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

Part 1:
Removal of nitric oxide

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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*.

A list of all parts in the ISO 17168 series can be found on the ISO website.

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.

Introduction

Photocatalyst is a substance that performs decomposition and removal of contaminants, self-cleaning, antifogging, deodorization and antibacterial actions under photoirradiation. Its application has expanded considerably in recent years. The application of photocatalysts for indoor spaces has increasingly been sought as a solution to indoor environmental problems. Since conventional photocatalysts are responsive only to ultraviolet light, studies have been made to develop an indoor-light-active photocatalyst that makes effective use of indoor light, which room lights mainly emit, and thus demonstrates high photocatalytic performance indoors. The development has recently led to the commercialization of various indoor-light-active photocatalytic products, and there has been demand for the establishment of test methods to evaluate the performance of this type of photocatalyst.

This document is based on ISO 22197-1, a test method for air purification performance of photocatalytic materials under UV light, and is intended to provide a testing method to determine the performance of indoor-light-active photocatalytic materials with regards to the removal of nitric oxide, enabling swift distribution of photocatalytic products and thus contributing to a safe and clean environment.

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

Part 1:
Removal of nitric oxide

1 Scope

This document specifies a test method for the determination of the air purification performance, with regards to removal of nitric oxide, 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 from indoor light.

This document is intended for use with different kinds of materials, such as construction materials in flat sheet, board or plate shape, which are the basic forms of materials for various applications. This document also applies to materials in honeycomb form and to plastic or paper materials containing ceramic microcrystals and composites. This document does not apply to certain test pieces that contain a large amount of adsorbent, due to unattained adsorption equilibrium. This document 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.

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

ISO 10304-1, *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, *Water quality — Determination of pH*

ISO 14605, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Light source for testing semiconducting photocatalytic materials used under indoor lighting environment*

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

ISO 80000-1, *Quantities and units — Part 1: General*

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 oxidation and reduction reactions under photoirradiation, including decomposition and removal of air and water contaminants, deodorization, and antibacterial, self-cleaning and antifogging actions; a type of functional fine ceramics

3.2
indoor light
light from an artificial light source for general lighting service that does not include sunlight

3.3
indoor-light-active photocatalyst
photocatalyst (3.1) that performs under indoor light irradiation

3.4
photocatalytic material
material in which or on which the photocatalyst is added by, for example, coating, impregnation or mixing

Note 1 to entry: Photocatalytic materials are intended primarily for use as building and road construction materials to obtain the above-mentioned functions.

3.5
zero-calibration gas
air in which common pollutants are below 0,01 µl/l

Note 1 to entry: Zero-calibration gas is prepared from indoor air using a laboratory air purification system, or supplied as synthetic air in a gas cylinder.

3.6
standard gas
diluted gas of known concentration supplied in cylinders and certified by an accredited laboratory

3.7
test gas
mixture of air and pollutant(s) of known concentration prepared from the *standard gas* (3.6) or the *zero-calibration gas* (3.5), or from the *standard gas* (3.6) only, to be used for the performance test of a *photocatalytic material* (3.4)

3.8
purified water
water with a specific conductivity lower than 1 µS/cm, prepared by the ion exchange method or distillation

3.9
dark conditions
test conditions of no light illumination by the light source for testing and room lighting

Note 1 to entry: Usually the test gas is supplied for comparison with the illuminated reaction.

4 Symbols

f	air-flow rate converted into that at the standard state (0 °C, 101,3 kPa) (l/min)
ϕ_{NO}	nitric oxide concentration at the reactor exit (μl/l)
$\phi_{\mathrm{NO}i}$	supply concentration of nitric oxide (μl/l)
ϕ_{NO2}	nitrogen dioxide concentration at the reactor exit (μl/l)
ϕ_{NO_x}	concentration of nitrogen oxides (ϕ_{NO} + ϕ_{NO2}) at the reactor exit (μl/l)
$\rho_{\mathrm{NO2-}}$	nitrite ion concentration in the eluent from the test piece (mg/l)
$\rho_{\mathrm{NO3-}}$	nitrate ion concentration in the eluent from the test piece (mg/l)
t	time of adsorption, removal or desorption operation (min)
n_{ads}	amount of NO_x adsorbed by the test piece (μmol)
n_{des}	amount of NO_x desorbed from the test piece (μmol)
n_{NO}	amount of NO removed by the test piece (μmol)
n_{NO2}	amount of NO_2 formed by the test piece (μmol)
n_{NO_x}	amount of NO_x removed by the test piece (μmol)
n_{w}	amount of nitrogen eluted from the test piece (μmol) [w_1, w_2 are the first and second elution, respectively]
V_{w}	volume of collected washings (ml) [w_1, w_2 are the first and second elution, respectively]
η_{w}	fractional recovery of nitrogen

