
**Fine ceramics (advanced ceramics,
advanced technical ceramics) —
Test method for water purification
performance of semiconducting
photocatalytic materials by measurement
of forming ability of active oxygen**

*Céramiques techniques — Méthode d'essai relative à la performance
des matériaux photocatalytiques semi-conducteurs pour la purification
de l'eau par mesurage de la capacité de formation de l'oxygène actif*



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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.

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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 10676 was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

Introduction

Photocatalysis has many excellent functions including self-cleaning, antifogging, antibacterial actions, deodorization and removal of pollutants under light irradiation and, therefore, its application fields have been enlarged recently.

Among these applications, photocatalysis for water purification, which eliminates the pollutants in water, is being developed and its products are arriving on the market. Accordingly, there is strong demand for a test method which enables correct evaluation of the water purification performance.

This International Standard describes a test method for determining the water purification performance of photocatalytic materials used for water purification application.

Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for water purification performance of semiconducting photocatalytic materials by measurement of forming ability of active oxygen

1 Scope

This International Standard describes a test method covering photocatalytic materials formed on, or attached to, another material surface for the purpose of decomposing, and thus eliminating the pollutants in water, using photocatalytic performance.

This test method is applicable to photocatalytic materials under UV irradiation, and not under visible light irradiation.

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

3 Terms and definitions

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

3.1

photocatalyst

a substance that carries out one or more functions based on oxidization and reduction reactions under photoirradiation, including decomposition and removal of all air and water contaminants, deodorization, and antibacterial, self-cleaning and antifogging actions

3.2

water purification

purification by decomposing contaminants contained in water

3.3

photocatalytic materials

materials in which, or on which, the photocatalyst is added by coating, impregnation, mixing, etc.

NOTE Such photocatalytic materials are intended for use as building and road construction materials to obtain the above-mentioned functions.

3.4

purified water

water purified by the ion exchange method, having an electrical conductivity below 1 $\mu\text{S}/\text{cm}$

4 Principle

This International Standard covers the development, comparison, quality assurance, characterization, reliability and design data of photocatalytic materials. The method is used to determine the water purification performance of photocatalytic materials by exposing a specimen to model water under illumination of ultraviolet (UV) light.

It is difficult to choose a specific pollutant as the reagent for the purification performance test, because there are many types of pollutants in water.

Since the mechanism of water purification by photocatalytic reaction is based on the formation of active oxygen from the photocatalyst activated by UV irradiation, which oxidizes and decomposes the pollutants in water, it is possible to evaluate the water purification performance by measuring the ability of active oxygen to form from the activated photocatalyst in water.

Therefore, dimethylsulfoxide (DMSO) is chosen as an indicator that gives methanesulfonic acid (MSA) as a product of the photocatalytic reaction, as shown in the following formula [methanesulfinic acid (MSI) is produced as an intermediate]. This reaction is often used for the determination of active oxygen. The specimen, set in a flow-type photoreactor, is activated by UV irradiation; the DMSO is decomposed, which results in the production of MSA on its surface. The water purification performance is determined based on the decrease in concentration of DMSO and the generation of MSA. The adsorption of DMSO by the specimen is evaluated by the test in the dark (without UV irradiation).

