



BSI Standards Publication

Photocatalysis — Continuous flow test methods

Part 1: Determination of the degradation of nitric oxide (NO) in the air by photocatalytic materials

National foreword

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English Version

**Photocatalysis - Continuous flow test methods - Part 1:
Determination of the degradation of nitric oxide (NO) in
the air by photocatalytic materials**

Photocatalyse - Méthodes d'essai en flux continu -
Partie 1 : Détermination de la dégradation du
monoxyde d'azote (NO) dans l'air par des matériaux
photocatalytiques

Photokatalyse - Prüfverfahren mit kontinuierlichem
Durchfluss - Teil 1: Bestimmung des Abbaus von
Stickstoffmonoxid (NO) aus der Luft durch
photokatalytische Werkstoffe

This Technical Specification (CEN/TS) was approved by CEN on 8 August 2016 for provisional application.

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European foreword

This document (CEN/TS 16980-1:2016) has been prepared by Technical Committee CEN/TC 386 "Photocatalysis", the secretariat of which is held by AFNOR.

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This document is part of the CEN/TS 16980 series that consists of the following parts:

- Part 1: *Determination of the degradation of nitric oxide (NO) in the air by photocatalytic materials*
- Part 2: [To be determined].

According to the CEN/CENELEC Internal Regulations, the national standards organisations of the following countries are bound to announce this Technical Specification: 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, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom

1 Scope

This standard describes a method for assessing the performance of photocatalytic inorganic materials contained in cement mortars and/or limes or ceramic-based matrices, paints or materials deposited as thin films or coatings on a variety of substrates for the photocatalytic abatement of nitric oxide in the gas phase. This method is not suitable for the assessment of samples to be applied with flow perpendicular to the surface or flow permeating the surface itself as polymeric and paper filters, honeycomb structures and suchlike.

The performance for the photocatalytic sample under test is evaluated by measuring the degradation rate of nitric oxide (NO) using the method described herein. The photocatalytic abatement rate is calculated from the observed rate by eliminating the effects of mass transfer. The intrinsic photocatalytic abatement rate is an intrinsic property of the material tested and makes it possible to distinguish the photocatalytic activities of various products with an absolute scale defined with physical and engineering meaning.

For the measurements and calculations described in this standard the concentration of nitrogen oxides (NO_x) is defined as the stoichiometric sum of nitric oxide (NO) and nitrogen dioxide (NO₂).

Safety statement

Persons using this document should be familiar with the normal laboratory practice, if applicable. This document cannot address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any regulatory conditions.

Environmental statement

It is understood that some of the material permitted in this standard may have negative environmental impact. As technological advantages lead to better alternatives for these materials, they will be eliminated from this standard to the extent possible.

At the end of the test, the user of the standard will take care to carry out an appropriate disposal of the wastes, according to local regulation.

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 16599:2014, *Photocatalysis - Irradiation conditions for testing photocatalytic properties of semiconducting materials and the measurement of these conditions*

EN ISO 9169, *Air quality - Definition and determination of performance characteristics of an automatic measuring system (ISO 9169)*

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

3 Terms, definitions and abbreviations

3.1 Terms and definitions

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

3.1.1

concentration of nitrogen oxides

NO_x

stoichiometric sum of nitric oxide (NO) and nitrogen dioxide (NO₂)

Note 1 to entry: For grade 999 nitrogen or air: the purity of the gas should be equal at least to 99,9 %.

3.1.2

photocatalyst

Catalyst able to produce, upon absorption of light, chemical transformations of the reaction partners

Note 1 to entry: The excited state of the photocatalyst repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of such interactions.

3.1.3

photocatalytic materials

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

3.2 Abbreviations

CSTR	Continuous Stirred-Tank Reactor
C^{IN}	concentration at reactor inlet
$C^{\text{OUT,DARK}}$	concentration of NO and NO ₂ at reactor outlet under stable conditions in the dark (no illumination)
$C^{\text{OUT,light}}$	concentration at reactor outlet under stable conditions with illumination (lamp on)
$C_{\text{NO}}^{\text{IN}}$	concentration of NO at reactor inlet
$C_{\text{NO}_2}^{\text{IN}}$	concentration of NO ₂ at reactor inlet
$C_{\text{NO}}^{\text{OUT,DARK}}$	concentration of NO at reactor outlet under stable conditions in the dark (no illumination) without sample
$C_{\text{NO}_2}^{\text{OUT,DARK}}$	concentration of NO ₂ at reactor outlet under stable conditions in the dark (no illumination) without sample
$C_{\text{NO,S}}^{\text{OUT,DARK}}$	concentration of NO at reactor outlet under stable conditions in the dark (no illumination) in presence of sample
$C_{\text{NO}_2,S}^{\text{OUT,DARK}}$	concentration of NO ₂ at reactor outlet under stable conditions in the dark (no illumination) in presence of sample
$C_{\text{NO}}^{\text{OUT,LIGHT}}$	concentration of NO at reactor outlet under stable conditions with illumination (lamp on) without sample
$C_{\text{NO},0}^{\text{OUT,LIGHT}}$	concentration of NO at reactor outlet under illumination of sample measured at fan speed at nominal voltage V_0

$C_{\text{NO}_2,0}^{\text{OUT,LIGHT}}$	concentration NO_2 at reactor outlet under illumination of sample measured at fan speed nominal voltage V_0
F	Flow
$F_{v,i}$	fan flow at i^{th} potential
I	irradiance
LED	light emitting diodes
MM	molecular mass
P	pressure in atmosphere
PTFE	Polytetrafluoroethylene
R	ideal gas constant
RH	gas relative humidity at 25 °C inside the reactor
$\eta_{\text{NO}}^{\text{dark}}$	conversion of NO in the dark
$\eta_{\text{NO}_2}^{\text{dark}}$	conversion to NO_2 in the dark
$\eta_{\text{NO,lamp}}^{\text{PHOTO}}$	conversion of NO under illumination without sample
$\eta_{\text{NO},i}^{\text{total}}$	conversion of NO measured with fan speed at i^{th} potential
$\eta_{\text{NO}_2,i}^{\text{total}}$	conversion to NO_2 measured with fan speed at i^{th} potential
$r_{\text{NO},i}^{\text{photo}}$	NO abatement rate at each fan speed ($i = 0..n$)
$r_{\text{NO}_2,i}^{\text{photo}}$	NO_2 photocatalytic production rate at each fan speed ($i = 0..n$)
$r_{\text{NO}_x,i}^{\text{photo}}$	NO_x abatement rate correspond to NO abatement rate minus NO_2 photocatalytic production rate
$r_{\text{NO}}^{\text{photoCAT}}$	NO photocatalytic degradation rate intrinsic to the surface of the material, after removing the mass transfer limitations
$r_{\text{NO}_x}^{\text{photoCAT}}$	NO_x photocatalytic degradation rate intrinsic to the surface of the material, after removing the mass transfer limitations
UV-A	ultraviolet with wavelength (λ) situated between 315 nm and 400 nm (IUPAC)
V_0	fan nominal operating potential (in Volt)
V_{min}	fan minimum operating potential (in Volt) set by the manufacturer
S	Sample
T	temperature in Kelvin
t_{stab}	time to reach the stability of NO concentration
UV	UltraViolet
Vr	Reactor net volume

4 Principle

The method consists in measuring the photocatalytic abatement of nitric oxide (NO) by photocatalytic materials as specified in paragraph 1 using a Continuous Stirred-Tank Reactor (CSTR) with flow tangential to the sample. Information on the theory is reported in the specialized literature (Minero et al. 2013). The residual NO and NO_x concentration at the CSTR outlet is measured by a chemiluminescence analyser (ISO 7996).

