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Coke — Determination of coke reactivity index (CRI) and coke strength after reaction (CSR)

Coke — Mesures de l'indice de réactivité du coke (CRI) et de la résistance post-réactionelle du coke (CSR)

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Foreword

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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.

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ISO 18894 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 3, *Coke*.

Coke — Determination of coke reactivity index (CRI) and coke strength after reaction (CSR)

1 Scope

This International Standard specifies the equipment and techniques used for determining lump-coke (> 20 mm) reactivity in carbon dioxide gas at elevated temperatures and its strength after reaction in carbon dioxide gas by tumbling in a cylindrical chamber.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 579, *Coke — Determination of total moisture*

ISO 3310 (all parts), *Test sieves — Technical requirements and testing*

ISO 1213–2, *Solid mineral fuels — Vocabulary — Part 2: Terms relating to sampling, testing and analysis*

ISO 2309, *Coke — Sampling*

ISO 13909-5, *Hard coal and coke — Mechanical sampling — Part 5: Coke — Sampling from moving streams*

ISO 13909-6, *Hard coal and coke — Mechanical sampling — Part 6: Coke — Preparation of test samples*

IEC 60584-1, *Thermocouples — Part 1: Reference tables*

IEC 60584-2, *Thermocouples — Part 2: Tolerances*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1213-2 and the following apply.

3.1
abrasion value
lack of resistance to abrasion of the coke after reaction with carbon dioxide in the CRI test, measured as the percentage of a sample passing through a 0,5 mm sieve after tumbling under conditions specified in this International Standard

NOTE See Annex D.

3.2
coke reactivity index
CRI
percentage weight loss of coke after reaction with carbon dioxide to form carbon monoxide under conditions specified in this International Standard

3.3
coke strength after reaction
CSR
strength of coke after reaction with carbon dioxide in the CRI test, measured as the percentage retained on either a 10,0 mm or a 9,5 mm sieve after tumbling under conditions specified in this International Standard