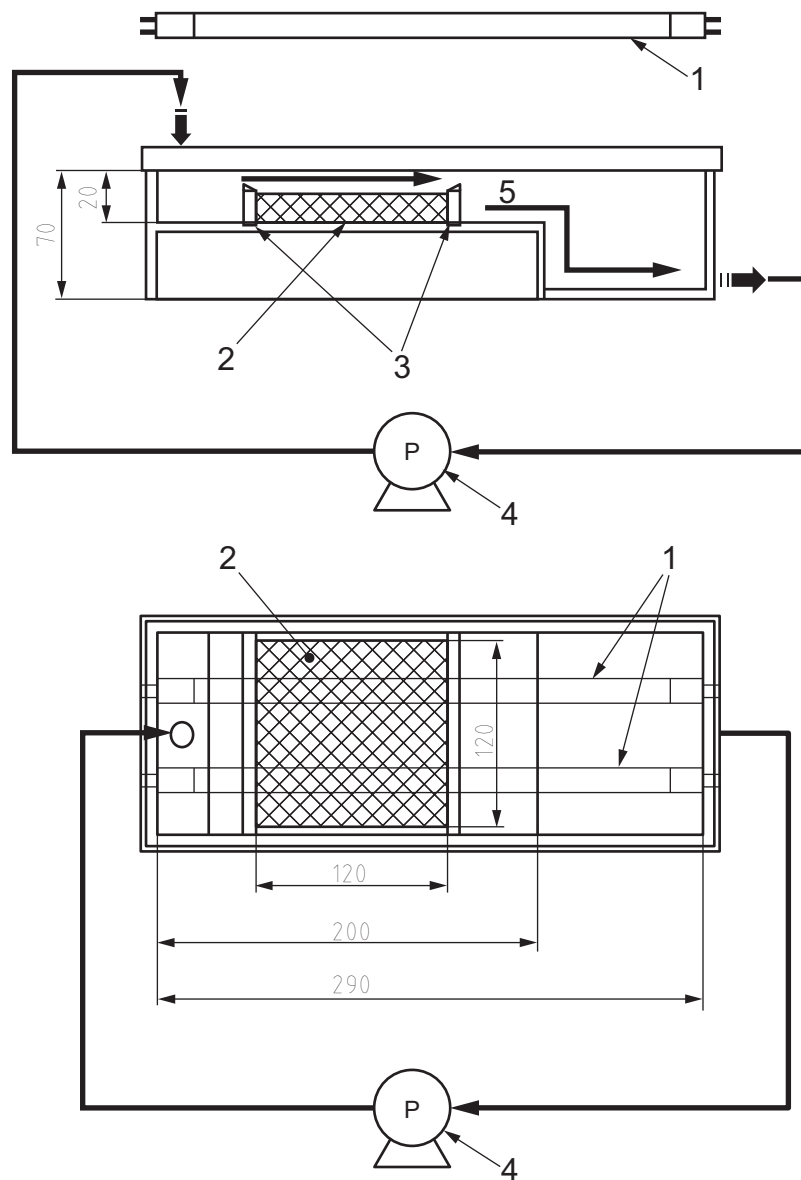
- a) $(\text{CH}_3)_2\text{SO}$ (DMSO) + $\cdot\text{OH}$ \rightarrow $\text{CH}_3\text{S}(\text{O})\text{OH}$ (MSI) + $\cdot\text{CH}_3$
- b) $\text{CH}_3\text{S}(\text{O})\text{OH}$ (MSI) + $\cdot\text{OH}$ + O_2 \rightarrow $\text{CH}_3\text{S}(\text{O})_2\text{OH}$ (MSA) + $\cdot\text{OOH}$
- c) $(\text{CH}_3)_2\text{SO}$ (DMSO) + $\cdot\text{OOH}$ \rightarrow $\text{CH}_3\text{S}(\text{O})_2\text{OH}$ (MSA) + $\cdot\text{CH}_3$
- d) $\text{CH}_3\text{S}(\text{O})_2\text{OH}$ (MSA) + $\cdot\text{OH}$ \rightarrow H_2SO_4 + $\cdot\text{CH}_3$

5 Apparatus

The testing equipment examines a photocatalytic material for its water purification performance by supplying and circulating the test water continuously, while providing photoirradiation to activate the photocatalyst. It consists of a test water supply, a photoreactor (with weirs), a light source and measurement equipment for testing the water. There is no cover in the photoreactor, i.e. the test is carried out in an open system.

An example of a testing system is shown in Figure 1.

Dimensions in millimetres



Key

- 1 lamp
- 2 test piece
- 3 weirs
- 4 pump
- 5 test solution

Figure 1 — Schematic diagrams of testing equipment

The testing equipment consists of the components described in 5.1 to 5.5

5.1 Test-water supply

The test-water supply consists of a flow controller (see Note) and a water pipe for circulating the test water with the predetermined speed and volume in the photoreactor.

NOTE The flow controller is an ejection pump which enables a determined volume of test water to be ejected and circulated to the test specimen in a photoreactor at a predetermined speed for a long time. For example, a peristaltic structure pump which ejects the solution by compressing the ejecting tube with a roller.

For the water pipe, use a material which adsorbs less reagent, such as silicon resin; the tube's diameter shall be suitable for the specification of the photoreactor's connecting-tube diameter and pump.

5.2 Photoreactor

The photoreactor holds a planar or spherical test piece and weirs over 1 cm high are placed in front of and behind the test piece in order to avoid distorting the test piece alignment during water supply. The reactor shall be fabricated from material (acryl resin) that adsorbs a small quantity of testing reagent and withstands irradiation of near-UV light.

