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

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

PROOF

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Foreword

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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;~~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~~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~~https://www.iso.org/obp

— IEC Electropedia: available at ~~https://www.electropedia.org/~~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 · 10^{-34} Js)	h	Js
Speed of light (c = 3 · 10^{8} m/s)	c	m/s
Avogadro constant (N_A = 6,022 · 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	$E_{av} = \frac{\int E dt}{t_m}$	W/m^2
Specific degradation rate	$R = \frac{\Delta A_\lambda \cdot V}{\Delta t \cdot \varepsilon \cdot d \cdot A}$	mol/(m^2·h)
Specific degradation rate under radiant exposure	$R_{irr} = \frac{\Delta A_{\lambda,irr} \cdot V}{\Delta t \cdot \varepsilon \cdot d \cdot A}$	mol/(m^2·h)

Designation	Symbol	Unit
Specific degradation rate without radiant exposure	$R_{dark} = \frac{\Delta A_{\lambda,dark} \cdot V}{\Delta t \cdot \varepsilon \cdot d \cdot A}$	mol/(m²·h)
Specific photocatalytic activity	$P_{MB} = R_{irr} - R_{dark}$	mol/(m²·h)
Photon irradiance	$E_P = \frac{\lambda_{max} \cdot E_{av}}{h \cdot c \cdot N_A}\ 3\,600$	mol/(m²·h)
Average photon irradiance	$E_{P,av}$	mol/(m²·h)
Photonic efficiency	$\zeta_{MB} = \frac{P_{MB}}{E_P} \times 100$	%

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 6.26.2 to 6.86.8 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 BAnnex 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).

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].~~[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).~~(11.3).

7 Calibration

The equipment according to ~~6.5, 6.6~~6.5, 6.6 and ~~6.7~~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/cm²), 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)~~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.

$$A_\lambda = \in \cdot c_{MB} \cdot d \qquad (1)$$

NOTE Methylene blue ($C_{16}H_{18}ClN_3S \cdot 3H_2O$; 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 m²/mol (see ~~[2]).~~[2]).

9 Preparation of the test specimens

The test specimens shall have a geometrical surface of (1 250 ± 50) mm² to (10 000 ± 100) mm². For tests according to method B (see ~~11.3),~~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

