INTERNATIONAL STANDARD

ISO 21066

First edition
2018-09

Fine ceramics (advanced ceramics, advanced technical ceramics) — Qualitative and semiquantitative assessment of the photocatalytic activities of surfaces by the reduction of resazurin in a deposited ink film

Céramiques techniques (céramiques avancées, céramiques techniques avancées) — Évaluation qualitative et semi-quantitative de l'activité photocatalytique des surfaces par réduction de résazurine dans un film d'encre déposé

Reference number
ISO 21066:2018(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

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 206, *Fine ceramics*.

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) — Qualitative and semiquantitative assessment of the photocatalytic activities of surfaces by the reduction of resazurin in a deposited ink film

1 Scope

This document specifies a method, the Resazurin (Rz) ink test, for the qualitative assessment of the activity of a photocatalytic surface, and its classification as below, within, or above the applicable range of the test. The method then allows for the subsequent semiquantitative evaluation of the activities of photocatalytic surfaces that are within the applicable range of the test. In all cases, artificial ultraviolet (UV) radiation is used.

The test method specified is appropriate for use with all flat, smooth, photocatalytic surfaces, which are not macroporous, examples of which include: commercial photocatalytic glass, paint, tiles and awning materials. The method is not applicable to assessing the visible-light activity of photocatalytic surfaces, nor their ability to effect: air purification, water purification, self-cleaning or disinfection, although some relevant correlations have been reported[4][5].

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 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 http://www.electropedia.org/

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

[SOURCE: ISO 22197-1:2016, 3.1, modified — The definition has been slightly rephrased.]

3.2
photocatalytic material
material in which, or on which, a *photocatalyst* (3.1) is added by coating, impregnation, mixing, etc.

[SOURCE: ISO 20507:2014, 2.1.60, modified — Note 1 to entry removed.]

3.3
macroporous surface
surface having sufficient cavities, typically larger than 75 µm, so that *Rz ink* (3.5) drains from it by gravity and is not held by capillary action

EXAMPLE Some concrete samples and most woven fabrics.

3.4
smooth surface
surface that can be uniformly coated with *Rz ink* (3.5) using a close wound standard *K-bar* (3.6), number 3, which delivers a wet film thickness of 24 µm

3.5
Rz ink
resazurin-based ink used to assess the activity of a photocatalytic surface

3.6
K-bar
steel rod, close wound with wire of a defined gauge so as to deliver a wet ink film of a desired thickness, as commonly used in the print industry

4 List of symbols, abbreviations and units

Designation	Symbol or abbreviation	Unit
Irradiation time	t	s
Irradiation end time	t_{end}	s
Average irradiation end time	$t_{end,av}$	s
Colour monitoring sampling time period	Δt $\Delta t = 0{,}1 \times t_{end,av}$	s
The absorbance due to Rz in aqueous solution alone, at 603 nm which is equal to absorbance of Rz solution – absorbance of water	ΔAbs	—
Average red RGB component of ink surface at t	$RGB(R)_t$	—
Average green RGB component of ink surface at t	$RGB(G)_t$	—
Average blue RGB component of ink surface at t	$RGB(B)_t$	—
Normalized $RGB(R)_t$ value	R_t $R_t = RGB(R)_t/[RGB(R)_t + RGB(G)_t + RGB(B)_t]$	—
Maximum value of R_t during irradiation	$R_{t,max}$	—
Minimum value of R_t during irradiation	$R_{t,min}$	—
Overall relevant change in R_t	$\Delta R_{t,tot}$ $\Delta R_{t,tot} = R_{t,max} - R_{t,min}$	—
Value of R_t when 90 % of the maximum change in R_t has occurred	$R_t(90)$ $R_t(90) = 0{,}9\Delta R_{t,tot} + R_{t,min}$	—
Time taken for $R_t = R_t(90)$	$ttb(90)$	s
Median of the eight $ttb(90)$ values	$median[ttb(90)]$	s

Designation	Symbol or abbreviation	Unit
Median absolute deviation[6] which is equal to the median of the eight |*ttb*(90) − *median*[*ttb*(90)]| values	*MAD*	s
Modified standard score (for each sample)[6]	Z_{mod} $Z_{mod} = 0{,}675\ 4\ \{ttb(90) - median[ttb(90)]\}/MAD$	—
Average time taken to achieve 90 % photocatalysis and its associated standard deviation, σ	$ttb(90)_{av} \pm \sigma$	s