The photocatalytic activity test is carried out using chromatographic grade air, also obtained by mixing pure gases, to which NO is added in such an amount as to simulate a high degree of air pollution. The NO concentration is set to $(0,50 \pm 0,05)$ ppmv.

5 Interferences

Any measurement interferences are reported in the technical specifications of the chemiluminescence analyser. As what is measured are all species that can be converted by reduction to NO, NO₂ concentration is here defined as $[NO_2] = [NO_x] - [NO]$. For interferences on chemiluminescence detection, see Winer et al. (1974).

6 Apparatus

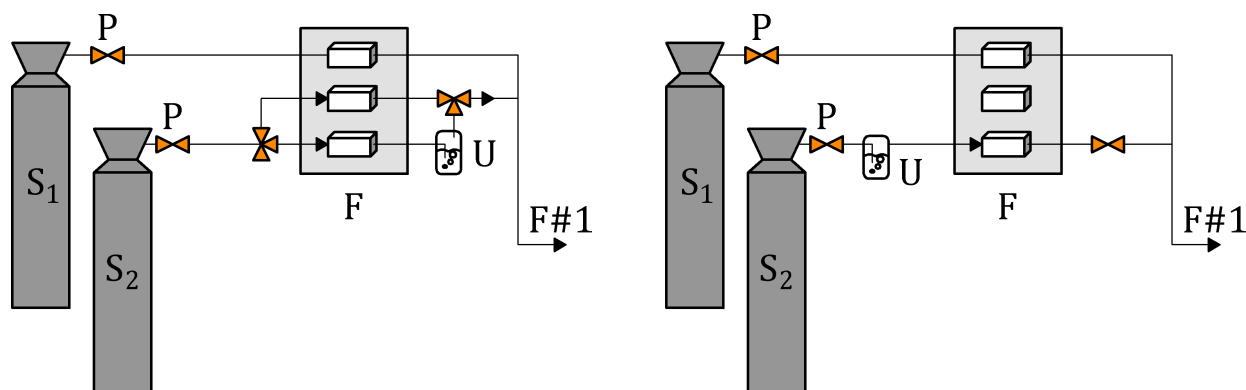
The test apparatus shall consist of the following main components.

6.1 Gas mixture preparation system.

The system used for preparing the reaction mixture is shown in Figure 1.

The mass flow controllers, calibrated and traceable, shall ensure a maximum flow consistent with that needed for a correct test execution. To ensure the necessary accuracy, the flow shall not exceed 90 % of the rated full scale.

As an example, to obtain the gas mixture only gases of chromatographic grade or higher purity shall be used. Instead of dry air cylinders, two separate cylinders of pure N₂ and O₂ can be used at the inlet of mass-flow controllers, adjusted so as to produce a mixture consisting of 20,8 % of O₂ and 79,2 % of N₂. The NO concentration to flow #1 is set to $(0,50 \pm 0,05)$ ppmv.



a) Relative humidity is set by regulating the flow to U, which is downstream to F

b) Relative humidity is set by regulating the pressure before U and F

Key

S_1 source of nitric oxide NO diluted in N_2

S_2 cylinder of air (chromatographic grade) or, alternatively, individual cylinders of N_2 and O_2 (chromatographic grade)

F flow controller with mass-flow controllers (2 or 3)

P pressure regulators with low-pressure manometers

U humidifier maintained at controlled temperature

$F\#1$ flow entering the reactor

Figure 1 — Gas mixture preparation system

The humidification of the gas mixture can be obtained with two different configurations:

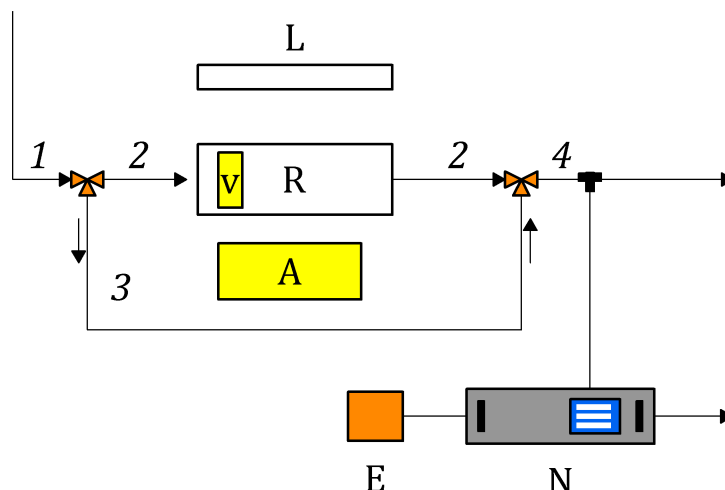
- using two mass flow controllers regulating the flow to U, as in Figure 1 left;
- using one mass flow controller regulating the pressure on U, as in Figure 1 right.

The gas mixture preparation system shall ensure a relative humidity of $(40 \pm 5) \%$ inside the CSTR reactor. The relative humidity shall be measured either inside the reactor R (Figure 2) or immediately at its outlet on flow 2 of Figure 2 by means of a hygro-thermometer.

6.2 Illumination and measuring system:

6.2.1 General:

The light source arrangement and the measuring system are shown in Figure 2.



Key

- R* reaction chamber, Continuous Stirred-Tank Reactor (CSTR) type
- V* fan
- A* power supply of fan *V*
- N* NO/NO₂ chemiluminescence analyser
- E* processing/logging unit
- L* illumination system
- 1, 2, 3, 4 flow paths, with valves and tubing

Figure 2 — Illumination, reaction and measuring system

All parts of the test apparatus, including connections and pipes, which come into contact with the nitric oxide mixture shall be made of chemically inert materials. For pipes and connections PTFE is recommended. The pipes of paths 1, 2, 3, 4 and the related connections shall have an outer diameter of 6 mm (1/4") and inner clearance of at least 4 mm to avoid overpressures that may affect the gas concentration inside the reactor.

Temperature shall be measured and recorded inside the reactor during the test or immediately at its outlet on flow 2 by means of a hygro-thermometer. The gas temperature inside the reaction chamber shall be $(25 \pm 5) ^\circ\text{C}$.

6.2.2 Illumination system *L*:

The illumination source shall consist of any lamp able to excite the photocatalyst (quartz mercury vapor lamps, UV-A fluorescent lamps, Xenon lamps, LEDs, lamps consisting of a metal vapor element combined with tungsten incandescence elements, etc.) as specified in the Technical Specification CEN/TS 16599.