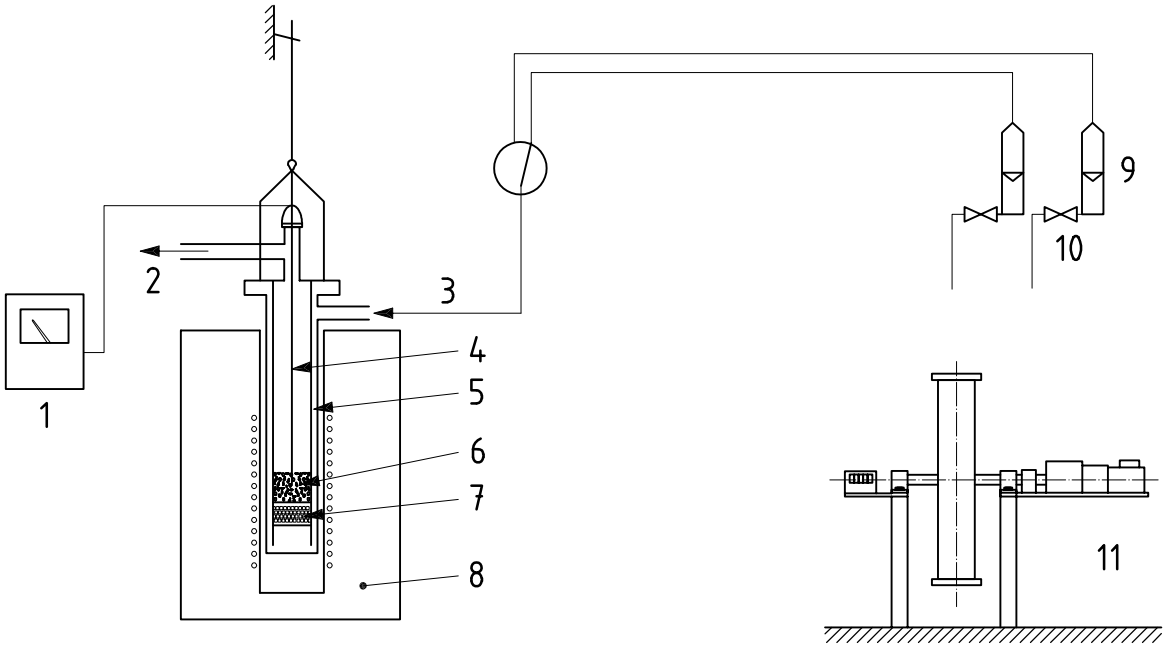
4 Principle

A test portion of the dried coke sample having a size range from 19,0 mm to 22,4 mm is heated in a reaction vessel to 1 100 °C in a nitrogen atmosphere. For the test, the atmosphere is changed to carbon dioxide for exactly 2 h. After the test, the reaction vessel is allowed to cool down to about 50 °C in a nitrogen atmosphere. The comparison of the sample weight before and after the reaction determines the coke reactivity index (CRI).

The reacted coke is treated in a specially designed tumbler for 600 revolutions for 30 min. The coke strength after reaction (CSR) value is determined by sieving and weighing the amount of coke passing through either a 10,0 mm or a 9,5 mm sieve.

An example of the arrangement of the test unit is shown in Figure 1.

NOTE During the development of this International Standard, it was found that 10,0 mm and 9,5 mm sieves are both commonly used for these types of test. When reacted coke is tumbled, abrasion usually takes place. Particles of about 20 mm lose some edges, but they do not break into pieces. Therefore, it makes almost no difference if the sieving after tumbling is made with a 10,0 mm or a 9,5 mm sieve, as the size of the coke pieces is either about 20 mm or 0 mm to 5 mm, but not in the range of 10 mm. This has been verified by experiments over a long period of time. It has been shown that the difference in CSR using both sieve sizes is within the precision range of this International Standard.



Key

1 plotter for recording temperature
2 gas outlet to stack
3 gas inlet
4 thermocouple
5 single or double wall retort with perforated plate as sample holder
6 test portion
7 layer of ceramic balls
8 electrically heated furnace
9 gas-flow meters
10 control valves
11 tumbler

Figure 1 — Example of test unit arrangement

5 Reagents

5.1 Nitrogen, having a purity of $> 99,9$ % by volume, dry and having a maximum oxygen and carbon dioxide ($CO_2 + O_2$) concentration of 100 mg/kg.

5.2 Carbon dioxide, having a purity of $> 99,5$ % by volume, dry and having an oxygen concentration < 100 mg/kg.

6 Apparatus

6.1 Electric furnace (see Annexes A and B), capable of housing the reaction-vessel assembly containing the test portion and providing a uniform temperature of (1 100 $\pm$ 3) °C in the centre of the test portion. The uniform temperature zone shall be at least three times longer than the sample height.

It is preferable that the furnace have independently controlled heating in three zones to achieve uniformity of heating in the reaction vessel.

6.2 Reaction vessel (see Annexes A and B), constructed from heat-resistant steel or nickel alloy to the dimensions required to fit inside the electric furnace selected for use.

The coke to be tested is placed on a perforated plate in the reaction vessel. Below this perforated plate, a gas preheater, such as a bed of ceramic Al_2O_3 balls on a second perforated plate, diffuses the nitrogen and carbon dioxide introduced into the vessel up through the coke bed during the course of the test. Both perforated plates are fixed between two sets of lugs in the reaction vessel. The gas enters through inlets at the bottom and exits through outlets positioned at the top of the reaction vessel.

The reaction vessel is positioned such that the coke sample contained in the vessel is in the centre of the uniform temperature zone of the furnace.

6.3 Flowmeters, **variable area flowmeter** or, preferably, **mass flowmeters**, used to monitor the nitrogen and carbon dioxide flow during the test, having an accuracy of gas flow rates of $\pm$ 5 % for both nitrogen and carbon dioxide.

NOTE Fluctuations in the gas flow can cause variability in the test results.

Gas pressures through the flowmeters shall be maintained at the manufacturer's calibration specification.

