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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

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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 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).

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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 $\lvert ttb(90) - median[ttb(90)]\rvert$ 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

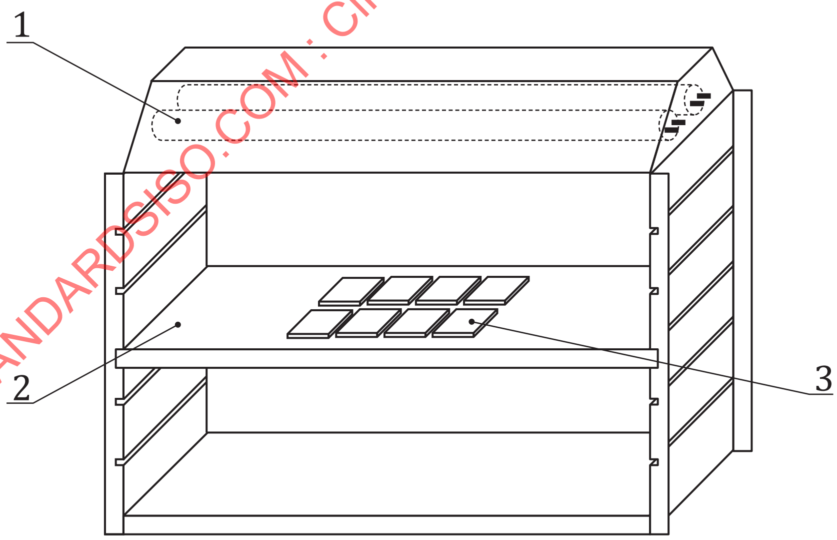
The UV-light source used shall be a black light (BL) lamp or black light blue (BLB) lamp, with a peak wavelength of 351 ± 2 nm as specified in ISO 10677.

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')

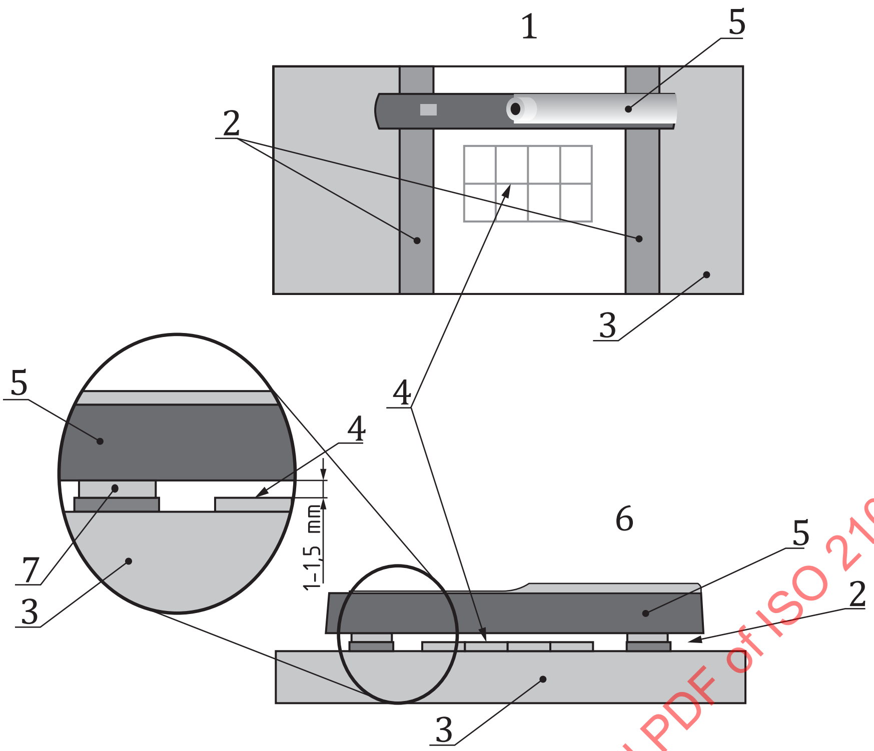
3 eight, Rz ink-coated, identical samples of the material under test on the irradiation shelf

