INTERNATIONAL STANDARD

ISO 22197-1

First edition
2007-09-01

Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for air-purification performance of semiconducting photocatalytic materials —

Part 1:
Removal of nitric oxide

Céramiques techniques — Méthodes d'essai relatives à la performance des matériaux photocatalytiques semi-conducteurs pour la purification de l'air —

Partie 1: Élimination de l'oxyde nitrique

Reference number
ISO 22197-1:2007(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 22197-1 was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

ISO 22197 consists of the following parts, under the general title *Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for air-purification performance of semiconducting photocatalytic materials*:

— *Part 1: Removal of nitric oxide*

The following parts are under preparation:

— *Part 2: Removal of acetaldehyde*

— *Part 3: Removal of toluene*

Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for air-purification performance of semiconducting photocatalytic materials —

Part 1:
Removal of nitric oxide

1 Scope

This part of ISO 22197 specifies a test method for the determination of the air-purification performance of materials that contain a photocatalyst or have photocatalytic films on the surface, usually made from semiconducting metal oxides, such as titanium dioxide or other ceramic materials, by continuous exposure of a test piece to the model air pollutant under illumination with ultraviolet light. This part of ISO 22197 is intended for use with different kinds of materials, such as construction materials in flat sheet, board or plate shape, that are the basic forms of materials for various applications. This part of ISO 22197 also applies to materials in honeycomb-form, and to plastic or paper materials if they contain ceramic microcrystals and composites. This part of ISO 22197 does not apply to powder or granular photocatalytic materials.

This test method is usually applicable to photocatalytic materials produced for air purification. This method is not suitable for the determination of other performance attributes of photocatalytic materials, i.e., decomposition of water contaminants, self-cleaning, antifogging and antibacterial actions. It concerns the removal of nitric oxide.

2 Normative references

The following referenced documents are indispensable for the application 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 31-0:1992, *Quantities and units — Part 0: General principles*

ISO 4677-1:1985, *Atmospheres for conditioning and testing — Determination of relative humidity — Part 1: Aspirated psychrometer method*

ISO 4892-1:—[1)], *Plastics — Methods of exposure to laboratory light sources — Part 1: General guidance*

ISO 4892-3:2006, *Plastics — Methods of exposure to laboratory light sources — Part 3: Fluorescent UV lamps*

ISO 5725-2:1994, *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*

ISO 6145-7:2001, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 7: Thermal mass-flow controllers*

1) To be published. (Revision of ISO 4892-1:1999.)

ISO 7996:1985, *Ambient air — Determination of the mass concentration of nitrogen oxides — Chemiluminescence method*

ISO 10304-1:—[2)], *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate*

ISO 10523:1994, *Water quality — Determination of pH*

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

3 Terms and definitions

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

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

3.2
photocatalytic materials
materials in which or on which the photocatalyst is added by coating, impregnation, mixing, etc.

NOTE Such photocatalytic materials are intended primarily for use as building and road construction materials to obtain the above-mentioned functions.

3.3
zero-calibration gas
air that does not contain pollutants (i.e. in which common pollutants are below 0,01 µl/l)

NOTE The zero-calibration gas is prepared from indoor air using a laboratory air-purification system, or supplied as synthetic air in a gas cylinder.

3.4
standard gas
diluted gases of known concentrations supplied in cylinders and certified by an accredited laboratory

3.5
test gas
mixture of air and pollutant(s) of known concentration prepared from a standard gas or a zero-calibration gas, to be used for the performance test of a photocatalytic material

3.6
purified water
water to be used for elution, etc., with a conductivity lower than 1 µS, prepared by the ion exchange method or distillation

2) To be published. (Revision of ISO 10304-1:1992.)