6.4 Thermocouple, conforming to the requirements of IEC 60584-1 and IEC 60584-2, used for measuring and controlling the sample temperature, which shall be designed according to the test conditions [e.g. platinum–rhodium/platinum (90 % Rh and 10 % Pt, percentage by mass)], enclosed in a heat-resistant steel or nickel alloy or ceramic protection tube. The protection tube shall be made of gas-tight casing to prevent faulty measurement caused by a poisoning of the thermocouple by gaseous products. The protection tube is fastened to the centre of the lid to ensure the positioning of the thermocouple tip in the centre of the coke bed.

6.5 Sieves, square hole conforming to the requirements of ISO 3310, with actual openings of 9,5 mm or 10,0 mm, 19,0 mm and 22,4 mm. A 0,5 mm sieve is also required if the abrasion test (see Annex D) is carried out.

6.6 Balance, capable of weighing to the nearest 0,1 g.

6.7 Tumbler (see Annex C), with a revolution counter and a time-relay device.

7 Preparation of test sample

Sample the coke in accordance with ISO 2309 or ISO 13909-5.

Crush approximately 50 kg of the gross sample with a representative size distribution in a jaw crusher or rolling crusher. The opening of the crusher shall be set such that the gross sample yields between 10 % and 30 % of the fraction 19,0 mm to 22,4 mm. Divide the crushed sample to obtain a mass of approximately 25 kg in accordance with ISO 13909-6.

The mass of sample required for the test depends on the following.

a) The minimum mass required for the test is governed by the minimum mass of the 19,0 mm to 22,4 mm fraction, i.e. 1 000 g.

b) A sample of large coke must be of sufficient size to ensure that it is representative. Therefore, smaller sample amounts may be used only when it is guaranteed that they are representative. This shall be indicated in the test report.

Sieve the crushed sample using a 22,4 mm sieve placed on top of a 19,0 mm sieve. Recycle the $>$ 22,4 mm fraction to the crusher until the oversize is less than 3 % of the crushed sample. Discard the $<$ 19,0 mm and $>$ 22,4 mm fractions.

Dry the 19,0 mm to 22,4 mm fraction in accordance with ISO 579 to less than 1 % moisture. Sieve the crushed and dried sample again using 22,4 mm and 19,0 mm sieves to remove adhering breeze. Divide the crushed and sieved sample to obtain a test sample of approximately 1 000 g.

Alternatively, the sample (fraction 19,0 mm to 22,4 mm) may be divided to approximately 1 000 g before drying and sieving.

Divide the test sample to get test portions of approximately 200 g each. For each test, prepare a test portion of 200 g $\pm$ 2 g and weigh accurately to the nearest 0,1 g. The final mass adjustment can be made by exchanging a single piece of coke for one slightly lighter or heavier as appropriate.

NOTE Recording the number of pieces in each test portion can be helpful for comparing the test runs.

8 Procedure

8.1 Number of tests

A minimum of two tests shall be carried out.

8.2 Determination of CRI

CAUTION — The waste gas leaving the reaction vessel during the CO_2 gas charging is CO-rich and therefore hazardous. It should be burnt or led to a ventilated stack. Care should be taken regarding the hot surface (1 100 °C) of the reaction vessel.

Preheat the furnace to a temperature that will allow the reaction vessel and sample, when placed in the furnace, to reach (1 100 $\pm$ 3) °C within 30 min to 40 min. Before the reaction vessel is placed in the electric furnace, place the weighed sample in the reaction vessel in a manner so as to ensure that the thermocouple sits vertically in the centre of the coke bed with its tip in the centre (at half the height of the test portion above the perforated plate) of the coke bed. Purge the reaction vessel for 5 min with nitrogen at 10 l/min $\pm$ 0,5 l/min before loading the vessel into the furnace.

Place the reaction vessel in the furnace such that the centre of the coke charge is positioned in the centre of the heating zone and heat the sample to (1 100 $\pm$ 3) °C within 30 min to 40 min in the nitrogen atmosphere.

Adjust the temperature to 1 100 °C; the allowed deviation of ± 3 °C is used only for temperature regulation during the test.

