BS EN 16845-1:2017

BSI Standards Publication

Photocatalysis — Anti-soiling chemical activity using adsorbed organics under solid/ solid conditions

Part 1: Dyes on porous surfaces

National foreword

This British Standard is the UK implementation of EN 16845-1:2017.

The UK participation in its preparation was entrusted to Technical Committee RPI/13, Advanced technical ceramics.

A list of organizations represented on this committee can be obtained on request to its secretary.

Published by BSI Standards Limited 2017

ISBN 978 0 580 89121 2

ICS 25.220.20

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 March 2017.

Amendments/corrigenda issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16845-1

March 2017

ICS 25.220.20

English Version

Photocatalysis - Anti-soiling chemical activity using adsorbed organics under solid/solid conditions - Part 1: Dyes on porous surfaces

Photocatalyse - Activité chimique anti-salissures à l'aide de matières organiques adsorbées dans des conditions solide/solide - Partie 1 : Colorants sur des surfaces poreuses

Photokatalyse - Schmutzabweisende, chemische Aktivität unter Verwendung adsorbierender organischer Stoffe im Zustand fest/fest - Teil 1: Farbstoffe auf porösen Oberflächen

This European Standard was approved by CEN on 14 November 2016.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 16845-1:2017 E

Contents

Page

European foreword

This document (EN 16845-1:2017) has been prepared by Technical Committee CEN/TC 386 “Photocatalysis”, the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2017, and conflicting national standards shall be withdrawn at the latest by September 2017.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

EN 16845, *Photocatalysis — Anti-soiling chemical activity using adsorbed organics under solid/solid conditions*, is dedicated to anti-soiling chemical activity using adsorbed organics under solid/solid conditions and is constituted by the following parts:

— *Part 1: Dyes on porous surfaces*;

— *Part 2: Simulated weathering conditions*.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This European Standard specifies a test method for the evaluation of the photocatalytic self-cleaning performance of materials showing photocatalytic activity, usually based on semiconducting metal oxides such as titanium dioxide, by the measurement under solid/solid conditions of the decolouring ability under irradiation with ultraviolet light (UV-A) of a test sample on which a dye solution is sprayed and dried.

This European Standard is intended for use with opaque and rough surfaces of different kinds, such as construction materials in flat sheet, board or plate shape, that are the basic forms of materials for various applications.

This European Standard also applies to fabric, plastic or composites containing photocatalytic materials that are not soluble in acetone. This European Standard does not apply to photocatalytic glass, granular materials (unless they are deposited in compact films or layers over flat solid surface) and flat non porous materials.

The method evaluates only the self-cleaning ability of the material under ultraviolet light irradiation. It cannot be applicable to evaluate other performance attributes of photocatalytic materials, i.e. decomposition of water contaminants in liquid or gas phases contacting the material, and antifogging and antibacterial actions.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

CEN/TS 16599, *Photocatalysis - Irradiation conditions for testing photocatalytic properties of semiconducting materials and the measurement of these conditions*

CEN/TS 16981, *Photocatalysis — Glossary of terms*

EN ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:2005)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in CEN/TS 16981 and the following apply.

3.1
self-cleaning
ability of a material to maintain clean or to clean itself if soiled on its surface

3.2
photocatalytic self-cleaning
self-cleaning ability of a material as a consequence of the irradiation of the material surface with UV-VIS-IR radiation

3.3
spraying distance
distance from the outlet of the spraying gun (see experimental setup) and the surface of the test sample

3.4
covered area
CA
area of the sample where the colour intensity is ≥ exp(−2)≈ 13,5% of the maximum intensity

3.5
dirt parameter
DP
dye amount spread or persistent over the sample surface

3.6
dirt parameter calibration function
mathematical function that describes the relation between the Dirt Parameter and the amount of dye spread over the sample surface

4 Symbols and abbreviations

a, b, c	polynomial constant parameters obtained by the fit using Formula (7)
$A_{net}(\lambda)$	Net Absorbance of the dye covering of the sample surface at the wavelength λ
CA	Covered Area (cm^2)
C_{dye}	concentration of the dye in the spraying solution (g cm^{-3})
d_{ac}	density of acetone at the temperature of the measurement (g cm^{-3})
DP	dirt parameter (nm): the parameter is indexed depending on the context
DR	deposition rate (g s^{-1} cm^{-2})
f	volumetric spraying flow (cm^3 s^{-1})
F_i	mass flow (g s^{-1})
k_{dye}	first order kinetic constant of the specified dye for the photocatalytic self-cleaning process (min^{-1})
MW	molecular weight
n	number of steps used for deposition of the dye on the sample surface; typically, $n = 5$, but can be larger if the surface is excessively wet
$R(\lambda)$	spectral reflectance at the wavelength λ of the sample surface; $R(\lambda)$ has indexes *i* and *j* referring to steps of spraying and illumination, respectively
$R_{background}(\lambda)$	reflectance of the pristine surface at the wavelength λ
SC	standard dye covering defined in Table 2 (g cm^{-2})
T	temperature in °C
t_i	irradiation time in min
t^{spr}	spraying time (s), calculated as $t^{spr} = t_{std}^{spr}/n$
W	the full width at half maximum (FWHM) of the sprayed dye colour peak (cm)
β	average covering of dye at the surface (g cm^{-2}); indexes *i* and *j* refer to steps of spraying and illumination, respectively
β_o	maximum average covering of dye at the surface (g cm^{-2}), obtained at t_{std}^{spr}

λ	wavelength (nm)
λ_{max}	wavelength (nm) at which there is a maximum of absorbance
t_{std}^{spr}	standard spraying time (s)
$\tau_{1/2}^{dye}$	half-life of the dye for the photocatalytic self-cleaning process (min)

5 Principle

This standard concerns the comparison and the quality assurance of photocatalytic materials used as self-cleaning materials. The method described is intended to measure the photocatalytic self-cleaning performance of a photocatalytic material by evaluating its ability to clean its surface, previously covered by a known amount of coloured organic compound, as a consequence of the exposition to ultraviolet light. A controlled amount of a dye solution dissolved in a volatile solvent (acetone) is spread on the tested surface by using a spraying gun.

The photocatalytic material turns out to be covered by the solid dye. The relation between the amount of the spread dye and the spectrophotometric reflectance is defined in the calibration step. The calibration function involves the measurement of the reflectance spectra of the sample surface as a function of the dyes covering. Dyes used in separate experiments are Metanil Yellow, Rhodamine B, and Methylene Blue. The test shall be carried out with the dye showing the maximum optical contrast with the material to be tested. Criteria for the choice of the best dye are here given (see 8.3.2). Optionally, the test can be carried out with the others dyes as the reactivity of each dye can depend on the specimen. The measurement with more than one dye is encouraged, but it is not compulsory. The self-cleaning activity measured by this test shall be referred to the used dye.

The soiled surface is then irradiated in air by UV-A light under defined conditions and the decrease of the dye amount on the surface is monitored by measuring the reflectance spectra of the surface of the test sample in the visible range. By using the calibration function the change of the reflectance spectra can be related to the kinetic of disappearance of the dye from the surface. The photocatalytic self-cleaning performance is determined as the half-life (minutes) of the dyes applied to the surface.