4 Symbols

f air-flow rate converted into that at the standard state (0 °C, 101,3 kPa, and dry gas basis) (l/min)

ϕ_{NO} nitric oxide volume fraction at the reactor exit (μl/l)

ϕ_{NO_i} supply volume fraction of nitric oxide (μl/l)

ϕ_{NO_2} nitrogen dioxide volume fraction at the reactor exit (μl/l)

ϕ_{NO_x} the volume fraction of nitrogen oxides (ϕ_{NO} + ϕ_{NO_2}) at the reactor exit (μl/l)

ρ_{NO_2-} nitrite ion concentration in the eluent from the test piece (mg/l)

ρ_{NO_3-} nitrate ion concentration in the eluent from the test piece (mg/l)

t time of adsorption, removal or desorption operation (min)

n_{ads} the amount of NO_x adsorbed by the test piece (μmol)

n_{des} the amount of NO_x desorbed from the test piece (μmol)

n_{NO} the amount of NO removed by the test piece (μmol)

n_{NO_2} the amount of NO_2 formed by the test piece (μmol)

n_{NO_x} the amount of NO_x removed by the test piece (μmol)

n_w the amount of nitrogen eluted from the test piece (μmol) [w_1, w_2 are the 1st and 2nd elutions, respectively]

V_w the volume of collected washings (ml) [w_1, w_2 are the 1st and 2nd elutions, respectively]

η_w the fractional recovery of nitrogen

5 Principle

This part of ISO 22197 concerns the development, comparison, quality assurance, characterization, reliability, and design data generation of photocatalytic materials[1]. The method described is intended to obtain the air-purification performance of photocatalytic materials by exposing a test piece to model polluted air under illumination by ultraviolet (UV) light[2]. Nitric oxide (NO) is chosen as a typical air pollutant that gives nonvolatile products on the photocatalyst. The test piece, placed in a flow-type photoreactor, is activated by UV illumination, and adsorbs and oxidizes gas-phase NO to form nitric acid (or nitrate) on its surface[3]. A part of the NO is converted to nitrogen dioxide (NO_2) on the test piece. The air-purification performance is determined from the amount of the net removal of nitrogen oxides (NO_x) (= NO removed – NO_2 formed). The simple adsorption and desorption of NO by the test piece (not due to photocatalysis) is evaluated by tests in the dark. Although the photocatalytic activity is reduced by the accumulation of reaction products, it is usually restored by washing with water[4]. The elution test provided here gives information about the ease of regeneration and material balance of the pollutants.