Once the sample temperature of (1 100 ± 3) °C is reached, soak the reaction vessel for a further 10 min in nitrogen before switching over to carbon dioxide with a flow rate of 5 l/min ± 0,25 l/min. Keep the sample at (1 100 ± 3) °C in an atmosphere of carbon dioxide. After the switch to carbon dioxide, the temperature will drop (endothermic reaction). The heat capacity of the furnace shall be such that, with an initial temperature of (1 100 ± 3) °C, the temperature drop is minimized and the test temperature is regained within 10 min.

NOTE The temperature drop can be minimized by turning up the furnace temperature just prior to introducing the carbon dioxide. For unknown samples, this increase can be determined by experiment.

After exactly 120 min exposure to carbon dioxide, switch back to nitrogen at 10 l/min ± 0,5 l/min for 5 min to purge the reactor vessel of carbon dioxide. Remove the reaction vessel from the furnace and allow it to cool down to less than 50 °C under nitrogen flow. After cooling, remove the test portion from the reaction vessel, weigh the reacted coke to the nearest 0,1 g and calculate the CRI in accordance with 9.1.

8.3 Determination of CSR

Transfer the reacted coke completely to the tumbler, close and check for complete tightness. Tumble the residue for exactly 600 revolutions for 30 min at (20 ± 0,1) min^{-1}.

Remove all coke from the drum. Sieve using either a 10,0 mm or a 9,5 mm sieve and weigh the coke remaining on the sieve to the nearest 0,1 g. Calculate the CSR in accordance with 9.2.

9 Expression of results

9.1 Coke reactivity index (CRI)

The CRI expressed as a percentage by mass is given by Equation (1):

$$\mathrm{CRI} = 100 \times \frac{m_0 - m_1}{m_0} \tag{1}$$

where

m_0 is the mass, in grams, of the sample before reaction;

m_1 is the mass, in grams, of the sample after reaction.

9.2 Coke strength after reaction (CSR)

The CSR, expressed as a percentage by mass, is given by Equation (2):

$$\mathrm{CSR} = 100 \times \frac{m_2}{m_1} \tag{2}$$

where

m_2 is the mass, in grams, of the fraction of the sample > 10,0 mm or > 9,5 mm after tumbling;

m_1 is the mass, in grams, of the sample after reaction.

10 Precision

10.1 Verification

Regular checking of apparatus and procedures is essential to verify the test results. The following items shall be checked at regular intervals.

a) Test sample preparation:

   1) sieves;

   2) balance.

b) For the reactivity test:

   1) condition of the reaction vessel;

   2) gas flow rate;

   3) thermocouple;

   4) timer.

c) For the strength test:

   1) tumbler condition;

   2) rotation speed;

   3) revolution counter;

   4) sieves;

   5) balance.

It is recommended that certified calibration equipment be used for checking and that internal reference material be prepared and used periodically to verify repeatability and reproducibility.

See also Annex E.

10.2 Repeatability limit

10.2.1 General

The results of duplicate determinations, carried out in the same laboratory by the same operator with the same apparatus within a short interval of time on representative portions taken from the same analysis sample, shall not differ by more than the values shown in Tables 1 and 2.

10.2.2 Coke reactivity index

For a paired result, the value of the range $|X_1 - X_2|$ shall govern whether additional tests are required as specified in Table 1 and 10.2.2 a) to 10.2.2 c).

Table 1 — Criteria for multiple determinations (CRI)

CRI	Range $\lvert X_1 - X_2 \rvert$		
	A	B	C
$\leqslant 10$	—	—	—
$> 10 \leqslant 20$	2,0	2,5	2,7
$> 20 \leqslant 30$	2,5	3,2	3,5
$> 30 \leqslant 40$	3,0	4,0	4,5
$> 40 \leqslant 60$	3,5	5,0	5,5
> 60	—	—	—

a) Given two results

— If range $|X_1 - X_2| \leqslant$ A, average the two results.

— If range $|X_1 - X_2| >$ A and range $|X_1 - X_2| \leqslant$ B, perform a third test.

— If range $|X_1 - X_2| >$ B, perform two more tests.

b) Given three results

— If $X_{(\max)} - X_{(\min)} \leqslant$ B, average the three results.