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

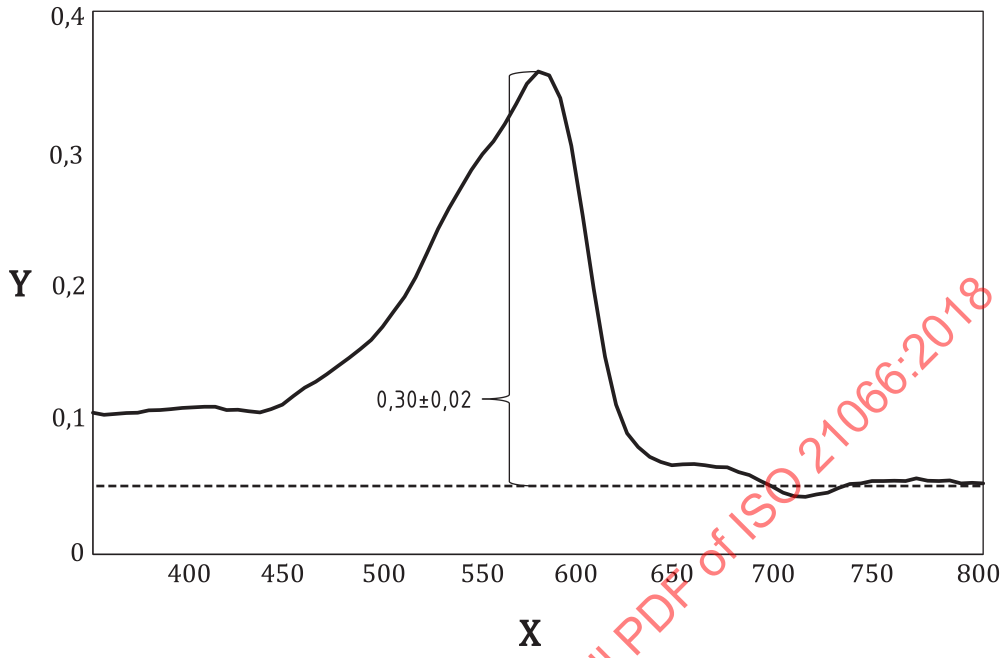
7.1 Rz ink preparation

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 the quality of the ink before use. Assess the quality of the Rz ink by diluting 1 g of the ink with 500 ml of water and record the UV/Vis absorbance spectrum of this dilute aqueous solution of the Rz ink using a 1 cm cuvette. The original Rz ink is acceptable for testing photocatalytic materials if the absorption spectrum of the diluted Rz ink is very similar to that illustrated in Figure 3, but with $\Delta Abs = 0{,}28 \pm 0{,}02$, which is that expected for a typical Rz ink using an Rz sample of 75 % purity, as stipulated in 7.1.2.

If, from the above work, the measured value for ΔAbs at 603 nm for the ink under (quality assurance) test is $<0{,}26$, then the ink is unsuitable for subsequent use. If the ΔAbs at 603 nm $> 0{,}30$, then dilute the ink with sufficient water so as to reduce the concentration of Rz so that the now diluted ink yields a ΔAbs value of $0{,}28 \pm 0{,}02$ in the above quality assurance test.

8 Test sample

8.1 Preparation of test samples

Prepare test samples with a (25 ± 2) mm × (25 ± 2) mm rectangular surface for coating with the Rz ink. For the qualitative test, three test samples shall be prepared. For the semiquantitative test, eight test samples shall be prepared.

8.2 Cleaning of test samples

Since one or both parts of the method (**qualitative** and **semiquantitative**) can be used to test a photocatalytic material, regardless of its history, it follows that the material for test can be used or unused, weathered or non-weathered, and/or pre-treated (with UV) or not (UV) pre-treated. As a consequence, in order to assess such materials in their 'as supplied' state, little or no preparation of the samples is recommended, although details of the material, its source and known conditioning history are required for the test report.

However, each sample shall be cleaned by wiping lightly with a water-soaked, silicone-free, tissue to remove any easily removed dirt and then be allowed to dry for 60 min in the dark under otherwise ambient conditions. If the sample's surface is considered delicate, such as a titania powder coated glass, or water-based paint sample, then even this modest cleaning step may be omitted, although this shall be noted in the test report.