5 Principle

This document deals with 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 indoor light[2]. Nitric oxide (NO) is chosen as a typical air pollutant that gives non-volatile products on the photocatalyst[2]. The test piece, placed in a flow-type photoreactor, is activated by indoor-light 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 gives information about the ease of regeneration and material balance of the pollutants.

The results of an interlaboratory test are given in Annex A.

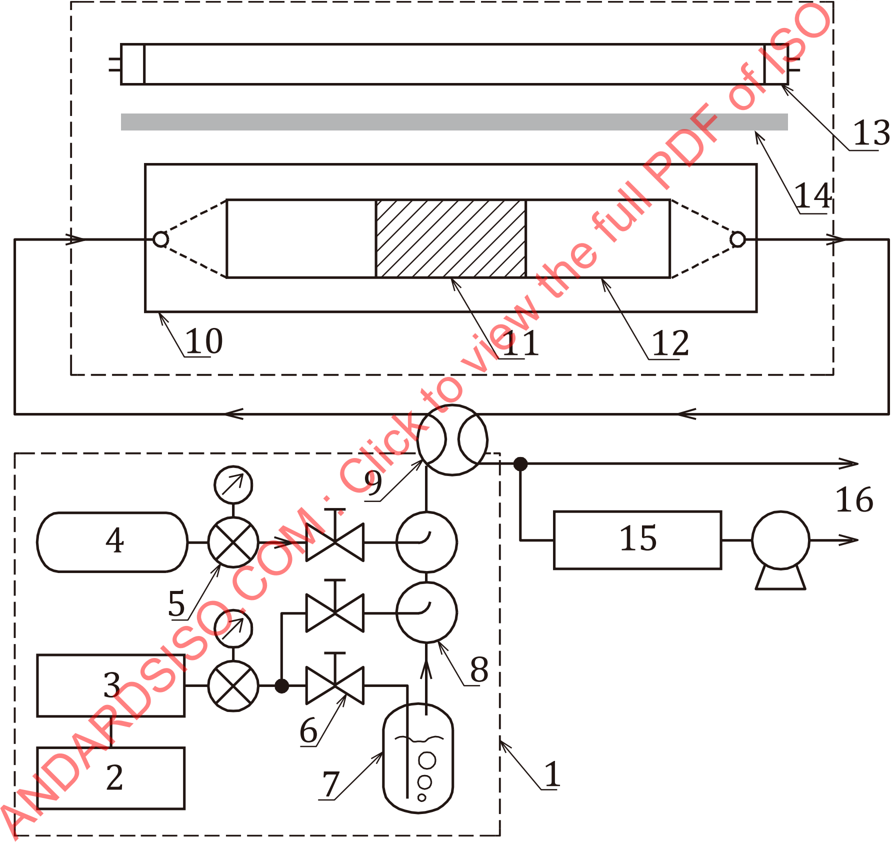
6 Apparatus

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, a UV sharp cut-off filter and pollutant measurement equipment. Since low concentrations of pollutants are to be tested, the system shall be constructed with materials of low adsorption, for example acrylic resin, stainless steel, glass and fluorocarbon polymers. An example of a testing 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 and so on. The flow rate of each gas should be within 5,0 % of the designated value, which is easily attained by using thermal mass-flow controllers with knowledge of calibrated gas flow rate and temperature (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 document is that converted to the standard state (0 °C, 101,3 kPa). The standard NO gas, normally balanced with nitrogen in a cylinder, shall have a concentration of 30 – 100 µl/l, because the oxidation of NO to NO_2 upon mixing with purified air becomes prominent with a higher concentration of NO.