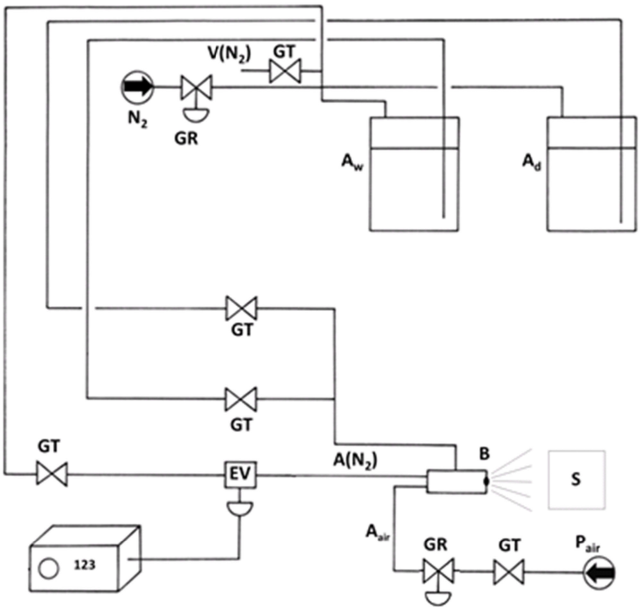
6 Instruments

6.1 Spraying system

The method described in this standard relies on the possibility to cover the sample surface with the dye in a controlled way. A spraying system shall be used to spread over the sample surface a solution of the dye (dye solution) in volatile solvent (acetone). The spraying system consists of a sample support and in a pneumatic system under pressure able to spray the dye solution over the sample for different definite times. The dye solution shall be spread by using a spraying gun that forms a circular spot. This involves a normal (Gaussian) distribution of the amount of dye centred in the spot of the dye on the surface. The amount of solution spread over the test sample is controlled by changing the spraying time (t^{spr}) with a timer that opens and closes, with a precision of ± 0,01 s, the dye solution flow. The relative distance and orientation between the gun and the sample shall be changed in a way to obtain a symmetric covering of the surface of the test sample and the desired surface covered area. Due to the normal distribution of the colour intensity at the test piece surface, the dye surface covered area is defined as the area of the sample where the colour intensity is $\geq \exp(-2)$approximately 13,5 % of the maximum intensity (see 8.2). The optimal distance from the gun outlet to the surface of the test sample is referred as the spraying distance.

A sketch of the pneumatic spraying system and of the sample support is shown in Figure 1 and Figure 2.

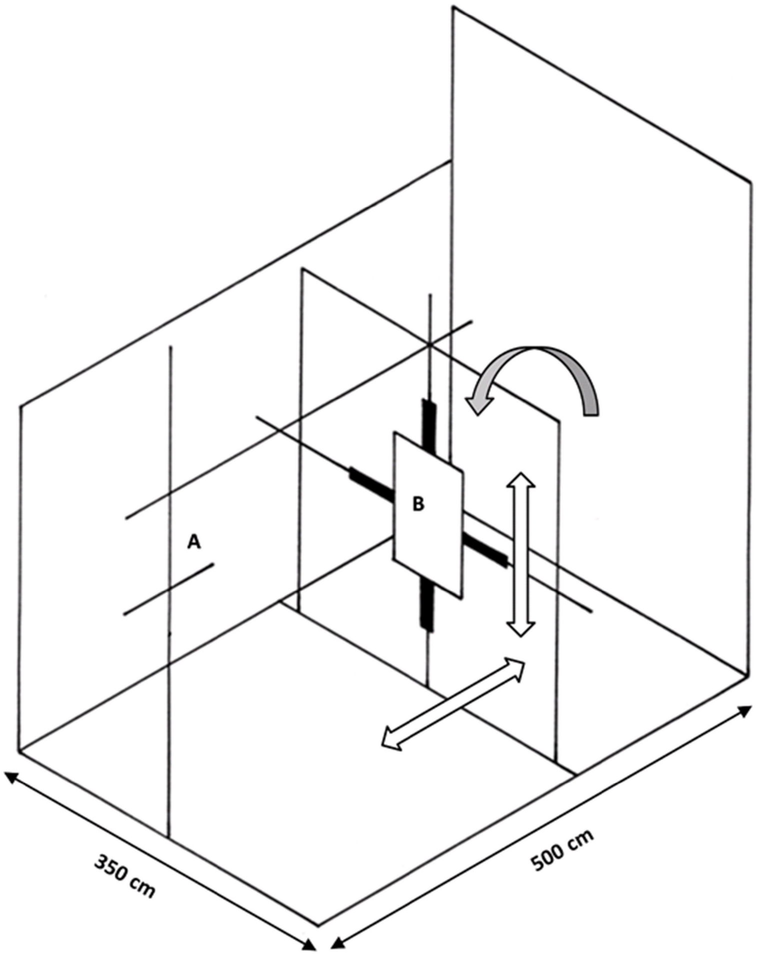
One pressurized ((3,0 ± 0,1) bar) bottle containing water and at least one pressurized ((3,0 ± 0,1) bar) bottle containing the dye solution (spraying liquids) are connected to the spraying gun by tubes made of materials resistant to the used solvent (for example PTFE (polytetrafluoroethylene)). The bottles and gun materials shall also be chemically inert to water and acetone. Bottles containing dye solutions or water can be selected acting on the corresponding valves. The gun is connected to air and N_2 pressurized lines ((3,0 ± 0,1) bar) that supply the atomization and the actuator gases. The actuator line is controlled by an electro-valve connected to a digital timer. The amount of solution spread over the test sample is controlled by changing the spraying time with a digital timer that opens and closes the actuator line with a precision of ± 0,01 s.



Key

A (N_2)	actuator gas line (N_2)
A_{air}	atomization AIR
A	tressurized bottles
A_w	water
A_d	dye/dyes solution
B	spraying gun
123	digital timer
EV	electrovalve
GR	gas regulator with manometer
GT	gastap
p_{air}	pressurized AIR
S	sample
V(N_2)	vent gas line (N_2)

Figure 1 — Pneumatic spraying system



Key

A	position of the spraying gun
B	sample
arrows	forward or back, up or down translation of the sample position

Figure 2 — Sample support

The spraying distance between the gun and the sample (see Figure 2) is typically fixed after setup of the instrumentation (see 8.2); the test samples are placed orthogonally to the spraying flow direction. The spraying gun shall provide a circular sprayed spot. Using a 0,8 mm fluid nozzle orifice under the given pressure, the typical spray distance is 200 mm. Typically, the fluid flow through the gun shall be regulated to obtain a value close to 0,2 $cm^3 s^{-1}$. For the accurate measurement of the spraying flow see 8.2.2. The atomization air flow is typically (270 ± 20) N $dm^3 min^{-1}$.

The system shall be operated under a ventilated chemical hood. Safety precautions shall be taken for use of acetone (CAS No: 67-64-1) such as safety glasses, good ventilation, removal of sources of ignition from the working area.

6.2 Analytical balance

An analytical balance with the precision of 10^{-4} g is used for all the gravimetric operations.

6.3 Diffuse Reflectance Spectrometer

The diffuse reflectance spectra of the sample surfaces shall be measured by using a diffuse reflectance spectrophotometer working in the VIS wavelength range from 400 nm to 750 nm excluding the specular component. Any commercial spectrophotometer with integrating sphere accessory can be used, including low cost instruments having wavelength band pass ≤ 3 nm. The reflectance spectra are measured by using a diffuse reflectance standard such as $BaSO_4$ as a reference of 100 % reflectance material.

6.4 Light source

The light source should agree with CEN/TS 16599. It shall provide UV-A irradiation within a wavelength range of 345 nm to 385 nm for a specimen containing TiO_2. Suitable sources include the so-called black light (BL) and black light blue (BLB) fluorescent lamps, with a maximum at 351 nm or 368 nm, and xenon arc lamps with optical filters that block radiation below 345 nm. In the case of xenon arc lamp, a cooling system shall be used.

The test sample shall be irradiated uniformly. The distance between the light source and the sample shall be adjusted so that the UV irradiance (300 nm to 400 nm) at the sample surface is (20 ± 0,5) $W m^{-2}$. A UV radiometer in conformity with CEN/TS 16599 shall be put at the same distance as the surface of the test sample to be tested. The irradiance along the length of the test sample shall also be constant within ± 5 %. The temperature of the sample during the test shall be (25 ± 5) °C.