The illumination system shall provide an average irradiance to the test sample surface within the range of wavelengths that are mostly adsorbed by the photocatalyst, equal to $(10,0 \pm 5 \%) \text{ W/m}^2$.

The geometry of the illumination system shall be such that uniform illumination of the sample surface is ensured. The illumination is considered uniform if 5 independent measurements performed on the surface (one in centre position and the other four in positions perpendicular to each other and next to the edge of the sample) show a percentage variation compared to the average value of less than 10 %. The control of the uniformity of illumination and average irradiance shall be repeated each time the system geometry changes (position of the lamp or any filters or reflectors, sample position, etc.).

Irradiance shall be measured by placing a radiometric sensor inside the reaction chamber in the same position occupied by the sample in order to measure real irradiance at its surface. A second measuring sensor for the control of source stability can be positioned outside the reaction chamber, provided that it has been calibrated with a reference radiometric sensor placed inside the reactor. Irradiance can be

measured continuously during the test or, alternatively, just before the beginning of the test and immediately after its conclusion. The irradiance values shall be measured only after the lamp intensity has stabilized as a result of its warming-up (typically 10 min after being turned on). The irradiance value as measured shall be recorded as average value in the test report.

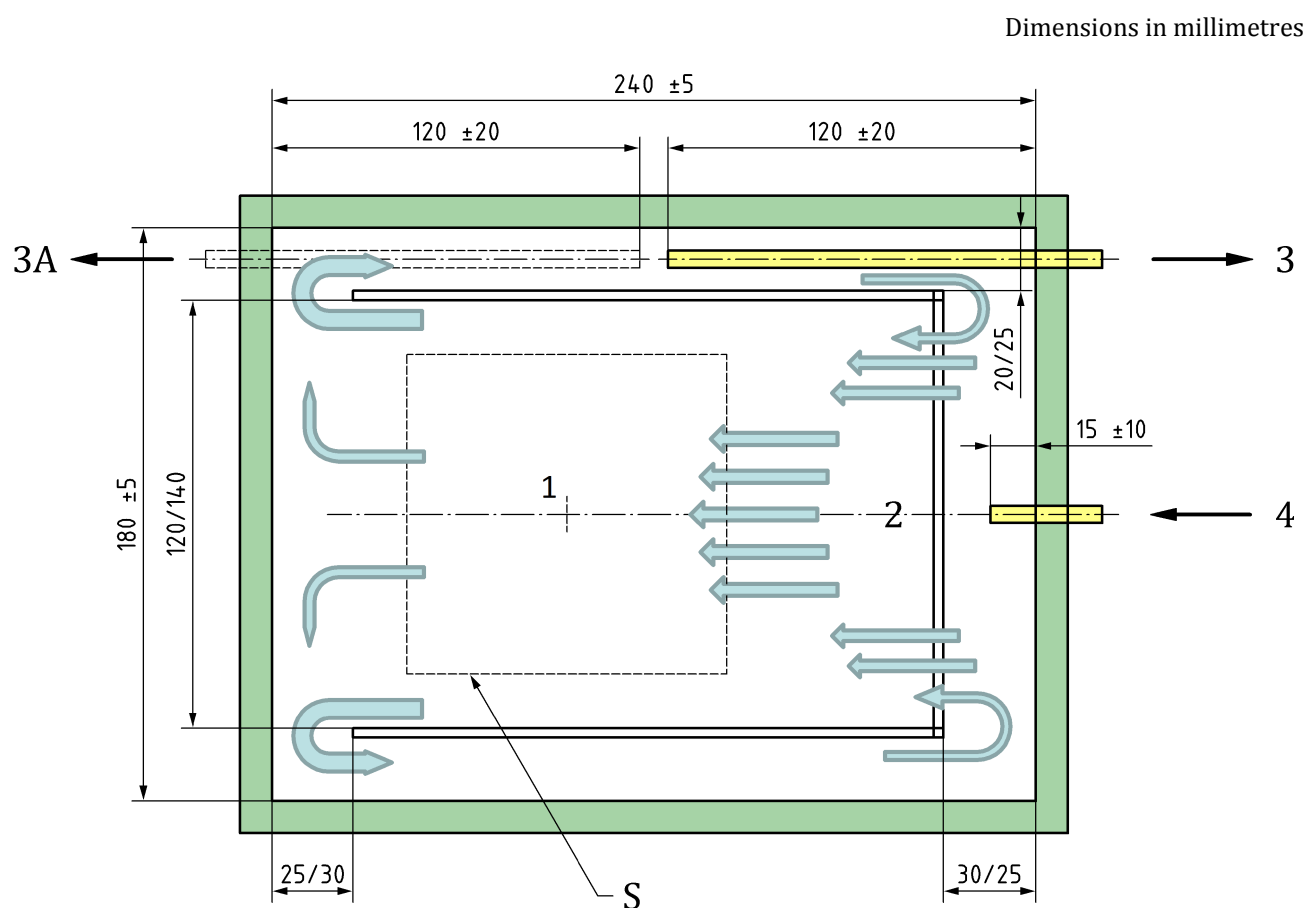
The radiometer used for the measurement shall have been previously calibrated by means of a spectroradiometer, which in turn has been previously calibrated by means of standard sources.

In order to avoid decomposition by direct photolysis of NO, the integrated irradiance at $\lambda < 340$ nm shall be less than $0,5 \text{ W/m}^2$. The direct NO photolysis rate shall be checked by performing the test using the empty reactor, where standard NO concentration ($0,5 \text{ ppmv}$) is introduced and the reactor outlet concentration is measured according to paragraph 8.3.a. For example, in the case of a photocatalyst consisting of pure TiO_2 , the illumination system that uses a mercury lamp shall be such as to ensure the surface of the sample receives a UV irradiance ($\lambda < 400 \text{ nm}$) mainly composed of the line at 365 nm of mercury, and an integrated irradiance for $\lambda < 340 \text{ nm}$ of less than $0,5 \text{ W/m}^2$.

The spectrum of the lamp used shall be acquired and reported in the test report, because the analysis result depends significantly on the lamp type used.

6.2.3 Reaction chamber R:

A schematic of the reaction chamber is given in Figure 3.