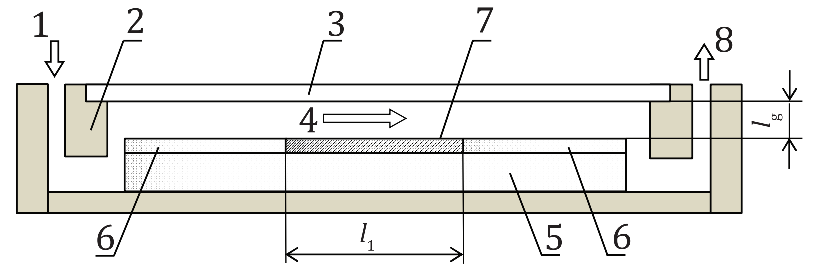
Key

1	test gas supply	9	four-way valve
2	air compressor	10	photoreactor
3	air-purification system	11	test piece
4	standard gas (pollutant)	12	air-tight optical window
5	pressure regulator with a gauge	13	light source
6	mass-flow controller	14	sharp cut-off filter
7	humidifier	15	analyser
8	gas mixer	16	vent

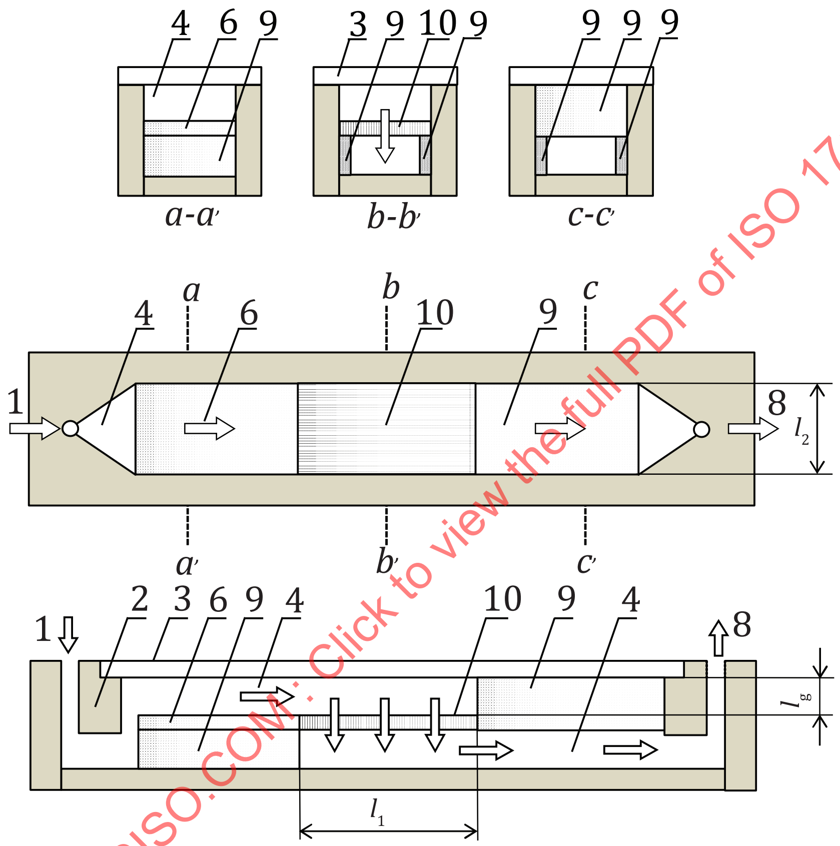
Figure 1 — A schematic of the test equipment

6.3 Photoreactor

The photoreactor holds a planar test piece within a 50 mm-wide trough, with its surface parallel to an air-tight 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 thickness, as shown in Figure 2a). 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 2b)]. Quartz or borosilicate glass that absorbs minimal light at wavelengths longer than 300 nm shall be used for the window.



a) For flat test pieces



b) For filter-type test pieces

Test piece length l_1	Test piece width l_2	Air layer thickness l_g
99,0 ± 1,0 mm	49,0 ± 1,0 mm	5,0 ± 0,5 mm

Key

1	test gas inlet
2	baffle
3	air-tight optical window
4	flow channel
5	height-adjusting plate
6	auxiliary plate
7	test piece (flat-type)
8	test gas outlet
9	test piece holder
10	test piece (filter-type)

Figure 2 — Cross-sectional views of photoreactor

6.4 Light source

A cool white halophosphate fluorescent lamp and a UV sharp cut-off filter specified in ISO 14605 shall be used. The test piece shall be illuminated 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 illuminance at the test piece surface is 6 000 lx ± 300 lx. The irradiance along the length of the test piece shall also be constant within ± 5 %. The illuminance shall be measured with an illuminance meter which conforms to ISO 14605. The reactor and light source shall be shielded from external light. The parts around the light source, such as luminaire and shielding device, shall have small reflectance, or flat spectral reflectance over the wavelength range of indoor light.

6.5 UV sharp cut-off filter

The UV sharp cut-off filter shall remove a small amount of UV light radiated from the light source. The transmittance of the UV sharp cut-off filter shall be less than 0,1 % (wavelength < 365 nm), less than 1 % (at 380 nm) and higher than 80 % (400 nm < wavelength < 780 nm), and the wavelength where the transmittance is half of the average transmittance between 400 nm and 780 nm is located at 390 nm ± 5 nm.

6.6 Analyser of pollutants

A chemiluminescent NO_x analyser as specified in ISO 7996, or equivalent, shall be used for accurate determination of NO_x concentration. The analyser shall be calibrated using calibration gases with zero NO_x and concentrations spanning the range of the test gas before testing. An ion chromatograph as described 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 a flat material or a honeycomb filter 49,0 mm ± 1,0 mm wide and 99,0 mm ± 1,0 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 minimize 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 honeycomb test piece shall not be thicker than 20 mm.

8 Procedure

8.1 General aspects

The test procedure consists of pretreatment of a test piece, adsorption process in the dark, and measurements of removal quantity and percentage of nitric oxide under photoirradiation. An example of concentration change of NO_x during the test is shown in Figure 3.

8.2 Pretreatment of test piece

8.2.1 The test piece shall normally be pretreated as specified in 8.2.1 and 8.2.2 in this order. If any smear is present, removal of organic matter (8.2.2) shall be performed before washing with water (8.2.2).

8.2.2 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 or 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 8.4. If the test pieces are not to be tested immediately after the pretreatment, they shall be kept in an airtight container.

8.2.3 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).

8.3 Pollutant removal test

8.3.1 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 concentration change of nitric oxide (NO) and nitrogen dioxide (NO_2) during the test procedure.

8.3.2 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 concentration is equivalent to a relative humidity of 50 % at 25 °C. The relative humidity shall be measured using a hygrometer (with accuracy of ± 3 % RH) that has been calibrated by a method traceable to a certified reference standard. Measure and record the illuminance from the light source. Warm up and calibrate the pollutant analyser during this period.

8.3.3 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. If necessary, height-adjusting plates are used to adjust the difference of the height of the front part of the test piece and that of the rear part to be within 1,0 mm based on the top of the test piece. Check that the reactor is sealed by visual examination of the sealing material such as an O-ring to tightly connect to the glass window.

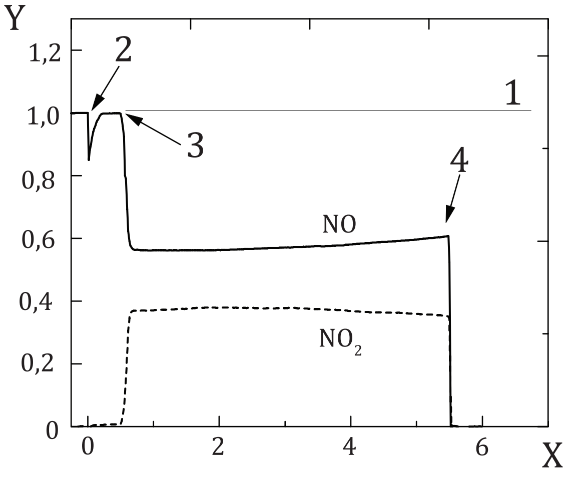
8.3.4 Place the UV sharp cut-off filter at the space between the light source and the photoreactor.

8.3.5 Flow the test gas 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 concentrations of NO and nitrogen dioxide (NO_2) under dark conditions. If the NO_x concentration is less than 90 % of the concentration supplied after 30 min, continue until it exceeds this percentage.