6 Apparatus

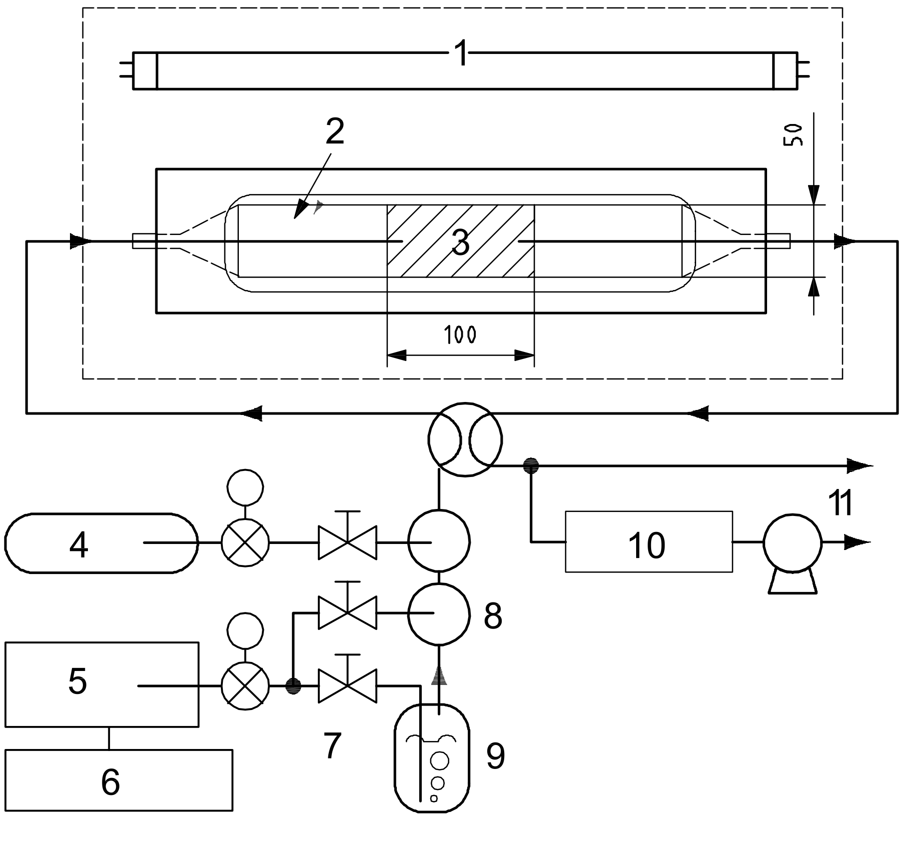
6.1 Test equipment

The test equipment enables a photocatalytic material to be examined for its pollutant-removal capability by supplying the test gas continuously, while providing photoirradiation to activate the photocatalyst. It consists of a test gas supply, a photoreactor, a light source, and pollutant measurement equipment. Since low concentrations of pollutants are to be tested, the system shall be constructed with materials of low adsorption and resistant to ultraviolet (UV) radiation, for example, acrylic resin, stainless steel, glass and fluorocarbon polymers. An example of a test system is shown in Figure 1.

6.2 Test gas supply

The test gas supply provides air polluted with the model contaminant at a predetermined concentration, temperature and humidity, and supplies it continuously to the photoreactor. It consists of flow regulators, a humidifier, gas mixers, etc. The flow rate of each gas should be within 5 % of the designated value, which is easily attained by using thermal mass-flow controllers, with a knowledge of calibrated gas flow rate and temperature in accordance with ISO 6145-7. Typical capacities of the flow controller for pollutant gas, dry air and wet air are 0,1 l/min, 2,0 l/min and 2,0 l/min, respectively. The expression of gas flow rate in this part of ISO 22197 is that converted to the standard state (0 °C, 101,3 kPa, and dry gas basis). The standard NO gas, normally balanced with nitrogen in a cylinder, shall have a volume fraction of 30 to 100 μl/l, because the oxidation of NO to NO_2 upon mixing with purified air becomes prominent with a higher concentration of NO.

Dimensions in millimetres

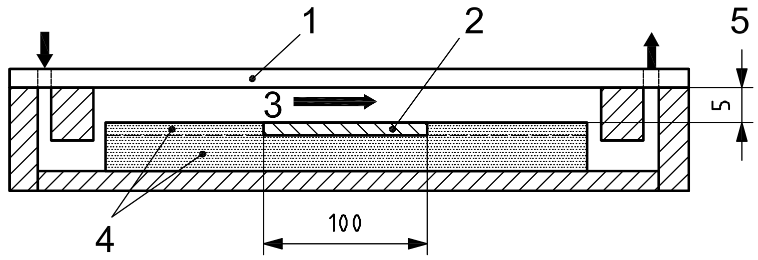


Key

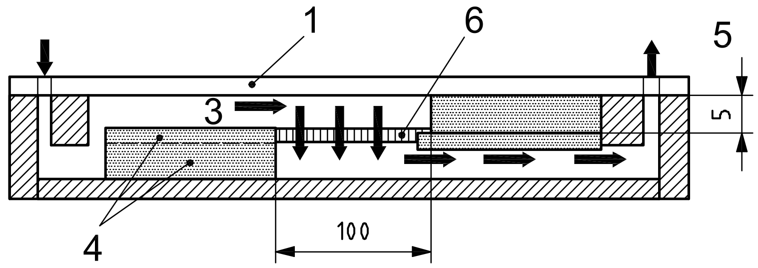
1 light source
2 optical window
3 test piece
4 standard gas (pollutant)
5 air-purification system
6 air compressor
7 mass-flow controllers
8 gas mixers
9 humidifier
10 analyser
11 vent

Figure 1 — A schematic of the test equipment

Dimensions in millimetres



a) **For flat test pieces**



b) **For honeycomb filters**

Key

1 optical window

2 test piece

3 test gas flow

4 height-adjusting plate

5 air layer thickness

6 test piece (honeycomb)