— If $X_{(\max)} - X_{(\min)} >$ B, perform a fourth test.

c) Given four results

— If $X_{(\max)} - X_{(\min)} \leqslant$ C, average the four results.

— If $X_{(\max)} - X_{(\min)} >$ C, discard $X_{(\max)}$ and $X_{(\min)}$ and average the remaining two results.

The mean index shall be rounded off to the first decimal place.

10.2.3 Coke strength after reaction

For a paired result, the value of the range $|X_1 - X_2|$ shall govern whether additional tests are required according to Table 2 and 10.2.3 a) to 10.2.3 c).

Table 2 — Criteria for multiple determinations (CSR)

CSR	Range $\lvert X_1 - X_2 \rvert$		
	A	B	C
> 80	—	—	—
$> 70 \leqslant 80$	2,0	2,5	2,7
$> 60 \leqslant 70$	2,5	3,2	3,5
$> 50 \leqslant 60$	3,0	4,0	4,5
$> 30 \leqslant 50$	3,5	5,0	5,5
$\leqslant 30$	—	—	—

a) Given two results

— If range $|X_1 - X_2| \leqslant$ A, average the two results.

— If range $|X_1 - X_2| >$ A and range $|X_1 - X_2| \leqslant$ B, perform a third test.

— If range $|X_1 - X_2| >$ B, perform two more tests.

b) Given three results

— If $X_{(\max)} - X_{(\min)} \leqslant$ B, average the three results.

— If $X_{(\max)} - X_{(\min)} >$ B, perform a fourth test.

c) Given four results

— If $X_{(\max)} - X_{(\min)} \leqslant$ C, average the four results.

— If $X_{(\max)} - X_{(\min)} >$ C, discard $X_{(\max)}$ and $X_{(\min)}$ and average the remaining two results.

The mean index shall be rounded off to the first decimal place.

11 Test report

The test report shall include the following information:

a) reference to this International Standard and its year of publication, i.e. ISO 18894:2006;

b) the identification of the sample tested;

c) the sieve size used for CSR determination (10,0 mm or 9,5 mm);

d) the results of the determination;

e) the sample mass if less than about 50 kg;

f) the date of the test.

Annex A
(normative)

Reactivity test apparatus “type A”, single wall

A.1 Electric furnace

The furnace, heated by electricity, shall be capable of housing the reaction vessel assembly and shall be designed for sufficient heating capacity to keep the coke sample at a temperature of (1 100 ± 3) °C during the test, measured in the centre of the test portions. The uniform temperature zone shall be a minimum of three times the sample height.

A.2 Reaction vessel

The reaction vessel shall be constructed of heat-resistant steel or nickel alloy.

Minimum length: 230 mm.

Outside diameter: ranges from 84 mm to 90 mm.

Inside diameter: (78 ± 1) mm.

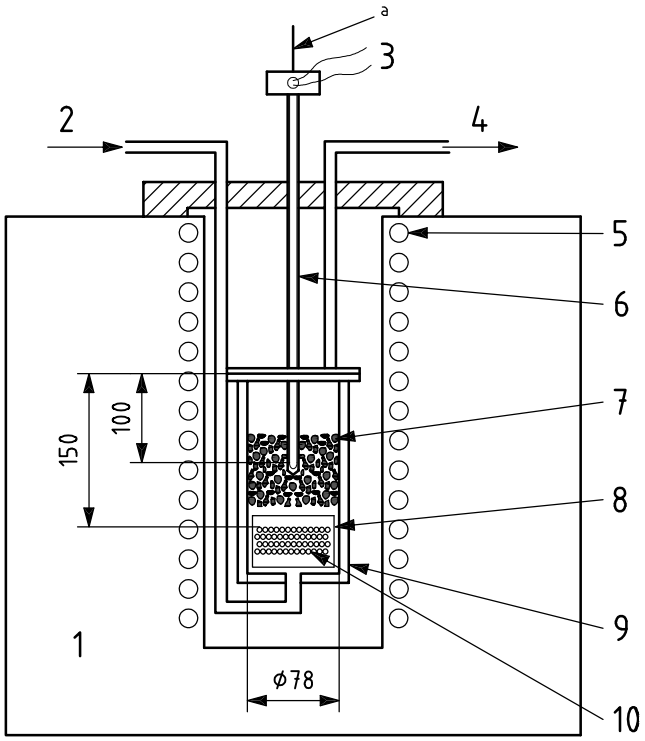
An example is shown in Figure A.1.