5 Principle

5.1 General

A photocatalyst activity indicator ink is deposited, using a K-bar, onto samples, 25 mm × 25 mm square, of the photocatalytic material under test, which have previously been wiped-clean and possibly UV-conditioned. If upon depositing the ink film on the material under test, but before irradiation, the ink changes from blue to pink or colourless, the sample is **reactive** (usually due to a highly alkaline surface) and the ink test is unsuitable for evaluating the photocatalytic material. Assuming the sample is not **reactive** and is photocatalytically active, then there are two possible tests the material under test can be subjected to as part of this method: a precursor qualitative test and then, for samples found to be within the applicable range of the test, a semiquantitative activity test. The Rz ink test is an example of reductive photocatalysis based on the photocatalysed reduction of Rz and concomitant oxidation of glycerol in an ink coating[5].

5.2 Qualitative test method (three samples)

Three identically Rz ink-coated samples of the material under test are exposed simultaneously to UVA light from a defined source (see 6.2), with a defined irradiance (see 6.3), and the colour of the ink on each sample is monitored at regular intervals by eye and/or using a digital image recording device, such as a digital scanner or camera, so as to observe the ink change colour, from blue to pink. This process allows, for each sample, an approximate value of the irradiation time required for this colour change to occur, t_{end}, to be determined, from which an average value, $t_{end,av}$ is calculated. The value of $t_{end,av}$ is used to classify the material under test. If $t_{end,av} < 1{,}5$ min, then it is classed as being above the applicable range of the test. If 1,5 min ≤ $t_{end,av}$ ≤ 45 min, then it is classified as being within the applicable range of the test. If $t_{end,av} > 45$ min, then it is classed as being below the applicable range of the test. If the material is **initially** classified as being 'above the applicable range of the test', then a reduced irradiance shall be used in a re-run of the test. If, using the low irradiance UV light, the material is found to be 'within the range of the test', then the **semiquantitative** test can be run to assess the activity of the material, also using the low UV irradiance. Further details regarding the decision-making strategy employed in this test are given in 9.1.

5.3 Semiquantitative test method (eight samples)

This subsequent test method is only used for materials which have been identified previously, using the **qualitative** test, as being within the applicable range of the test, i.e. samples which exhibit 1,5 min ≤ $t_{end,av}$ ≤ 45 min. In the **semiquantitative** test method, eight Rz ink-coated samples of the material under test are exposed simultaneously to UVA of a defined irradiance from a defined source, and the colour of each sample is monitored at a regular time interval, Δt (see Clause 4), either using a digital camera or hand-held scanner, until the ink turns pink. RGB colour analysis of the central part of each digital image of the ink film for each sample, for each irradiation time, t, is used to calculate average values for $RGB(R)_t$, $RGB(G)_t$ and $RGB(B)_t$, for that time point.

A plot of the normalized value of the RGB colour analysis parameter, R_t, (see Clause 4) vs. irradiation time, t, is then constructed for each of the eight samples from which the time taken to bleach 90 % of the red component of the image of the ink film on each sample is determined, i.e. $ttb(90)$, along with

other key parameters. See 10.3 for further details and for a typical example of an R_t vs. t plot for a Rz ink on a photocatalytically active sample.

A statistical analysis of the eight *ttb*(90) values generated by the method, based on the modified score method (see 10.4 and Clause 4), is then used to exclude any outliers. Then, an average value for *ttb*(90) and associated standard deviation is calculated, i.e. $ttb(90)_{av} \pm \sigma$, and is taken as an inverse measure of the photocatalytic activity of the material under test.

6 Apparatus

6.1 Coating device

The coating device for the Rz ink shall be a stainless-steel K-bar No. 3 delivering a uniform wet film thickness of 24 µm on a smooth surface using a draw-down method of application.

