International Standard

ISO 10678

Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue

Second edition
2024-10

Céramiques techniques — Détermination de l'activité photocatalytique des surfaces dans un milieu aqueux par dégradation du bleu de méthylène

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

This second edition cancels and replaces the first edition (ISO 10678:2010), which has been technically revised.

The main changes are as follows:

— normative references have been updated;

— procedures for "Testing with intermittently stirred test cylinders" and "Testing with continuously stirred test cells" as "method A" and "method B" have been clarified and the whole document has been revised accordingly;

— precision data and interlaboratory test results for both methods have been updated and included in Annex C;

— document has been editorially revised.

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.

Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue

1 Scope

This document specifies a method for the determination of the photocatalytic activity of surfaces by means of degradation of methylene blue (MB) in an aqueous medium under artificial irradiation, and characterises photocatalytically active surfaces with respect to their activity for degradation of dissolved organic molecules under radiant exposure to ultraviolet light.

This document does not apply for the characterization of surfaces with respect to their photocatalytic activity under visible light. A correlation of photocatalytic activity with the removal of direct soiling, the degradation of gaseous molecules in the environmental air or the antimicrobial efficacy can exist, especially for surfaces with low photonic efficiency.

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

3 Terms and definitions

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

ISO and IEC maintain terminology 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
specific photocatalytic activity
P_{MB}
measure for the photochemical conversion

Note 1 to entry: P_{MB} is expressed in moles per square metre and hour [mol/(m²·h)].

3.2
photonic efficiency
ζ_{MB}
measure for the selectivity of the incident photons for methylene blue decolouration

Note 1 to entry: It is assumed that one photon is sufficient for the decolouration of a molecule.

Note 2 to entry: ζ_{MB} is expressed as a percentage of the incident photons.

3.3
testing solution
aqueous solution of methylene blue, which serves as the reactive solution for the determination of the photocatalytic activity of surfaces

3.4
measurement solution
portion of the testing solution, the volume of which is < 10 % of the volume of the *testing solution* (3.3), used for the external determination of absorbance in a photometer

3.5
conditioning solution
aqueous methylene blue solution used for the pre-adsorption of methylene blue on the test surface prior to the determination of the optical absorbance employing a spectrometer

4   Symbols and abbreviations

For the purposes of this document, the symbols and units given in Table 1 apply.

Table 1 — Symbols and units

Designation	Symbol	Unit
Planck constant ($h = 6{,}626 \cdot 10^{-34}$ Js)	h	Js
Speed of light ($c = 3 \cdot 10^8$ m/s)	c	m/s
Avogadro constant ($N_A = 6{,}022 \cdot 10^{23}$ mol^{-1})	N_A	mol^{-1}
Relative molecular mass	M	g/mol
Molar extinction coefficient	ε	m^2/mol
Time	t	h
Measuring time	t_m	h
Concentration of methylene blue	c_{MB}	mol/l
Initial concentration of methylene blue in the testing solution	c_{MB0}	mol/l
Absorbance	A_λ	1
Gauge length	d	mm
Volume	V	l
Internal diameter	d_i	mm
Irradiated surface	A	m^2
Wavelength	λ	m
Irradiance	E	W/m^2
Average irradiance	$E_{av} = \dfrac{\int E dt}{t_m}$	W/m^2
Specific degradation rate	$R = \dfrac{\Delta A_\lambda \cdot V}{\Delta t \cdot \varepsilon \cdot d \cdot A}$	mol/(m^2·h)
Specific degradation rate under radiant exposure	$R_{irr} = \dfrac{\Delta A_{\lambda,irr} \cdot V}{\Delta t \cdot \varepsilon \cdot d \cdot A}$	mol/(m^2·h)
Specific degradation rate without radiant exposure	$R_{dark} = \dfrac{\Delta A_{\lambda,dark} \cdot V}{\Delta t \cdot \varepsilon \cdot d \cdot A}$	mol/(m^2·h)
Specific photocatalytic activity	$P_{MB} = R_{irr} - R_{dark}$	mol/(m^2·h)

Table 1 *(continued)*

Designation	Symbol	Unit
Photon irradiance	$E_P = \dfrac{\lambda_{max} \cdot E_{av}}{h \cdot c \cdot N_A}\,3\,600$	mol/(m²·h)
Average photon irradiance	$E_{P,av}$	mol/(m²·h)
Photonic efficiency	$\zeta_{MB} = \dfrac{P_{MB}}{E_P} \times 100$	%

5 Principle

In an aqueous solution, methylene blue is brought into contact with the photocatalytically active surface of a test specimen; this surface is irradiated through the supernatant solution with photolytically non-active radiation (320 nm ≤ λ ≤ 400 nm). The solution will decolour. The dye content in the solution is determined at regular intervals (method A) or continuously (method B) during measurement using UV/visible spectroscopy. For the determination of the apparent photocatalytic decolourisation due to e.g. adsorption, a reference measurement is either made by using a photocatalytically active coating of a test specimen without radiant exposure or by measuring an equivalent test specimen in parallel in a second vessel whose surface is shaded against radiation (darkness specimen). The specific degradation rate and the photonic efficiency of the test specimen's surface are calculated from the measurements.

6 Apparatus

6.1 General

In addition to standard laboratory equipment, the following equipment according to 6.2 to 6.8 shall be used. All equipment that comes into contact with the methylene blue solutions shall be made of materials which only show a low adsorption of methylene blue, e.g. glass, stainless steel, polyethylene, polypropylene, polyacrylate or certain polysiloxanes with low organic emissions. Care shall be taken to ensure that the amount of scattered light in the test setup is as low as possible.

6.2 Measuring device

The measuring device either consists of two test cylinders that are glued to the test specimen, or of two test cells, each consisting of a vessel into which a specimen holder is embedded (see Annex B for a schematic representation of the measuring device).

6.3 Glass pane

For covering the test cylinders or the test cells in order to prevent evaporation, with low absorption within the spectral region of the light source (6.4).

6.4 Light source

Narrow-band radiator with emissions only in the range of 320 nm ≤ λ ≤ 400 nm (ultraviolet A spectrum) with an irradiance of E = (10 ± 0,5) W/m², measured at the height of the specimen underneath the glass pane cover.

NOTE 1   A suitable selection of light sources is given in ISO 10677.

NOTE 2   UV-LED light sources can be used to irradiate the test specimens, provided that their application complies with the specifications for testing semiconducting photocatalytic materials[1].

6.5 UV radiometer

Device for measuring the UV irradiance, calibrated to the characteristics of the light source and in accordance with ISO 10677.

6.6 Photometer or UV/visible spectrometer

Device for the determination of the methylene blue concentration, calibrated in the measurement range of 600 nm ≤ λ ≤ 700 nm in accordance with the instrument manual.

6.7 Measuring cuvette

Cuvette made of glass or plastic with an optical path length of 10 mm and a transmission of > 80 % in the wavelength range of 600 nm ≤ λ ≤ 700 nm, used in a spectrometer for the external determination of the methylene blue concentration.

6.8 Magnetic stirrer

Electric device with a cylindrical magnetic stir bar (20 mm × 3 mm), used for stirring the methylene blue solution according to method B (11.3).

7 Calibration

The equipment according to 6.5, 6.6 and 6.7 as well as the balances used shall be calibrated in accordance with the equipment manual.

8 Testing and conditioning solutions

For the purposes of testing and conditioning, methylene blue solutions shall be used. On the basis of distilled water (conductivity < 5 μS/cm^2), the initial methylene blue concentration in the testing solution shall be c_{MB0} = (10 ± 0,5) μmol/l. The conditioning solution shall be prepared with a concentration of c_{MB} = (20 ± 1,0) μmol/l. The absorbance A_λ of the solutions shall be calculated according to Formula (1) and is $A_{\lambda,max}$ = 0,74 for the testing solution or $A_{\lambda,max}$ = 1,48 for the conditioning solution at a gauge length d = 10 mm.

$$A_\lambda = \epsilon \cdot c_{MB} \cdot d \tag{1}$$

NOTE   Methylene blue (C$_{16}$H$_{18}$ClN$_3$S · 3H$_2$O; molar mass M = 373,90 g/mol; CAS-No. 7220-79-3) is a low-absorptive dye when it is used in the wavelength range of 350 nm ≤ λ ≤ 450 nm. At a concentration of c_{MB} = 10 μmol/l in an aqueous solution (pH = 5,5), methylene blue shows a molar extinction coefficient of $\varepsilon_{\lambda,max=664\ nm}$ = 7 402,8 m^2/mol (see [2]).