6.5 Other experimental needs

a) A bottle with a neck diameter larger than the spot dye spot size, as determined under b) in 8.2.3.

b) Ventilated chemical hood.

c) Sonication bath.

d) Safety glasses.

e) Vial (from 20 ml to 30 ml in volume) for use in a) and c) in 8.2.3.

7 Materials

7.1 Dyes used

Three different dyes can be used in the test (see Table 1). The dyes shall be dissolved in acetone (2-propanone), a volatile organic solvent that allows a perfect solubilisation of the dyes. The dyes have different optical contrast on the test sample depending on their colour. When a dye is chosen, a calibration function shall be performed (see 8.3). Depending on the effective test sample chromatic properties and the obtained calibration function, the proper dye is selected.

Table 1 —Dyes used in the test

Dyes	CAS Number	IUPAC name	Synonyms	Empirical Formula	MW	λ_{max} (nm)	Amount (mg) for 1 L solution
Methylene Blue (hydrated)	7220–79–3	3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride	Basic blue 9	$C_{16}H_{18}ClN_3S \cdot x H_2O$ where x = 3	373,90	657	187,0
Rhodamine B	81–88–9	[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride	Basic Violet 10, Brilliant Pink B, Rhodamine O, Tetraethylrhodamine	$C_{28}H_{31}ClN_2O_3$	479,01	556	239,5
Metanil Yellow	587–98–4	3-(4-Anilinophenylazo)benzenesulfonic acid	Acid Yellow 36	$C_{18}H_{14}N_3NaO_3S$	375,38	411	187,7

7.2 Preparation of Solutions to Spray

The dye solution shall be prepared dissolving the corresponding amount of the compound (Methylene Blue, Rhodamine B or Metanil Yellow) in acetone. To facilitate the dissolution a sonicator bath is recommended. The required concentration of the dye in solution is $5x10^{-4}$ MW (see, in Table 1, the amount needed to prepare 1 L of such a solution). The solution shall be filtered on a common laboratory filter paper (see 7.4) before transferring it into the pressurized bottle to avoid the presence of suspended solids in the bottles.

7.3 Test Samples

The test sample shall be a flat material; its form shall be square (side size ≥ 7 cm x 7 cm) or circular (diameter ≥ 7 cm). The thickness of the test sample can changed as it is not relevant. The right distance from the light source to obtain the specified light power intensity as outlined in 6.4, and the right distance from the spraying gun (see below in 8.2.1) shall be fixed. This standard needs three identical test samples to be used, as three samples are needed, either for the evaluation of the dye that gives the best optical contrast (see 8.3.2), or for performing the full measurement using three dyes.

7.4 Other experimental needs

Laboratory filter paper[1] made of pure cellulose, about 80 g m^{-2}, porosity from 10 µm to 20 µm, for routine applications with funnels having a medium retention and flow rate.

8 Procedure

8.1 General Aspects

8.1.1 General

This clause details the procedure for the measurement of the disappearance rate of a dye on the surface of the test sample to quantify the photocatalytic self-cleaning rate of the test sample.

---

1) For example Grade I, Whatman, available in sheets.

8.1.2 Initial set up and calibration

Initially is necessary to setup and calibrate the spraying system to obtain a regular dye spot and to evaluate the dye deposition rate. This consists in the procedure (see 8.2) for the optimization of the experimental setup. It is performed once for the initial setup of the system.

The test procedure consists of two different steps:

a) calibration of the change in the spectral features of the surface (see 8.1.3) of the test sample as a function of the amount of the spread dye. This calibration shall be performed for every test sample (see 8.3).

b) evaluation of the change in the reflectance spectra of the test sample covered be the dye after different times under ultraviolet light (see 8.1.3). This evaluation shall be performed for every test sample (see 8.3.2).

8.1.3 Measurement of the Reflectance Spectra of the Surface

The diffuse reflectance spectra of the sample surfaces shall be measured in the (400-750) nm range excluding the specular component. The reflectance spectra are measured by using a diffuse reflectance standard such as $BaSO_4$ as a reference of 100 % reflectance material. The spectra of each sample shall be the average of at least three spectra acquired in three different places of the sample near the centre of the colour spot on the test piece. The spectra of the sample surface shall be collected before the spraying (pristine surface), along the dye covering on the test sample (calibration function development, see 8.3), after the spraying (time zero condition) and after different irradiation times (i-time condition).

8.2 Optimization of the Experimental Setup

8.2.1 General

The calibration of the test apparatus shall be performed once and controlled every 200 samples have been tested. Once optimized the experimental setup is fixed.

8.2.2 Optimization of the Spraying Distance and Flow

It consists in spraying a volume of a chosen dye solution (e.g. methylene blue) under the adopted conditions (tank pressure, gun model) on a white, flat and absorbing substrate (e.g. laboratory filter paper).

The spraying distance and orientation between the gun and the sample shall be changed in a way to obtain a circular spot with a normal (Gaussian) distribution of the amount of dye centred in the spot of the dye on the surface. The spots obtained at different spraying distances, different spraying times and different spraying flows are compared. The optimal spraying distance, flow and optimal spraying time shall be set when a good chromatic contrast between the bare substrate and the spread surface is obtained, and normal distribution of the colour intensity at the surface is obtained. An example is reported in A.2 where the optimum distance is at 25 cm from the gun outlet and a spraying time of 12 s.

8.2.3 Measurement of the Spraying Flow Rate

It consists in measuring for the experimental setup adopted under 8.2.2 the mass of water and acetone sprayed at different spraying times by using an analytical balance with sensitivity ≤ 0,001 g. Three different measurements shall be made:

a) using water from Tank A (see Figure 1), the water is recovered in a vial positioned near as possible to the outlet of the gun to recover all the flow from the gun;

b) using water from Tank A (see Figure 1), the water is recovered in a bottle located in place of the sample at the spraying distance adopted under 8.2.2. The bottle shall have a neck of proper diameter to collect the whole net spray reaching the sample. The bottle neck diameter shall be larger than the spot diameter previously determined (see 8.2.2). A typical value is 1,70 times the full width at half maximum (FWHM) of the spot colour ($\pm 2\sigma$) (see 8.2.4). The internal walls of the bottle are covered by laboratory filter paper, and its bottom filled with facial tissue paper, in such a way to completely absorb the water spray entering through the bottle neck.

c) using acetone from Tank B (see Figure 1), the acetone is recovered in a vial positioned near as possible to the outlet of the gun to recover all the flow from the gun. The measurement of the acetone recovered at the spraying distance is discouraged because the easy volatilization.

The net content of the bottle or the vials in each of the above steps a)-c) is measured gravimetrically by an analytical balance. The amount sprayed is measured at least at four different spraying times each lasting one to six seconds. The duration of this spraying time shall allow the collection of a measurable mass on the balance, say grams (see A.3). For each spraying time the measurement is performed at least three times.

The temperature of the sprayed liquids shall be also measured or controlled to have an accurate value of the acetone density necessary to calculate the volumetric flow. The flow of acetone solution reaching the surface of the test sample is computed in accordance to Formula (1).

Example of a measurement of the spraying flow rate with a typical experimental arrangement is reported in A.3.

8.2.4 Evaluation of the Deposition Rate (DR)

After spraying a colour spot using one dye (e.g. Methylene Blue) on the filter paper, the procedure is as follows:

a) Record the reflectance spectra of the sprayed dye on paper on a straight line passing from the centre of the sprayed area. The contiguous points where the spectra shall be collected shall be separated from at least 5 mm.

b) Evaluate the Dirt Parameter (DP) in accordance with proper Formula (3a)-(3c) for all the points on the straight line.

c) On the normal distribution obtained evaluate the full width at half maximum (FWHM) of the peak (see an example in A.4), and compute the covered area (CA) according to Formula (4). The value of CA shall be the average of at least five independent tests.

d) The deposition rate (DR) is computed with Formula (5).