8.3.6 Maintain the gas flow and commence irradiation of the sample, recording the NO and NO_2 concentrations under photoirradiation for 5 h continuously.

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

8.3.8 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

8.4 Elution test

8.4.1 Immerse the test piece in a known quantity of purified water (ca. 50 ml) for 1 h. Remove the test piece and record the volume of the water (hereafter called Washing 1). Immerse the test piece again in a second known quantity of purified water for 1 h. Remove the 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, for example due to strong water absorption, a retest after drying the test piece can be performed, omitting the procedure in 8.2.2 to show that the removal performance is constant for the repeated tests.

8.4.2 Measure the pH of washings 1 and 2 according to 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 specified in 9.2 to 9.8. The calculated values are usually rounded to one decimal place according to ISO 80000-1. 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 using Formula (1).

$$n_{\text{ads}} = (f / 22{,}4)\left[\int(\phi_{\text{NO}i} - \phi_{\text{NO}})\,\mathrm{d}t - \int\phi_{\text{NO2}}\,\mathrm{d}t\right] \tag{1}$$

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) (l/min);

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

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

ϕ_{NO2} is the nitrogen dioxide concentration 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 using Formula (2).

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

where n_{NO} is the amount of NO removed by the test piece (µmol). The 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 using Formula (3).

$$n_{\text{NO2}} = (f / 22{,}4)\int\phi_{\text{NO2}}\,\mathrm{d}t \tag{3}$$

where n_{NO2} is the amount of NO$_2$ formed by the test piece (µmol). 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 using Formula (4).

$$n_{\text{des}} = (f / 22{,}4)\left(\int\phi_{\text{NO}}\,\mathrm{d}t + \int\phi_{\text{NO2}}\,\mathrm{d}t\right) \tag{4}$$

where n_{des} is the amount of NO$_x$ desorbed from the test piece (µmol). 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 using Formula (5).

$$n_{\mathrm{NO}_x} = n_{\mathrm{ads}} + n_{\mathrm{NO}} - n_{\mathrm{NO2}} - n_{\mathrm{des}} \tag{5}$$

where n_{NO_x} is the amount of NO$_x$ removal by the test piece (µmol).

9.7 Nitrogen eluted from the test piece

The amount of nitrogen eluted is calculated using Formula (6).

$$n = n_{\mathrm{w1}} + n_{\mathrm{w2}} = V_{\mathrm{w1}}\left(\rho_{\mathrm{NO3\text{-},w1}}/62 + \rho_{\mathrm{NO2\text{-},w1}}/46\right) + V_{\mathrm{w2}}\left(\rho_{\mathrm{NO3\text{-},w2}}/62 + \rho_{\mathrm{NO2\text{-},w2}}/46\right) \tag{6}$$

where

n	is the nitrogen from the test piece (µmol);
V	is the volume of collected washings (ml);
$\rho_{\mathrm{NO3\text{-}}}$	is the nitrate ion concentration in the eluent from the test piece (mg/l);
$\rho_{\mathrm{NO2\text{-}}}$	is the nitrite ion concentration in the eluent from the test piece (mg/ l);
w1, w2 (subscripts)	are the first and second elution, respectively.

9.8 Recovery of washing with water

The fractional recovery of nitrogen is calculated to two decimal places using Formula (7).

$$\eta_{\mathrm{w}} = \left(n_{\mathrm{w1}} + n_{\mathrm{w2}}\right)/n_{\mathrm{NO}_x} \tag{7}$$

where η_{w} is the fractional recovery of nitrogen.

10 Test method for test pieces with lower performance

When the removal quantity in Formula (5) is less than 2 µmol and a more certain result is demanded, both the number of test pieces and the flow rate of test gas may be altered simultaneously as shown in Table 1. However, the amounts of NO$_x$ removed, NO$_2$ generated, NO$_x$ adsorbed and NO$_x$ desorbed which appear in the test report shall be half of the values calculated in Formula (2) to Formula (5). In cases where the removal quantity is less than 0,25 µmol, this shall be indicated.

Table 1 — Alternative test conditions

Alterable test conditions	Value after change
Flow rate of test gas	1,5 ± 0,075 l/min
Number of test pieces	Two pieces in series (surface of 50 mm × 200 mm)

11 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 test establishment;