INTERNATIONAL STANDARD

ISO 14720-1

First edition
2013-03-01

Testing of ceramic raw and basic materials — Determination of sulfur in powders and granules of non-oxidic ceramic raw and basic materials —

Part 1:
Infrared measurement methods

Essais des matières premières pour produits réfractaires — Dosage du soufre dans les matières premières non oxydantes sous forme de poudre et de granulés —

Partie 1: Méthodes d'essai par infrarouge

Reference number
ISO 14720-1:2013(E)

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Published in Switzerland

Contents

Page

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.

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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.

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

ISO 14720-1 was prepared by Technical Committee ISO/TC 33, *Refractories*.

ISO 14720 consists of the following parts, under the general title *Testing of ceramic raw and basic materials — Determination of sulfur in powders and granules of non-oxidic ceramic raw and basic materials*:

- *Part 1: Infrared measurement methods*
- *Part 2: Inductively coupled plasma optical emission spectrometry (ICP/OES) or ion chromatography after burning in an oxygen flow*

Testing of ceramic raw and basic materials — Determination of sulfur in powders and granules of non-oxidic ceramic raw and basic materials —

Part 1:
Infrared measurement methods

1 Scope

This part of ISO 14720 defines a method for the determination of sulfur in powdered and granular non-oxidic ceramic raw materials and materials, such as silicon carbides, silicon nitrides, graphites, carbon blacks, cokes, carbon powders. If proved by the recovery rate, this method can also be applied for other non-metallic powdered and granular materials, e.g. silicon dioxide.

This part of ISO 14720 is applicable for materials with mass fractions of sulfur from 0,005 % to 2 %.

This part of ISO 14720 can also be applied for materials with higher mass fractions of sulfur after verification of the particular case.

2 Principle

The sample and added combustion accelerators (mostly tungsten- or iron-granules) are heated in an inductive furnace under oxygen atmosphere. The high-frequency field of the furnace couples with electrically conductive components of sample and combustion accelerators. The sample is heated to temperatures above 1 800 °C and the total sulfur content of the sample is released as sulfur dioxide. The reaction gas is transferred to the infrared absorption cell of the analyser. The molecular absorption of sulfur dioxide is measured by using a narrow-band optical filter which is translucent for the wavelength of the characteristic infrared absorption of sulfur dioxide. The mass fraction of sulfur dioxide in the reaction gas is proportional to peak-height and peak-area, respectively, of the transient absorption signal. The mass fraction of sulfur in the sample is calculated by using a calibration function established by suitable calibration standards measured under comparable conditions.

3 Apparatus

3.1 Device with induction furnace or alternatively resistance furnace and infrared cell.

NOTE The correctness of the analysis result can be proved by using matrix-analogous reference materials or by comparing with an independent alternative test method. If determining mass fractions below 100 mg/kg, it has to be considered that some analytical devices may deliver incorrect results.

3.2 Analytical balance, capable of reading to the nearest 0,01 mg.

3.3 Ceramic crucible, e.g. mullite or alumina.

3.4 Crucible lid with hole, e.g. mullite or alumina.

4 Reagents

4.1 General

Reagents of known analytical grade shall be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Tungsten granules

NOTE Depending on the material, the decomposition of the sample in the furnace may be improved by partially replacing tungsten granules by tin granules. Tungsten/tin-mixtures are commercially available.

4.3 Iron granules

4.4 Calibration standards, preferably certified reference materials with composition and sulfur content similar to the analysed material.

NOTE See Annex C. Also suitable are primary substances, preferably sulfates.

4.5 Oxygen, purity ≥ 99,998 % *V*/*V*.

5 Sampling and sample preparation

Sampling shall be performed in a way such that the sample to be analysed is representative for the total amount of material, for example according to ISO 8656-1.[1]

In an unknown drying state, the sample shall be dried at (110 ± 5) °C to constant mass. The sample shall be cooled to ambient temperature in a desiccator and stored therein.

The sample material shall have a particle size of ≤ 160 µm. If necessary, it shall be crushed and homogenized.

6 Calibration

The calibration shall be performed according to the manufacturer’s manual. It shall be ensured that the mass of sulfur in the calibration sample and test sample are within the same order of magnitude.