The data obtained during the measurement of the Covered Area with a typical experimental arrangement are reported in A.4.

8.3 Test Procedure

8.3.1 Evaluation of the Dirt Parameter Calibration Function

The relation between the amount of spread dye and the reflectance is needed to bypass the problem related to nonlinearity of reflectance with surface concentration. The dye solution shall be spread on the surface of the test sample at different spraying times.

In the case of one-dye test, the dye shall have a good optical contrast.

This condition is fulfilled when DP > 3 at the standard spraying time (t_{std}^{spr}). For the one-dye test, only one calibration function is calculated following the below procedure. The procedure applies to other dyes if they are used.

To use only one test sample for the test (for each dye), the standard spraying time (t_{std}^{spr}) is calculated by Formula (6) (see 9.6); this value is divided into at least five different spraying times ($t^{spr} = t_{std}^{spr}/n$, where $n = 5$). The spraying time (t^{spr}) is such that the solvent of the dye solution does not excessively wet the sample surface, in order to avoid the penetration of the dye below the sample surface. If the surface is excessively wetted, the spot will not be regular as that observed on the filter paper (see 8.2.2). In this case reduce the spraying time (t^{spr}) by increasing the steps n ($t^{spr} = t_{std}^{spr}/n$, where $n > 5$). Then, after the first spraying for a duration t^{spr}, allow a complete evaporation of acetone in the dark (wait 20-30 min, or put the sample in an oven at 50°C), and then measure the reflectance spectrum. The procedure is repeated for a further t^{spr} (j = 1...n) until the standard spraying time (t_{std}^{spr}) is reached at the stage j = n.

For each recorded reflectance spectrum at stage j, where the cumulative spraying time is $j \times t^{spr}$, compute the relative Dirt Parameter and record DP_j (computed by Formula (3) for the j-step of spraying) and β_j calculated by Formula (8).

Then, the *DP* Calibration Function is calculated by using Formula (7). A polynomial of second order is used to fit the data DP_j -β_j. The coefficients of the second order polynomial are obtained by using the least squares method on a standard spreadsheet on the series of coupled data DP_j-β_j. The Dirt Parameter Calibration Function is the mathematical function that correlates *DP* and the average dye covering at the surface (g cm^{-2}) of the test piece.

An example of the calibration function obtained experimentally by using methylene blue as standard dye on a test sample is reported in A.5.

8.3.2 Choice of Test Sample Covered with Dye for Irradiation

The selected dye is suitable for the self-cleaning test if DP > 3 at the standard spraying time (t_{std}^{spr}). In this case the evaluation of DP at the standard spraying time (t_{std}^{spr}) for others dyes is not compulsory.

A value of DP calculated at the standard spraying time (t_{std}^{spr}) less than 3 indicates that the contrast between the deposited dye and the test sample is insufficient. Then the dye is not suitable for photocatalytic self-cleaning evaluation.

Optionally, because the relative performance of different photocatalytic surfaces with respect to different dyes is not always correlated, as many as possible dyes shall be used. As stated in Clause 5, the measurement with more than one dye is encouraged, but it is not compulsory. The self-cleaning activity measured by this test shall be referred to dye used.

8.3.3 Evaluation of the Photocatalytic Self-cleaning Performance

The procedure is executed on the dye covered test sample chosen in 8.3.2, or optionally for the other dyes.

Using the sample spread with dye for a cumulative standard spraying time (t_{std}^{spr}) previously prepared (see 8.3.1) irradiate with light of proper wavelength and intensity (see 6.4) and record the surface reflectance spectra at different irradiation times. For each recorded reflectance spectrum at irradiation time t_i, record DP_i (computed by Formula (3)) and calculate (using Formula (9) the average covering of dye at the surface remaining at the irradiation time t_i (g cm^{-2}) given by β_i.

The irradiation time can change as a function of the photocatalytic self-cleaning ability of the test piece. Adjust the step between each irradiation time (also by eye evaluation) with the aim to well-describe the eventually observed dye disappearance. For example, irradiate for 10 min.

If the DP is lower than 10 % of its initial value, increase the time step for the next measurement by a factor of 1,5 (15 min, next measurement at a total time 25 min); otherwise decrease the time step for the next measurement by a factor of 1,5 (6 min, next measurement at a total time of 16 min), and so on.

The maximum irradiation time for the test is 8 h. At this time the test can be considered completed. The test can be stopped before 8 h if the DP of the surface reached 50 % of the initial one. The photocatalytic self-cleaning performance is determined as the half-life (minutes) of the dye covering at the surface computed according to 9.7.

An example of the data obtained in a typical experimental arrangement on a photocatalytic white pigment, deposited as a film on a flat rigid substrate, using Methylene Blue is reported in A.6.

8.3.4 Results

The calculation of the dye half-life is performed according to 9.9. The results are then summarized in a report according to Clause 12 specifications.

9 Calculation

9.1 General

The test results shall be calculated as follows. The calculated values are usually rounded to one decimal place.

9.2 Spraying Flow (*f*)

The slope of linear regression between the mass recovered and the spraying time would give the mass flow. For the three measures above depicted (see 8.2.3) one calculates F_1 (flow of water recovered in a vial positioned at the outlet of the gun (g s^{-1})), F_2 (flow of water recovered at the spraying distance (g s^{-1})) and F_3 (flow of acetone recovered in a vial positioned at the outlet of the gun (g s^{-1})).

The volumetric flow of dye solution reaching the surface of the test sample (cm^3 s^{-1}) (*f*) is calculated by Formula (1).

$$f = \frac{F_3 \times F_2}{d_{ac} \times F_1} \tag{1}$$

where

f is the volumetric flow of dye solution reaching the surface of the test sample (cm^3 s^{-1});

F_1 is the mass flow of water recovered in a vial positioned at the outlet of the gun (g s^{-1});

F_2 is the mass flow of water recovered at the spraying distance (g s^{-1});

F_3 is the mass flow of acetone recovered in a vial positioned at the outlet of the gun (g s^{-1});

d_{ac} is the density of acetone at the temperature of the measurement.

The density of acetone in the range 10-30°C can be evaluated by using the following formula:

$$d_{ac} = 0{,}809\ 22 - 9{,}601\ 3 \times 10^{-4} \cdot T$$

where

T is the temperature in Celsius degrees.

9.3 Dirt Parameter

The measurement of the Dirt Parameter depends from the adopted spraying solution and is based on the measurement of the percent reflectance spectra of the surface of the pristine and soiled test sample.

From the values of reflectance measured the net absorbance (A_{net}) is computed by Formula (2) where log refer to the base 10 logarithm:

$$A_{net}(\lambda) = \frac{\log\left[R_i(\lambda)\right] - \log\left[R_{background}(\lambda)\right]}{2} \qquad (2)$$

where

$A_{net}(\lambda)$	is the net absorbance at the wavelength λ;
$R_i(\lambda)$	is the reflectance of the sample at the wavelength λ;
$R_{background}(\lambda)$	is the reflectance of the pristine surface at the wavelength λ.

NOTE The value of reflectance is the corresponding value of Percent Reflectance divided by 100.

From the spectra of the soiled surfaces expressed in A_{net} the Dirt Parameter (DP) is calculated by Formula (3). Use Formula (3a) in the case of Metanil Yellow, Formula (3b) for Rhodamine B and Formula (3c) in the case of Methylene Blue.

$$DP = \int_{410nm}^{440nm} A_{net}(\lambda)d\lambda \text{ (Metanil Yellow)} \qquad (3a)$$

$$DP = \int_{520nm}^{550nm} A_{net}(\lambda)d\lambda \text{ (Rhodamine B)} \qquad (3b)$$

$$DP = \int_{660nm}^{690nm} A_{net}(\lambda)d\lambda \text{ (Methylene Blue)} \qquad (3c)$$

Common commercial worksheets can be used to implement the trapezoidal rule or the Simpson's rule for numerical integration of a set of data $A_{net}(\lambda)$ vs λ [3].