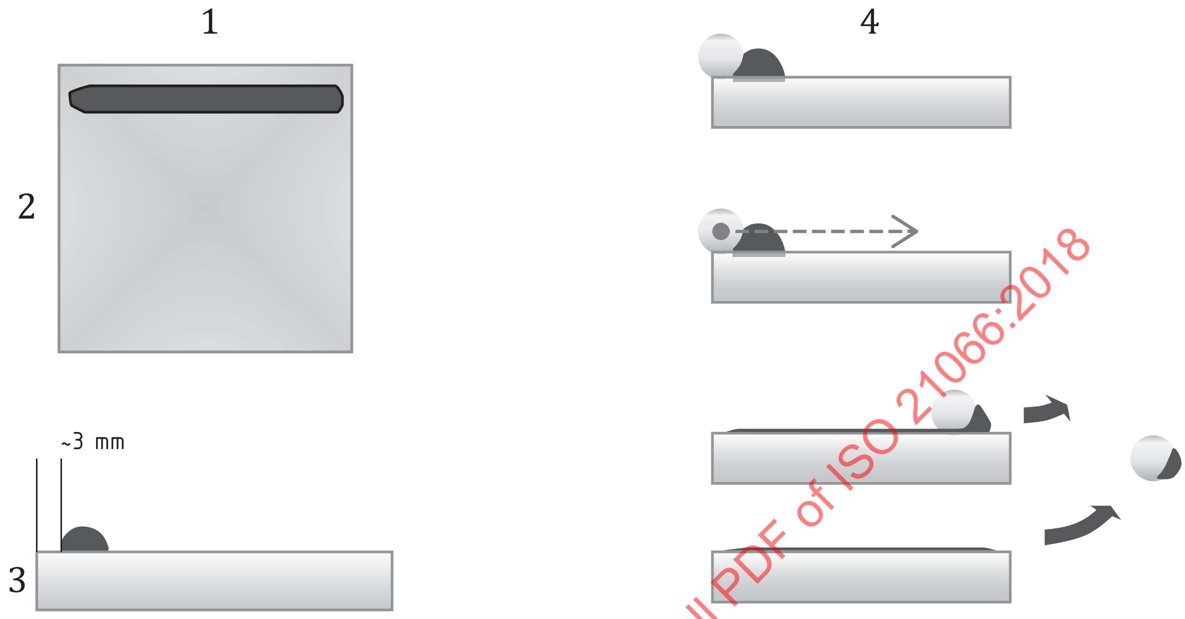
If the material has been subjected to one or more pre-treatment process(es), such as accelerated weathering, or – more usually – pre-conditioning with UV light over a long period, then full details of the pre-conditioning history shall be given in the test report. When testing unused, i.e. lab- or factory fresh, samples they shall be pre-conditioned with UV light ($2\ mW \cdot cm^{-2}$) for 8 h.

8.3 Coating test samples with Rz ink

Once cleaned, the samples of the material under test shall be coated with the ink as described below. To do this, secure each 25 mm × 25 mm square sample to an impression bed (e.g. a clipboard) and deposit a line of ink, ca. 25 mm long, along the top of the sample and ca. 3 mm from the top edge; the amount of ink deposited should be ~65 µL. Figure 4, key reference 1, illustrates a typical deposit of a line of Rz ink on a sample before drawing down. Spread and coat the ink onto the sample, using a wire wound rod (K-bar No. 3), by drawing the bar down from the top of the sample (where the line of ink is) to the bottom using sufficient and equal hand pressure, on both sides of the k-bar, to ensure the spiral wire of the K-bar remains in contact with the sample throughout the drawdown process, but not so much that the K-bar is bowed. A uniform coating of the ink over the sample, particularly the central 1 cm^2 on each sample, shall be generated in this manner, as illustrated in Figure 4, key reference 4.

NOTE An ink coating is considered uniform if it yields a standard deviation of <5 % in the measured average initial (before irradiation) $R_{t=0}$, value (see Clause 4), derived from colour measurements taken of the three or eight samples (see 5.2 and 5.3). If, for any reason, a uniform ink film cannot be formed, then it is inappropriate to continue with the test with that/those samples.

Each sample shall be prepared as described above and the process repeated until the requisite number of ink-coated samples is generated. Ink-coating of the required three or eight samples of a material shall be completed in no more than 15 min and, upon coating the last sample, all the ink-coated samples shall be left to dry for 60 min in the dark, but otherwise under ambient conditions, before irradiation.



Key

1 schematic illustrating the correct initial placement of the Rz ink line

2 top view

3 side view

4 schematic illustrating the correct drawdown method

Figure 4 — Schematic illustration of the correct placement of the Rz ink line on a sample and correct drawdown method to yield a uniform, homogeneous film

9 Procedure for the qualitative assessment of activity

9.1 General

The **qualitative** assessment method, outlined in 5.2, is for the rapid identification of the presence of a photocatalytically active surface **and** for the assessment of its activity as being below, within or above the applicable range of the test. It also identifies materials that are within the applicable range of the test and the approximate irradiation time, $t_{end,av}$, required for a subsequent **semiquantitative** assessment of its activity.

The key steps in the decision making are based on the observed interaction of the Rz ink with the three samples of the material under test, thus:

a) if Rz ink reacts with surface in the **dark**, the sample is **reactive** and the ink test is inappropriate – go to test report;

b) if $t_{end,av}$ < 1,5 min, the photocatalytic activity is considered above the applicable range of the test – go to test report. If so classified, a reduced irradiance of 0,50 ± 0,05 mW·cm^{-2} shall be used instead in a re-run of the test. If, when using the low irradiance UV light, the activity is found to be 'within the range of the test', then the **semiquantitative** test may be run to assess the activity of the material, also using the low (0,5 ± 0,05 mW·cm^{-2}) UV irradiance;

c) if 90 min < $t_{end,av}$, the photocatalyst material is considered below the applicable range of the test – go to test report;

d) if 1,5 min ≤ $t_{end,av}$ ≤ 45 min, the photocatalytic activity is considered within the applicable range of the test and so suitable for a subsequent **semiquantitative** assessment of its activity – go to test report;

e) details of the format of the test report are given in Clause 11.

9.2 Procedure

Prepare three samples of the material, coat with the Rz ink and let dry for 60 min, as described in Clause 8. If, at this stage, the Rz ink film on any of the samples changes colour (usually blue to pink) **before** irradiation, the surface is identified as being **reactive** and the test is inappropriate. Assuming this is not the case, digitally photograph (using a scanner or a camera) the three Rz ink-coated samples and then irradiate together using a UV light source and conditions described in 6.2 to 6.5. Monitor any UV-induced change in the colour of the ink periodically, by eye and/or (preferably) via digital photography. Record the approximate time taken, t_{end}, for the Rz ink coating, on each sample, to change from blue to pink and photograph the samples at this (end) point. A useful approach to monitoring the change in the colour of the ink periodically is to start with a sampling time of 30 s. If, after 3 lots of this sampling time, i.e. after 1,5 min, the sample has still not turned pink, then the sampling time should be doubled and the process repeated until either the ink has started to change colour (and so the current sampling time is appropriate) or an irradiation time of >90 min has occurred, and no change in the colour of the sample has been observed and the activity is below the applicable range of the test. The average value of t_{end}, i.e. $t_{end,av}$, determined from the results of this work, then identifies if the material is below, within, or above the applicable range of the test, see 9.1.

10 Procedure for the semiquantitative assessment of activity

10.1 General

The **semiquantitative** assessment method is appropriate for a material that has been identified as exhibiting a photocatalytic activity that is within the applicable range of the test, using the **qualitative** ink test. For the **semiquantitative** test, the value for $t_{end,av}$ sets the values of both: (i) the overall irradiation time [= 1,5 × $t_{end,av}$] and (ii) the sampling period, Δt [= 0,1 × $t_{end,av}$], for taking digital images of the eight samples during their irradiation.

10.2 Procedure

The key steps in the **semiquantitative** test method are as follows:

(1) cleaning: wipe clean and coat uniformly with the Rz ink the eight samples of the material under test and let dry for 60 min, as described in Clause 8;

(2) irradiation and colour measurement: record, through digital photography using a camera, or hand-held scanner, the colour change of the ink before and during UV irradiation, as described in 6.2 to 6.4, [in time steps of Δt from t = 0 to 1,5 $t_{end,av}$];

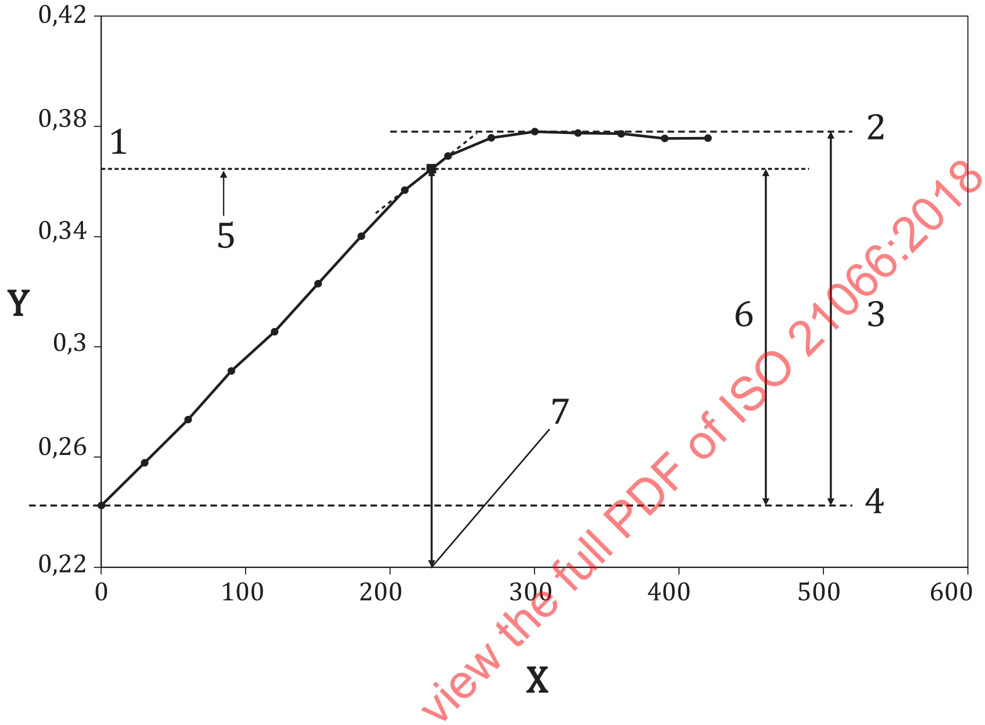
(3) data analysis: for each time step, process, through an RGB analysis, each of the eight digital images, so that, at the end of the irradiation, for each sample, a plot R_t vs. t can be constructed and an associated value of *ttb*(90) can be determined, as described in 10.3;

(4) test report: generate a test report, details of which are given in Clause 11, and which contains a reciprocal measure of the photocatalytic activity of the material under test, namely: $ttb(90)_{av} \pm \sigma$.

10.3 Digital image (RGB) analysis (for one sample)

Each digital image of each sample, of which there are eight, shall be analysed as follows. For each sample, after an irradiation time, t, available software, as described in 6.5 shall be used to determine the average individual RGB values, $RGB(R)_t$, $RGB(G)_t$, and $RGB(B)_t$, of the central area of each image of the sample, this area is *the region of interest*. Note that this is typically: ca. 100 pixels × 100 pixels for a scanned image of the 25 mm × 25 mm square sample, with a resolution of 300 dpi.

For each sample, the $RGB(R)_t$, $RGB(G)_t$, and $RGB(B)_t$ vs. t data, shall be used to calculate a value for R_t, i.e. the normalized value for the red component, at the centre of the RGB digital image at time t, see Figure 5.



Key

X t, s

Y R_t

1 $R_t(90)$

2 $R_{t,max}$

3 $\Delta R_{t,tot}$

4 $R_{t,min}$

5 broken line between two points that straddle $R_t(90)$, which is then used to calculate $ttb(90)$ *via* X = $(Y - c)/m$

6 span = 0,9 × $\Delta R_{t,tot}$ used to calculate $R_t(90)$

7 $ttb(90)$ = 233 s

Figure 5 — Schematic representation of the typical R_t vs. t plot with the various key parameters and an illustration of the simple, least squares method of determining the value of $ttb(90)$

As a consequence, each sample of a material under test will yield a set of R_t vs. irradiation time, t data, a plot of which usually reveals a shape similar to that illustrated in Figure 5. Once an irradiation is completed, for each of the eight samples plot the respective R_t vs. t data and determine the values of $R_{t,max}$ and $R_{t,min}$, from which a value for $\Delta R_{t,tot}$, is calculated, see Figure 5. For each of the samples calculate a value for $R_t(90)$, then use this to determine the associated unique irradiation time value, $ttb(90)$, for the sample, see Figure 5.

For any sample, calculate the value for $ttb(90)$ from a plot of the R_t vs. t for the sample, and values of the gradient, and intercept for the straight line which joins the two data points identified that straddle the value of $R_t(90)$, as illustrated in Figure 5.

10.4 Data analysis

Analyse statistically the eight *ttb*(90) values, derived from the eight samples under test, using the modified standard score test. In the latter test, calculate the value of Z_{mod}, see Clause 4 for the key equations, for each of the eight samples, with their respective *ttb*(90) values (see Reference [5]). If, for a particular sample, the value of Z_{mod} is >3,5 it is defined as an outlier and shall not be used in the subsequent calculation of the average of the *ttb*(90) value of the samples. The maximum number of outliers allowed in any test is three, any greater and the test is invalid. Once any outliers are eliminated, calculate the value of the average of the *ttb*(90) and its standard deviation, i.e. $ttb(90)_{av} \pm \sigma$. In addition, plot the R_t vs t curve for each of the eight samples of the material under test on one graph, see Figure B.1.

11 Test report

11.1 Qualitative assessment of activity

The test report shall include the following:

a) name of operator and address of testing establishment;

b) date of test, report identification and number, and signatory;

c) a reference to this document, i.e. determined in accordance with ISO 21066;

d) a description of the test material: type of product, type of photocatalyst (if known), date of receipt;

e) details of any pre-conditioning of the samples of the material under test (e.g. 8-h UV pre-treatment, 2 mW·cm^{-2}, under otherwise ambient conditions);

f) a description of the testing equipment used, i.e. details of: source of Rz ink, the light source, irradiation rig, UV radiometer, digital scanner or digital camera, software (for RGB analysis of digital images). The following details should be included for each piece of equipment used: manufacturer, model, specification, any modifications and – with respect to the UV radiometer, date of last calibration;

g) testing conditions used (T and RH);

h) a statement on whether the material under test is: (i) **reactive**, (ii) below, (iii) within or (iv) above the applicable range of the test;

i) digital photographic images of the three samples together; (i) before and (ii) after irradiation;

j) a value for $t_{end,av}$ if measurable.

NOTE A value for $t_{end,av}$ will not be measurable for a material that is **reactive**, or with a $t_{end,av}$ value >90 min or <1,5 min.

See Annex A for an example set of data for a test report.

11.2 Semiquantitative assessment of activity

The test report shall include at least the same general components (a) to (g) as stipulated in 11.1 above. In addition, the test report shall provide:

a) a plot of R_t vs. irradiation time for all eight samples tested (see Figure B.1);

b) a list of the *ttb*(90) and values for the eight samples of the material under test determined from an analysis of the data in the plot specified in (a); highlighting any outliers in red (see Figure B.1);

c) a value for $ttb(90)_{av} \pm \sigma$.

See Annex B for an example set of data for a test report and Annex C provides details of the results arising from a round-robin exercise involving this test.

Annex A
(informative)

Example of Rz ink qualitative test report on samples of a commercial type of photocatalyst-based, self-cleaning glass

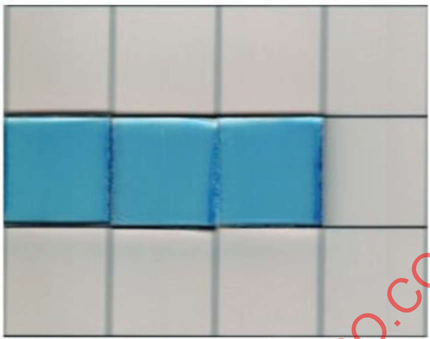
Operator: Y

Date: 28/08/14

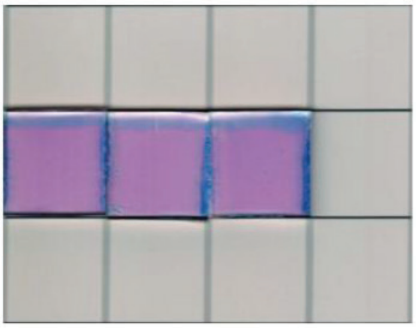
Material: From supplier X, pristine (unused) samples of commercial self-cleaning glass

Preconditioning: none, except samples wiped with a damp cloth and allowed to dry as specified in test method (Clause 8).