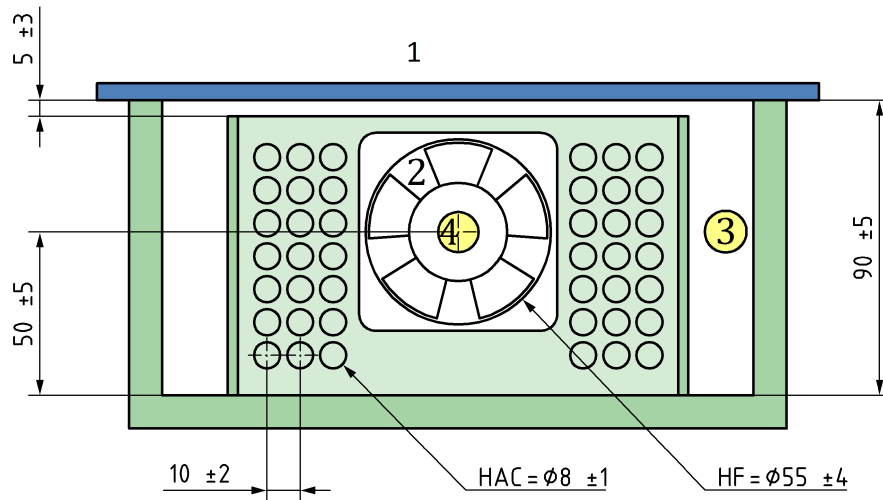
- Key**
- 1, S sample
 - 2 fan
 - 3 outflow
 - 3A gas output (alternative)
 - 4 inflow

Figure 3 — Top view of the CSTR reaction chamber, with dimensional details and indication of flows for thorough mixing and location of the sampling point

Other dimensional details of the reaction chamber with related sample positions are also shown in the Figures 4-5 below.

The reaction chamber shall be built with NO inert materials, i.e. glass, polymethylmethacrylate or other inert plastic materials. The chamber shall be gas-tight. On top, the chamber shall be provided with a flat window that is transparent to the light emitted by the illumination system and vertically incident to the sample. This flat window, transparent to the wavelengths used (e.g. made up of borosilicate glass) shall be (3-4) mm thick to ensure sufficient strength and also removable to allow for sample positioning.

Dimensions in millimetres

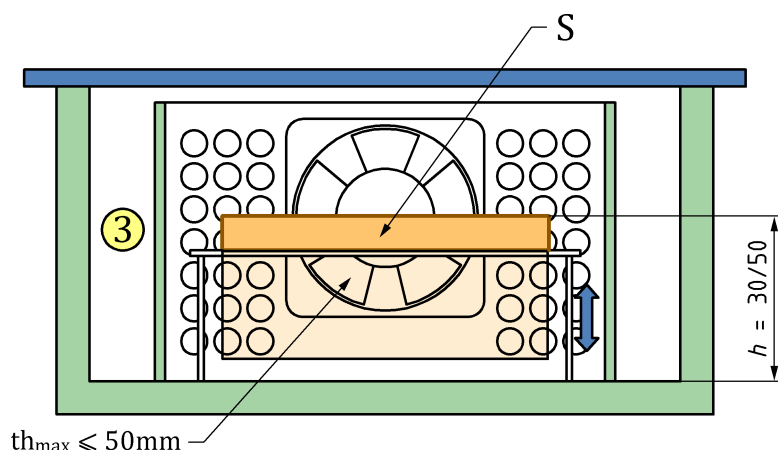


Key

- HAC holes for air circulation
- HF hole for a fan with $\phi = 60$ mm
- 1 top window
- 2 fan 60 mm nominal
- 3 gas outlet
- 4 gas inlet

Figure 4 — Side view (back of fan side) of the CSTR reactor

Dimensions in millimetres



Key

- 3 gas outlet
- h distance to the surface of the sample
- S sample
- th_{max} sample on the support, any thickness, max 50mm

Figure 5 — Side view (fan front side) of reactor CSTR, with indications of sample position

The reaction chamber shall comply with the dimensions shown in Figures 3 to 5. Considering the volumes occupied by internal barriers, fan, sample and sample support, the total net volume is (2,8 to 3,5) dm³. This volume is not critical. The gas flow is maintained constant throughout the whole test, and shall be equal to 1,6 dm³ min⁻¹. It shall be at least 20 % higher than the sampling flow of the NO/NO₂ analyser. The max flow variation allowed is 10 %.

The fan ensures perfect mixing inside the reaction chamber. The fan is placed inside the reactor on a support having a hole with diameter equal to the fan aperture and axial to the fan axis. The support has lateral holes that ensure full air mixing inside the chamber. The fan shall provide nominal flows at the nominal supply voltage of 70 m³ h⁻¹.

Fans with external dimensions of 60 mm × 60 mm and thickness from 25 mm to 35 mm are suitable for this purpose. The fan flow shall be varied by varying the supply voltage by an appropriate power supply of continuous variable output voltage (see A of Figure 2).

6.2.4 NO/NO₂ analyser

The analyser shall be calibrated according to the procedures described in ISO 7996 or according to EN ISO 9169. The instrument's calibration can be performed using NO and/or NO₂ mixtures at a known and certified concentration of either grade 999 nitrogen or air. For the measurement range adopted during calibration, at least 4 standard gas mixtures shall be analysed, supported by the related calibration certificates, with different NO contents in N₂ (or in any other inert gas) with concentrations equal to approx. 0,2 ppmv, 0,4 ppmv, 0,6 ppmv, 0,8 ppmv.

Alternatively, the concentrations needed to check the analyser calibration can be generated starting from a single gas cylinder with certified NO concentration and with the help of a calibrated flow controller provided with calibration certificates for mass-flow controllers.

Adjustments and calibrations shall be always carried out when the measuring device is under steady conditions.

By comparing the measured NO concentration values and the related certified values it is possible to obtain, for each concentration level, the corresponding analyser calibration condition, which can be expressed in table form, as a calibration curve or a response factor.

If calibration provides a linear response as nitrogen oxide concentrations vary within the calibration range, then a single level measurement can be adopted during the control of the instrument calibration condition. The frequency of such control operations depends on the accuracy level desired in accordance with the time drift of the instrumental signal typical of each NO_x-analyser.

7 Sample preparation

7.1 Precaution

Samples shall be preconditioned under supplier advices to ensure that the conversion is constant under the test conditions.

7.2 Sample characteristics

The samples being analysed shall have a surface area of 64 ± 6 cm². For larger samples, use a mask. The surface area value shall be carefully assessed being a parameter necessary for the normalization of the test result.

The sample shall be positioned on a support made of borosilicate glass, polytetrafluoroethylene (PTFE) or ceramic material that is not photocatalytically active, paying attention that its surface is as close as possible to the level of the fan rotation axis and central to the free space between fan and reactor wall in the lateral direction (see Figure 5). As to distance tolerances, the sample surface can be at a distance of (30 to 50) mm from the internal base, that is (60 to 40) mm from the inner surface of the upper transparent window of the reactor. This means that the sample shall have a maximum usable thickness of 50 mm. Solid samples of 50 mm thickness can be positioned in the reaction chamber without any support.

The geometric surface area exposed to the gas flow can be square, rectangular or circular, provided that the illumination uniformity conditions are met (see paragraph 6.2.2). The sample width in axial direction should not exceed 120 mm. Typically a cylindrical sample has a surface area of (64 ± 6) cm² (± 10 %).

The required surface area can be achieved by combination of various samples, provided that they are coplanar and the resulting surface meets the specifications above.

The surfaces of the tested sample other than those exposed orthogonally to the incident light flow, shall be isolated from gas containing nitric oxide by means of a coating of commercial silicones, paraffin waxes, inert polymer films or composite materials. The test shall be performed only after these protective films have completely dried. All coatings shall withstand irradiance conditions for at least 6 h, should not release potentially interfering substances and should have no photocatalytic activity. The type of the used product shall be specified in the final report.