6.2 UV-radiation light source

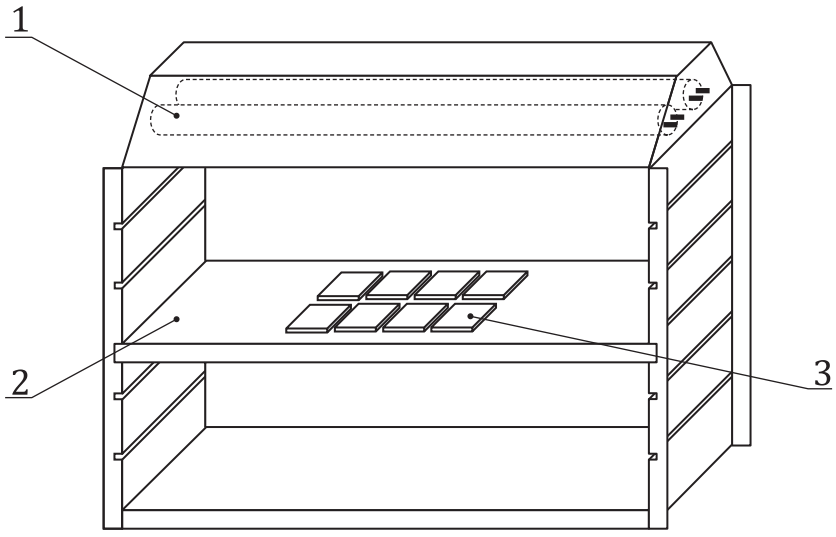
The UV-light source used shall be a black light (BL) lamp or black light blue (BLB) lamp, with a peak wavelength of 351 ± 2 nm as specified in ISO 10677.

6.3 UV radiometer

A radiometer with a detector whose sensitivity peak is at λ = 351 ± 2 nm shall be used to measure the UV-light intensity. The radiometer, traceably calibrated, shall be selected so that its response is appropriate for measuring accurately (to better than ± 0,05 mW·cm^{-2}) the UV irradiance of the UV light irradiation source as specified in ISO 10677.

6.4 Irradiation system

An example of an irradiation system is illustrated Figure 1.



Key

1 two BL or BLB UV fluorescent tubes

2 a shelf placed at a distance so that the irradiance at the shelf is 2,0 ± 0,1 mW·cm^{-2} (or 0,50 ± 0,05 mW·cm^{-2}, if samples initially classified as 'above the applicable range of the test')

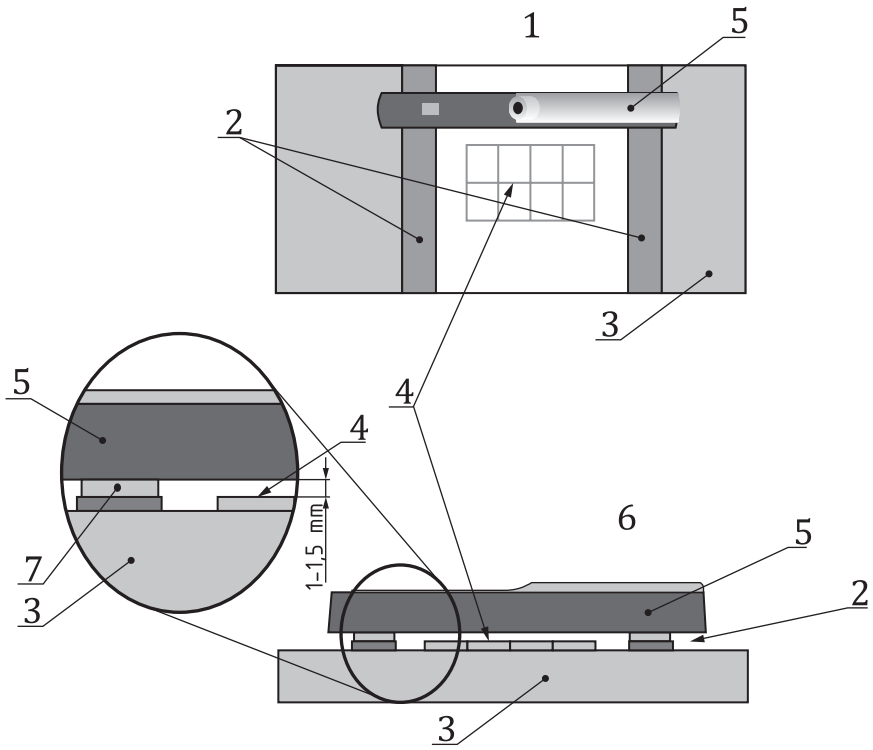
3 eight, Rz ink-coated, identical samples of the material under test on the irradiation shelf

