
**Fine ceramics (advanced ceramics,
advanced technical ceramics) —
Test method for air-purification
performance of semiconducting
photocatalytic materials —**

**Part 5:
Removal of methyl mercaptan**

*Céramiques techniques — Méthodes d'essai relatives à la performance
des matériaux photocatalytiques semi-conducteurs pour la
purification de l'air —*

Partie 5: Élimination du mercaptan méthylique





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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 2.

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 22197-5 was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

ISO 22197 consists of the following parts, under the general title *Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for air-purification performance of semiconducting photocatalytic materials*:

- Part 1: Removal of nitric oxide
- Part 2: Removal of acetaldehyde
- Part 3: Removal of toluene
- Part 4: Removal of formaldehyde
- Part 5: Removal of methyl mercaptan

Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for air-purification performance of semiconducting photocatalytic materials —

Part 5: Removal of methyl mercaptan

1 Scope

This part of ISO 22197 specifies a test method for the determination of the air-purification performance of materials that contain a photocatalyst or have photocatalytic films on the surface, usually made from semiconducting metal oxides, such as titanium dioxide or other ceramic materials, by continuous exposure of a test piece to the model air pollutant under illumination with ultraviolet light (UV-A). This part of ISO 22197 is intended for use with different kinds of materials, such as construction materials in flat sheet, board or plate shape, that are the basic forms of materials for various applications. This part of ISO 22197 also applies to structured filter materials including honeycomb-form, woven and non-woven fabrics, and to plastic or paper materials if they contain ceramic microcrystals and composites. This part of ISO 22197 does not apply to powder or granular photocatalytic materials.

This test method is usually applicable to photocatalytic materials produced for air purification. This method is not suitable for the determination of other performance attributes of photocatalytic materials, i.e. decomposition of water contaminants, self-cleaning, antifogging and antibacterial actions. It concerns the removal of methyl mercaptan.

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 2718:1974, *Standard layout for a method of chemical analysis by gas chromatography*

ISO 4677-1:1985, *Atmospheres for conditioning and testing — Determination of relative humidity — Part 1: Aspirated psychrometer method*

ISO 4892-3, *Plastics — Methods of exposure to laboratory light sources — Part 3: Fluorescent UV lamps*

ISO 6145-7:2001, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 7: Thermal mass-flow controllers*

ISO 10677:2011, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Ultraviolet light source for testing semiconducting photocatalytic materials*

ISO/IEC 17025:2005, *General requirements for the competence of testing and calibration laboratories*

ISO 22197-1:2007, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for air-purification performance of semiconducting photocatalytic materials — Part 1: Removal of nitric oxide*

ISO 80000-1:2009, *Quantities and units — Part 1: General*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

**3.1
photocatalyst**
substance that performs one or more functions based on oxidation and reduction reactions under photoirradiation, including decomposition and removal of air and water contaminants, deodorization, and antibacterial, self-cleaning and antifogging actions

**3.2
photocatalytic materials**
materials in which or on which the photocatalyst is added by coating, impregnation, mixing, etc

Note 1 to entry: Such photocatalytic materials are intended primarily for use as building and road construction materials to obtain the above-mentioned functions.

**3.3
zero-calibration gas**
air that does not contain pollutants (i.e. in which common pollutants are below 0,01 µl/l)

Note 1 to entry: The zero-calibration gas is prepared from indoor air, using a laboratory air-purification system, or supplied as a synthetic air in a gas cylinder

**3.4
standard gas**
diluted gases of known concentrations supplied in cylinders and certified by an accredited laboratory

**3.5
test gas**
mixture of air and pollutant(s) of known concentration prepared from a standard gas or a zero-calibration gas, to be used for the performance test of a photocatalytic material

Note 1 to entry: The flow rate, concentration, etc. are expressed at the standard state (0 °C, 101,3 kPa) and dry gas basis (exclusion of water vapour).

**3.6
dark condition**
test condition with no light illumination by the light source for testing and room lightings

Note 1 to entry: Usually the test gas is supplied for comparison with the illuminated reaction.

4 Symbols

For the purposes of this document, the following symbols apply.

