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

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Contents

Page

Foreword	v
Introduction	vi
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Principle	1
5 Reagents	2
5.1 General.....	2
5.2 Toluene.....	2
5.3 Grignard reagent.....	2
5.4 Reaction solution.....	2
5.5 Carrier gas and diluent gas.....	2
5.6 Auxiliary gases.....	2
5.7 Calibration substance.....	2
6 Apparatus	3
6.1 Gas chromatograph.....	3
6.2 Headspace system.....	3
6.3 Oven.....	3
6.4 Capillary column.....	3
6.5 Sample vials.....	4
6.6 Analytical balance.....	4
6.7 Gas collecting bag.....	4
6.8 Syringe.....	4
7 Sample pre-treatment and reaction	4
7.1 Sample pre-treatment.....	4
7.1.1 Determination of matter volatile at 105 °C in fumed silica.....	4
7.1.2 Preparation of the test sample.....	4
7.2 Blank test.....	4
7.3 Reaction.....	5
7.4 Analysis.....	5
7.4.1 Headspace system conditions.....	5
7.4.2 Gas chromatographic conditions.....	5
7.4.3 Identification.....	5
7.4.4 Calibration.....	5
7.4.5 Measurement.....	6
8 Calculation	6
8.1 Calculation of the methane quantity produced in the vials.....	6
8.2 Calculation of the silanol group content.....	7
8.2.1 Calculation of fumed silica volatile at 105 °C.....	7
8.2.2 Calculation of the silanol group content on the surface of fumed silica.....	7
9 Expression of results	7
10 Precision	7
10.1 General.....	7
10.2 Repeatability limit, <i>r</i>	7
10.3 Reproducibility limit, <i>R</i>	8
11 Test report	8
Annex A (informative) Representative chromatogram of methane	9
Annex B (informative) Information about precision	10

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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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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.

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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*

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3 Terms and definitions [iteh.ai/catalog/standards/sist/99bc49c4-20c6-47dd-88bf-61f7b0ba635b/iso-prf-23157](https://www.iso.org/obp/ui/#iso:prf:23157)

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.



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.

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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.

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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 $1,013\ 25 \times 10^5$ 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.

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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 ($40\text{ °C} \pm 1\text{ °C}$).

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 l) 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.

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7 Sample pre-treatment and reaction

ISO/PRF 23157

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