9.4 Covered Area

The covered area (CA) is calculated according to Formula (4):

$$CA = \frac{\pi \times W^2}{2 \times \ln(2)} \qquad (4)$$

where

W is the full width at half maximum (FWHM) of the sprayed dye colour peak.

CA is the covered area (cm^2)

W is evaluated at the half of the maximum DP observed by reporting the DP calculated according Formula (3) (see an example in A.4).

9.5 Deposition Rate

Deposition Rate (DR) is the average mass of dye spread over 1 cm² of the sample surface area in one second. It is calculated by Formula (5):

$$DR = f \times C_{dye} \times \frac{0{,}9545}{CA} \tag{5}$$

where

DR is the deposition rate (g s^{-1} cm^{-2});

f is the Spraying flow rate (cm^3 s^{-1}) calculated according to Formula (1);

C_{dye} is the concentration of the dye in the spraying solution (g cm^{-3});

CA is the covered area (cm^2).

NOTE 1 Given that the required concentration of the dye in solution is $5x10^{-4}$ M (according to 7.2), the value of C_{dye} is $1{,}87 \times 10^{-4}$, $2{,}40 \times 10^{-4}$, $1{,}88 \times 10^{-4}$ g cm^{-3} for Methylene Blue, Rhodamine B and Metanil Yellow, respectively.

NOTE 2 The factor 0,954 5 is the fractional area evaluated at $\pm 2\sigma = \frac{W}{\sqrt{2 \times \ln(2)}}$ according to Formula (4) with respect to the total area of the Gaussian function.

9.6 Standard Spraying Time

The standard spraying time (t_{std}^{spr}) is the spraying time the gives, under the adopted conditions, the dye covering given in Table 2. It is calculated by Formula (6):

$$t_{std}^{spr} = \frac{SC}{DR} \tag{6}$$

where

SC is the standard dye covering in g cm^{-2}, see Table 2;

t^{spr}_{std} is the standard spraying time (s).

Table 2 — Standard dye covering (SC)

Dye	Standard Covering (SC) g cm^{-2}
Methylene Blue (CAS Number: 7220–79–3)	$1{,}5 \times 10^{-5}$
Rhodamine B (CAS Number: 81–88–9)	$7{,}5 \times 10^{-6}$
Metanil Yellow (CAS Number: 587–98–4)	$1{,}5 \times 10^{-5}$

9.7 Dirt Parameter Calibration Function

The function that correlates the dye covering of the sample surface and the Dirt Parameter is obtained by using the least squares method on the series of coupled data DP_j- β_j obtained in 8.3.1. The fit function to DP shall be a second order polynomial (Formula (7)

$$DP_j = a \times \beta_j + b \times \beta_j{}^2 + c \tag{7}$$

where

DP_j is the Dirt Parameter computed by Formula (3) for the j-step of spraying;

a, *b*, *c* is thepolynomial constant parameters obtained by the fit.

β_j is the average dye covering at the surface in g cm^{-2}. It is given by:

$$\beta_j = j \times DR \times t^{spr} \tag{8}$$

where

t^{spr} is the spraying time defined in 8.3.1 and j is the j-step of spraying.

9.8 Remaining Dye (βi) after Different Times of Irradiation

The evaluation of the remaining dye at the surface (g cm^{-2}) of the test sample after a definite number of minutes of irradiation t_i shall be evaluated calculating the corresponding DP_i by the proper Formula (3) and by using Formula (9):

$$\beta_i = \frac{-b + \sqrt{b^2 - 4 \times a \times (c - DP_i)}}{2 \times a} \tag{9}$$

where:

β_i is the average covering of dye at the surface (g cm^{-2}) remaining at the irradiation time t_i;

DP_i is the Dirt Parameter at the irradiation time t_i;

a, *b*, *c* is the parameters of the calibration function (see 9.7).

9.9 Dye Half-Life

For the calculation of the dye half-life the method is based on the evaluation of the first order kinetic constant. This evaluation shall be performed for all the dyes used.

The disappearance of the dye from the surface of the test sample follows a first order kinetic expressed by Formula (10):

$$\ln\left(\frac{\beta_i}{\beta_0}\right) = -k_{dye} \times t_i \tag{10}$$

where

β_i is the average covering of dye at the surface remaining at the irradiation time t_i g cm^{-2};

β_o is the average covering of dye at the surface before irradiation in g cm^{-2};

t_i is the irradiation time in min;

k_{dye} is the first order kinetic constant in min^{-1}, referring to a chosen dye.

The application of the least squares method to the experimental points $\ln(\beta_i/\beta_o)$ vs t_i allows to obtain the value of k_{dye} as a slope of the resulting linear function and from this value the dye half-life $\tau_{1/2}^{dye}$ for a given dye is calculated by using Formula (11):

$$\tau_{1/2}^{dye} = \frac{\ln(2)}{k_{dye}} \tag{11}$$

The dye half-life $\tau_{1/2}^{dye}$ for the chosen dye, and eventually those of other dyes, shall be reported as result of the test method of this standard.

10 Precision and Reproducibility

Precision, repeatability and reproducibility of the test method are strongly affected by i) the surface roughness of the test piece that can cause low homogeneity of the surface reflectance and of the dye covering; ii) the intrinsic self-cleaning activity.

A relative error on the evaluation of the dye half time $\tau_{1/2}^{dye}$ equal to ± 15 % can be foreseen from intra laboratory tests.

NOTE The results of a Round Robin Test will be available as an Addendum and/or upon request to CEN/TC 386. They will be integrated in the text in a future revision.

11 Test Method for Samples with Low to Negligible Performance

It is considered a sample with “low to negligible photocatalytic self-cleaning activity” a specimen characterized by a dye life time ≥ 1500 min (β_i / $\beta_0 \geq 0{,}8$ after eight hours of irradiation). In this case an accurate quantification of $\tau_{1/2}$ is impossible due to the method precision. Specify the low activity of the sample in the report as reported in Clause 12 h) of the present standard.

12 Test Report

The test report shall include the reporting provisions of EN ISO/IEC 17025, and shall include the following information:

a) the name and address of the testing establishment;

b) the date of the test, a unique identification of the report and of each page, customer name and address, signatory of the report;

c) a reference to this standard, i.e. determined by accordance with EN 16845-1;

d) experimental conditions: temperature, relative humidity, etc.;

e) description of the identical test samples (material, size, shape, etc.);

f) description of testing equipment (gun specifications, tank pressure, spraying distance, size of the dye spot as covered area, detailed description of light source, irradiance, reflectance spectrophotometer used).;

g) testing conditions (number of dye used, dye concentrations, covering of dye per surface area, conditions of measurements, etc.);

h) the DP at the standard spraying time for the dye used. If the DP at the standard spraying time of the dye is ≤ 3 indicate “the dye (name) is not suitable for photocatalytic self-cleaning evaluation because DP is less than 3,0”. Indicate that other dyes have been checked;

i) the polynomial constant parameters obtained by the fit using Formula (7);

j) the experimental determined DP_i, and calculated β_i using Formula (9), versus t_i in graphical or tabular form;

k) the half-life of the dye(s) at the surface of the test sample, or the wording “sample with low to negligible photocatalytic self-cleaning activity” in the case of specimens with dye life time ≥ 1 500 min.