Figure 2 — Cross-sectional view of photoreactor

6.3 Photoreactor

The photoreactor holds a planar test piece within a 50 mm wide trough, with its surface parallel to an optical window for photoirradiation. The reactor shall be fabricated from materials that adsorb minimal test gas and withstand irradiation of near-UV light. The test piece shall be separated from the window by a 5,0 mm ± 0,5 mm thick air layer. The test gas shall pass only through the space between the test piece and the window. This gap shall be accurately set up, for example by using height-adjusting plates with different thicknesses, as shown in Figure 2 a). When a filter-type photocatalyst is tested, an alternative type of test-piece holder shall be used, which holds the test piece while allowing the test gas to pass through the cells of the filter under illumination (Figure 2 b). Quartz or borosilicate glass that absorbs minimal light at wavelengths longer than 300 nm shall be used for the window.

6.4 Light source

The light source shall provide UV-A illumination within a wavelength range of 300 nm to 400 nm. Suitable sources include the so-called black light (BL) and black light blue (BLB) fluorescent lamps, with a maximum at 351 nm, as specified in ISO 4892-3, and xenon lamps with optical filters that block radiation below 300 nm and above 400 nm. The test piece shall be irradiated uniformly through the window by the light source. In the case of testing honeycomb-form photocatalysts, the light source shall illuminate one face of the test piece. A light source that requires warming up shall be equipped with a shutter. The distance between the light source and the reactor shall be adjusted so that the UV irradiance (300 nm to 400 nm) at the sample surface is 10 W/m^2 ± 0,5 W/m^2. The irradiance along the length of the test piece shall also be constant within ± 5 %. The UV irradiance shall be measured with a radiometer which conforms to ISO 4892-1. The reactor shall be shielded from external light if necessary.

6.5 Analyser of pollutants

A chemiluminescent NO_x analyser as specified in ISO 7996, or equivalent, shall be used for the accurate determination of NO_x concentration. The analyser shall be calibrated using calibration gases having zero NO_x and concentrations spanning the range of the test gas before testing. An ion chromatograph as specified in ISO 10304-1, or equivalent, shall be used for the analysis of nitrate and nitrite in water samples.

7 Test piece

The test piece shall be 49,5 mm ± 0,5 mm wide and 99,5 mm ± 0,5 mm long. It may be cut to these dimensions from a larger bulk material or coated sheet, or may be specially prepared for the test by coating a pre-cut substrate. The thickness of the test piece shall ideally be less than 5 mm, in order to minimise the photocatalytic contribution from the side faces. If thicker test pieces are to be tested, the side faces shall be sealed with an inert material before testing. The same requirements apply to filter-type materials.

8 Procedure

8.1 Pretreatment of test piece

8.1.1 Removal of organic matter

Irradiate the test piece with an ultraviolet lamp for at least 5 h to decompose residual organic matter on the test piece. The UV irradiance at the sample surface shall be high enough to secure complete decomposition of organic matter (10 W/m^2 or higher).

8.1.2 Washing with water

Immerse the test piece in deionised water for 2 h or more, remove it, and air-dry at room temperature. The test piece may be dried by heating within a temperature range that does not cause physical and chemical changes to the test piece (maximum 110 °C). Dryness is confirmed when a constant mass is reached. The method of drying and any observations, such as the appearance of sediment in the wash water, shall be recorded. The pH and the concentrations of nitrate and nitrite ions are measured by the method described in 8.3. If the test pieces are not to be tested immediately after the pretreatment, they shall be kept in an airtight container.

8.2 Pollutant-removal test

8.2.1 This test uses the following procedure to obtain the amount of the pollutant adsorbed under dark conditions, that removed by photoirradiation, and that desorbed after photoirradiation. Figure 3 shows a typical volume fraction change of nitric oxide (NO) and nitrogen dioxide (NO_2) during the test procedure.

8.2.2 Adjust the test gas supply beforehand so that it can stably supply the test gas containing 1,0 µl/l ± 0,05 µl/l of NO and 1,56 % ± 0,08 % of volume fraction of water vapour at 25,0 °C ± 2,5 °C. This water-vapour volume fraction is equivalent to a relative humidity of 50 % at 25 °C. The measurement of humidity shall be made using the procedure in ISO 4677-1. Measure and record the irradiance from the light source. Warm up and calibrate the pollutant analyser during this period.