NOTE This is achieved by choosing a suitable calibration substance (4.4) and adapted masses.

For a mass fraction below 100 mg/kg, the trueness of the result shall be verified using a suitable reference material, preferably a certified reference material.

The calibration shall be carried out according to the procedure in 7.3.

7 Performance

7.1 Preparation of analysis

Ceramic crucibles (3.3) and lids (3.4) have to be pre-cleaned by heating to 1 200 °C for 1 h prior to analysis, preferably using a muffle furnace. The sulfur content of the iron granules (4.3) shall be determined batch-wise. In the case of a too high and irreproducible sulfur content of the iron granules in relation to the expected sulfur content in the sample, they shall be pre-cleaned by the following procedure: weigh 1 g of iron granules into each ceramic crucible used for analysis. Cover with a lid and melt the iron granules under oxygen atmosphere in the inductive furnace of the analytical device. If the sulfur content of the sample is less than 100 mg/kg, the iron granules can be alternatively purified by heating in hydrogen atmosphere at approximately 800 °C for 1 h.

7.2 Determination of blank value

Use the procedure in 7.3 but without any sample.

7.3 Determination of sulfur content

According to the expected sulfur content, a sub-sample of 20 mg to 200 mg is weighed to the nearest 0,01 mg into the crucibles prepared according to 7.1.

The sub-sample is covered with approximately 1 g and 2 g of iron and tungsten granules (4.2 and 4.3), respectively. If the crucible already contains pre-cleaned iron (see 7.1), no further iron has to be added. For mixing, the crucible has to be shaken carefully. Afterwards, the crucible is closed with the lid, placed in the analysis device and the combustion cycle is started.

Each sample has to be analysed at least two times. If the single values of the double-test deviate more than a given degree, depending on the repeatability of the method, then the analysis has to be repeated according to this Clause. If necessary, the sample has to be homogenized according to Clause 5.

8 Calculation and report of the results

The sulfur content of the sample shall be calculated under consideration of sample mass and blank values. The sulfur content as the mean of the corrected single values of the multiple determinations shall be expressed as a mass fraction and rounded off in accordance with the uncertainty of measurement (Annex B).

NOTE Most state-of-the-art analysers automatically calculate the mass fraction of sulfur for each measurement after input of blank values and sample masses.

9 Precision

9.1 Repeatability

The repeatability limit *r* will not be exceeded in more than 5 % of cases by the absolute difference between two single test results, determined in rapid succession by the same analyst with the same sample material using the same analytical procedure and the same equipment in the same laboratory.

NOTE The repeatability limit *r* depends on the examined material type and the determined mass of sulfur.

The precision data determined within a round robin test are listed in Annex A.

9.2 Reproducibility

The reproducibility limit *R* will not be exceeded in more than 5 % of cases by the absolute difference between two single test results, determined by different analysts with the same sample material using the same analytical procedure and different equipments in different laboratories.

The reproducibility *R* depends on the examined material type and the determined mass of sulfur.

The precision data determined within a round-robin test are listed in Annex A.

10 Test report

Test reports shall include the following information

a) sample identification;

b) a reference to this part of ISO 14720;

c) test results for the sulfur content, expressed as the mean of the single values of the multiple determinations;

d) if required, uncertainty of the mean (see Annex B) or standard deviation;

e) if required, information for calibration;

f) any discrepancy of the procedure used for sample testing according to this part of ISO 14720;

g) name and address of the laboratory, analysis date and, if required, signature of the responsible person.

Annex A

(informative)

Results of the round-robin test

The round-robin test was carried out using a sample of carbon black (see Tables A.1 and A.2) and silicon carbide (see Tables A.3. and A.4). The sulfur content of the carbon black sample was near the lower limit of the application range (see Clause 1) which leads to a worsening of the achievable precision data (see Tables A.1 and A.2). The maximum grain size of all samples was less than 100 µm. The evaluation of the results was done according to ISO 5725-2.[2]