The coke to be tested is placed on a perforated plate in the reaction vessel. Below this perforated plate, a gas preheater, such as a bed of ceramic Al_2O_3 balls (approximately 10 mm in diameter) on a second perforated plate, diffuses the nitrogen and carbon dioxide introduced into the vessel up through the coke bed during the course of the test. The height of the preheater is approximately 80 mm. To prevent leakage, insert a seal between the cover and the lower part of the reaction vessel.

The gas enters through inlets positioned at the bottom and exits at the top of the reaction vessel. The reaction vessel is positioned such that the coke sample contained in the vessel is in the centre of the controlled-temperature zone of the furnace.

The thermocouple is enclosed in a heat-resistant steel or nickel alloy or ceramic protection tube. This protection tube works as a centring guide; it is normally fastened to the centre of the lid to ensure correct positioning of the thermocouple tip. The tip is positioned in the centre, at half the height to the test portion above the perforated plate. Variations in coke density can result in different total coke-bed heights in the reaction vessel; adjust the tip of the thermocouple accordingly.

Dimensions in millimetres



Key

1 furnace
2 N_2 and CO_2 gas inlet
3 thermocouple leads
4 gas outlet
5 heating element
6 thermocouple
7 coke sample (≈100 mm in height)
8 gas diffuser and preheater
9 reaction tube
10 Al_2O_3 balls

a Suspended from a cantilever.

Figure A.1 — Example of reaction vessel and test unit design — "Type A", single wall

Annex B
(normative)

Reactivity test apparatus “type B”, double wall

B.1 Electric furnace

The furnace, heated by electricity, shall be capable of housing the reaction vessel assembly and designed for sufficient heating capacity to keep the coke sample at a temperature of (1 100 ± 3) °C during the test, measured in the centre of the test portions. The uniform temperature zone shall be a minimum of three times the sample height.

B.2 Reaction vessel

The reaction vessel shall be constructed of heat-resistant steel or nickel alloy.

Length: dependent on furnace length.

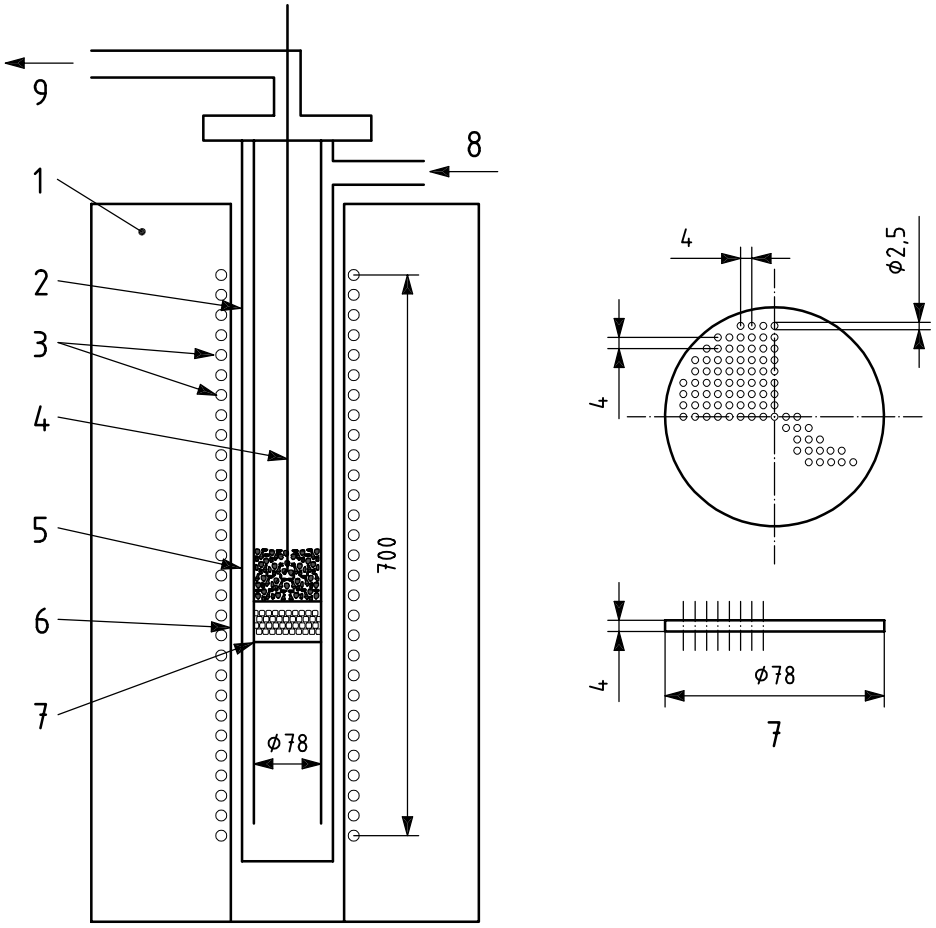
Inside diameter of inner pipe: (78 ± 1) mm.