5.3 Black light blue lamp (light source)

The light source shall provide UV-A illumination within a wavelength range of 300 nm to 400 nm. Suitable sources include the so-called black light (BL) and black light blue (BLB) fluorescent lamps, with a maximum wavelength of 351 nm or 368 nm, as specified in ISO 10677, and xenon arc lamps with optical filters that block radiation below 300 nm. In the case of a xenon arc lamp, a cooling system shall be used according to ISO 10677.

5.4 Ultraviolet radiation apparatus

An ultraviolet radiation apparatus holds two black light blue lamps parallel to each other [tubular-bulb fluorescent lamps, 20 W, type FL20S BLB¹⁾]. It consists of a structure that emits homogenous light radiation to the test specimen and alters the position of the test specimen or lamp in order to adjust the radiation intensity. If setting the lamp reflecting plate, use the material which is less likely to deteriorate when subjected to ultraviolet light. The ultraviolet radiation apparatus shall have a structure that enables the measurement of the radiation intensity at the test piece position.

5.5 UV-radiation intensity meter

The radiation intensity meter shall enable the measurement of UV radiation intensity at the test piece position; it shall consist of a photoreceiver with a good cosine property and a range of vision of 2π sr. It shall be corrected to the light source used or to the fixed sensitivity in the range of wavelengths absorbed by the photocatalytic material.

6 Reagent (test solution)

6.1 Dimethylsulfoxide (DMSO)

DMSO of assay above 99,5 % shall be used.

1) A type FL20S BLB lamp is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

7 Preparation of test piece

7.1 Test piece

Cut the photocatalytic material with a size of $100\text{ mm} \pm 2\text{ mm}$ square, which is the standard size of the test piece. When preparing test pieces, organic contaminants, such as oil and pollution by adsorbing organic substances in air, shall be removed.

The test piece should be taken from photocatalytic material itself. However, when the shape of the photocatalytic material makes preparing the test piece difficult, a test piece from the same raw material and with the same fabrication process as photocatalytic material can be used. Furthermore, when it is difficult to cut a $100\text{ mm} \pm 2\text{ mm}$ square of photocatalytic material or when the material has the form of a bead instead of a plate, a test piece big enough to place on the test piece platform in the photoreactor can be used.

7.2 Pretreatment of test piece

7.2.1 Follow the procedure below. If the test piece is not tested immediately after this pretreatment, it shall be stored in the resin desiccator. Before treating the test piece, fresh air shall be blown on the upper, under and side surfaces of the test piece to remove contaminants such as dust.

7.2.2 Removal of organic materials. Irradiate the test piece with an ultraviolet lamp for at least 5 h using the ultraviolet radiation apparatus adjusted to an irradiance of $2,0\text{ mW/cm}^2$ at the test piece surface.

Heat-resistant photocatalytic materials that show no physical or chemical change after heating may be heated to remove residual organic substances adhered to the test piece surface.

The test piece after pretreatment should be handled with polyethylene gloves in order to prevent contamination by hydrophobic substances.

7.2.3 Washing with water. The test piece is immersed in purified water stirred for 2 h or more, then taken out and air-dried at room temperature. The test piece may be dried by heating within a temperature range (temperature limit $110\text{ }^\circ\text{C}$) that does not cause physical and chemical changes. It shall be confirmed that its weight remains constant.

8 Procedure

8.1 Dissolve 10 mg of DMSO in 1 000 ml of purified water to obtain 1 000 ml of DMSO solution of 10 mg/l. If this solution is not used immediately after preparation, it shall be stoppered tightly, light-blocked, and stored at a temperature range of $5\text{ }^\circ\text{C}$ to $10\text{ }^\circ\text{C}$. A DMSO solution shall be used within 1 month after preparation.

8.2 Set up the two weirs in the reactors as shown in Figure 1, and place the test piece between the two weirs. The height of the weirs shall be adjusted depending on the thickness of the test pieces to maintain the water surface at a constant level (5 mm) from the test piece surface. If adjusting the weir height is not possible, the additional plate should be placed under the test pieces, if necessary. In the case of spherical test pieces, test pieces should be set in a wire net or an aluminum foil saucer in order to make handling the test piece and adjusting the weir height easy.

Before setting the test piece, the distance between the light source and the test specimen shall be adjusted so that radiation intensity is $2,0\text{ mW/cm}^2$ at the upper surface of the test specimen, and it shall be confirmed that the UV intensity is stable enough.

