.01 N.

6.3.3.5 *Saturated boric acid solution*, same as in **6.2.3.7**

6.3.3.6 *Mixed indicator solution*, same as in **6.2.3.8**.

6.3.3.7 *Sucrose*, same as in **6.2.3.4**.

6.3.4 *Procedure*

6.3.4.1 Mix the air-dried sample of coal, ground to pass 212 micron IS Sieve for at least 1 min preferably by mechanical means. Weigh to the nearest 0.1 mg about 0.1 g of the sample and transfer to the dry digestion flask. Add 2.0 g of the mixed catalyst and shake to mix. Add 4 ml of concentrated sulphuric acid and mix again.

6.3.4.2 Switch on the electric heating unit at approximately half load for 20 min, and then at the maximum load for 10 min before placing the flask on the unit. Alternatively, with gas heating, place the digestion flask over the fully aerated flame of the micro-burner and adjust the flame so that clearing of the solution is affected in a time of 7 to 10 min, for example, by using a flame 5 cm high with the lowest part of the bulb of the flask 4 cm above the top of the burner. After the solution becomes clear, continue boiling to give a total digestion of 25 to 30 min to complete the conversion of the nitrogenous compounds into ammonium sulphate.

NOTE — The total digestion time should be rigorously followed for the conditions specified.

6.3.4.3 During the digestion, steam out the distillation apparatus, close the connection to the distillation flask, and blow out the waste from the previous distillation. Pour 20 ml of the alkaline sodium sulphide solution into the distillation flask through the funnel, and rinse with water. Measure 2 ml of the boric acid solution into the receiver, and add 4 drops of the mixed indicator solution, adjusting a block under the receiver so that the end of the condenser tube dips below the surface of the liquid.

NOTE — The distillation apparatus should be conditioned by steaming through for 30 min before commencing a batch of distillation. There is no need, however, to do this between individual distillations in a batch.

6.3.4.4 Allow the acid digest to cool for 5 min, and dilute by adding 10 ml of distilled water, in drops at first, and shaking, until the reaction is less violent, Pour the diluted digest through the tap funnel into the distillation flask; rinse the digestion flask into the tap funnel with water, then rinse the tap funnel with water. The total volume of liquid in the distillation flask should not exceed half the capacity of the flask, or frothing and priming may occur.

6.3.4.5 Heat the distillation flask with a small flame and pass steam into the apparatus. Distil for 5 min from the time steam enters the condenser, at a rate of about 4 ml of distillate per minute. Lower the receiver so that the condenser end is about 2.5 cm above the surface of the liquid and continue distillation for 1 min longer. The contents of the receiver should remain cold. Rinse the end of the condenser tube with water. Titrate the ammonia present in the distillate with the

standard sulphuric acid until the grass green colour changes to steel grey, a further drop then giving the purple acid colour.

6.3.4.6 Carry out a blank determination in exactly the same manner but using 0.1 g of the sucrose instead of coal sample.

NOTE — Splash head should remove all entrained sodium hydroxide. Double bulb splash heads are preferred. The results of the blank determination should not exceed 0.1 ml of 0.01 N sulphuric acid. Steam remove alkali compound from some glasses and, if higher blank results are found, the central tube of condenser should be replaced by a fused silica or other suitable glass tube.

6.3.5 *Calculation*

Calculate the percentage of nitrogen by mass, as prescribed in **6.2.5**.

7 EXPRESSION OF RESULTS AND PRECISION OF DETERMINATIONS

7.1 Expression of Result

The results, preferably the mean of duplicate determinations, shall be reported to the nearest 0.1 percent.

7.2 Precision of Determinations

7.2.1 *Repeatability*

The minimum acceptable difference between 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 analysis sample, shall not exceed 0.05.

7.2.2 *Reproducibility*

The maximum acceptable difference between the means of the results of duplicate determinations in each of two different laboratories, on representative portions taken from the same analysis sample, shall not exceed 0.10.