An example is shown in Figure B.1.

The coke to be tested is placed on a perforated plate in the reaction vessel. Below this perforated plate, a gas preheater, such as a bed of ceramic Al_2O_3 balls (approximately 10 mm in diameter), on a second perforated plate, diffuses the nitrogen and carbon dioxide introduced into the vessel up through the coke bed during the course of the test. The height of the preheater is approximately 80 mm. To prevent leakage, insert a seal between the cover and the lower part of the reaction vessel.

The gas enters through the inlet positioned on the side of the reaction vessel near the top, flows down between the two walls of the vessel and into the central part of the reaction vessel, up through the coke sample, then exits from the top. The reaction vessel is positioned such that the coke sample contained in the vessel is in the centre of the controlled-temperature zone of the furnace. The tip of the thermocouple is positioned in the centre, at half the height of the test portion above the perforated plate.

Dimensions in millimetres



Hole diameter:	2,5 mm
Pitch between holes:	4 mm
Number of holes:	241
Total hole area	11,8 cm^2
Thickness of plate	4 mm

Key

1 furnace (10 kVA)
2 reduction tube
3 heating element
4 thermocouple
5 test portion
6 layer of ceramic balls (80 mm in height)
7 perforated plate
8 gas inlet
9 gas outlet

Figure B.1 — Example of reaction vessel and test unit design — "Type B", double wall

Annex C
(normative)

Coke-strength-after-reaction tumbler

The tumbler has a revolving drive, controlled by a revolution counter and a time relay. The drive shall be designed for exactly 600 revolutions in 30 min at $(20 \pm 0{,}1)\ \text{min}^{-1}$. The tumbler shall stop after exactly 600 revolutions.

Length of inside cylindrical chamber: (700 ± 1) mm.

Inner diameter: (130 ± 1) mm.