Annex A
(informative)

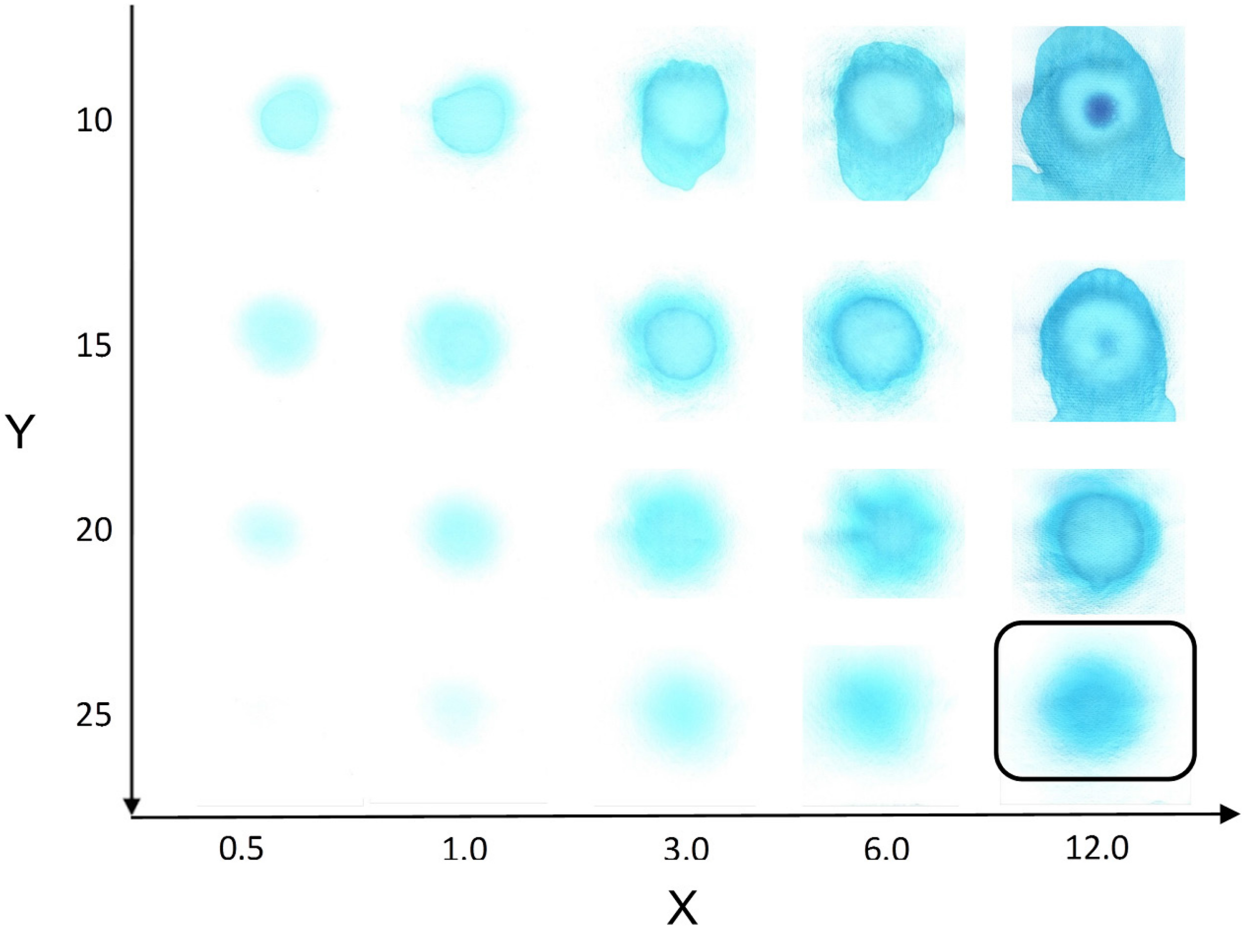
Typical Experimental Data

A.1 General

For the sake of clearness in Annex A are reported the experimental data obtained in each step of the method object of this part of EN 16845 during a real test.

A.2 Optimization of the Spraying Conditions (example)

Figure A.1 reports a comparison among the spots obtained on laboratory filter paper with methylene blue as test dye at different spraying distance (sees ordinate Y) and spraying time (on the abscissa X). The best conditions are underlined with the black rectangle.



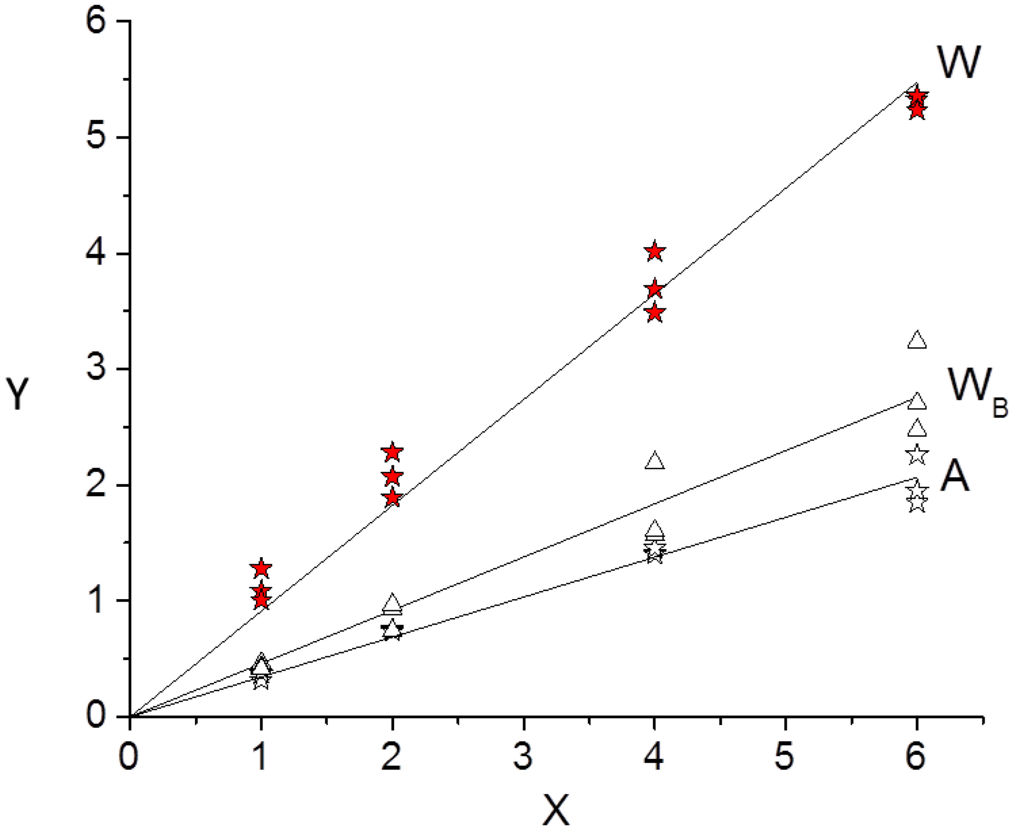
Key

X spraying time, expressed in s

Y distance, expressed in cm

Figure A.1 — Example of the results obtained during the step of optimization of the spraying conditions

A.3 Measurement of the Spraying Mass Flows (example)



Key

X	spraying time, expressed in s
Y	solvent mass, expressed in g
W	curve referring to water as solvent. The slope is F1
W_B	curve referring to water recovered in a bottle positioned at the outlet of the gun. The slope is F2
A	curve referring to acetone as solvent. The slope is F3
F1	mass flow of water recovered in a vial positioned at the outlet of the gun: 0,91 g s^{-1}
F2	mass flow of water recovered at the spraying distance: 0,46 g s^{-1}
F3	mass flow of acetone recovered in a vial positioned at the outlet of the gun: 0,34 g s^{-1}

Figure A.2 — Example of mass of solvent (water or acetone) sprayed as function of the spraying time in a typical experimental arrangement

A.4 Measurement of the Covered Area (example)