7.3 Conditioning

Samples can be conditioned according to the manufacturer's guidelines before being tested.

8 Measurement of concentrations

8.1 General

All concentrations can be expressed either in ppmv or $\mu\text{g m}^{-3}$.

Assuming an ideal behaviour for the gases in question, the conversion from ppmv to $\mu\text{g m}^{-3}$ is given by the following equation:

$$C(\mu\text{g m}^{-3}) = 10^3 \frac{\text{ppmv} \times MM \times P}{R \times T} = \text{ppmv} \times k \quad (1)$$

where

MM is the gas molecular mass ($MM^{\text{NO}} = 30,0061 \text{ g mol}^{-1}$, $MM^{\text{NO}_2} = 46,0055 \text{ g mol}^{-1}$);

R , P and T are, respectively, the ideal gas constant ($0,0821 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$), the pressure expressed in atm and the temperature in K ;

the factor k is $k_{\text{NO}} = 1226$ for NO and $k_{\text{NO}_2} = 1879$ for NO_2 at $T = 298,15 \text{ }^\circ\text{K}$ and $P = 1 \text{ atm}$.

With reference to Figure A.1 that shows the variation of concentrations during a typical experiment, the following values shall be measured in sequential order.

- C^{IN} : concentration of NO and NO_2 at reactor inlet;
- $C^{\text{OUT,DARK}}$: concentration of NO and NO_2 at reactor outlet under stable conditions in the dark (no illumination);
- $C^{\text{OUT,light}}$: concentration of NO and NO_2 at reactor outlet under stable conditions with illumination (lamp on).

8.2 Measurement of the initial concentration of nitrogen oxides before entering the photochemical reactor

The test gas, fed with constant and controlled rate (typically $1,6 \text{ dm}^3 \text{ min}^{-1}$) by mixer F, is conveyed directly to the analyser through a by-pass (via the path 1 - 3 - 4) excluding the reactor. The NO/ NO_2 concentration ($C_{\text{NO}}^{\text{IN}}, C_{\text{NO}_2}^{\text{IN}}$) shall be measured when the concentration has remained constant for at least 10 min (deviation $< 5 \%$). The measured concentration value shall be recorded in the test report. Typically, $C_{\text{NO}_2}^{\text{IN}}$ shall be less than 5 % of $C_{\text{NO}}^{\text{IN}}$ and remain stable, otherwise the NO cylinder shall be replaced.

8.3 Conversion without sample

This measurement shall be carried out only once to verify the suitability of the illumination system and the chemical inertia properties of the reactor building elements. This measurement shall be carried out in the absence of the sample but in the presence of the sample support:

- a) with the lamp OFF (i.e. ON but properly shielded) and the fan running at speed at the nominal voltage, the test gas, coming with constant and controlled flow ($1,6 \text{ dm}^3 \text{ min}^{-1}$) from mixer F, is conveyed to the reaction chamber (via the path 1 - 2 - 4) and the NO/ NO_2 concentration leaving the reactor is monitored continuously. In these conditions, $C_{\text{NO}}^{\text{OUT,DARK}}$ and $C_{\text{NO}_2}^{\text{OUT,DARK}}$ are measured without sample;

- b) the measurement is continued with the lamp ON (and not shielded) without interrupting the gas flow to the reactor and the ventilation. The test can be considered completed when the NO/NO₂ concentrations are stable for at least 10 min (deviation < 5 %) and, anyway after 3 h when concentrations are still changing. However, if after 3 h the concentrations are still changing, this behaviour will be indicated in the test report.

The value $C_{NO}^{OUT,LIGHT}$ corresponds to the value measured at the end of the test.

The test result is expressed as conversion $\eta_{NO,lamp}^{PHOTO}$ calculated as follows:

$$\eta_{NO,lamp}^{PHOTO} = \frac{C_{NO}^{OUT,DARK} - C_{NO}^{OUT,LIGHT}}{C_{NO}^{OUT,LIGHT}} \quad (2)$$

The conversion values in the absence of sample are acceptable if $\eta_{NO,lamp}^{PHOTO} < 0,02$ (2 %). Otherwise, the system is not suitable for the measurement referred to in this standard because of defective lighting system or inappropriate material types.

8.4 Conversion in the dark and in the presence of sample

This measurement is carried out by conveying the test gas inside the reaction chamber (via the path 1-2-4). The fan shall be running with a speed at the nominal voltage V_0 that can be obtained with the applied nominal potential V_0 , while illumination from the lamp shall be totally shielded.

The values $C_{NO,S}^{OUT,DARK}$ and $C_{NO_2,S}^{OUT,DARK}$ in the presence of sample correspond to the NO/NO₂ concentrations at the outlet of the reactor containing the sample S in the dark. These values correspond to the concentration value when they are stable for at least 10 min (deviation < 5 %) or after 3 h when the concentrations are still changing.

If $C_{NO,S}^{OUT,DARK}$ is more than 5 % less than $C_{NO_2}^{IN}$ it is necessary to verify that the reactor or pipes show no leaks, cracks or pressure drops, and the sample has no shielding defects. If the system has no defects, the concentration difference is due to adsorption or reactivity in the dark and therefore it is necessary to allow the concentrations to stabilize as specified above.

The test result is expressed as conversions η_{NO}^{dark} and $\eta_{NO_2}^{dark}$ and calculated as follow:

$$\eta_{NO}^{dark} = \frac{C_{NO}^{IN} - C_{NO,S}^{OUT,DARK}}{C_{NO}^{IN}} \quad (3)$$

$$\eta_{NO_2}^{dark} = \frac{C_{NO_2,S}^{OUT,DARK} - C_{NO_2}^{in}}{C_{NO}^{IN}} \quad (4)$$

8.5 Conversion under illumination in the presence of sample

The concentration is measured by conveying the test gas into the reaction chamber (via the path 1 - 2 - 4) with the lamp on. The fan (at V_0) and the illumination system shall run as for the measurement in the dark (see paragraph 8.4).

The NO and NO₂ concentrations at reactor outlet shall be monitored continuously. When the NO/NO₂ concentrations are stable for at least 30 min (deviation < 5 %) and, anyway after 3 h when

concentrations are still changing, the concentrations $C_{NO,0}^{OUT,LIGHT}$, $C_{NO_2,0}^{OUT,LIGHT}$ measured at fan speed corresponding to the nominal voltage V_0 are recorded.

In order to determine the mass transfer effect on the total NO photocatalytic degradation rate, measurements at different fan speeds are carried out. The fan speed can be modified by changing the direct current (DC) voltage supplied to the fan and assuming a flow proportional to the potential applied. The assumption that the flow is proportional to the applied potential can be checked by measuring the fan electrical resistance in the reactor. In the region according to the Ohm law where V (voltage) is linear with I (current), the assumption is valid. Instead of measuring the resistance, the wind speed can be measured using an anemometer placed at the sample position with its axis coaxial to fan axis. or any other possible strategies to ensure that the fan flow is proportional to the potential applied to the fan. The chamber shall be closed to do this measurement. See Annex C.