8.3 Pour 500 ml of DMSO solution into the vessel tank, and take 10 ml of solution from this as the initial concentration reference sample. The collected sample shall be stored within a temperature range of $5\text{ }^\circ\text{C}$ to $10\text{ }^\circ\text{C}$, in a tightly stoppered flask and protected from light prior to measurement.

8.4 Supply and circulate the DMSO solutions at a flow rate of 500 ml/min into the reactor where the photocatalytic test piece is situated. This circulation treatment shall be continued for 5 h. Then collect 10 ml of the sample for measurement from the solution tank every 1 h, starting from 0 h up to 5 h. The circulation treatment shall be carried out both under light irradiation (bright condition) and no irradiation (dark condition).

8.5 Measure DMSO and MSA concentrations of collected samples by gas chromatography or ion chromatography. Other methods besides gas chromatography and ion chromatography may be used provided the accuracy is ensured. In formula d) in Clause 4, MSA is oxidized to sulfuric acid (H_2SO_4). The formation of the sulfuric acid is much slower than that of MSA.

8.6 Test condition

The temperature in the testing room shall be kept in the range of 20 °C to 25 °C.

8.7 Valid condition

When the following conditions are satisfied, the test is considered valid.

The final concentration of DMSO in the bright conditions is lower than that in dark conditions and the MSA products accompanied with DMSO oxidative decomposition is confirmed.

9 Calculation

The test results shall be calculated as described in 9.1 to 9.5.

9.1 DMSO adsorption by test specimen under dark conditions

Measure the test solution (DMSO), taken at a certain interval under dark conditions, by the gas chromatography or the ion chromatography method, and calculate the concentration from the DMSO peak area using the calibration curve created from the standard specimen. Next, calculate the value by deducting the concentration measured from the initial concentration, using Equation (1), and record the calculated value at each collection time.

$$c_t = c_{D0} - c_{D4} \quad (1)$$

where

c_t is the concentration of DMSO absorbed by the test piece, in milligrams per litre (mg/l);

c_{D0} is the initial concentration of DMSO, in milligrams per litre (mg/l);

c_{D4} is the final concentration of DMSO in dark conditions, in milligrams per litre (mg/l).

9.2 DMSO concentration change in bright conditions

DMSO, which is decomposed by oxidation by the test piece under bright conditions, is measured using gas chromatography or ion chromatography. The obtained peak area is applied to the calibration curve created by the standard sample. Thus, calculate the DMSO concentration at each collection time. When DMSO is adsorbed under dark conditions, calculate the DMSO concentration using Equation (2).

$$c_{D2} = c_{D1} - c_t \quad (2)$$

where

c_{D2} is the DMSO concentration in bright conditions where the absorbed one is deducted, in milligrams per litre (mg/l);

c_{D1} is the DMSO concentration in bright conditions in the sample taken at a certain interval, in milligrams per litre (mg/l);

c_t is the concentration of DMSO absorbed by the test piece, in milligrams per litre (mg/l).

9.3 MSA products

Measure the MSA products along with DMSO decomposition by the test piece under bright conditions by ion chromatography, and apply the obtained peak area to the calibration curve created by the standard sample. Calculate the MSA concentration (c_{MSA}) at each collection time. c_{MSA} is the MSA concentration in the sample taken at a certain interval, in milligrams per litre (mg/l).

9.4 Comparison of final DMSO concentrations under dark and bright conditions

Confirm that the DMSO final concentration in bright conditions is lower than that in dark conditions [satisfy Inequality (3)].

$$c_{D3} < c_{D5} \quad (3)$$

where

c_{D3} is the DMSO final concentration in bright conditions, in milligrams per litre (mg/l);

c_{D5} is the DMSO concentration in dark conditions in the sample taken at a certain interval, in milligrams per litre (mg/l).

9.5 Calculation of half-life time of DMSO

The half-life time of DMSO shall be calculated as follows. Plot the natural logarithm of c_{D2}/c_{D0} value on the ordinate axis and the UV irradiation time on the abscissa axis, and calculate the half-life time of DMSO when the DMSO concentration becomes 50 % of the initial concentration, using the approximate curve obtained by 6 points between 0 h and 5 h.

