INTERNATIONAL STANDARD ISO 333

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

Coal and coke — Determination of nitrogen — Semi-micro Kjeldahl method

Charbon et coke — Dosage de l'azote — Méthode Kjeldahl semi-micrométrique

First edition — 1975-01-15

UDC 662.66 : 662.642 : 662.749.2 : 543.846

Ref. No. ISO 333-1975 (E)

Descriptors : coal, chemical analysis, determination of content, nitrogen.

Price based on 5 pages

Coal and coke – Determination of nitrogen – Semi-micro Kjeldahl method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method of determining the nitrogen content of hard coal, brown coal, lignite and coke by the semi-micro Kjeldahl method. An alternative macro method for coal is given in ISO 332.[1]

2 PRINCIPLE

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

In bituminous coals and anthracite, the nitrogen is fairly uniformly distributed, even when the seam is banded. In some lignites the nitrogen varies in the different bands of the seam and sampling difficulties make it undesirable to employ a semi-micro method using only a 0,1 g sample; in these circumstances, the macro Kjeldahl method using a 1 g sample should be adopted for such banded lignites.

Since coke is less reactive than coal and takes longer to digest, the coke is ground very finely. The catalytic mixture used does not cause loss of ammonia during the long period of digestion.

3 REAGENTS

All reagents shall be of analytical reagent quality, and distilled water shall be used throughout.

3.1 Mixed catalyst for coal, containing by mass :

- 32 parts of anhydrous potassium sulphate;
- 1 part of selenium powder;
- 5 parts of mercury(II) sulphate.

Grind the above reagents in a mortar and mix them thoroughly.

3.2 Mixed catalyst for coke, containing by mass :

- 87 parts of anhydrous potassium sulphate;
- 13 parts of mercury(II) sulphate.

Grind the above reagents in a mortar and mix them thoroughly.

3.3 Sucrose.

3.4 Sulphuric acid, ρ 1,84 g/l.

3.5 Boric acid solution, saturated.

Dissolve 60 g of boric acid in 1 l of hot water, cool and allow to mature for 3 days before decanting the clear liquid.

3.6 Alkaline sodium sulphide solution.

Dissolve 20 g of sodium sulphide ($Na_2S.9H_2O$) in water, and dilute to 50 ml; add a solution of 240 g of sodium hydroxide in 600 ml of water, and mix well.

3.7 Sulphuric acid, 0,01 N.

3.8 Mixed indicator solution :

Solution A – Dissolve 0,125 g of 4'-dimethylamino-azobenzene-2-carboxylic acid (methyl red) in 60 ml of ethanol or industrial spirit, and dilute to 100 ml with water.

Solution B – Dissolve 0,083 g of 3,7-bisdimethylamino-phenothiazinium chloride (methylene blue) in 100 ml of ethanol or industrial spirit. Store in a dark glass bottle.

Mix equal volumes of solutions A and B. Discard the mixed solution after 1 week.

4 APPARATUS

All volumetric apparatus shall be of the best analytical quality obtainable, and the balance used shall be sensitive to 0,1 mg.

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[1] ISO 332, *Coal – Determination of nitrogen by the macro Kjeldahl method.*

4.1 Digestion flask, of borosilicate glass, of bulb capacity 50 ml, preferably pistol-shaped, with a light borosilicate blown-glass bulb which is a loose fit in the neck of the flask, to prevent loss of acid.

4.2 Distillation apparatus : a suitable water steam distillation apparatus of borosilicate glass, fitted with a splash head to arrest the passage of any entrained sodium hydroxide from the distillation flask (see figure 1).

4.3 Receiver : a wide-necked, flat-bottomed conical flask, capacity 100 ml.

4.4 Burette, capacity 25 ml.

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

5 PREPARATION OF SAMPLE

The coal or coke used for the determination of nitrogen content is the analysis sample ground to pass a sieve of 0,2 mm aperture. If necessary expose the sample in a thin layer for the minimum time required for the moisture content to reach approximate equilibrium with the laboratory atmosphere. For coke grind a part of the analysis sample to pass a sieve of 0,06 mm aperture.

Before commencing the determination, mix the air-dried sample of coal for at least 1 min, preferably by mechanical means.

6 PROCEDURE

6.1 Coal sample

Weigh, to the nearest 0,1 mg, about 0,10 g of the sample, transfer carefully to the digestion flask, add 2,0 g of the mixed catalyst (3.1) and shake to mix. Add 4 ml of the sulphuric acid (3.4) and mix again.

Switch on the electric heating unit at approximately half load for 20 min, and then at 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 a micro-burner and adjust the flame so that clearing of the solution is effected in a time of 7 to 10 min, for example by using a flame 50 mm high with the lowest part of the bulb of the flask 40 mm above the top of the burner. After the solution becomes clear, continue boiling to give a total digestion time of 25 to 30 min, in order to complete the conversion of the nitrogenous compounds into ammonium sulphate (see note 1 in 6.4).

6.2 Coke sample

Weigh, to the nearest 0,1 mg, about 0,10 g of the crushed sample, transfer carefully to the digestion flask, add 2,0 g of the mixed catalyst (3.2) and shake to mix. Add 4 ml of the sulphuric acid (3.4) and mix again.

Switch on the electric heating unit at approximately half load for 20 min, and then at maximum load for 10 min before placing the flask on the unit. Alternatively, with gas heating, place the flask over the fully aerated flame of a micro-burner and adjust the flame so that the solution boils rapidly. After the solution boils, continue boiling until the solution becomes clear (see note 2 in 6.4).

6.3 Distillation

During the digestion, steam out the distillation apparatus (see note 3 in 6.4), 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 (3.6) into the distillation flask through the funnel, and rinse with water. Measure 2 ml of the boric acid solution (3.5) into the receiver, and add 4 drops of the mixed indicator solution (3.8), adjusting a block under the receiver so that the end of the condenser tube dips below the surface of the liquid.

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.

Heat the distillation flask with a small flame and pass steam into the apparatus. Distil for 5 min from the time the 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 25 mm 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 sulphuric acid (3.7) until the grass-green colour changes to steel grey, a further drop then giving the purple (acid) colour.

6.4 Blank test

Carry out a blank test in exactly the same manner, but using 0,1 g of the sucrose (3.3) instead of the sample (see note 4).

NOTES

1 The total digestion time shall be rigorously followed for the conditions specified.

2 An unreactive coke may take over 10 h before the solution becomes clear; no loss of nitrogen will occur even with this long digestion period, and clearing of the solution shall always be taken as a guide to the completion of the reaction.

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

4 If the splash head removes all entrained sodium hydroxide, the results of the blank test should not exceed 0,1 ml of 0,01 N sulphuric acid. Steam removes alkali compounds from some glasses and, if higher blank results are found, the central tube of the condenser shall be replaced by a fused silica or borosilicate glass tube.

7 EXPRESSION OF RESULTS

The nitrogen (N) content of the sample as analysed[1], expressed as a percentage by mass, is given by the formula

$$N = \frac{1{,}4\,T\,(V_1 - V_2)}{m}$$

where

m is the mass, in grams, of sample taken;

V_1 is the volume, in millilitres, of 0,01 N sulphuric acid used in the determination;

V_2 is the volume, in millilitres, of 0,01 N sulphuric acid used in the blank test;

T is the normality of sulphuric acid (i.e. 0,010 0 if the solution is exactly centinormal).

The results (preferably the mean of duplicate determinations, see clause 8) shall be reported to the nearest 0,1 %.

8 PRECISION OF THE METHOD

Nitrogen	**Maximum acceptable differences between results** (calculated to the same moisture content)	
	Same laboratory (Repeatability)	**Different laboratories** (Reproducibility)
	0,05 % absolute	0,10 % absolute

8.1 Repeatability

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 differ by more than the above value.

8.2 Reproducibility

The means of the results of duplicate determinations, carried out in each of two laboratories on representative portions taken from the same sample after the last stage of sample preparation, shall not differ by more than the above value.

9 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

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[1] Calculation of the results to other bases is dealt with in ISO 1170.