In operational terms, after the first measurement with the nominal fan flow $F_{V,0}$ at voltage V_0 without changing any other experimental parameter, the voltage applied to the fan is reduced to allow the execution of at least $n = 5$ subsequent measurements with decrease of the electric potential applied. The potential decrease applied in each stage could be estimated by the following formula and rounded to two digits:

$$\Delta V = \frac{V_0 - V_{min}}{n} \quad (5)$$

where

V_0 and V_{min} are the fan nominal operating potential (in Volt) and the minimum operating potential (in Volt) set by the manufacturer. Once ΔV is fixed (for example to 1,5 V), from Formula (5) the nominal value of n to be used in Formula (6) is given by $n_{calc} = (V_0 - V_{min}) / \Delta V$.

The fan flow $F_{V,i}$ corresponding to the variation of the applied potential $V_i = (V_0 - i \Delta V)$ is calculated with the following formula:

$$F_{V,i} = F_{V0} \left(1 - \frac{i}{n_{calc}} \right) \quad (6)$$

where

$i = 0,1,2,3,4$ and $F_{V,nom}$ is the nominal fan flow set by the manufacturer at the applied nominal potential V_0 .

After decreasing the potential at step i , the NO and NO₂ concentrations at reactor outlet $C_{NO,i}^{OUT,LIGHT}$, $C_{NO_2,i}^{OUT,LIGHT}$ are measured.

The test can be considered completed for each potential applied to the fan when the NO conversion has stabilized during 30 min (deviation < 5 %) or, in the case of higher variation in time of the conversions (and concentrations), after 3 h of irradiance for $i = 0$, and after 30 min for $i > 0$.

The conversion value for a given potential applied to the fan is evaluated with the concentrations measured at the end of each measurement at the stabilization time t_{stab} .

The test result for fan flow $F_{V,i}$ is expressed as conversions $\eta_{NO,i}^{total}$ and $\eta_{NO_2,i}^{total}$ calculated from the following equations:

$$\eta_{NO,i}^{total} = \frac{C_{NO}^{IN} - C_{NO,i}^{OUT,light}}{C_{NO}^{IN}} \quad (7)$$

$$\eta_{NO_2,i}^{total} = \frac{C_{NO_2,i}^{OUT,light} - C_{NO_2}^{IN}}{C_{NO}^{IN}} \quad (8)$$

At the end of the test ($n+1$) quadruplets of values (t_{stab} , $F_{V,i}$, $\eta_{NO,i}^{total}$ and $\eta_{NO_2,i}^{total}$) are obtained.

If the conversions measured exceed the value 0,7 (70 %) the photocatalyst is extremely active. In this case the conversion and the consequent abatement/production rates (as calculated in paragraph 9) are strongly controlled by mass transfer limitation. The rates can still be calculated according to paragraph 9, but in this case the test report shall specify “the sample shows conversions exceeding 70 % under test conditions, therefore its activity is so high that is limited by the mass transfer effects under the test conditions”.

9 Calculation of photocatalytic degradation rate

9.1 The observed rate of photocatalytic degradation

The actual conversions (η) inside the reactor in the dark (η^{dark}) [see Formulae (3) and (4)] and with illumination (due to the summation of the processes in the dark and those photoinduced, η^{total} , [see Formulae (7) and (8)] are calculated starting from the concentrations recorded at the end of the measurement according to the previous points, or at every single experimental time in the case of continuous acquisition. In this test method, it is assumed that nitric oxide degradation occurs according to a first order kinetics and with negligible adsorption, therefore the following equations apply.

The NO abatement rate at each fan speed ($r_{NO,i}^{photo}$) ($i = 0..n$) and the NO₂ photocatalytic production rate ($r_{NO_2,i}^{photo}$) ($i = 0..n$) are expressed as mass (micrograms) of NO consumed or mass of NO₂ produced by the sample per unit of time and unit of exposed surface area. These rates are calculated as the difference between the abatement/production rates and the rates observed in the dark according to Formulae (9)-(11).

$$r_{NO,i}^{photo} = \frac{613F}{S} \left(\frac{\eta_{NO,i}^{total}}{(1-\eta_{NO,i}^{total})} - \frac{\eta_{NO}^{dark}}{(1-\eta_{NO}^{dark})} \right) \quad (9)$$

$$r_{NO_2,i}^{photo} = \frac{940F}{S} \left(\frac{\eta_{NO_2,i}^{total}}{(1-\eta_{NO,i}^{total})} - \frac{\eta_{NO_2}^{dark}}{(1-\eta_{NO}^{dark})} \right) \quad (10)$$

$$r_{NO_x,i}^{photo} = 1,53 r_{NO,i}^{photo} - r_{NO_2,i}^{photo} \quad (11)$$

where

all rates are expressed in $\mu\text{g m}^{-2} \text{h}^{-1}$;

the NO_x abatement rate ($r_{NO_x}^{photo}$) is expressed as NO₂ equivalents;

all rates are normalized to a nominal input NO concentration of 0,5 ppmv;

F is the actual flow of reactant gas entering the reactor via the path (1) expressed in m³ h⁻¹ (cubic meters per hour, i.e. according to this standard nominally equal to 0,096 m³ h⁻¹ ± 10 %);

S is the sample illuminated surface area in m².

At the end of the calculation (n+1) triples of values (FV_i, $r_{NO,i}^{photo}$, $r_{NO_x,i}^{photo}$) are obtained.

9.2 Intrinsic rate of photocatalytic transformation

The intrinsic NO photocatalytic abatement rate and NO₂ photocatalytic production rate, with deduction of the mass transfer limitation effects, are calculated by plotting in a graph (see Figure B.1) the inverse of the NO abatement rate ($1/r_{NO,i}^{photo}$) as a function of the inverse of the fan flow (1 / FV_i) and by extrapolating to 1 / FV_i = 0 by means of linear regression. This graph and the regression can be easily evaluated with commercial spreadsheets. The inverse of the intercept (the value $1/r_{NO}^{photo}$ with abscissa = 0) provides the photocatalytic degradation rates $r_{NO}^{photoCAT}$ (and $r_{NO_x}^{photoCAT}$ optional) intrinsic to the surface of the material, after removing the mass transfer limitations. The first order reaction constant (also called deposition velocity could also be calculated as $k_R = r_{NO}^{photoCAT} / C_{NO}^{IN}$.

Note that generally the calculated values of $r_{NO}^{photoCAT}$ and the optional $r_{NO_x}^{photoCAT}$ are not the values that are found in real material applications, but they represent the maximum intrinsic limit value of photocatalytic activity that the material can provide. In reality, the values are lower depending on the application because of the various limitations that intervene at mass transfer from the gas phase to the photocatalyst surface.

10 Acceptability ranges of main test parameters

The photocatalytic conversion rates can be calculated if the following experimental critical parameters fall within the acceptability ranges shown in Table 1.