- f air-flow rate of test gas converted into that at the standard state (l/min, 0 °C, 101,3 kPa, dry gas basis)
- ϕ_M the volume fraction of methyl mercaptan at the reactor exit (µl/l)
- ϕ_{M0} the supply volume fraction of methyl mercaptan (µl/l)
- n_M the removal quantity, by test piece, of methyl mercaptan (µmol)
- R_M the removal percentage, by test piece, of methyl mercaptan (%)

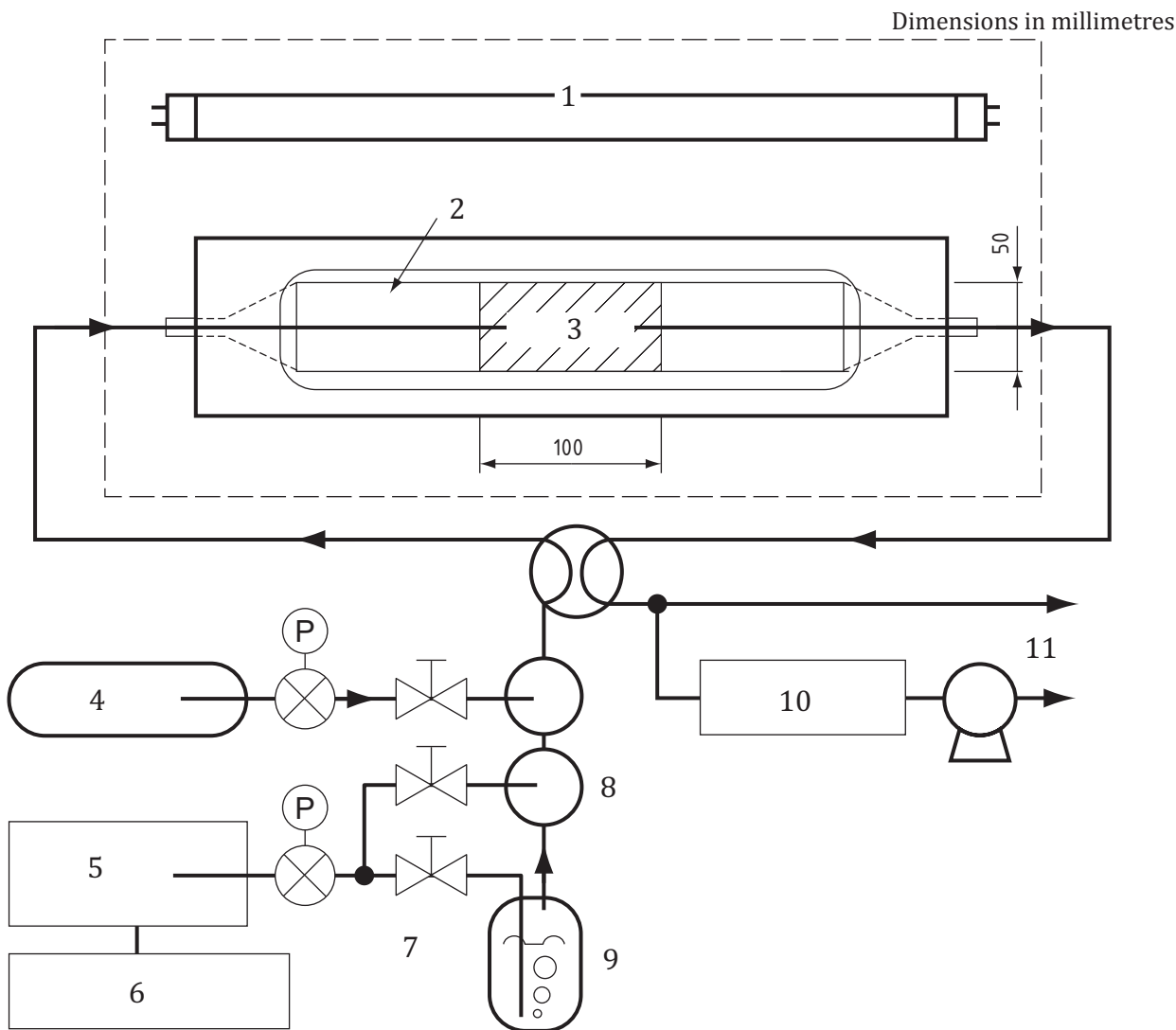
5 Principle

This part of ISO 22197 concerns the development, comparison, quality assurance, characterization, reliability, and design data generation of photocatalytic materials. The method described is intended to obtain the air-purification performance of photocatalytic materials by exposing a test piece to model polluted air under irradiation by ultraviolet (UV-A) light. Methyl mercaptan (methanethiol, CH₃SH) is chosen as a typical malodorous substance. The test piece, placed in a flow-type photoreactor, is activated by UV irradiation, and adsorbs and oxidizes gas-phase methyl mercaptan. The air-purification performance is determined from the amount of the net removal of methyl mercaptan (μmol). The simple adsorption and desorption of CH₃SH by the test piece (not due to photocatalysis) is evaluated by tests in the dark. However, this standard cannot be applied to the test piece which does not give a stable concentration of methyl mercaptan in the designated time of test. The photocatalytic activity may depend on physical and chemical properties of pollutants mainly due to the adsorption process involved. For complete evaluation of air purification performance of photocatalytic materials, it is recommended to combine one or more suitable test methods as provided in other parts of ISO 22197.