Figure 1 — Schematic diagram of the irradiation system

The irradiation system shall provide simultaneous and uniform irradiation of the test samples (three or eight; see 5.2 and 5.3, respectively) from above by the light source. The distance between the light source and the shelf, directly below, supporting the test samples shall be adjusted so that the irradiance is 2,0 ± 0,1 mW·cm^{-2}. One or more mini labjacks can be used to adjust the shelf height so that the irradiance is at the required value. If the material is **initially** classified as 'above the applicable range of the test', an irradiance of 0,50 ± 0,05 mW·cm^{-2} may be used instead. The irradiance along the length of the part of the shelf with the test samples shall be constant within ±5 %. The irradiance shall be measured with a calibrated radiometer (see 6.3). The test arrangement shall be such that any ambient light incident on the samples under test has a UV irradiance of <0,05 mW·cm^{-2}. The irradiation system shall be shielded from external light if the latter exposes the samples to a UV irradiance detectable by the UV radiometer. All illuminations shall be carried out at 22,0 ± 2,0 °C and a RH of 50 ± 5 %. The maximum irradiation time employed on any sample shall be 90 min.

6.5 Digital imaging device and analysis software

The test method requires that digital images of each of the samples of the material under test be recorded at a regular time interval, Δ*t*, as a function of irradiation time. The digital images of the three or eight samples of the material under test shall always be recorded together. This can be achieved using a hand-held digital scanner, as illustrated in Figure 2, or other similar system, e.g. a digital camera, providing it generates digital images of the 25 mm × 25 mm square samples, with a resolution of at least 300 dpi. To ensure adequate clearance between the samples and scanner (so the scanner does not accidentally touch the samples) spacers shall be placed on either side of the sample area to support the scanner as it is moved back and forth over the samples for multiple scans. As such, the supports shall be of even thickness and wide enough to support the roller which the scanner runs on. A suitable material would be rigid and of thickness equal to that of the samples, made thicker with a cardboard (such as greyboard craft card, available from most art and craft shops and the internet) or paper 'shim' to raise the scanner above the samples by a distance of 1 mm to 1,5 mm.



Key

1 overhead view
2 tracks of material (usually cardboard) to support scanner above samples and ensure a gap of 1,0 mm to 1,5 mm
3 block supporting samples
4 samples
5 scanner
6 side view
7 rollers of scanner

Figure 2 — Schematic diagram of the scanner

A generic digital imaging software package is required to carry out an RGB colour analysis of each scanned image of each sample, see Annex B for example software packages.

7 Materials

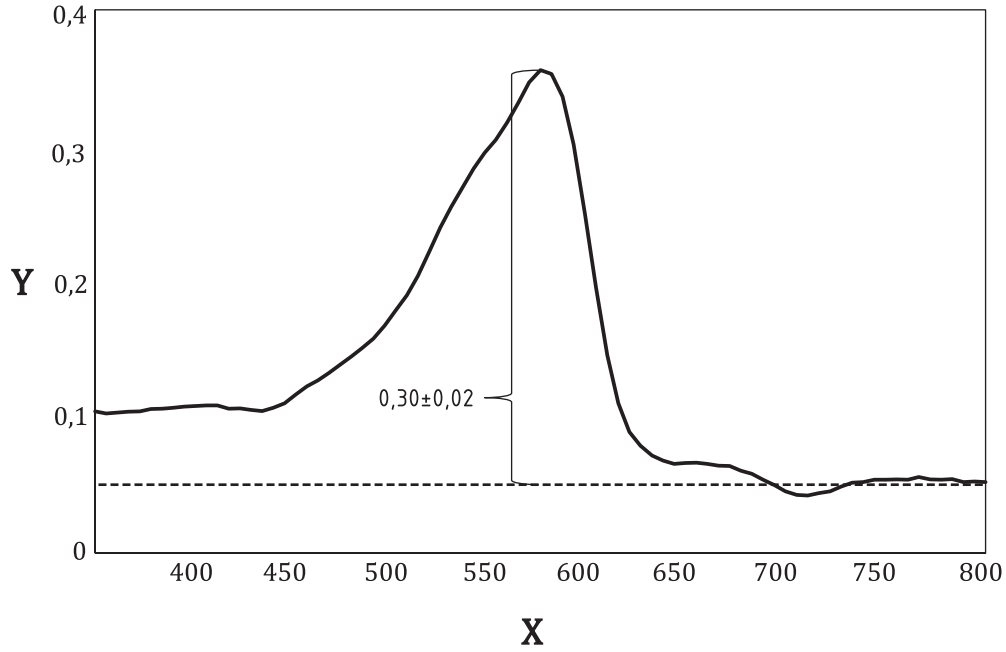
7.1 Rz ink preparation

7.1.1 Dye purity test (if purity is unknown)

Before making up the Rz ink, assess the purity of the sample Rz dye (CAS No.: 62758-13-8; purity: 75 %) by recording the UV/Vis absorbance spectrum of an aqueous solution of the dye. Compare the absorbance due to the dissolved Rz dye in the solution at 603 nm (ΔAbs, see Clause 4) derived from this spectrum, to that of a standard Rz solution made using a high purity (75 %) sample of the Rz dye, the absorption spectrum of which is illustrated in Figure 3, then measure all absorbances with an accuracy of ±0,003. This test is necessary since other work[7] has established that many commercial samples of Rz dye do not stipulate dye purity or, sometimes, do not provide a reliable value.

In this dye purity test, dissolve 10,0 ± 0,1 mg of the sample Rz dye in 100 ml of high purity (conductivity ≤ 2 $\mu S \cdot cm^{-1}$) water, then further dilute with water by a factor of 5. Stir the resulting solution with a magnetic stirrer bar for a minimum of 1 h. Measure the absorbance of this solution at

603 nm using a 1 mm cuvette. For a dye sample of the correct purity, i.e. 75 %, the measured absorbance due to the Rz alone (Δ*Abs*, at 603 nm) should be 0,30 ± 0,02; see Figure 3.



Key

X wavelength, nm

Y absorbance

Figure 3 — Visible absorbance spectrum of an aqueous Rz solution, of 75 % purity, recorded in a 1 mm cuvette

If the Δ*Abs* absorbance value is larger or smaller than 0,30 ± 0,02, then use instead a corresponding, proportionately larger or smaller amount of sample Rz dye compared to the specified amount of 10 mg, to make the Rz ink solution. For example, if a value of Δ*Abs* = 0,25 is determined, then make up the Rz ink using (10 × 0,30/0,25) = 12,0 mg of Resazurin, rather than the usual 10 mg stated in 7.1.2.

7.1.2 Ink preparation

First, dissolve 0,15 g hydroxyethyl cellulose (HEC; CAS No.: 9004-62-0; viscosity: 145 mPa·s for 10 g/kg solution in water) into 9,85 g high purity (conductivity ≤2 μS·cm^{-1}) water to give an HEC solution of 15 g/kg; stir this solution with a magnetic stirrer bar for a minimum of 12 h in order to ensure the complete dissolution of the polymer, HEC. Next, add to the HEC solution 1 g of glycerol (CAS No.: 56-81-5, purity: ≥99 %), followed by 20 mg polysorbate 20 (CAS No.: 9005-64-5, purity: ≥97 %) surfactant and stir the resulting solution mixture with a magnetic stirrer bar until the additives are fully dissolved. Finally, add 10 mg of the dye Resazurin, Rz, (CAS No.: 62758-13-8; purity: 75 %) to the solution and stir, with a magnetic stirrer bar, for a minimum of 8 h to ensure complete dissolution of the dye.

Weigh each component out to within 1 % of the mass stipulated.

Store the Rz ink in a refrigerator at ca. 5 °C and use within 12 weeks of its preparation. At least 1 h before use, remove the refrigerated Rz ink from the refrigerator and stir with a magnetic stirrer bar at room temperature.

7.2 Rz ink quality assurance

If an already made Rz ink has been supplied by a third party, or if a prepared Rz ink is suspected to have undergone some degradation (e.g. through incorrect storage or contamination of the ink), then assess