Table A.1 — Data of precision determined using the sample of carbon black

Description	Precision data
Number of participants	5
Number of accepted single values of all laboratories	28
Number of outliers	0
Mean value $\bar{w}(\text{S})$, in mg/kg	67,0
Repeatability (standard deviation), s_r, in mg/kg	9,6
Repeatability limit r: $r = 2{,}8 \times s_r$, in mg/kg	26,9
Coefficient of variation of repeatability $C_{V,r}$: $C_{V,r} = (s_r / \bar{w}(\text{S})) \times 100$, in %	14,4
Reproducibility (standard deviation) s_R, in mg/kg	10,4
Reproducibility limit R: $R = 2{,}8 \times s_R$, in mg/kg	29,2
Coefficient of variation of reproducibility $C_{V,R}$: $C_{V,R} = (s_R / \bar{w}(\text{S})) \times 100$, in %	15,6

Table A.2 — Single values determined using the sample of carbon black

No.	Mass fraction of sulfur of the sample of carbon black mg/kg				
	Laboratory 1	Laboratory 2	Laboratory 3	Laboratory 4	Laboratory 5
1	62,0	84,0	72,6	74,0	58,0
2	67,0	54,4	71,3	66,0	57,0
3	61,0	65,6	76,3	68,0	73,0
4	61,0	54,4	75,6	51,0	58,0
5	75,0	85,6	81,3	–	65,0
6	65,0	45,5	83,0	–	66,0
$\bar{w}(\text{S})$	65,2	64,0	76,7	64,8	62,8
s	5,4	16,7	4,7	9,8	6,3
s_{rel}	8,3	25,7	6,1	15,1	10,0

Table A.3 — Data of precision determined using the sample of silicon carbide

Description	Precision data
Number of participants	5
Number of accepted single values of all laboratories	30
Number of outliers	0
Mean value $\bar{w}(\mathrm{S})$, in mg/kg	658
Repeatability (standard deviation), s_r, in mg/kg	17
Repeatability limit r: $r = 2{,}8 \times s_r$, in mg/kg	47
Coefficient of variation of repeatability $C_{V,r}$: $C_{V,r} = (s_r/\bar{w}(\mathrm{S})) \times 100$, in %	2,5
Reproducibility (standard deviation) s_R, in mg/kg	25
Reproducibility limit R: $R = 2{,}8 \times s_R$, in mg/kg	71
Coefficient of variation of reproducibility $C_{V,R}$: $C_{V,R} = (s_R/\bar{w}(\mathrm{S})) \times 100$, in %	3,9

Table A.4 — Single values determined using the sample of silicon carbide

No.	Mass fraction of sulfur of the sample of silicon carbide mg/kg				
	Laboratory 1	**Laboratory 2**	**Laboratory 3**	**Laboratory 4**	**Laboratory 5**
1	673	682	665	676	625
2	675	687	670	633	653
3	654	705	650	644	635
4	659	675	675	623	657
5	662	678	655	640	624
6	628	709	645	611	660
$\bar{w}(\mathrm{S})$	659	689	660	638	642
s	17	14	12	22	16
s_{rel}	2,6	2,1	1,8	3,5	2,5

Annex B
(informative)

Information regarding the validation of the uncertainty of the mean value

The specification of the measurement uncertainty of the results may be desired by the customer. The specification of the expanded uncertainty U is recommended which can be calculated by multiplication of the combined measurement uncertainty u_{comb} with the expanding factor $k = 2$. The calculation of the combined uncertainty can be carried out by a mathematical summarization of all contributions to the uncertainty as described in detail by ISO/IEC Guide 98-3 (GUM) [3] and as specified for analytical measurements by the Eurachem-Citac-Guide.[4] However, also other possibilities can be used to estimate the measurement uncertainty alternatively to that procedure based on a detailed analysis and modelling of the entire measurement process. To do so, laboratory internal data of validation processes or data of interlaboratory comparisons can be used, Reference.[5] In this case, a detailed knowledge of all contributions to the combined uncertainty is not necessary. A practical way is the analysis of a certified reference material (CRM) with similar properties to the investigated analytical samples. In this case, the combined measurement uncertainty can be calculated based on the standard deviation of the mean value determined by measurement of the CRM in the laboratory, the uncertainty of the certified value and the deviation of the measured and the certified value. (For more information see ISO 21748,[6] ISO 5725-4,[7] EUROLAB Technical Report 1/2007 [8] and EURACHEM Guide [9]).