TECHNICAL SPECIFICATION

ISO/TS 11725

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Solid mineral fuels — Determination of nitrogen — Semi-micro gasification method

Combustibles minéraux solides — Détermination de la teneur en azote — Méthode semi-micrométrique par gazéification

Reference number
ISO/TS 11725:2002(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years with a view to deciding whether it should be confirmed for a further three years, revised to become an International Standard, or withdrawn. In the case of a confirmed ISO/PAS or ISO/TS, it is reviewed again after six years at which time it has to be either transposed into an International Standard or withdrawn.

Attention is drawn to the possibility that some of the elements of this Technical Specification may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 11725 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

Annex A of this Technical Specification is for information only.

Introduction

A method for the determination of nitrogen in coals, ISO 333, has been in use for many years, but experience has shown that it is unsuitable for cokes and some high carbon content coals and chars which require long reaction times with the potential loss of nitrogen from the system before completion of the test. The method described in this Technical Specification, based on JIS M 8813, addresses that shortcoming and is applicable to all solid fuels.

It has been prepared as a Technical Specification since there is at present little experience with the method outside Japan, where it was developed and tested.

Solid mineral fuels — Determination of nitrogen — Semi-micro gasification method

1 Scope

This Technical Specification specifies a method of determining the nitrogen content of hard coals, brown coals and lignites, cokes and chars by a semi-micro gasification method.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this Technical Specification. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this Technical Specification are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 331, *Coal — Determination of moisture in the analysis sample — Direct gravimetric method*

ISO 687, *Coke — Determination of moisture in the general analysis test sample*

ISO 1015, *Brown coals and lignites — Determination of moisture content — Direct volumetric method*

ISO 1988, *Hard coal — Sampling*

ISO 2309, *Coke — Sampling*

ISO 5068, *Brown coals and lignites — Determination of moisture content — Indirect gravimetric method*

ISO 5069-2, *Brown coals and lignites — Principles of sampling — Part 2: Sample preparation for determination of moisture content and for general analysis*

ISO 9411-1, *Solid mineral fuels — Mechanical sampling from moving streams — Part 1: Coal*

ISO 9411-2, *Solid mineral fuels — Mechanical sampling from moving streams — Part 2: Coke*

3 Principle

A known mass of the sample is mixed with a flux and pyrolyzed at temperatures up to 1 000 °C in a silica tube through which steam is passing. Ammonia, which is formed from the nitrogen present, is absorbed in boric acid solution and determined by titration with sulfuric acid.

4 Reagents

WARNING — Care should be exercised when handling reagents, many of which are toxic and corrosive.

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water, or water of equivalent purity.

4.1 Boric acid solution, saturated

Dissolve 60 g of boric acid in 1 l of hot water, cool and allow to stand for three days before decanting the clear solution.

4.2 Sodium hydroxide, 250 g/l solution

Dissolve 250 g of sodium hydroxide in water and dilute to 1 l; mix thoroughly.

4.3 Ammonia, approximately 0,17 g/l solution

Dissolve 0,535 g of ammonium chloride in 30 ml of water. Transfer the solution to a steam distillation apparatus as described in 5.4. Transfer 4 ml of the boric acid (4.1) to the receiver. Add 150 ml of the sodium hydroxide solution (4.2) to the distillation flask and pass steam through the apparatus whilst maintaining the temperature at approximately 125 °C.

When approximately 250 ml of distillate have been collected, cease the distillation. Dilute the distillate to 1 l with water and mix well.

4.4 Helium, purity > 99,8 %

4.5 Soda-lime, powdered

Granular soda-lime (NaOH solution absorbed on CaO) may be crushed using a porcelain pestle and mortar.