10 Test report

The test report shall include the following information:

- a) a reference to this International Standard (ISO 10676:2010);
- b) the manufacturer's name and the grade of reagent used;
- c) the manufacturer's name and lamp's number of the black-light fluorescent lamp and its specification;
- d) the name of the manufacturer of the irradiation intensity meter and its specification;
- e) the manufacturer's name of measuring apparatus for DMSO and MSA and its specification;
- f) the pretreatment method and ultraviolet irradiation time;
- g) the distance between the ultraviolet light source and the upper surface of the test specimen;
- h) the temperature in the test room during the test;
- i) the detailed description of the light source, irradiance and radiometer;
- j) the DMSO and MSA concentrations under bright and dark conditions;
- k) the half-life time of the DMSO.

Annex A (informative)

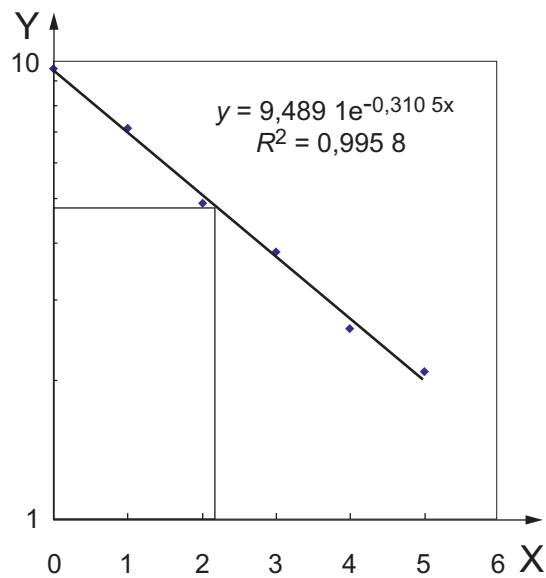
Examples of test results

Examples of test results are shown in Tables A.1 and A.2.

A.1 Granular photocatalyst

Table A.1 — Example of test result in granular photocatalyst

UV irradiation time h	Bright conditions		Dark conditions	
	DMSO concentration mg/l	MSA concentration mg/l	DMSO concentration mg/l	MSA concentration mg/l
0	9,6	0	9,6	0
1	7,1	2,2	9,5	0
2	4,9	4,5	9,5	0
3	3,8	6,4	9,5	0
4	2,6	8,4	9,5	0
5 (final)	2,1	9,2	9,5	0



Half-life time of DMSO: 2,2 h

Key

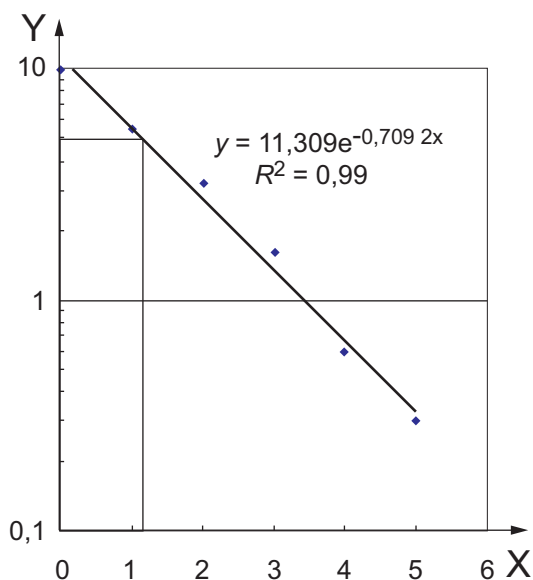
- X UV irradiation time, h
- Y DMSO concentration, mg/l

Figure A.1 — Calculation of half-life time of DMSO

A.2 Photocatalytic filter (ceramic filter)

Table A.2 — Example of test result in photocatalytic filter

UV irradiation time h	Bright conditions		Dark conditions	
	DMSO concentration mg/l	MSA concentration mg/l	DMSO concentration mg/l	MSA concentration mg/l
0	9,9	0	9,9	0
1	5,5	3,1	9,9	0
2	3,2	5,6	9,9	0
3	1,6	8,3	9,9	0
4	0,6	9,5	9,9	0
5 (final)	0,3	9,9	9,9	0



Half-life time of DMSO: 1,2 h

Key

- X UV irradiation time, h
- Y DMSO concentration, mg/l

Figure A.2 — Calculation of half-life time of DMSO

Bibliography

- [1] ISO 80000-1:2009, *Quantities and units — Part 1: General*
- [2] BARDOUKI, H., MIHALOPOULOS, N. et al. Kinetics and mechanism of the oxidation of dimethylsulfoxide (DMSO) and methanesulfinic acid (MSI) by OH radicals in aqueous medium, *Atmospheric Environment* 36 (2002), pp. 4627-4634

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