6 Apparatus

6.1 Test equipment

The test equipment enables a photocatalytic material to be examined for its pollutant-removal capability by supplying the test gas continuously, while providing photoirradiation to activate the photocatalyst. It is the same as that used in the test method for the removal of nitric oxide (ISO 22197-1) and consists of a test gas supply, a photoreactor, a light source, and pollutant-measurement equipment. Since low concentrations of pollutants are to be tested, the system shall be constructed with materials of low adsorption and resistant to ultraviolet (UV) radiation, for example, acrylic resin, stainless steel, glass and fluorocarbon polymers. An example of a test system is shown in [Figure 1](#).



Key

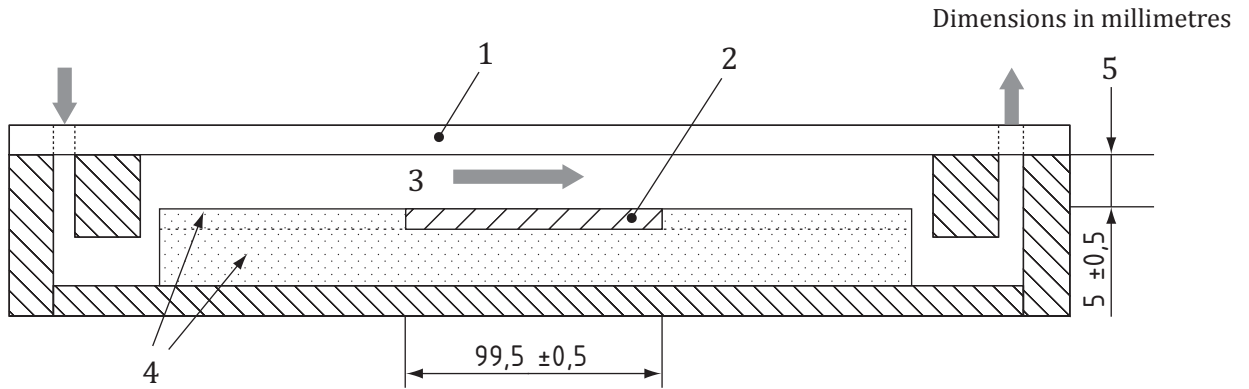
- | | |
|----------------------------|------------------------|
| 1 light source | 7 mass-flow controller |
| 2 optical window | 8 gas mixers |
| 3 test piece | 9 humidifier |
| 4 standard gas (pollutant) | 10 analyser |
| 5 air-purification system | 11 vent |
| 6 compressor | |