4.6 Activated alumina, neutral, pore size approximately 9 nm

4.7 Silica fibre, diameter 1 µm to 5 µm

4.8 Sulfuric acid, standard volumetric solution, concentration $c(H_2SO_4) = 0{,}005$ mol/l

4.9 Mixed indicator solution

— solution A — dissolve 0,125 g of 2-(4-dimethylaminophenylazo) benzoic acid, sodium salt (methyl red), in 100 ml of water.

— solution B — dissolve 0,083 g of 3,7-bis(dimethylamino)phenothiazine-5-ylium chloride (methylene blue), in 100 ml of water. Store in a dark glass bottle.

Mix equal volumes of solutions A and B. Store in a dark glass bottle. Discard the mixed solution after 1 week.

4.10 Graphite, powdered, spectroscopy electrode purity

5 Apparatus

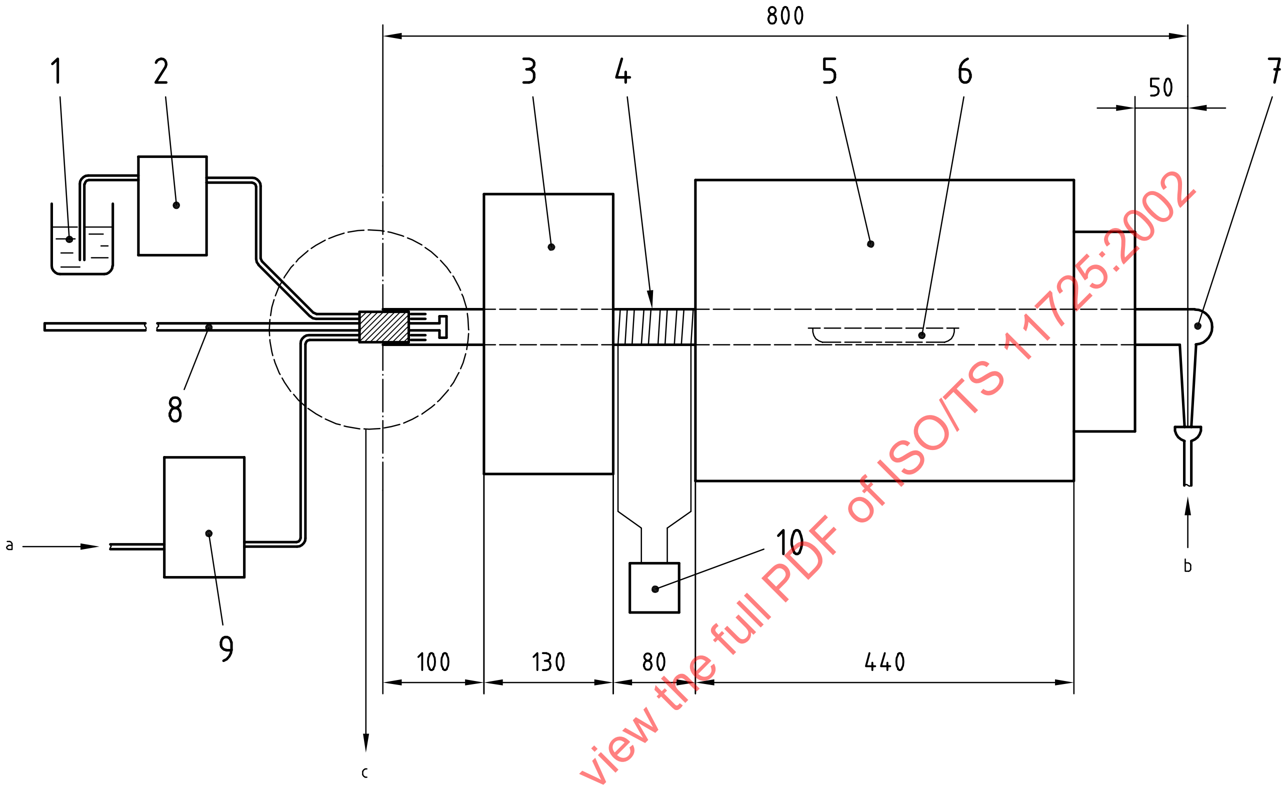
5.1 Analytical balance, capable of weighing to 0,1 mg

5.2 Graduated glassware, conforming to the requirements for Grade “A” in the International Standards prepared by ISO/TC 48, “Laboratory glassware and related apparatus”

5.3 Gasification apparatus

See Figure 1.

Dimensions in millimetres



Key

1	Water	6	Boat
2	Peristaltic pump	7	Pyrolysis tube
3	Steam-raising surface	8	Pusher rod
4	Pre-heater	9	Helium flow controller
5	Main furnace	10	Voltage regulator

[a] Helium in

[b] Entry to distillation flask (see Figure 3)

[c] See Figure 2

Figure 1 — Gasification apparatus

5.3.1 Steam-raising furnace, of sufficient capacity to maintain a portion of the pyrolysis tube (5.3.4) at about 450 °C.

5.3.2 Pre-heater, formed by wrapping insulated heating tape, of heat capacity 800 W at 100 V, supplied through a variable voltage regulator, around the pyrolysis tube. The tape shall completely cover the length of tube between the steam-raising furnace (5.3.1) and the main furnace (5.3.3).

5.3.3 Main furnace, capable of maintaining the pyrolysis tube at approximately 1 000 °C.

NOTE A furnace with a heating element constructed from a double spiral of silicon carbide has been found to be suitable for this purpose.

5.3.4 Pyrolysis tube, consisting of a translucent silica tube, 30 mm internal diameter and 800 mm long.

A silica adapter, which is 80 mm long and reduces to 8 mm outside diameter, is fused to the outlet end of the pyrolysis tube. This in turn is fitted with a spherical ground glass joint to enable the distillation apparatus (5.4) to be connected. A silicone rubber stopper, containing a sample pusher rod (5.3.7) and entry tubes for water and helium, is fitted to the inlet end of the pyrolysis tube as illustrated in Figure 2.

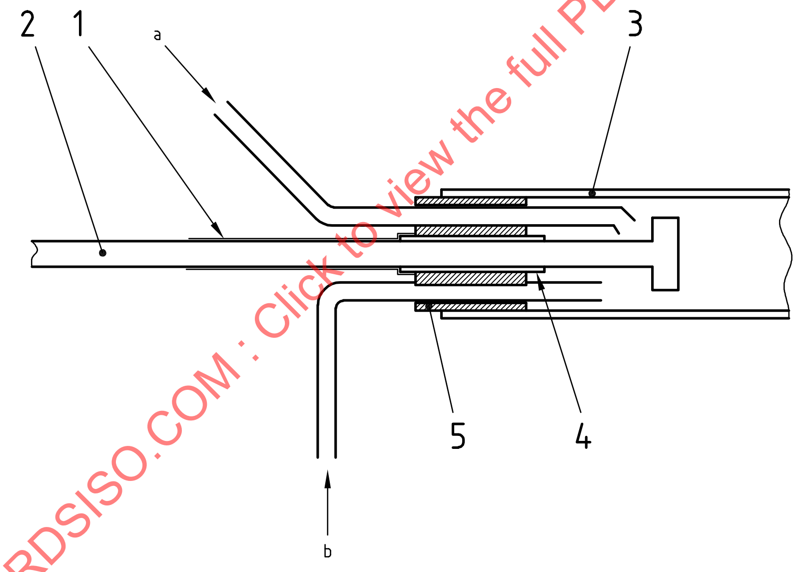
5.3.5 Peristaltic pump, capable of maintaining a steady water flow of 2 ml/min to 3 ml/min.

5.3.6 Helium flow control apparatus, consisting of a flowmeter of 500 ml/min capacity, adjustable needle valve and an electromagnetic on/off switch.

5.3.7 Pusher rod, made of silica, 650 mm long and 7 mm diameter, to which is attached, centrally at one end, a 20 mm diameter quartz disc.

5.4 Distillation apparatus, constructed of alkali-resistant glass.

See Figure 2.



Key

1	Rubber seal	4	Glass tube
2	Pusher rod	5	Silicone rubber stopper
3	Pyrolysis tube		

[a] Water in

[b] Helium in

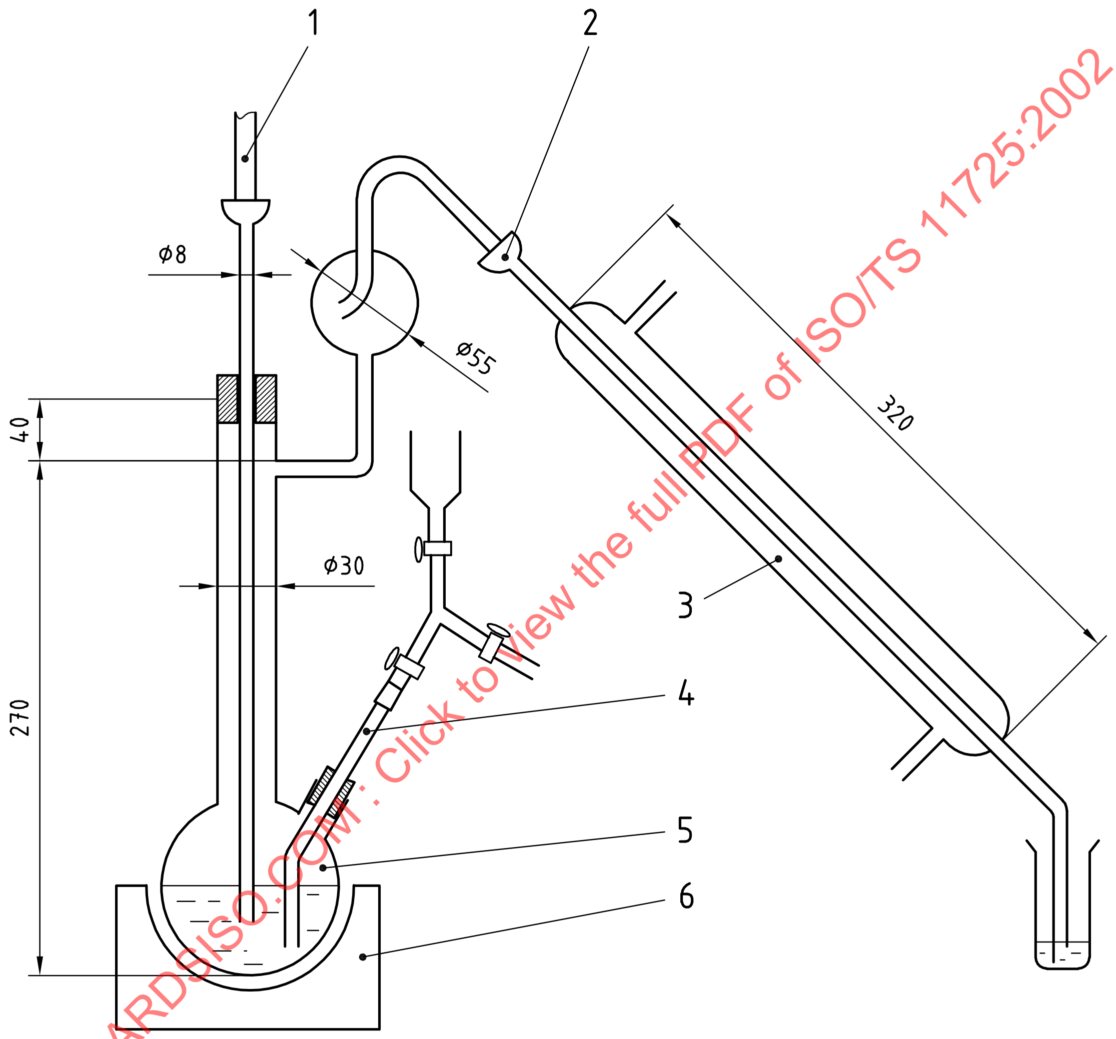
Figure 2 — Detail of gasification apparatus