Other details: All irradiations were conducted using a Blak-Ray® XX-15 lamp and exposure stand[1)] purchased from Cole-Parmer. The radiometer used was a UVX Radiometer with UVX-36 sensor[1)] from UVP LLC, USA (www.UVP.com), last calibrated 20/8/14. The UV light was derived from two 15 W Blacklight tubes[1)] (Eiko) with λ_{max} emission of 352 nm and an emission spectrum as reported in ISO 10677. Digital images of the ink-coated glass samples (see Figure A.1) were recorded using an Ion CopyCat hand-held document scanner[1)] (https://www.ionaudio.com/downloads/COPY_CAT_Quickstart_Guide_v1.3.pdf). Irradiations conducted at: T = 22,0 ± 0,5°C and a RH of 50 ± 5 %.



1



2

Key

1 before irradiation (all blue)

2 after irradiation (all pink)

Figure A.1 — Scanned images of three samples of Rz coated commercial, self-cleaning glass before and after exposure to the UV light for 260 s

Irradiation times: $t_{end,av}$ = 260 s.

Statement on the material's suitability, with regard to the range of the test: The material is within the applicable range of the test.

1) This 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 the product named. Equivalent products may be used if they can be shown to lead to the same results.

Annex B
(informative)

Example of Rz ink semiquantitative test report on samples of a commercial type of photocatalyst-based, self-cleaning glass[8]

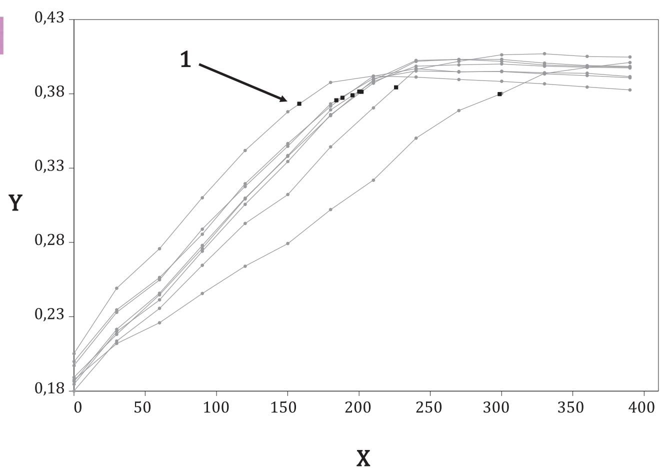
Operator: Y; Date: 28/08/14

Material: From supplier X, pristine (unused) samples of commercial self-cleaning glass

Preconditioning: none, except samples wiped with a damp cloth and allowed to dry as specified in test method (Clause 8).

Other details: All irradiations were conducted using a Blak-Ray® XX-15 lamp and exposure stand2) purchased from Cole-Parmer. The radiometer used was a UVX Radiometer with UVX-36 sensor2) from UVP LLC, USA (www.UVP.com), last calibrated on 20/8/14. The UV light was derived from two 15 W Blacklight tubes2) (Eiko) with λ_{max} emission of 352 nm and an emission spectrum as reported in ISO 10677. Digital images of the ink-coated glass samples were recorded using an Ion CopyCat hand-held document scanner2) (https://www.ionaudio.com/downloads/COPY_CAT_Quickstart_Guide_v1.3.pdf). Irradiations conducted at: T = 22,0 ± 0,5°C and a RH of 50 ± 5 %. *ImageJ* from: https://imagej.nih.gov/ij/ free software was used for carrying out the RGB analyses of the digital images, although there are numerous others, including Adobe Photoshop®2), which can be used instead.

Typical observed colour changes – blue to pink - (optional):



Key

X t, s

Y R_t

1 solid square points identify the respective *ttb*(90) values on each of the R_t *vs t* curves

Figure B.1 — Plot of the calculated values of R_t vs t for the eight samples of the commercial self-cleaning glass

2) This 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 the product named. Equivalent products may be used if they can be shown to lead to the same results.