Figure 1 — Schematic diagram of the test equipment

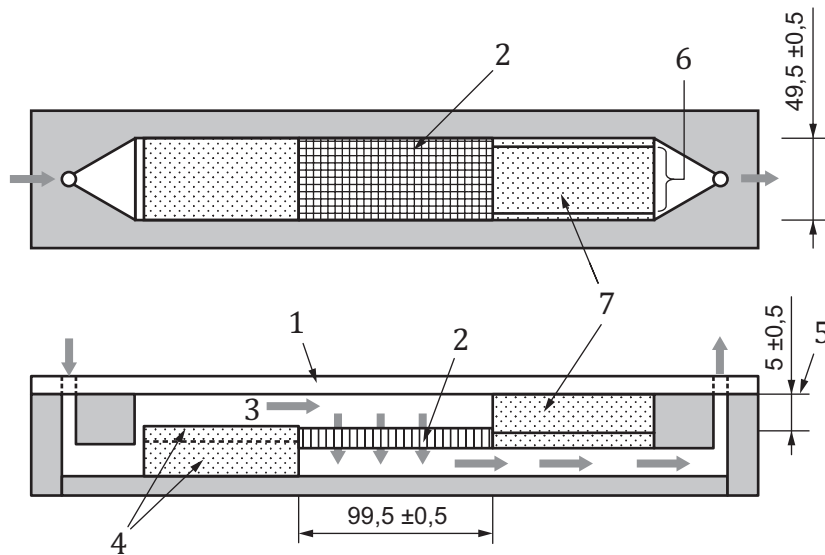
6.2 Test gas supply

The test gas supply provides air polluted with model contaminant at a predetermined concentration, temperature and humidity, and supplies it continuously to the photoreactor. It consists of flow regulators, a humidifier, gas mixers, etc. The flow rate of each gas should be within 5 % of the designated value, which is easily attained by using thermal mass-flow controllers with knowledge of temperature and gas type at calibration in accordance with ISO 6145-7. The expression of gas flow rate in this part of ISO 22197 is that converted to the standard state (0 °C, 101,3 kPa and dry gas basis). Typical capacities of flow controller for pollutant gas, dry air and wet air are 50 ml/min, 1000 ml/min and 1000 ml/min,

respectively. The standard methyl mercaptan gas in a cylinder, normally balanced with nitrogen, shall have a volume fraction of 100 µl/l to 1000 µl/l.



a) For flat test pieces



b) For filter-type test pieces

Key

- 1 window
- 2 test piece
- 3 test gas
- 4 height-adjusting plate
- 5 air layer thickness
- 6 flow channel
- 7 test piece holder

Figure 2 — Cross-sectional view of photoreactor

6.3 Photoreactor

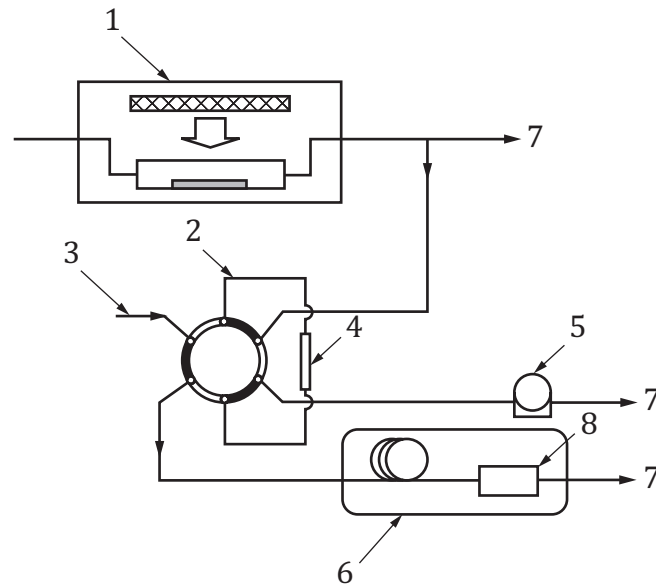
The photoreactor holds a planar test piece within a 50 mm wide trough, with its surface parallel to an optical window for photoirradiation. The reactor shall be fabricated from materials that adsorb little test gas and withstand irradiation of near-UV light. The test piece shall be separated from the window by a $5,0 \text{ mm} \pm 0,5 \text{ mm}$ thick air layer. The test gas shall pass only through the space between the test piece and the window. This gap shall be accurately set up according to the thickness of the test piece, for example, by using height-adjusting plates with different thicknesses, as shown in [Figure 2 a](#)). When a filter-type material is tested, an alternative type of test-piece holder shall be used, which holds the test piece while allowing the test gas to pass through the cells of the filter under irradiation [[Figure 2 b](#)]). Quartz or borosilicate glass that absorbs minimal light at wavelengths longer than 300 nm shall be used for the window.

6.4 Light source

The light source shall provide UV-A irradiation within a wavelength range of 300 nm to 400 nm. Suitable sources include the so-called blacklight (BL) and blacklight blue (BLB) fluorescent lamps, with a maximum at 351 nm, as specified in ISO 4892-3 and ISO 10677. The test piece shall be irradiated uniformly through the window by the light source. In the case of testing honeycomb-form photocatalysts, the light source shall irradiate one face of the test piece. A light source that requires warming up shall be equipped with a shutter. The distance between the light source and the reactor shall be adjusted so that the UV irradiance (300 nm to 400 nm) at the sample surface is $10 \text{ W/m}^2 \pm 0,5 \text{ W/m}^2$. The irradiance along the length of the test piece shall also be constant within $\pm 5 \%$. The UV irradiance shall be measured with a radiometer which conforms to ISO 10677. The reactor shall be shielded from external light if necessary.

6.5 Analytical system

The concentration of methyl mercaptan shall be determined by gas chromatography. Either packed column or capillary column, as described in ISO 2718, can be used as long as it can separate methyl mercaptan from related organic compounds. The detection shall be made by either flame ionization detector (FID) or flame photometric detector (FPD). The test gas is sampled with a gas-tight syringe. However, use of a 6-way valve is recommended for reproducible and automatic sampling. The flow diagram when a 6-way valve is used is shown in [Figure 3](#). A small sampling pump continuously ventilates the metering tube with the test gas. The pump is stopped when the test gas is sampled by switching the 6-way valve. The volume of the metering tube is typically 0,5 ml, but it shall be determined by the sensitivity of the analytical system.



Key

- 1 photoreactor
- 2 six-way valve
- 3 carrier gas
- 4 metering tube
- 5 sampling pump
- 6 gas chromatograph
- 7 vent
- 8 FID

Figure 3 — Gas sampling system

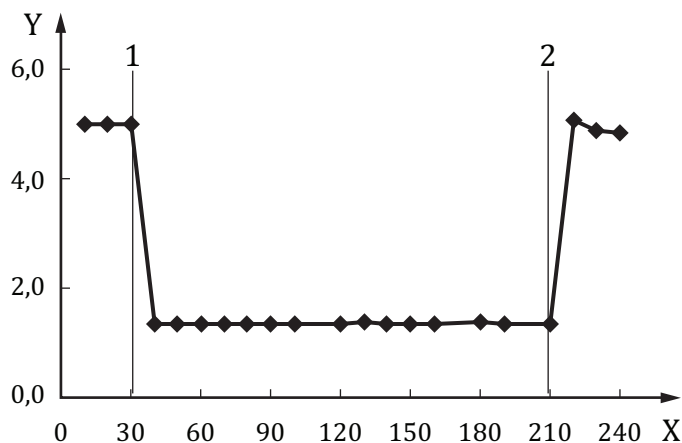
7 Test piece

The test piece shall be a flat material or a honeycomb filter of $49,5 \text{ mm} \pm 0,5 \text{ mm}$ wide and $99,5 \text{ mm} \pm 0,5 \text{ mm}$ long. It may be cut to these dimensions from a larger bulk material or coated sheet, or may be specially prepared for the test by coating a pre-cut substrate. The thickness of the test piece shall ideally be less than 5 mm, in order to minimize the contribution from the side faces. If thicker test pieces are to be tested, the side faces shall be sealed with an inert material before testing. The honeycomb test piece shall not be thicker than 20 mm.

8 Procedure

8.1 General aspects

The test procedure consists of pretreatment of the test piece, an adsorption process in the dark, and measurements of removal of methyl mercaptan under photoirradiation. An example of the concentration change of methyl mercaptan during the test is shown in [Figure 4](#). Some test pieces may not give accurate removal of methyl mercaptan due to lower photocatalytic activity. In this case, loading of methyl mercaptan per test piece can be reduced following the procedure in [Clause 10](#).

**Key**

- X Time (min)
 Y Concentration of methyl mercaptan (µl/l)
 1 Irradiation start
 2 Irradiation stop

Figure 4 — Typical trace of methyl mercaptan concentration during the test operation

8.2 Pretreatment of the test piece

Irradiate the test piece with an ultraviolet lamp for at least 16 h (up to 24 h) to decompose residual organic matter on the test piece. The UV irradiance at the sample surface should be high enough to secure complete decomposition of organic matter (15 W/m² or higher). If the test pieces are not to be tested immediately after this pretreatment, they shall be kept in an airtight container.

8.3 Removal test

8.3.1 Adjust the test gas supply beforehand so that it can stably supply the test gas containing 5,0 µl/l ± 0,25 µl/l of methyl mercaptan and 1,56 % ± 0,16 % of volume fraction of water vapour at 25,0 °C ± 2,5 °C. This water-vapour volume fraction is equivalent to a relative humidity of 50 % at 25 °C. The measurement of humidity shall be made using the procedure in ISO 4677-1. Adjust the flow regulator in order for the flow rate at the inlet of the reactor to be 1,0 l/min (0 °C, 101,3 kPa, dry gas basis). Measure and record the irradiance from the light source at the surface of the test piece. For the light source that requires warming up, turn the power on well before the measurement of irradiance and irradiation for the acetaldehyde removal test. Use the shutter appropriately to avoid unnecessary irradiation to the photoreactor.

8.3.2 Place the test piece in the centre of the photoreactor and attach the glass window after adjusting the air layer between the test piece and window to be 5,0 mm ± 0,5 mm thick. If necessary, height-adjusting plates are used for this purpose, and adjusting the height before and after of the test piece to be within 1,0 mm difference based on the top of the test piece. Check that the reactor is sealed by visual examination of the sealing material, such as an O-ring to tightly contact the glass window.

8.3.3 Allow the test gas to flow into the photoreactor, without photoirradiation. The flow rate shall be 1.0 l/min. Record the change in the concentrations of methyl mercaptan under dark conditions for 30 min. Adsorption of methyl mercaptan onto the test piece can be observed by this procedure. When the concentration at the outlet of the reactor returns to the supply gas concentration within 30 min, photoirradiation may be started at the time. If the methyl mercaptan concentration is less than 90 % of

the concentration supplied, continue until it exceeds this. If the concentration does not exceed 90 % after 90 min, stop the gas supply and finish the test.

8.3.4 Maintain the gas flow and commence irradiation of the test piece, and record the concentration of methyl mercaptan under photoirradiation for 3 h. The concentration decreases, as shown in [Figure 4](#), if methyl mercaptan is decomposed by photocatalyst and then stabilizes. The concentration of methyl mercaptan at the outlet of photoreactor should be the average of three or more measurements in the last 1-h test period.

8.3.5 Stop photoirradiation and confirm that the concentration of methyl mercaptan returns to supply gas concentration. Stop gas supply to the reactor and take the test piece out of the reactor.

9 Calculation

The test results shall be calculated as follows. The calculated values are usually rounded to one decimal place according to ISO 80000-1. The observed concentration of methyl mercaptan before water vapour correction shall be used for calculation. The flow rate of test gas f is 1,0 l/min normalized for 0 °C, 101,3 kPa and dry gas basis, and is then multiplied by a factor of 1,016 for water vapour correction.

The removal percentage of methyl mercaptan (R_M) is calculated by Formula (1). When R_M is either below 5 % or more than 95 %, R_M is expressed as “below 5 %” or “more than 95 %”, respectively. Then, the quantity of methyl mercaptan removed per hour (n_M) is calculated by Formula (2). When R_M is either below 5 % or more than 95 %, n_M is expressed as “below (0,136 $\phi_{M0}f$) μmol ” or “more than (0,136 $\phi_{M0}f$) μmol ”, respectively.

$$R_M = \frac{\phi_{M0} - \phi_M}{\phi_{M0}} \times 100 \quad (1)$$

$$n_M = R_M \times \frac{\phi_{M0} \times f \times 60 \times 1,016}{100 \times 22,4} \quad (2)$$

where

R_M is the removal percentage, by test piece, of methyl mercaptan (%);

n_M is the removal quantity, by test piece, of methyl mercaptan (μmol);

ϕ_{M0} is the supply volume fraction of methyl mercaptan ($\mu\text{l/l}$);

ϕ_M is volume fraction of methyl mercaptan at the reactor exit ($\mu\text{l/l}$);

f is the flow rate of test gas converted into that at the standard state (l/min, 0 °C, 101,3 kPa, dry gas basis).

10 Test method for test pieces with lower performance

In the case where the removal percentage is less than 5 % and a more certain result is demanded, the number of test pieces and the flow rate of test gas may be altered at the same time as shown in [Table 1](#). However, the removal quantity of formaldehyde to appear in the test report shall be half of the values calculated from Formula (2), as well as using the flow rate of 0,5 l/min. When the test conditions are altered, it is required to confirm the time of adsorption (dark condition) at the altered test conditions.

Table 1 — Alternative test conditions

Alternative test conditions	Value after change
Test gas flow rate	0,5 l/min
Number of test pieces	2 pieces

11 Test report

The test report shall include the reporting provisions of ISO/IEC 17025, and shall include the following information. Items g), h) and i) shall be reported for each test.

- a) The name and address of the testing establishment.
- b) The date of the test, a unique identification of the report and of each page, the customer's name and address, signatory of the report.
- c) A reference to this part of ISO 22197, i.e. determined in accordance with ISO 22197-5:2013.
- d) Date of test, atmospheric temperature, relative humidity, etc.
- e) Description of the test piece (material, size, shape, etc.).
- f) Description of test equipment (specifications, etc.).
- g) Test conditions (kind of pollutant gas, supply concentration, water-vapour concentration, flow rate, detailed description of light source, irradiance, analyser and radiometer used, condition of pretreatment, modification under [Clause 10](#), etc.).
- h) The amount of methyl mercaptan removed during the last 1 h, removal percentage of methyl mercaptan (optional).
- i) Any other matters of special importance, such as a change in the test piece noticed during the test.

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