5.4.1 Distillation flask, round-bottomed of 300 ml capacity, with two inlets, a long one for admitting gases from the pyrolysis tube and a short one for adding the sodium hydroxide solution and emptying the flask. The distillate exit from the flask has an integral splash head which connects directly to a Liebig condenser (5.4.2).

5.4.2 Liebig condenser, 300 mm to 400 mm long.

5.4.3 Heating mantle, suitable for the distillation flask.

Dimensions in millimetres



Key

1 Pyrolysis tube exit (see Figure 1)
2 Spherical ground glass joint
3 Condenser
4 Glass tube for admission and extraction of sodium hydroxide solution
5 93 mm diameter flask
6 Heating mantle

Figure 3 — Suitable distillation apparatus

5.5 Sample boat, porcelain, of 8 ml capacity.

5.6 Silica boat, 25 mm × 15 mm × 130 mm, or as required, to contain the sample boat and any alkali that may spill out during the pyrolysis of the sample.

6 Preparation of the test sample

The test sample is the general analysis test sample prepared in accordance with ISO 1988, ISO 2309, ISO 5069-2, ISO 9411-1 or ISO 9411-2 as appropriate. Expose the test sample for the minimum time required for the moisture content to reach approximate equilibrium with the laboratory atmosphere.

Before commencing the determination, mix the equilibrated sample for at least 1 min.

If results are to be calculated other than on the “air-dried” basis (see clause 9) then, after weighing the test portion, determine the moisture content of a further portion of the test sample by the method described in ISO 331, ISO 687, ISO 1015 or ISO 5068 as appropriate.

7 Procedure

7.1 Preparation of the test portion

Transfer approximately 1 g of the powdered soda lime (4.5) to a clean, dry watch glass. Weigh to the nearest 0,1 mg, about 0,10 g of the sample, transfer to the watch glass and mix well with the soda lime.

Heat the sample boat (5.5) to 1 000 °C for a few minutes and allow to cool.

Carefully transfer the mixture to the sample boat to form an even layer. Cover with about 2 g of the activated alumina (4.6) and finally with about 0,1 g of the silica fibre (4.7), to reduce the loss of alkali during pyrolysis and hence prolong the life of the tube.

7.2 Preparation of the apparatus

Check that the apparatus is airtight, then raise the temperature of the main furnace (5.3.3) to 1 000 °C ± 5 °C and that of the steam-raising furnace (5.3.1) to 450 °C ± 5 °C.

NOTE 1 This is conveniently carried out by fitting a manometer to the exit from the empty distillation flask and connecting a small hand pump to one of the tubes passing through the silicone rubber stopper at the inlet end of the pyrolysis tube. Close all other exits and inlets in the system of the pyrolysis tube and distillation flask and introduce air by means of the hand pump until there is a small positive pressure as shown by the manometer. Close the air inlet and observe the manometer for loss of pressure. If a pressure drop occurs, locate and rectify the source of the leak.

Ensure that water is passing through the condenser. Add 150 ml of the sodium hydroxide solution (4.2) to the distillation flask and raise it to the boiling temperature of approximately 125 °C using the heating mantle (5.4.3).

NOTE 2 One filling of the sodium hydroxide solution will serve several determinations. Renew once a day in apparatus which is in regular use.

Condition the apparatus, after placing a receiver under the end of the condenser, by introducing water at a rate of 2,5 ml/min, by means of the peristaltic pump (5.3.5) and helium at a rate of 50 ml/min, by means of the helium flow control apparatus (5.3.6). Maintain these conditions for 10 min.

7.3 Gasification of the sample

Remove the receiver (discarding the contents), and replace with one into which 2 ml of the saturated boric acid solution (4.1) and 2 ml of the ammonia solution (4.3) have been transferred by means of a pipette. Adjust the receiver so that the delivery tube of the Liebig condenser (5.4.2) dips below the liquid level.

Turn off the peristaltic pump and remove the silicone stopper from the inlet end of the pyrolysis tube (5.3.4). Put the sample boat (5.5) containing the sample, into the silica boat (5.6), place at the inlet end of the pyrolysis tube and re-insert the silicone stopper. Carry out these operations as quickly as possible.

Re-introduce the water and maintain the helium flow as described in 7.2 for a maximum of 2 min until traces of liquid water appear within the pyrolysis tube at the exit of the steam-raising furnace.

NOTE 1 If liquid water does not appear within 2 min, the temperature of the steam-raising furnace is too high and should be reduced until the condition is met.

While maintaining the water and helium flows, transfer the silica boat to the pre-heater (5.3.2) zone of the pyrolysis tube, by means of the pusher rod (5.3.7). Withdraw the pusher rod and switch on the pre-heater.

For coals, set the pre-heater regulator to raise the temperature to 500 °C in 5 min and then to 800 °C in a further 5 min, or longer, until all the volatile matter has evolved.

For coke, set the pre-heater regulator to raise the temperature to 800 °C in 2 min to 3 min and maintain at this temperature for a total of 10 min.

Switch off the pre-heater and push the silica boat into the heated zone of the main furnace. Withdraw the pusher rod and leave the boat in this position for 20 min while still maintaining the water and helium flows.

Remove the receiver containing the distillate from the condenser and set it aside for titration (see 7.4). Switch off the water supply, disconnect the silicone rubber stopper, remove the boat and re-insert the stopper. Examine the residue in the boat. If unburnt sample is evident, discard the test.

If another determination is to be made, condition the system by passing water and helium through the empty pyrolysis tube for 10 min as in 7.2. Collect the distillate in an empty receiver. Re-commence the procedure as at 7.3 using another test portion prepared as at 7.1.

NOTE 2 The water and helium should remain turned on at all times between determinations while the main furnace is at operating temperature.

7.4 Titration of the distillate

Add to the receiver containing the distillate, 2 drops to 4 drops of the mixed indicator solution (4.9) and titrate the ammonia present with the sulfuric acid solution (4.8) until the green colour changes to steel grey. Confirmation that the end point has been reached can be obtained by adding a further drop of sulfuric acid solution which will give a purple colour.

8 Blank test

Carry out a blank test by exactly the same procedure, but using approximately 0,1 g of powdered graphite (4.10) instead of the sample.

9 Expression of results

The nitrogen content, N, of the sample as analysed, expressed as a percentage by mass, is given by the formula:

$$N = 2{,}8 \times c \times (v_1 - v_2)/m$$

where

c is the concentration, expressed in moles per litre, of the sulfuric acid solution (4.8);

v_1 is the volume, in millilitres, of the sulfuric acid solution (4.8) used in the determination;

v_2 is the volume, in millilitres, of the sulfuric acid solution (4.8) used in the blank test;

m is the mass, in grams, of the test portion taken.

Report the results, as the mean of duplicate determinations, to the nearest 0,01 %.

The results of the determination described in this Technical Specification are reported on the “air-dried” basis. Calculation of results to other bases is dealt with in ISO 1170.

NOTE The derivation of the factor used in the above calculation is detailed in annex A.

10 Precision

10.1 Repeatability limit

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 test sample, shall not differ by more than 0,06 % absolute.

10.2 Reproducibility critical difference

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 0,10 % absolute.

11 Test report

The test report shall include the following information:

a) identity of the sample tested;

b) reference of the method used;

c) result and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this Technical Specification, or regarded as optional;

f) date of the test.