INTERNATIONAL STANDARD

ISO 23157

First edition
2021-07

Determination of the silanol group content on the surface of fumed silica — Reaction gas chromatographic method

Reference number
ISO 23157:2021(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 256, *Pigments, dyestuffs and extenders*.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Fumed silica (pyrogenic silicon dioxide) has a relatively high concentration of silanol groups formed during high-temperature flame hydrolysis and the following cooling process. This specified property enables fumed silica to be widely used as a reinforcing filler, thickener, thixotropy-increasing and anti-sagging additive in numerous industries, for example silicone rubber, coating materials, adhesives and sealants.

The determination of the silanol group content on the surface of fumed silica is essential for both manufacturers and users to develop a high-performance, surface modified fumed silica and improve existing products. Further, it also facilitates the communication among interested parties.

In practice, methods of titration, thermogravimetry (TG), infrared spectroscopy (IR) and reaction gas chromatography can be a choice for the determination of the silanol group content on the surface of fumed silica. Among these methods, the method of reaction gas chromatography is preferred by users due to the advantage of higher sensitivity and better reproducibility.

This document provides a detailed procedure for how to conduct the testing of the silanol group content on the surface of fumed silica by means of the reaction gas chromatographic method.

Determination of the silanol group content on the surface of fumed silica — Reaction gas chromatographic method

SAFETY STATEMENT — Persons using this document should be familiar with usual laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine applicability of any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted in accordance to this document be carried out by suitably qualified staff.

1 Scope

This document specifies a method for the determination of the silanol group content on the surface of fumed silica by reaction gas chromatographic method.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 18451-1, *Pigments, dyestuffs and extenders — Terminology — Part 1: General terms*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18451-1 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

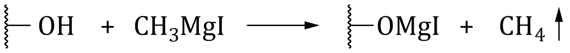
3.1
fumed silica
amorphous silica produced from silicon halides by high-temperature flame hydrolysis

[SOURCE: ISO 18473-3:2018, 3.1]

3.2
silanol group
hydroxyl group on the surface of fumed silica

4 Principle

A suitable amount of the dried fumed silica sample reacts with the Grignard reagent dispersed in toluene in an airtight reaction bottle to produce methane, which is injected into a gas chromatograph for separation, and further detected by a flame ionization detector (FID). The amount of methane produced is directly proportional to the silanol group content on the surface of fumed silica and is quantified from the peak areas using the external standard method. Then, the silanol group content in the sample is calculated according to the following reaction.



$$\text{—OH} + CH_3MgI \longrightarrow \text{—OMgI} + CH_4\uparrow$$

5 Reagents

5.1 General

During the analysis, use only reagents of recognized analytical grade. Other grades may also 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.

Information about the major reagents is given in Table 1.

Table 1 — Information about major reagents

Reagent	CAS No.[a]
Toluene	108–88–3
Methyl magnesium iodide[b]	917–64–6
Methane	74–82–8
Diethyl ether	60–29–7

[a] Chemical Abstracts System Registry Number.

[b] Dissolved in diethyl ether.

5.2 Toluene

Toluene (AR, purity ≥ 99,9 %, see Table 1) is used as a dispersion agent to promote the contact and reaction between the fumed silica sample and the Grignard reagent. Trace water is removed with calcium hydroxide before use.

5.3 Grignard reagent

The Grignard reagent is a solution of 3,0 mol/l methyl magnesium iodide (see Table 1), which reacts with hydroxyl to produce methane.

5.4 Reaction solution

Dilute the Grignard reagent (5.3) 10 times with toluene (5.2) (volume ratio) as a reaction solution. The reaction solution shall be used immediately after dilution. A volumetric flask or another clean glass container may be used for dilution. Ensure that the samples to be tested and the calibration substances react with the identical reaction solution. Carry out the injection with the syringe immediately.

5.5 Carrier gas and diluent gas

Use nitrogen of 99,999 % or higher purity. High-purity helium may also be used.

5.6 Auxiliary gases

Use hydrogen of high purity and air for the flame ionization detector.

Suitable filters shall be installed in the gas chromatograph connection pipes to adsorb residual impurities.

5.7 Calibration substance

Use methane (see Table 1, purity ≥ 99,9 %) for the calibration. For a representative chromatogram of methane, see Annex A.

With a 1 000 ml gas collecting bag (6.7), syringe (6.8) and diluent gas, dilute methane into at least five different concentrations. Then, inject 10 ml diluted methane gas into a sealed vial that contains 2,0 ml toluene to obtain five calibration substances with different methane masses (see Table 2).

Table 2 — Example for five calibration substances

Calibration substance	Methane ml	Diluent gas ml	Mass of methane in the vial mg
1	10	490	0,143 5
2	25	475	0,358 2
3	50	450	0,716 5
4	150	350	2,150
5	250	250	3,583
6	500	0	7,168

NOTE The methane density at 25 °C and 1,013 25 × 10^5 Pa is 0,716 8 g/l.

6 Apparatus

6.1 Gas chromatograph

The apparatus shall be set up and used in accordance with the manufacturer's instructions. All of the instrumental parts that get in contact with the sample or reagents shall be made of material that is inert to the sample or reagents, and shall not affect the sample or reagents chemically.

The apparatus shall be equipped with a flame ionization detector (FID), recorder, electronic integrator and data handling system.

6.2 Headspace system

A totally automated equilibrium headspace analyser available from commercial sources is used which shall meet the following specifications:

The system shall be capable of keeping the vials at a constant temperature (40 °C ± 1 °C).

The system shall be capable of transferring accurately a representative portion of the headspace gas into a gas chromatograph fitted with capillary columns.

6.3 Oven

The oven shall be capable of being heated between 40 °C and 300 °C isothermally and under programmed temperature control. The temperature fluctuations of the oven shall be within 1 °C. The final temperature of the temperature programme shall not exceed the maximum operating temperature of the column.

6.4 Capillary column

The column shall be made of glass or fused silica. Porous layer, open, tubular column coated with molecular sieve with a suitable film thickness, and maximum internal diameter of 0,32 mm, has been found to give good results of peak separation. Proper stationary phase and column length is needed to meet the requirement of separation. Other type columns that satisfy the test requirement may also be used.

Examples are given in 7.4.2.

6.5 Sample vials

Glass vials with a septum [e.g. a rubber membrane coated with polytetrafluoroethylene (PTFE)] and a metallic cap, compatible with the headspace system connected to the gas chromatograph, are used as containers for reactions. It is recommended to use 22 ml glass vials.

6.6 Analytical balance

Capable of weighing to an accuracy of 0,1 mg.

6.7 Gas collecting bag

Gas collecting bags are used to prepare calibration substances. Appropriate volume size (e.g. 500 ml or 1 000 ml) of PTFE bags with a valve is recommended. Purge the gas collecting bags with diluent gas (5.5). Drain the bags before use.

6.8 Syringe

A syringe with a suitable size (e.g. 1 ml, 2,5 ml, 5 ml, 10 ml, 100 ml) is used to measure and transfer the reaction solution, methane gas and calibration substance.

All of the syringe parts that get in contact with the reaction solution shall be made of material (e.g. glass, polypropylene (PP), PTFE, stainless steel) that is inert to the reaction solution and will not affect the reaction solution chemically. The gas syringe for manual sampling shall be provided with a locking valve to avoid gas leakage.

7 Sample pre-treatment and reaction

7.1 Sample pre-treatment

7.1.1 Determination of matter volatile at 105 °C in fumed silica

Heat the weighing bottle (squat form, wide-mouthed), with the ground glass stopper removed, in the oven at 105 °C for 2 h. Allow to cool in the desiccator, insert the stopper and weigh to the nearest 1 mg.

Spread 10 ± 1 g (m_0) of fumed silica in a uniform layer on the bottom of the weighing bottle, insert the stopper and weigh to the nearest 1 mg.

Heat the weighing bottle and contents, with the stopper removed, in the oven at 105 °C for 2 h. Allow to cool in the desiccator, insert the stopper and weigh to the nearest 1 mg. Repeat this procedure until two successive weightings differ by no more than 5 mg. Record the lower mass (m_1).

If the results of the two determinations differ by more than 10 % of the higher value, repeat the whole procedure.

Calculate the fumed silica volatile at 105 °C, expressed as mass fraction in percent (%).

7.1.2 Preparation of the test sample

Weigh about 0,1 g of fumed silica (m_2) to the nearest 0,1 mg into a sample vial. Heat the sample vial, with the stopper removed, in the oven at 105 °C for 2 h, then insert the stopper. Allow to cool in the desiccator.

7.2 Blank test

For each batch of samples, a blank test shall be carried out by injecting 2,0 ml reaction solution accurately into a sealed sample vial. Traces of water in the solvent and water vapour in the air will cause a certain amount of methane gas to be produced in the blank. Carry out the blank tests in triplicate. Make sure the methane peak areas in chromatograms of three blank tests are consistent and calculate the average of the blank tests(S_0).

If the standard deviation is greater than 5 %, the experimental conditions shall be examined and improved.

7.3 Reaction

Inject precisely 2,0 ml of the reaction solution into the sealed sample vial. Shake to disperse the test sample (see 7.1.2).

When the silanol group on the surface of fumed silica gets in contact with methyl magnesium iodide, it immediately reacts and produces methane.

Put the prepared sample vial on the sample tray of the headspace system and wait for the injection.

7.4 Analysis

7.4.1 Headspace system conditions

An example for the headspace system conditions is given in Table 3:

Table 3 — Example for the headspace system conditions

Heating temperature of sample:	40 °C
Needle temperature:	50 °C
Transfer line temperature:	60 °C
Sampling volume:	1,0 ml
Vial equilibrium time:	15 min

7.4.2 Gas chromatographic conditions

An example for the gas chromatographic conditions is given in Table 4:

Table 4 — Example for the gas chromatographic conditions

Column:	HP-MOLESIEVE (30 m × 0,32 mm × 25 µm) or equivalent column
Oven temperature:	50 °C for 10 min
Detector (FID) temperature:	200 °C
Carrier gas:	Nitrogen (99,999 %)
Carrier gas flow:	1,6 ml/min
Split ratio:	25 : 1

7.4.3 Identification

Methane is identified by comparison of the retention time of the peak in the sample chromatogram with the methane peak in the calibration substance chromatogram, obtained under the same conditions. The deviation of retention time shall be within ±0,05 min.

7.4.4 Calibration

Prepare a series of calibration substances according to 5.7. Put the calibration substance vials on the sample tray of the headspace system. Analyse the calibration substances in order of methane content from low to high (see Table 2).

For a graphical presentation of the calibration curve, plot the methane peak area, *s*, in the calibration substances chromatogram on the ordinate against the methane quantity, *m*, on the abscissa.

Use data obtained from a series of calibration substances to establish the linear regression function. See Formula (1):

$$s = am + b \tag{1}$$

where

s is the measuring value (signal area) of methane depending on m (unit depends on evaluation);

a is the gradient of the reference line for methane;

m is the mass, in milligrams (mg), of the methane in a vial;

b is the intersection of the reference line on the ordinate.

NOTE b has the same unit as the measuring value, s, and can be positive or negative.

7.4.5 Measurement

Analyse the samples prepared according to 7.3 in the same manner as described for the calibration (7.4.4) after the calibration substances.

Identify the methane peak by retention time.

Record the methane peak area in the chromatogram (s).

8 Calculation

8.1 Calculation of the methane quantity produced in the vials

Calculate the methane quantity, *m*, in milligrams (mg), of methane produced in the sample vials by calibration with an external standard using Formula (2):

$$m = \frac{(s - s_0) - b}{a} \tag{2}$$

where

s is the peak area of methane in the chromatogram of the sample, the unit of which depends on the type of evaluation performed;

s_0 is the peak area of methane in the chromatogram of the blank, the unit of which depends on the type of evaluation performed;

a and b are defined in Formula (1).

8.2 Calculation of the silanol group content

8.2.1 Calculation of fumed silica volatile at 105 °C

Calculate the fumed silica volatile at 105 °C, w, as mass fraction in percent (%), using Formula (3)

$$w = \frac{(m_0 - m_1)}{m_0} \times 100 \tag{3}$$

where

m_0 is the mass, in grams (g), of the test portion;

m_1 is the mass, in grams (g), of the residue.

8.2.2 Calculation of the silanol group content on the surface of fumed silica

Calculate the silanol group content, P, in milligrams per grams (mg/g), on the surface of fumed silica using Formula (4):

$$P = \frac{\left(\frac{m}{M_1}\right) \times M}{m_2 \times (1 - w)} \tag{4}$$

where

m is the mass, in milligrams (mg), of methane produced by the sample reaction;

M_1 is 16,04, molar mass, in grams per mol (g/mol), of methane;

M is 17,01, molar mass, in grams per mol (g/mol), of hydroxyl groups;

m_2 is the mass, in grams (g), of the sample;

w is fumed silica, as mass fraction in percent (%), volatile at 105 °C.

9 Expression of results

If the two determinations differ by more than the maximum value indicated in 10.2, repeat the procedure. Calculate the mean of two valid determinations and report the result to the nearest 0,01 mg/g.

10 Precision

10.1 General

The precision of the test method was determined by interlaboratory comparison in accordance with ISO 5725-1 and ISO 5725-2. Details can be found in Annex B.

10.2 Repeatability limit, *r*

The repeatability limit, r, is the value below which the absolute difference between two single test results, each the mean of duplicates, obtained on identical material by one operator in one laboratory within a short interval of time using the standardized test method, may be expected to lie.

The repeatability for this test method, expressed as the repeatability coefficient of variation, lies between 1,0 % and 3,0 %.

10.3 Reproducibility limit, *R*

The reproducibility limit, *R*, is the value below which the absolute difference between two test results, each the mean of duplicates, obtained on identical material by operators in different laboratories using the standardized test method, might be expected to lie.

The reproducibility for this test method, expressed as the reproducibility coefficient of variation, lies between 2,0 % and 7,0 %.

11 Test report

The test report shall contain at least the following information:

a) all information necessary to completely identify the product tested;

b) the test method used, together with a reference to this document (i.e. ISO 23157:2021);

c) reagents and the gas chromatographic conditions (see 7.4.1 and 7.4.2) to be used;

d) the results of the test and the method of calculation as indicated in 8.1 and 8.2;

e) any deviation from the test method specified;

f) the date and location of the test;

g) any details not specified in this document or which are optional, as well as any factors which may have affected the results.