8.2.3 Place the test piece in the photoreactor and attach the glass window after adjusting the space between the test piece and the window to 5,0 ± 0,5 mm. Check that the reactor is sealed by visual examination of the sealing material, such as an O-ring to tightly contact the glass window.

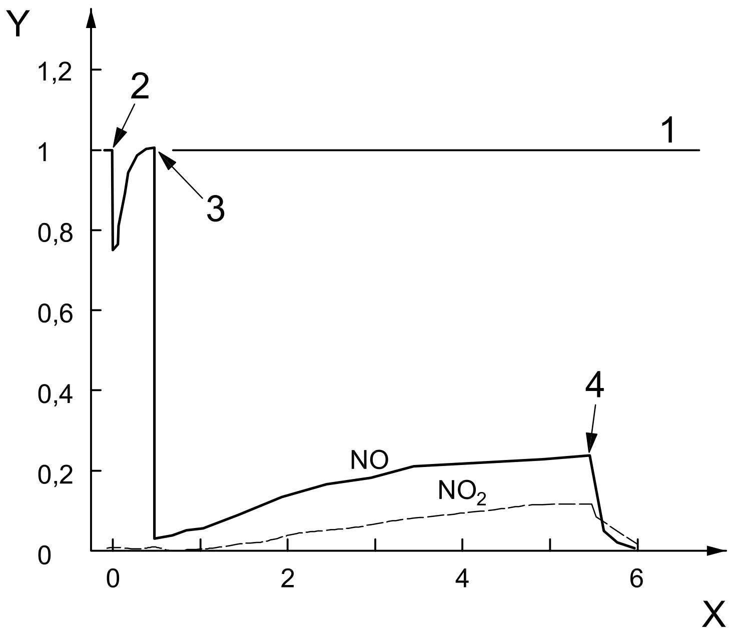
8.2.4 Allow the test gas to flow into the photoreactor, without photoirradiation. The flow rate shall be 3,0 l/min ± 0,15 l/min (equivalent to a velocity of approximately 0,2 m/s for the vessel dimensions described above). Continue the flow for 30 min and record the change in the volume fraction of NO and nitrogen dioxide

(NO_2) under dark conditions. If the NO_x volume fraction is less than 90 % of the volume fraction supplied after 30 min, continue until it exceeds this.

8.2.5 Maintain the gas flow and commence irradiation of the sample, and record the NO and NO_2 volume fractions under photoirradiation for 5 h.

8.2.6 Stop photoirradiation, switch to the zero-calibration gas under the same flow conditions and record the NO_x volume fraction for 30 min.

8.2.7 Stop the gas supply to the reactor and remove the test piece from the reactor.



Key

1 NO feed level

2 contact start

3 lights on

4 lights off, zero-calibration gas

X time (h)

Y NO, NO_2 (µl/l)

Figure 3 — Typical trace of NO_x concentration during the test operation

8.3 Elution test

8.3.1 Immerse the test piece in a known quantity of purified water (about 50 ml) for 1 h. Remove the test piece and record the volume of the water (hereinafter called Washing 1). Immerse the test piece again in a second known quantity of purified water for 1 h. Remove the test piece and record the volume of the water (Washing 2). Record any observations, such as discoloration of the washings or the presence of sediment.

NOTE 1 When the test piece absorbs water, the quantity of water can be increased appropriately.

NOTE 2 For test pieces presenting difficulties with elution, e.g. due to strong water absorption, a retest after drying the test piece can be performed omitting the procedure in 8.1.2, to show that the removal performance is constant for the repeated tests.

8.3.2 Measure the pH of Washings 1 and 2 in accordance with ISO 10523, together with the concentrations of nitrate and nitrite determined in accordance with ISO 10304-1.