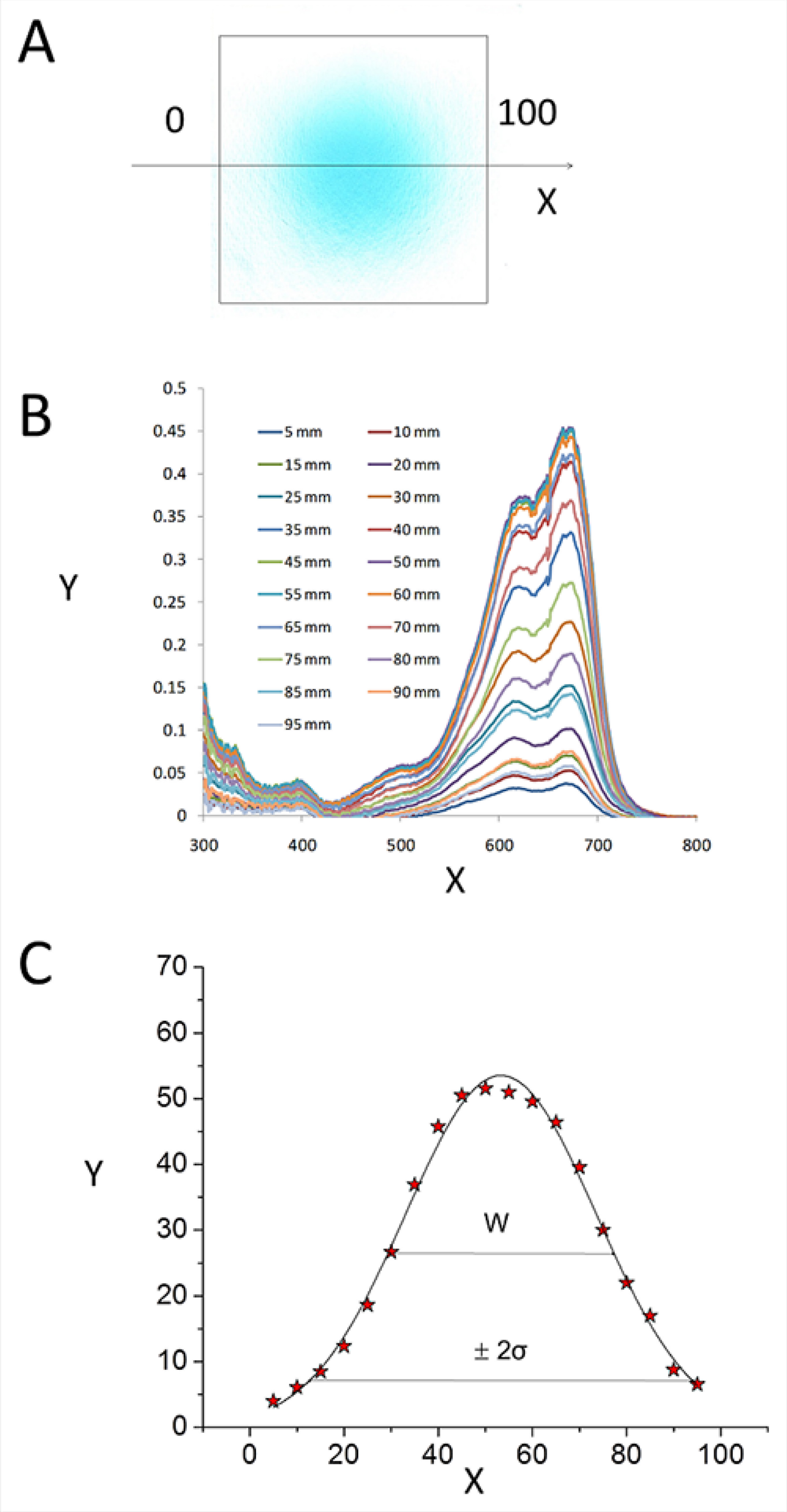


Figure A.3 — Example of evaluation of the Covered Area with a typical experimental arrangement

A.3.A) Image of the dye (Methylene Blue) spread over filter laboratory paper, the reflectance spectra are collected along the arrow starting from the border; X is the distance from the border in mm;

A.3.B) Spectra in the 300-800 nm range expressed as $A_{net}(\lambda)$ (see Formula (2)) recorded at different distance from the border. X is the wavelength in nm; Y is $A_{net}(\lambda)$, a.u.;

A.3.C) Nominal distribution of the colour intensity, expressed as Dirt Parameter DP, as a function of the distance from the support border. X is the distance from the support border in mm; Y is the DP; the arrows indicate the full width at half maximum (W) and the interval corresponding to ± 2σ, where σ is the standard deviation.

A.5 Evaluation of the Dirt Parameter Calibration Function (example)

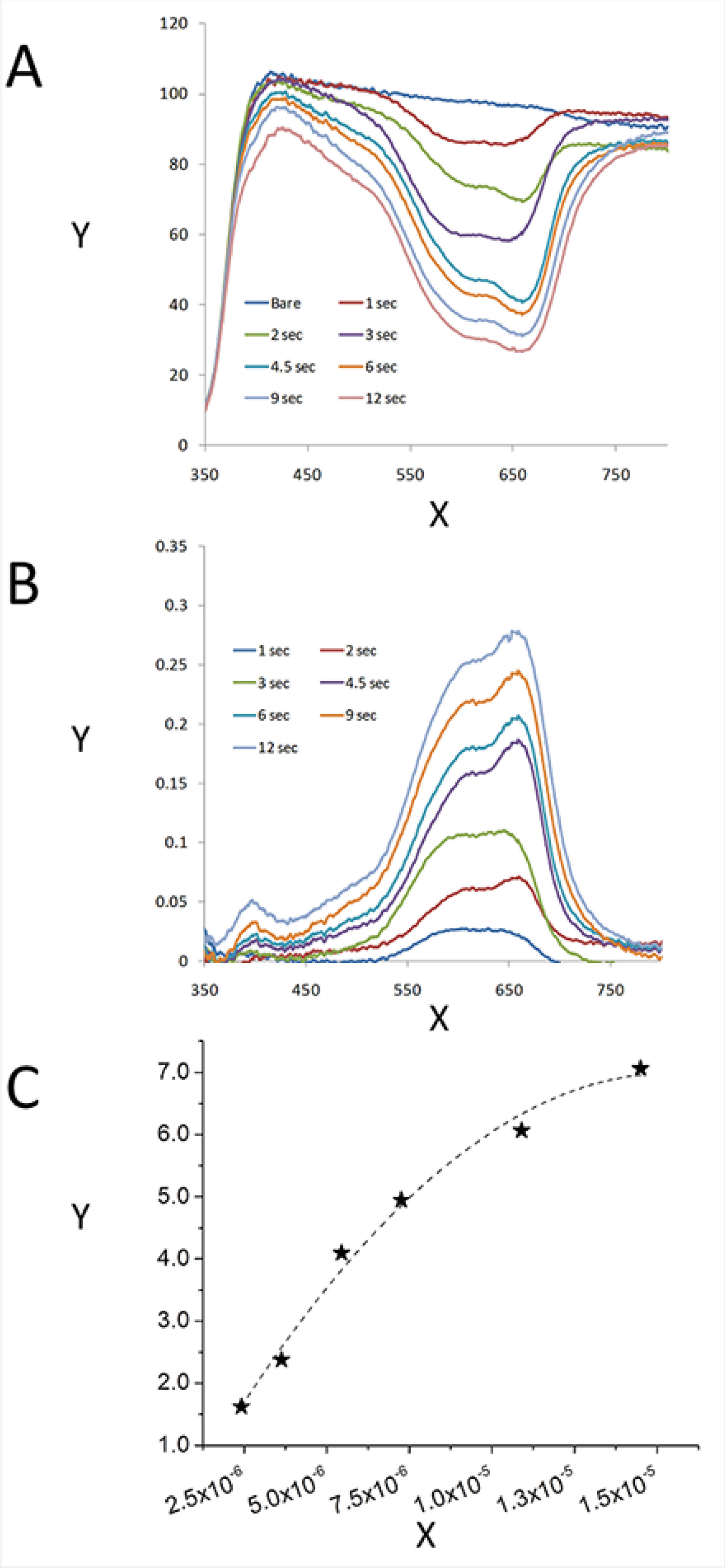


Figure A.4 — Example of evaluation of the Dirt Parameter Calibration Function by using Methylene Blue as dye on a white photocatalytic pigment deposited as a compact film on a flat and rigid substrate