9 Preparation of the test specimens

The test specimens shall have a geometrical surface of (1 250 ± 50) mm^2 to (10 000 ± 100) mm^2. For tests according to method B (see 11.3), a specimen size of (49,5 ± 0,5) mm × (24,5 ± 0,5) mm is defined. Prior to the measurement all specimens shall be cleaned according to the manufacturer's instructions. In case no manufacturer's instructions are available, the specimens should be used at the earliest 12 h after its preparation and stored under free air circulation at (23 ± 5) °C and (50 ± 10) % relative humidity at least 1 h before starting the final cleaning step. For more detailed information on storage and preconditioning of specimens see [3]. For strongly absorbing specimens, the lateral surfaces shall be covered with an inert material, e.g. hard lacquer or aluminum tape. In the last cleaning step, the specimens shall be kept under ultraviolet radiation with a wavelength λ < 400 nm and an irradiance E > 10 W/m^2 for 24 h to 72 h.

For the purposes of conditioning, two equal specimens (test specimen and darkness reference specimen) shall each be placed in a vessel containing the conditioning solution (see Clause 8). Either the conditioning solution shall be poured into the cylinders in case the test cylinders are glued (V = (35 ± 0,5) ml), or the test specimens shall be placed directly into the conditioning solution (V = (90 ± 0,5) ml). Both vessels containing the test specimens and the conditioning solution shall be stored in the dark for an equal duration of at least 12 h. Once the concentration of the conditioning solution is below that of the testing solution, the test specimen is not suitable for measurements according to this document and the result shall be recorded in the test report.

10 Preparation of the measurement

In case of test cylinders that are glued (method A; see B.1), the conditioning solutions shall be exchanged for the testing solutions at the time t_0 (see Figure 1). Cylinders with an internal diameter d_i = (41 ± 1) mm and a length of (35 ± 5) mm shall be used as test cylinders. The volume of the testing solution is V = (35 ± 0,5) ml, which shall be determined exactly.

NOTE   Commercially available ISO-KF DN40 flanges according to ISO 2861[4] with pipe extension of steel or borosilicate glass can be used as test cylinders.

When using test cells (method B; see B.2), the two conditioned test specimens shall be inserted into the measuring device (6.2) with the testing solutions and be stored in the dark until time t_0 (see Figure 1). Commercially available large cuvettes with a gauge length of d = (50 ± 0,5) mm and a nominal volume of V = (90 ± 0,5) ml shall be used as test cells.

Test cylinders, test cells and measuring cuvettes shall be cleaned with a commercially available cuvette cleaner to remove any adhering methylene blue residues prior to use.
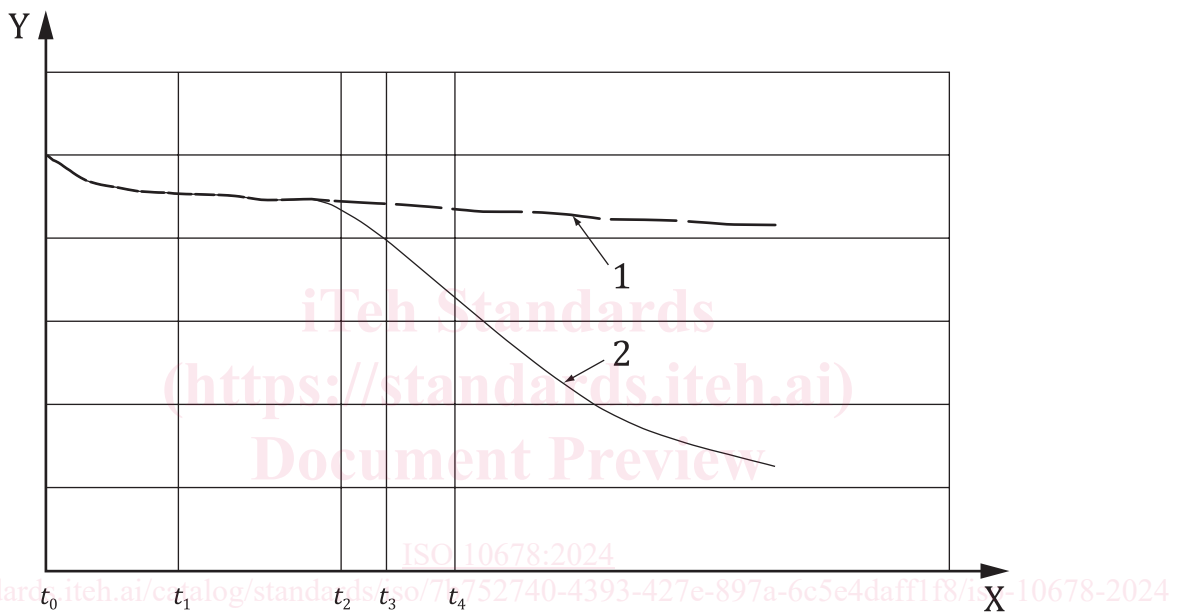
Key

X	time	t_0	start of measurement
Y	absorbance, A_λ	t_1	start of linear range
1	absorbance-time curve of the testing solution in the dark (without radiant exposure)	t_2	start of UV irradiation
		t_3	start of measurement time; $t_m = 0$
2	absorbance-time curve of the testing solution under radiant exposure	t_4	end of linear range

Figure 1 — Schematic representation of the course of the absorbance-time curves in the dark and under radiant exposure

11 Measurement procedure

11.1 General

The test cells or test cylinders shall be covered with the glass pane (6.3). The vessel containing the darkness specimen shall be additionally shielded from UV radiation. Irradiation of the specimen is started as soon as the absorbance-time curve of the testing solution (see curves 1 and 2 in Figure 1) is nearly constant, i.e. in the range from t_1 to t_2. The light source (6.4) shall ensure an irradiance E = (10 ± 0,5) W/m², measured

underneath the glass pane at the height of the test specimen. The test temperature of the testing solution shall be (22 ± 3) °C and shall be recorded. Measurement and verification of the temperature is permitted inside as well as near the test cylinders or test cells. The absorbance shall be measured at a wavelength of λ = (664 ± 5) nm.

11.2 Testing with intermittently stirred test cylinders (method A)

The methylene blue testing solution shall be homogenised during the test by brief stirring (for about 3 s) every 20 min using a glass bar or stirrer. The absorbance shall be determined during the irradiation process by external measurements of the measurement solutions (3.4) extracted from the testing solution (3.3), and subsequent recirculation of the measurement solution into the testing solution. The absorbance shall be measured at intervals of 20 min each, where the measurement solution shall always be extracted immediately after stirring. The measurement under radiant exposure shall be carried out over a period of 3 h, but at most until the solution has decoloured.

If the evaluation of results (see Clause 12) shows a high average photonic efficiency of ζ_{MB} > 0,10 %, the measurement shall be repeated with an irradiance of E = (2,5 ± 0,13) W/m². If the subsequent data analysis results in a higher value for the photonic efficiency than that obtained at a higher irradiance, the value that has been determined at an irradiance of E = (2,5 ± 0,13) W/m² shall be stated in the test report. The observation of a high average photonic efficiency at an irradiance of E = (10 ± 0,5) W/m² shall be stated in the test report.

11.3 Testing with continuously stirred test cells (method B)

In order to be able to obtain an evenly mixed testing solution, the test cells are placed on a magnetic stirrer. For the tests applied with continuous stirring, the test specimens shall be supported on specimen holders at a distance of (10 ± 0,5) mm above the vessel bottom of the test cells (see B.2). Therefore, a distance of at least 5 mm from the edge of the test cells must be ensured on at least two sides of the specimen holder to enable uniform mixing. Stirring is carried out using a cylindrical magnetic stir bar (20 mm × 3 mm) with a stirring speed of (400 ± 20) min⁻¹. For the direct measurement of the testing solution inside the test cell, the absorption-concentration curve of the methylene blue solution shall first be determined by means of a calibration measurement within the concentration range of 7,5 µmol/l ≤ c_{MB} ≤ 10,5 µmol/l. The measurement under radiant exposure shall be carried out over a period of 3 h, but at most until the calibrated measurement range is undercut.

Equivalent to both procedures, a curve without radiant exposure (darkness specimen) shall be measured under otherwise identical conditions (see curve 1 in Figure 1).

12 Evaluation of results

12.1 General

For the evaluation of measurement results, only values in the linear range corresponding to those from t_3 to t_4 in Figure 1 may be used. The linear range should therefore extent over at least 5 measured values at intervals of 20 min, where a maximum of one value is permitted to be an outlier which shall be justified in the test report. Deviations from linearity shall be stated in the test report (Clause 14). The absorbance values shall be rounded to three decimal places and summarised in a time/absorbance table (see Table A.1). A determination of the measured values via linear regression is permitted (see evaluation example in A.2).

An example of evaluation is given in Annex A.

12.2 Specific degradation rate R

The specific degradation rate R, in mol/(m²·h), shall be calculated according to Formula (2):

$$R = \frac{\Delta A_\lambda \cdot V}{\Delta t \cdot \varepsilon \cdot d \cdot A} \tag{2}$$