9 Calculation

9.1 Calculation method

The test results shall be calculated as follows. The calculated values are usually rounded to one decimal place in accordance with ISO 31-0. The fractional recovery of nitrogen is rounded to two decimal places.

9.2 Amount of NO_x adsorption by the test piece

The amount of adsorption from the test gas is calculated by the following formula:

$$n_{\text{ads}} = (f / 22{,}4) \left\{ \int (\phi_{\text{NO}i} - \phi_{\text{NO}}) \mathrm{d}t - \int \phi_{\text{NO}_2} \mathrm{d}t \right\} \tag{1}$$

where

n_{ads} is the amount of NO_x adsorbed by the test piece (µmol);

f is the air-flow rate converted into that at the standard state (0 °C,101,3 kPa, and dry gas basis) (l/min);

$\phi_{\text{NO}i}$ is the supply volume fraction of nitric oxide (µl/l);

ϕ_{NO} is the nitric oxide volume fraction at the reactor exit (µl/l);

ϕ_{NO_2} is the nitrogen dioxide volume fraction at the reactor exit (µl/l);

The integrations are taken over the time, in minutes, of the adsorption operation, i.e. the time between *contact start* and *lights on* as shown in Figure 3.

9.3 Amount of NO removed by the test piece

The amount of NO removed from the test gas is calculated by the following formula:

$$n_{\text{NO}} = (f / 22{,}4) \int (\phi_{\text{NO}i} - \phi_{\text{NO}}) \mathrm{d}t \tag{2}$$

where

n_{NO} is the amount of NO removed by the test piece (µmol);

the other symbols are as defined in 9.2.

The integration is taken over the time, in minutes, for which the sample is illuminated, i.e. the time between *lights on* and *lights off* as shown in Figure 3.

9.4 Amount of NO_2 formed by the test piece

The amount of NO_2 formed is calculated by the following formula:

$$n_{\text{NO}_2} = (f / 22{,}4) \int \phi_{\text{NO}_2} \mathrm{d}t \tag{3}$$

where

n_{NO_2} is the amount of NO_2 formed by the test piece (µmol);

The other symbols are as defined in 9.2.

The integration is taken over the time, in minutes, for which the sample is illuminated, i.e. the time between *lights on* and *lights off* as shown in Figure 3.

9.5 Amount of NO_x desorbed from the test piece

The amount of NO_x desorbed is calculated by the following formula:

$$n_{des} = (f/22{,}4)\left\{\int \phi_{NO} dt + \int \phi_{NO_2} dt\right\} \quad (4)$$

where

n_{des} is the amount of NO_x desorbed from the test piece (μmol);

the other symbols are as defined in 9.2.

The integration is taken over the time, in minutes, between *lights off* and the end of the test as shown in Figure 3.

9.6 Net amount of NO_x removed by the test piece

The net amount of NO_x removed is calculated by the following formula:

$$n_{NO_x} = n_{ads} + n_{NO} - n_{NO_2} - n_{des} \quad (5)$$

where

n_{NO_x} is the amount of NO_x removal by the test piece (μmol);

the other symbols are as defined in 9.2 to 9.5.

9.7 Nitrogen eluted from the test piece

The amount of nitrogen eluted is calculated by the following formula:

$$n = n_{w1} + n_{w2} = V_{w1}\left(\rho_{NO_3^-,\,w1}/62 + \rho_{NO_2^-,\,w1}/46\right) + V_{w2}\left(\rho_{NO_3^-,\,w2}/62 + \rho_{NO_2^-,\,w2}/46\right) \quad (6)$$

where

n	is the amount of nitrogen eluted from the test piece (μmol);
V	is the volume of collected washings (ml);
$\rho_{NO_3^-}$	is the nitrate ion concentration in the eluent from the test piece (mg/l);
$\rho_{NO_2^-}$	is the nitrite ion concentration in the eluent from the test piece (mg/l);
w1, w2 (subscripts)	are the 1st and 2nd elutions, respectively.