Table 1 — Acceptability ranges

Parameter	Symbol	Measurement unit	Nominal value	Variation allowed
Average irradiance	<i>I</i>	W m ⁻²	10	5 %
Inlet NO ₂ concentration	$C_{NO_2}^{IN}$	ppmv	< 0,025	-
Inlet NO concentration	C_{NO}^{IN}	ppmv	0,50	10 %
Temperature inside the reactor	<i>T</i>	°C	25	±5 °C
Gas relative humidity at 25 °C inside the reactor	<i>RH</i>	%	40 %	±5 %
Flow	<i>F</i>	dm ³ min ⁻¹	1,6	10 %
Reactor net volume	V_R	Dm ³	3,2	20 %

An example of experimental concentration profile is shown in Annex A, while Annex B describes an example of the method used to calculate the intrinsic degradation rate $r_{NO}^{photoCAT}$.

11 Test report

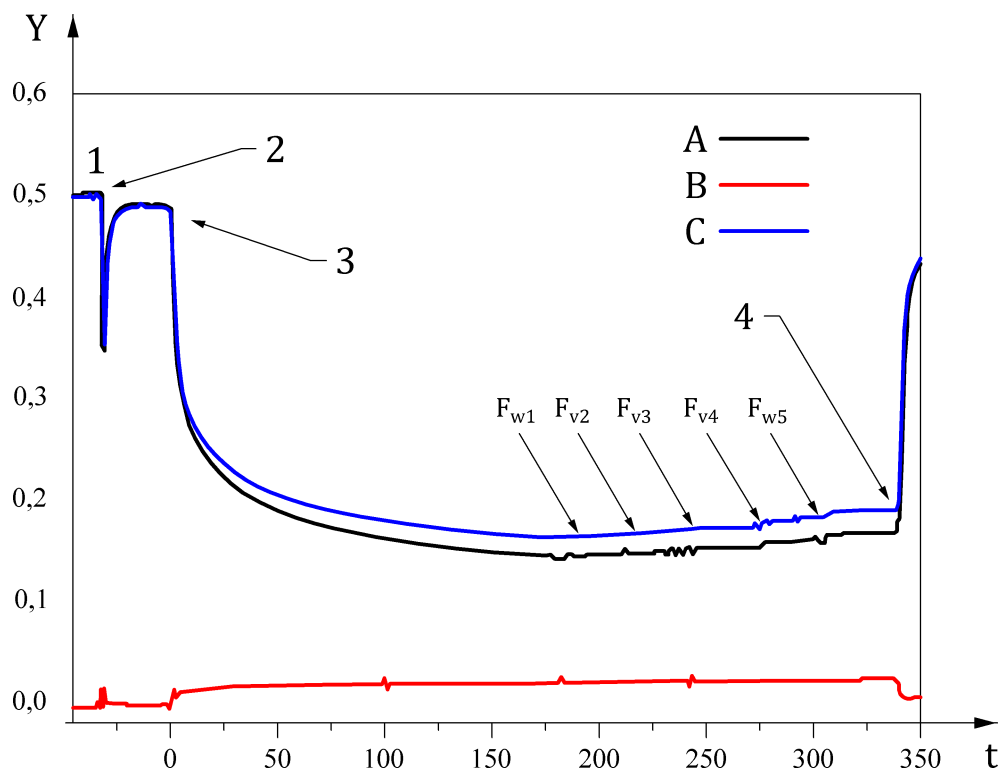
The test report shall include the following minimum information:

- 1) a reference to this standard;
- 2) a declaration stating that the conditions required by this method for the determination of NO degradation rate in the presence of sample have been met;
- 3) type and serial number of the NO_x analyser used;
- 4) reactor volume;
- 5) type, voltage and nominal flow of the fan used;
- 6) type and spectrum of the lamp used;
- 7) surface area of the sample under test;
- 8) main characteristics of the sample analysed and type of photocatalyst contained, if known, or identification code provided by the manufacturer;
- 9) specifications of the material used for sample shielding (side and bottom), as described in paragraph 7.2;
- 10) the information about sample conditioning including the statement “the sample has been measured as is”, or “specify the type of conditioning”;
- 11) concentration of gases used, as measured according to paragraph 8.2;
- 12) gas flow F ;
- 13) temperature inside the reactor;
- 14) relative humidity inside the reactor;
- 15) lamp irradiance to sample surface in $W\ m^{-2}$ in the catalyst adsorption area;
- 16) time elapsed between the time the UV lamp was switched ON and recording of the stabilized concentration;
- 17) the values $C_{NO}^{OUT,DARK}$, $C_{NO_2}^{OUT,DARK}$, $C_{NO}^{OUT,LIGHT}$ and $\eta_{NO,lamp}^{photo}$ as calculated in paragraph 8.3;
- 18) the values of conversion in the dark in the presence of sample η_{NO}^{dark} e $\eta_{NO_2}^{dark}$ as calculated in paragraph 8.4; If after 3 h the concentrations are still changing, indicate this in the test report
- 19) the diagram showing the trend of C_{NO} and C_{NO_2} concentrations during the various test steps or alternatively the diagram with the trend of $\eta_{NO,i}^{total}$ and $\eta_{NO_2,i}^{total}$ conversions as a function of test time; raw test results expressed in table form of (n+1) quadruples of values (t_{stab} , $F_{V,i}$, $\eta_{NO,i}^{total}$ and $\eta_{NO_2,i}^{total}$) calculated according to the Formulae (6) to (8) for total conversion at different fan flows;

- 20) if any conversions measured exceed 70 %, the statement “the sample shows conversions exceeding 70 % under test conditions, therefore its activity is so high that it is limited by the effects of mass transfer under test conditions”;
- 21) If after three hours test the constant conversion is not achieved, the test is stopped. In this case the test report shall include the sentence “the sample is not stable under test conditions and therefore the photocatalytic degradation rate cannot be reported”;
- 22) the abatement/production rates observed at various fan flows in table form of (n + 1) triples of values $(F_{V,i}, r_{NO,i}^{photo}, r_{NO_x,i}^{photo})$, calculated according to the Formulae (6), and (9) to (11) for total conversions at various fan flows, also in correlation with the data referred to in paragraph 19;
- 23) the value of intrinsic photocatalytic degradation rate $r_{NO}^{photoCAT}$ obtained by linear interpolation of data $1/r_{NO,i}^{photo}$ versus $1/F_{V,i}$, for NO according to the procedure explained in paragraph 9.2 and demonstrated in Annex B, including the statement “The reported value represents the *maximum* intrinsic limit of photocatalytic activity that the material can provide. In practice, the values are lower depending on the application because of the various limitations that intervene at mass transfer from the gas phase to the photocatalyst surface”;
- 24) the deposition velocity calculated as $k_R = r_{NO}^{photoCAT} / C_{NO}^{IN}$;
- 25) (optional) the value of intrinsic photocatalytic abatement rate $r_{NO_x}^{photoCAT}$ obtained by linear interpolation of data $1/r_{NO_x,i}^{photo}$ to $1/F_{V,i}$, for NO_x;
- 26) any aspect observed during the test run which may be of some importance;
- 27) the graph of inverse rate versus inverse fan flow with regression coefficient R².