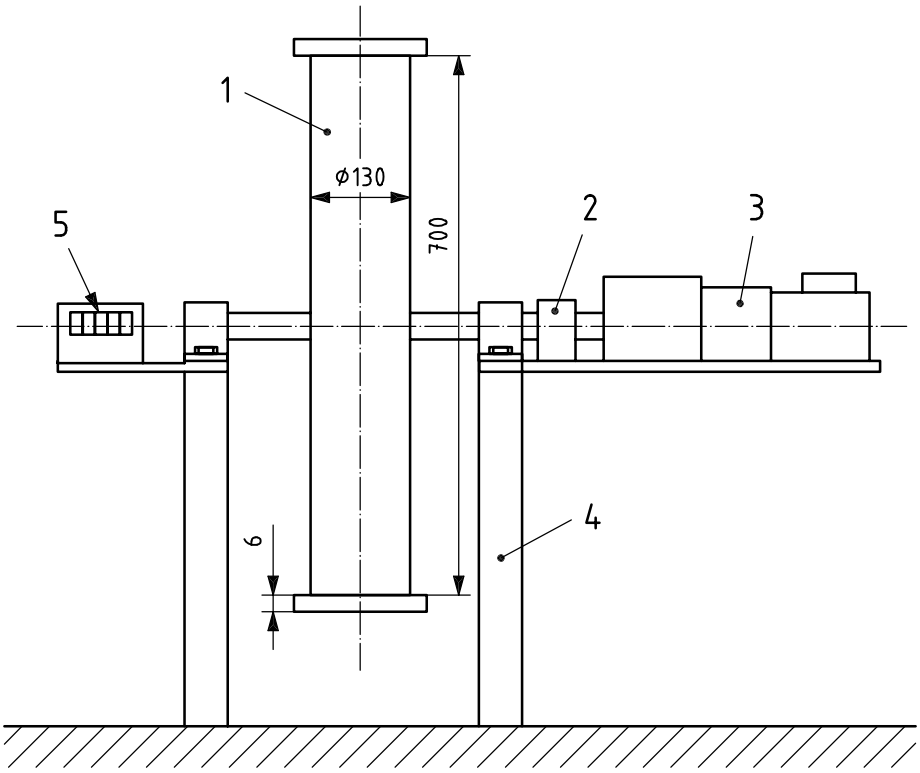
Thickness of cylindrical chamber: 5 mm.

Minimum thickness of end caps: 6 mm.

Both the inside of the cylinder and the end plates shall be without any intrusions (e.g. bolt heads).

See Figure C.1.

Dimensions in millimetres



Key

1 tumbler
2 safety-friction clutch
3 geared motor
4 porter bar
5 revolution counter

Figure C.1 — Tumbler

Annex D
(informative)

Determination of abrasion value

D.1 Principle

The abrasion value reflects the amount of fines (< 0,5mm) resulting from tumbling the reacted coke and indicates the resistance to mechanical degradation.

D.2 Procedure

Re-sieve the portion of the reacted coke (from the CSR determination) that passed the 10,0 mm or 9,5 mm sieve using a 0,5 mm sieve and weigh the coke that passed through the sieve. Calculate the abrasion value according to Equation (D.1).

D.3 Expression of results

The abrasion value (AV), expressed as a percentage by mass, is given by Equation (D.1):

$$AV = 100 \times \frac{m_3}{m_1} \qquad \text{(D.1)}$$

where

m_3 is the mass, in grams, of the fraction < 0,5 mm after tumbling;

m_1 is the mass, in grams, of the sample after reaction.

Annex E
(informative)

Reproducibility critical difference

The determination of precision data, especially the reproducibility critical difference, is very time- and money-consuming. In three proficiency tests sponsored by the European Coal and Steel Community in 1997 and 1999, precision data were obtained. In these series, 22 participants from Europe analyzed coke samples that had already been prepared, i.e. coke in the size range of 19,0 mm to 22,4 mm. Therefore, the precision data given in this annex exclude the effect of sample preparation. Of the three samples analyzed, acceptable results were obtained for only two coke samples, which had a CSR $>$ 55. (The consensus CSR values were 64,3 and 63,3). However, additionally, data are presented for coke having a CSR $<$ 55 (consensus CSR value 35,3) only as an approximate value.

NOTE ISO criteria for the determination of reproducibility from inter-laboratory testing were not met as not enough samples have been measured in the proficiency test described above. Therefore, it was decided to present the reproducibility critical difference in an informative annex only.

The means of the results of duplicate determinations, performed in each of two laboratories, on representative portions taken from the same test sample, prepared to the last stage of sample preparation, shall not differ by more than the values specified in Table E.1.

Table E.1 — Reproducibility critical difference

CRI		CSR	
Value	**Critical difference**	**Value**	**Critical difference**
$>$ 33	5 [a]	$<$ 55	8 [a]
$<$ 33	3,5	$>$ 55	4,5
[a] Approximate values only.			

Among other criteria (e.g. temperature control, gas flow, quality of sample preparation), sieving is critical. Sieving results are influenced strongly by the sieve-shaker characteristics. Therefore, in cases where two or more laboratories need to compare results for commercial or technological purposes, they shall use identical sieving conditions in order to obtain comparable results for the same test sample.

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