9.8 Recovery of washing with water

The fractional recovery of nitrogen is calculated to two decimal places by the following formula:

$$\eta_{\mathrm{W}} = \left(n_{\mathrm{W1}} + n_{\mathrm{W2}}\right) / n_{\mathrm{NO}_x} \quad (7)$$

where

η_{W} is the fractional recovery of nitrogen;

the other symbols are as defined in 9.6 and 9.7.

10 Test report

The test report shall be in accordance with the reporting provisions of ISO/IEC 17025, and shall include the following information. Items g) and h) shall be reported for each test.

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 part of ISO 22197, i.e., determined in accordance with ISO 22197-1:2007.

d) Date of test, temperature, relative humidity, etc.

e) Description of the test piece (material, size, shape, etc.).

f) Description of testing equipment (specifications, etc.).

g) Testing conditions (kind of pollutant gas, supply concentration, water-vapour concentration, flow rate, kind of light source, irradiance, analyser and radiometer used, etc.).

h) The amounts of NO_x removed, NO_2 generated, NO_x adsorbed, and NO_x desorbed by the test piece, and fractional recovery by washing with water.

i) Any other matters of special importance, such as a change in the test piece noticed during the test.

Annex A
(informative)

Results of round-robin test

A round-robin test was undertaken between four collaborating laboratories. Each prepared the testing equipment including the photoreactor separately. The organizing laboratory visited each party during the test with a standard gas cylinder (about 50 µl/l NO/nitrogen), calibrated gas flowmeter and UV-A radiometer to check and calibrate its equipment. Each laboratory made four tests using the paper-based photocatalyst supplied. The original data are shown in Table A.1.

Table A.1 — Results of round-robin test

Unit: µmol

Laboratory (run No.)	NO removed	NO_x removed	NO_2 formed	Laboratory (run No.)	NO removed	NO_x removed	NO_2 Formed
A (1)	24,3	15,2	8,9	C (1)	24,3	13,8	10,5
A (2)	24,1	14,6	9,1	C (2)	24,2	14,5	9,6
A (3)	24,1	14,9	8,8	C (3)	24,2	14,7	9,4
A (4)	24,8	15,4	8,9	C (4)	24,3	14,5	9,7
B (1)	24,8	14,6	10,2	D (1)	25,2	15,5	9,7
B (2)	24,8	15,5	9,4	D (2)	24,7	15,3	9,4
B (3)	24,8	15,4	9,4	D (3)	24,2	15,0	9,2
B (4)	25,1	15,7	9,3	D (4)	24,7	15,2	9,5

The overall mean, repeatability standard deviation and reproducibility standard deviation as computed in accordance with ISO 5725-2 are summarized in Table A.2.

Table A.2 — Statistical data obtained in accordance with ISO 5725-2

Unit: µmol

	Overall mean	Repeatability standard deviation	Reproducibility standard deviation
NO removed	24,54	0,28	0,38
NO_x removed	14,99	0,37	0,53
NO_2 formed	9,44	0,33	0,46

For the light source, some laboratories used a BL fluorescent lamp, while others used a BLB fluorescent lamp. However, no significant difference was observed as long as the UV-A irradiance was set at the specified value. In further tests, the NO_x removal results obtained with different photocatalyst samples, such as tile, cement-coated plate, painted aluminum plate, etc. varied from < 1,0 µmol to 20,0 µmol, which indicated that this method can differentiate the samples with different photocatalytic performance.

Bibliography

[1] FUJISHIMA, A., HASHIMOTO, K. and WATANABE, T. *TiO_2 Photocatalysis. Fundamentals and Applications*, BKC Inc., Tokyo (1999)

[2] Japanese Industrial Standard Committee, *Photocatalytic materials – Air purification test procedure*, TR Z 0018, Japanese Standard Association (2002)

[3] IBUSUKI, T. and TAKEUCHI, K. Removal of low concentration nitrogen oxides through photoassisted heterogeneous catalysis, *J. Mol. Catal.*, **88**, pp. 93-102 (1994)

[4] TAKEUCHI, K. Purification and remediation of ambient air by photocatalysis *(in Japanese)*, *J. Jpn. Soc. Atmos. Environ.*, **33**(3), pp. 139–150 (1998)

ICS 81.060.30

Price based on 12 pages