Annex A
 (informative)

Typical trend of NO, NO₂ and NO_x concentrations during a photocatalytic test



Key

- t* time (expressed in min)
- Y concentration of NO, NO₂ and NO_x (expressed in ppmv)
- A curve of NO
- B curve of NO₂
- C curve of NO_x
- 1 reactor by-passed
- 2 gas flow inside the reactor
- 3 illumination start
- 4 illumination end

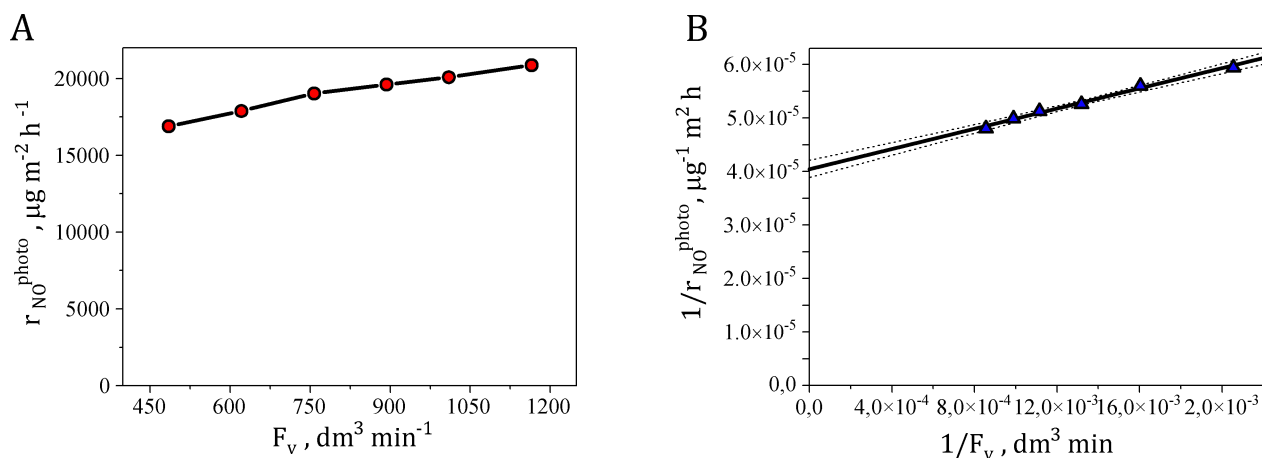
NOTE The start time of sample illumination is considered as value 0 of the time scale.

Figure A.1 — Typical trend of NO, NO₂ and NO_x concentrations during a photocatalytic test

Annex B (informative)

Example of test for the control of mass transfer conditions

In order to assess the mass transfer effect on the total rate of NO photocatalytic degradation, a graph of the inverse of NO abatement rate ($1/r_{NO}^{photo}$) versus the inverse of fan flow ($1/F_v$) shall be plotted (see Figure B.1). This last parameter can be modified by changing the potential of the fan direct current supply and assuming that fan flow is proportional to the potential applied. The points are arranged approximately along a straight line.



a) NO degradation rate (r_{NO}^{photo}) as a function of the fan flow

b) Variation of $1/r_{NO}^{photo}$ as a function of the inverse of fan flow ($1/F_v$)

Key

F_v expressed in $dm^3\ min^{-1}$

r_{NO}^{photo} expressed in $\mu g\ m^{-2}\ h^{-1}$

F_v^{-1} expressed in $min\ dm^{-3}$

$1/r_{NO}^{photo}$ expressed in $\mu g^{-1}\ m^2\ h$

$$1/r_{NO}^{photo} = 9,39\ 10^{-3} \times F_v^{-1} + 4,04\ 10^{-5}$$

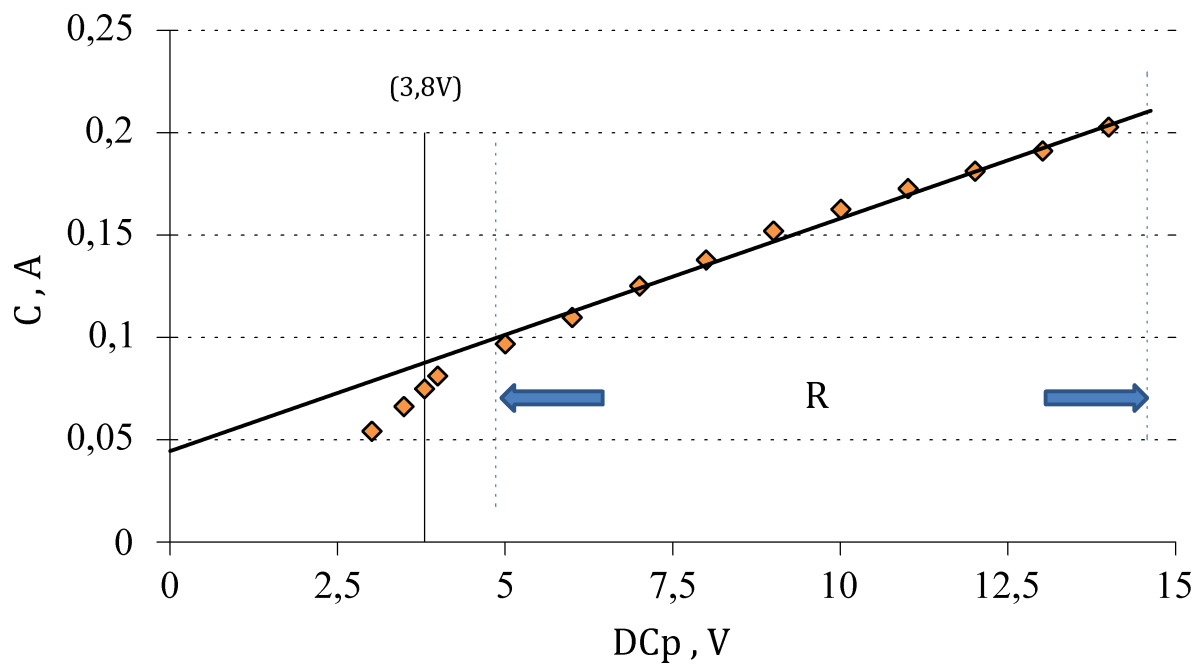
When $F_v^{-1} = 0$, then $1/r_{NO}^{photo} = 4,04\ 10^{-5}\ \mu g^{-1}\ m^2\ h$, that means that $r_{NO}^{photoCAT} = 24752\ \mu g\ m^{-2}\ h^{-1}$

Figure B.1 — Example of test for the control of mass transfer conditions

NOTE The rate extrapolated at $1/F_v = 0$ (fan flow hypothetically infinite) is the rate involving no limitations due to mass transfer phenomena.

Annex C (informative)

Typical Ohmic response of the fan



Key
R available range
3,8 V on set

Figure C.1 — Ohmic response of the fan

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