A.4.A) Percent Reflectance spectra in the (350-800) nm range at different spraying time; X is the wavelength in nm; Y is the % $R_i(\lambda)$; different curves refer to different t^{spr} (see Formula (8));

A.4.B) Spectra in the (350-800) nm range expressed as $A_{net}(\lambda)$ (see Formula (2)) as a function of wavelength expressed in nm; X is the wavelength in nm; Y is the $A_{net}(\lambda)$, a.u.; different curves refer to different t^{spr}, s (see Formula (8)).

A.4.C) Dirt Parameter DP as a function of dye coverings with the corresponding second order polynomial fit (Dirt Parameter Calibration Function). Significance of parameters is indicated in Formula (9). X is the β_j (see Formula (8)); Y is the DP.

A.6 Evaluation of the Self-cleaning Effect (example)

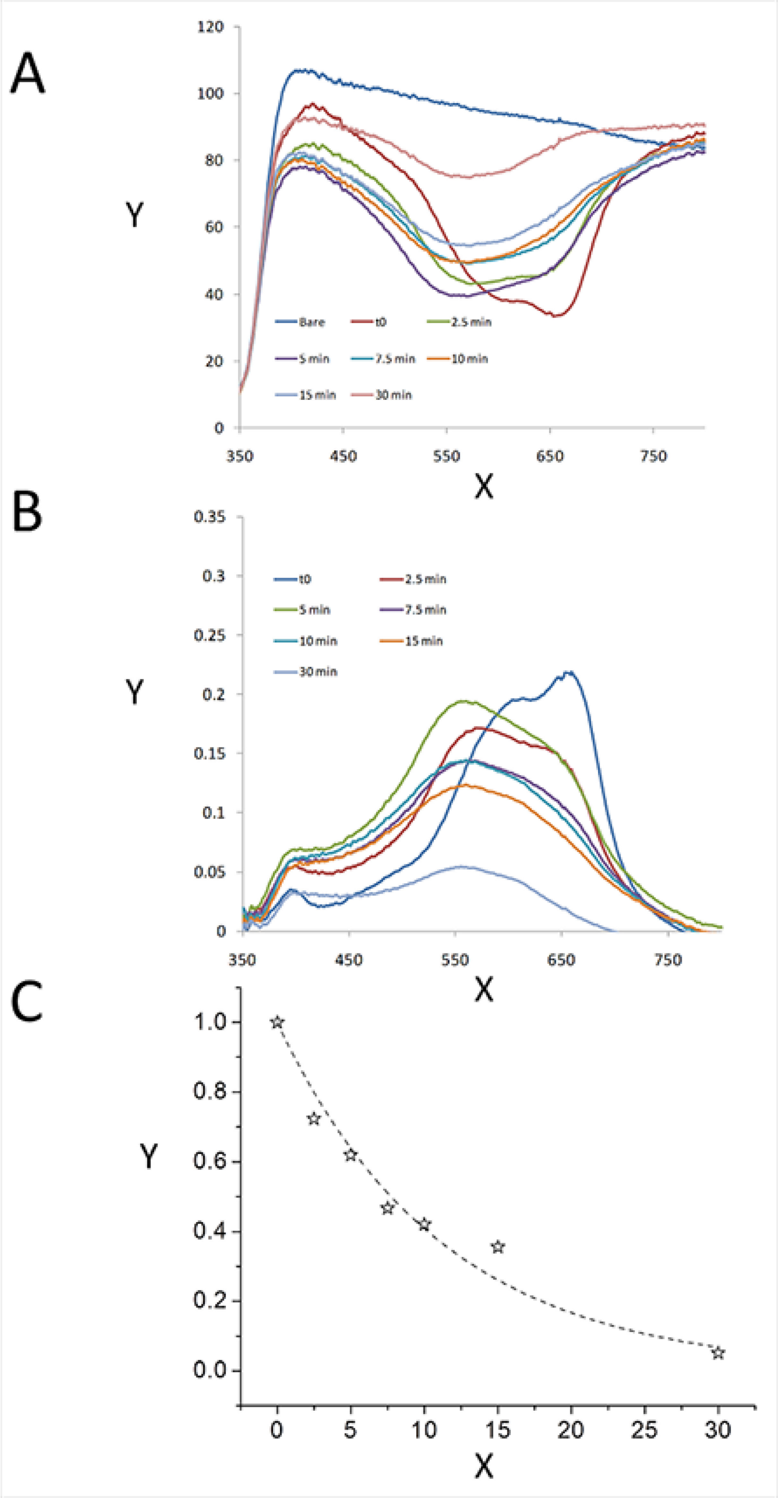


Figure A.5 — Example of evaluation of the disappearance of dye covering by using Methylene Blue as dye on a white photocatalytic pigment deposited as a compact film on a flat and rigid substrate

A.5.A) Percent Reflectance spectra in the (350-800) nm range at different irradiation time; X is the wavelength in nm; Y is the % $R_i(\lambda)$; different curves refer to different t_i (see Formula (9));

A.5.B) Spectra in the (350-800) nm range expressed as $A_{net}(\lambda)$ (see Formula (2)) as a function of wavelength expressed in nm; X is the wavelength in nm; Y is the $A_{net}(\lambda)$, a.u.; different curves refer to different t_i (see Formula (9));

A.5.C) Fraction of the average covering of dye β_i/β_o (see Formula (10)), remaining at the surface as a function of the irradiation time t_i with the corresponding exponential fit function; X is the t_i in min; Y is the β_i/β_o.

Bibliography

[1] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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

[3] EL-GEBEILY M., YUSHAU B. Numerical Methods with MS Excel, *The Montana Mathematics Enthusiast*, ISSN 1551-3440, Vol. 4, no.1, pp. 84-92, 2007

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards-based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Copyright in BSI publications

All the content in BSI publications, including British Standards, is the property of and copyrighted by BSI or some person or entity that owns copyright in the information used (such as the international standardization bodies) and has formally licensed such information to BSI for commercial publication and use.

Save for the provisions below, you may not transfer, share or disseminate any portion of the standard to any other person. You may not adapt, distribute, commercially exploit, or publicly display the standard or any portion thereof in any manner whatsoever without BSI's prior written consent.

Storing and using standards

Standards purchased in soft copy format:

- A British Standard purchased in soft copy format is licensed to a sole named user for personal or internal company use only.
- The standard may be stored on more than 1 device provided that it is accessible by the sole named user only and that only 1 copy is accessed at any one time.
- A single paper copy may be printed for personal or internal company use only.

Standards purchased in hard copy format:

- A British Standard purchased in hard copy format is for personal or internal company use only.
- It may not be further reproduced – in any format – to create an additional copy. This includes scanning of the document.

If you need more than 1 copy of the document, or if you wish to share the document on an internal network, you can save money by choosing a subscription product (see 'Subscriptions').

Reproducing extracts

For permission to reproduce content from BSI publications contact the BSI Copyright & Licensing team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email subscriptions@bsigroup.com.

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Useful Contacts

Customer Services
Tel: +44 345 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 345 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK