Fine ceramics - Test method for air-purification performance of semiconducting photocatalytic materials -

Removal of nitric oxide: Modified ISO 22197-1:2007

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Please find attached the results of NO_x removal capability on 1 sample of photocatalytic coating on concrete base, supplied by PURETi.

The sample was pretreated in order to decompose any residual organic matter by irradiating with an ultraviolet lamp (2 mW/cm^2) for 16 h, under a flow of zero-calibration gas at 1.5 L/min. The test piece was placed in the photoreactor with the space between the test piece and the window a constant 5.0 ± 0.5 mm.

The test gas supply was adjusted so as to stably supply 0.8 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, *i.e.* a relative humidity of 50 % at 25 °C. The test gas was allowed to flow into the photoreactor, without photoirradiation, with a flow rate of 1.5 L/min ± 0.15 L/min, for 30 min whilst the change in the volume fraction of NO and NO_2 were recorded. After 30 minutes, the gas flow was maintained and irradiation of the sample commenced. The NO and NO_2 volume fractions under photoirradiation were recorded for 5 h. After this 5 h period, irradiation was halted, but the test gas flow maintained for a further 30 minutes, during which time the NO fraction was seen to return to its original level.

Using the data recorded, by an Enviro Technology Service plc NO_x analyser – Model T200, during the 5 h photoirradiation, the amounts of NO_x removed, NO_2 generated, and therefore net amount of NO_x removed by the test piece were calculated, both in units of µmol, and %. NO_x adsorbed, and NO_x desorbed by the test piece supplied were found to be negligible.

The data recorded is firstly summarised by a histogram, shown in *Figure 1*, in units of µmol, and in Figure 2, in units as a % of NO supplied to the reactor. Included in this histogram are example data for a TiO_2 paste dipcoated onto glass (example 1) and a typical photocatalytic paper (example 2) tested under ISO 22197-1:2007 (3 L/min ± 0.15 L/min of test gas, 1 µL/L ± 0.05 µL/L of NO).

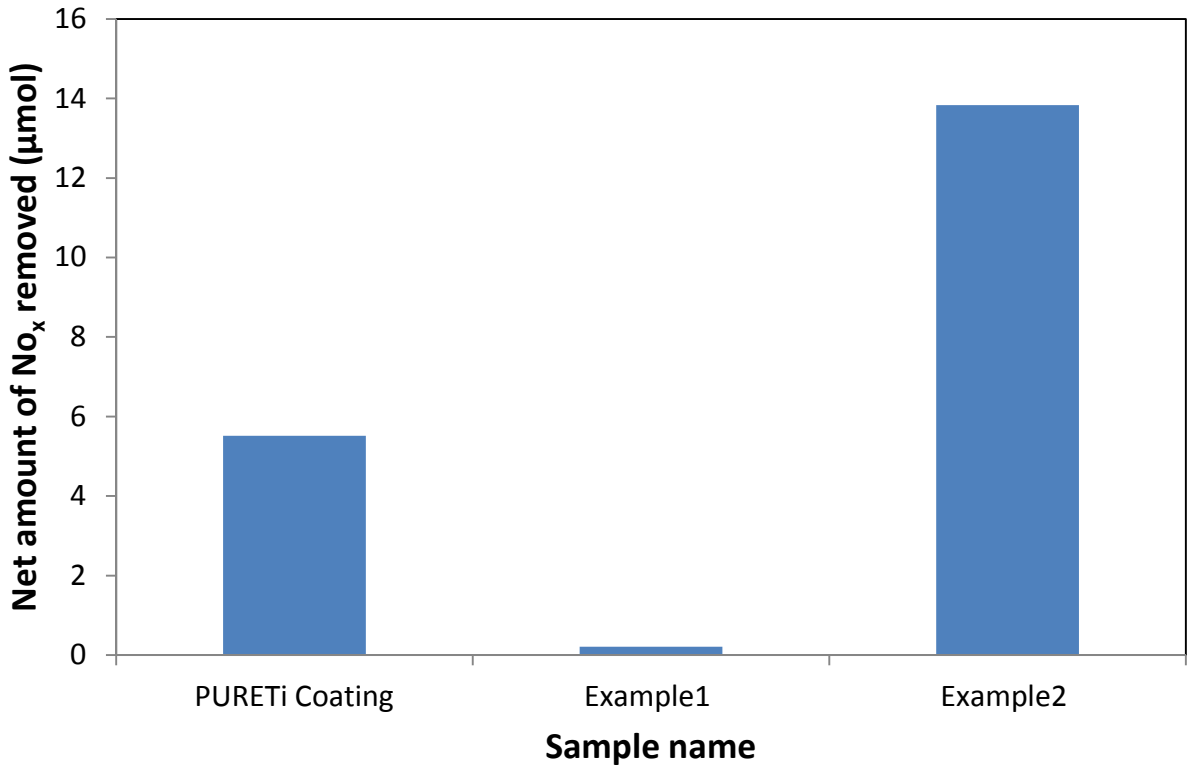

Figure 1 – Histogram illustrating the ability of supplied test pieces to remove NO_x from a 1.5 L/min air stream containing 0.41 ppm NO over a 5 hour period, and 2 example test pieces to remove NO_x in accordance with ISO 22197-1:2007 (3.0 L/min air stream containing 1.00 ppm NO) over a 5 hour period (units: µmol). The supplied sample was of photocatalytic coating on a concrete base, whilst example 1 is a sample of TiO_2 paste dipcoated onto glass, and example 2 is a sample of photocatalytic paper.

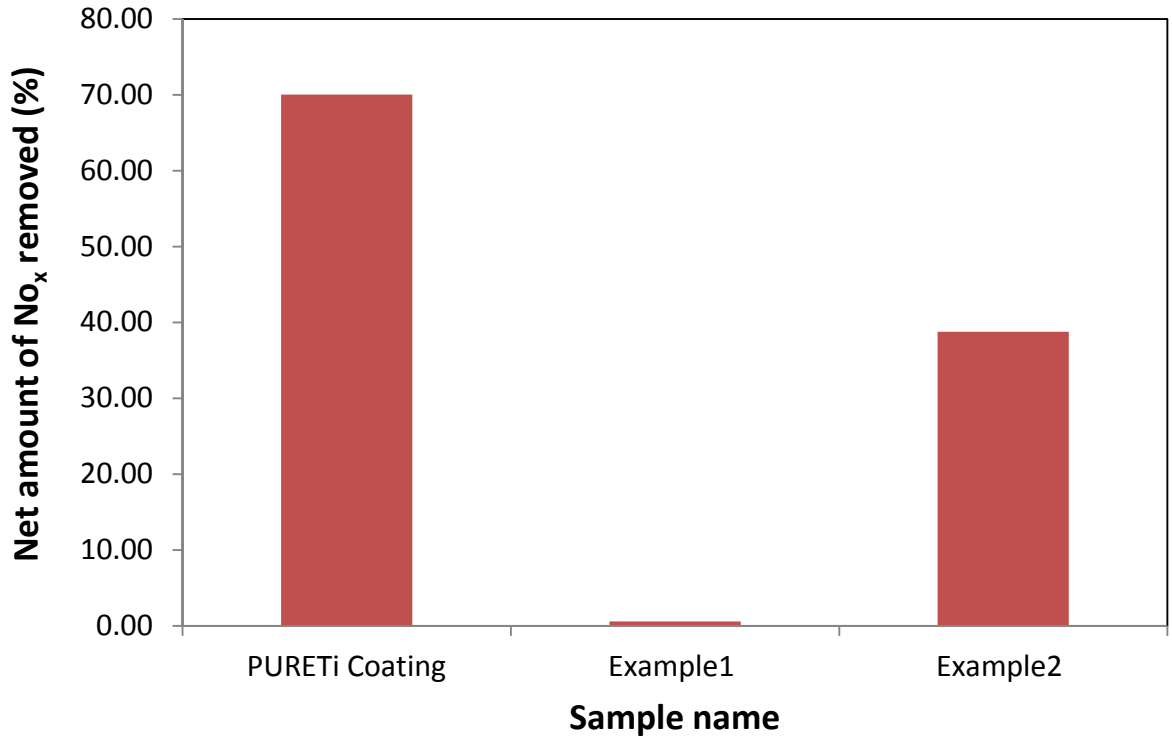

Figure 2 – Histogram illustrating the ability of supplied test pieces to remove NOx from a 1.5 L/min air stream containing 0.41 ppm NO over a 5 hour period , and 2 example test pieces to remove NOx in accordance with ISO 22197-1:2007 (3.0 L/min air stream containing 1.00 ppm NO) over a 5 hour period (units: µmol). (units: % of NO supplied to the reactor). The supplied sample was of photocatalytic coating on a concrete base, whilst example 1 is a sample of TiO¬2 paste dipcoated onto glass, and example 2 is a sample of photocatalytic paper.

Table 1 summarises (i) NO supplied to the reactor (ii) NO removed by the test piece (iii) total NO unreacted (iv) amount of NO_2 generated by the test piece and (v) net amount of NO_x removed by the test piece = ((ii)-(iv)) for the supplied sample, and for the two example test pieces, in units µmol, and Table 2 in units %.

The remainder of this report gives a breakdown of these results along with the original data figure and reaction conditions for each sample under test. Finally, the appendix of this report contains a detailed method of the ISO analysis, along with the original data figure and reaction conditions for the example test pieces of TiO_2 paste on glass and of photocatalytic paper, for your comparison.

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semiconducting photocatalytic materials -

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	Units: µmol				
Sample number (and name)	*(i) NO supplied to the reactor*	*(ii) NO removed by the test piece*	*(iii) total NO unreacted*	*(iv) amount of NO_2 generated by the test piece*	*(v) net amount of NO_x removed by the test piece = ((ii)-(iv))*
PURETi Coating	7.88	6.79	1.09	1.27	**5.52**
Example1 - TiO_2 paste coated on glass	36.86	5.59	31.26	5.38	**0.21**
Example2 - Typical photocatalytic paper	35.69	23.85	11.84	10.02	**13.83**

Table 1 – Summary of (i) NO supplied to the reactor (ii) NO removed by the test piece (iii) total NO unreacted (iv) amount of NO_2 generated by the test piece and (v) net amount of NO_x removed by the test piece = ((ii)-(iv)) for the tested sample (modified conditions) and example test pieces (ISO 22197-1:2007), in units of µmol.

	Units: % of NO supplied to the reactor				
Sample number (and name)	*(i) NO supplied to the reactor*	*(ii) NO removed by the test piece*	*(iii) total NO unreacted*	*(iv) amount of NO_2 generated by the test piece*	*(v) net amount of NO_x removed by the test piece = ((ii)-(iv))*
PURETi Coating	100	86.10	13.90	16.10	**70.05**
Example1 - TiO_2 paste coated on glass	100.00	15.18	84.82	14.60	**0.58**
Example2 - Typical photocatalytic paper	100.00	66.82	33.18	28.07	**38.76**

Table 2 – Summary of (i) NO supplied to the reactor (ii) NO removed by the test piece (iii) total NO unreacted (iv) amount of NO_2 generated by the test piece and (v) net amount of NO_x removed by the test piece = ((ii)-(iv)) for the tested sample (modified conditions) and example test pieces (ISO 22197-1:2007) as a % of NO supplied to the reactor.

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Customer name:	Pureti
Customer contact:	bikash@pureti.com
Sample name:	**PURETi Coating**
Sample description:	Grey concrete panel

Testing conditions

Date (dd/mm/yy)	17/10/2013
T (°C)	25.7
RH (%)	52
STP flow (L/min)	1.4231
Irradiance (mW/cm^{-2})	2.00
NO supply conc. (ppm)	413.0

Results	Amount (mmol)	Area (%)
(i) NO supplied to the reactor	7.88	100.0
(ii) NO removed by the test piece	6.79	86.1
(iii) total NO unreacted	1.09	13.9
(iv) amount of NO2 generated by the test piece	1.27	16.1
(v) net amount of NOx removed by the test piece = ((ii)-(iv))	**5.52**	**70.0**

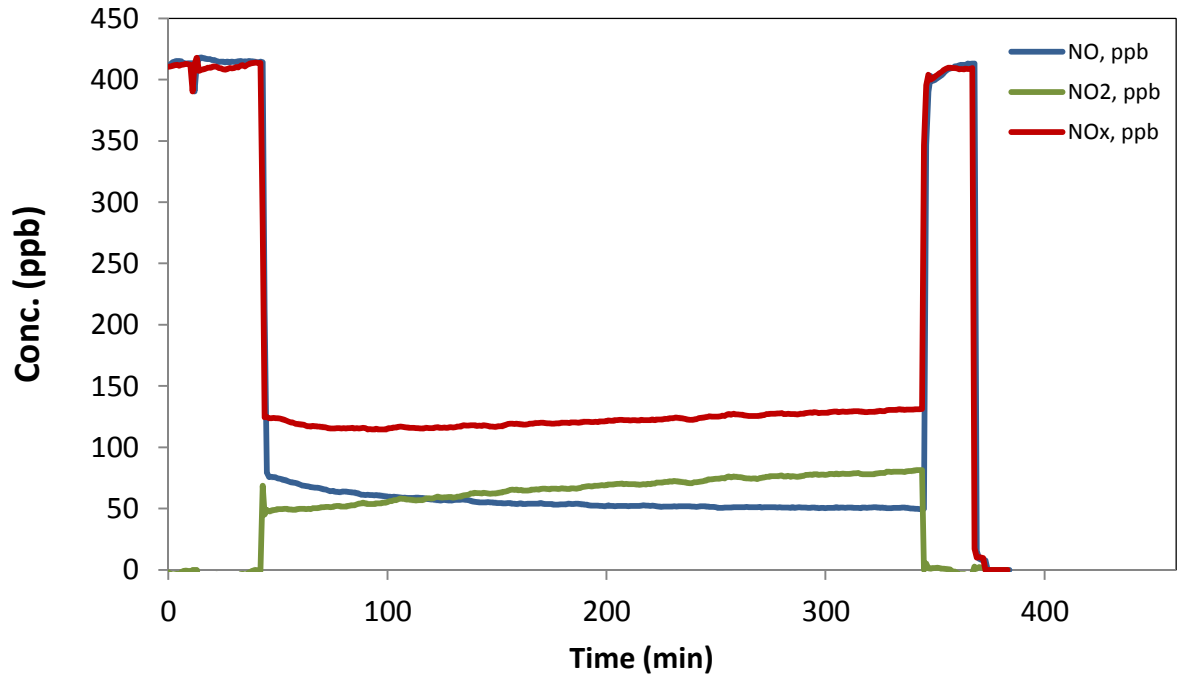

Figure 3 – Trace of NO/NO$_x$/NO$_2$ concentration during the ISO test for sample PURETi Coating

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Appendix

ISO 22197: test methods for air-purification performance of semiconductor photocatalytic materials [1-3]

To date there are three published photocatalyst air-purification ISO methods, each dedicated to the removal of a different air-borne pollutant, namely: nitric oxide (NO), ISO 22197-1: 2007 [1]; acetaldehyde (CH_3CHO), ISO 222197-2: 2011 [2] and toluene ($CH_3C_6H_5$), ISO 22197-3: 2011 [3], although others are almost at the publication stage (e.g. for: formaldehyde and methyl mercaptan).

The NO test system: ISO 22197-1 [1]

Nitric oxide is an important intermediate in the chemical industry and a major air pollutant produced by the combustion of substances in air, such as gasoline in automotives and fossil fuels in power stations. In the absence of a catalyst NO is oxidised relatively slowly to nitric oxide by oxygen ($t_{1/2}$ ~ 70 h for 1 ppmv of NO in air). It is used on a large scale in the manufacture of nitric acid, the bleaching of rayon, and as a stabiliser in the production of propene and methyl ether. It is an important signalling molecule in most biological systems and, along with NO_2, is associated with sick building syndrome and acid rain production. Given its widespread commercial use and, maybe more importantly, its occurrence as a common air-borne, environmentally damaging pollutant, the removal of NO and its NO_x counterpart, NO_2, by semiconductor photocatalysis has attracted a great deal of attention. Although the apparent efficacy of the NO removal process by semiconductor photocatalysis is not particularly high (quantum efficiency ca. 0.5%) [4], the attraction of removing such a ubiquitous indoor and outdoor pollutant using light has resulted in the promotion of many commercial photocatalyst products, such as paint, tiles, paving stones, for their NO_X removing ability.

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Key reactions

The titania-sensitised, photocatalytic oxidation of NO proceeds to nitric acid, via nitrous acid and a radical based mechanism.[4-8] The two key photocatalytic reactions are:

$$4NO + O_2 + 2H_2O \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 4HNO_2 \qquad (1)$$

and

$$2HNO_2 + O_2 \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 2HNO_3 \qquad (2)$$

Recent work [4] reveals that the accumulation of nitric acid on the surface promotes its photocatalysed reaction with NO that generates the toxic product NO_2, i.e.

$$2HNO_3 + NO \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 3NO_2 + H_2O \qquad (3)$$

This can lead to an eventual steady state where the rate of NO removal is matched by the rate of NO_2 production; which is clearly highly undesirable. It follows that for any NO_x-removing photocatalyst product to work effectively it is necessary that the HNO_3 photogenerated, via reactions (1) and (2), must be removed at regular intervals, by rinsing with water, e.g. from rain or a damp cloth.

The standard sets out to measure the photocatalyst's overall ability to remove the oxides of nitrogen, i.e. NO_x, using a NO-containing (1 ppmv) air stream. A measure of this ability is

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taken as the difference between the total NO removed (n_{NO}) and NO_2 generated (n_{NO2}) during the irradiation period.

Procedure

All three photocatalyst, air-purification published standards use the same photoreactor system, the key features of which are illustrated in Figure .

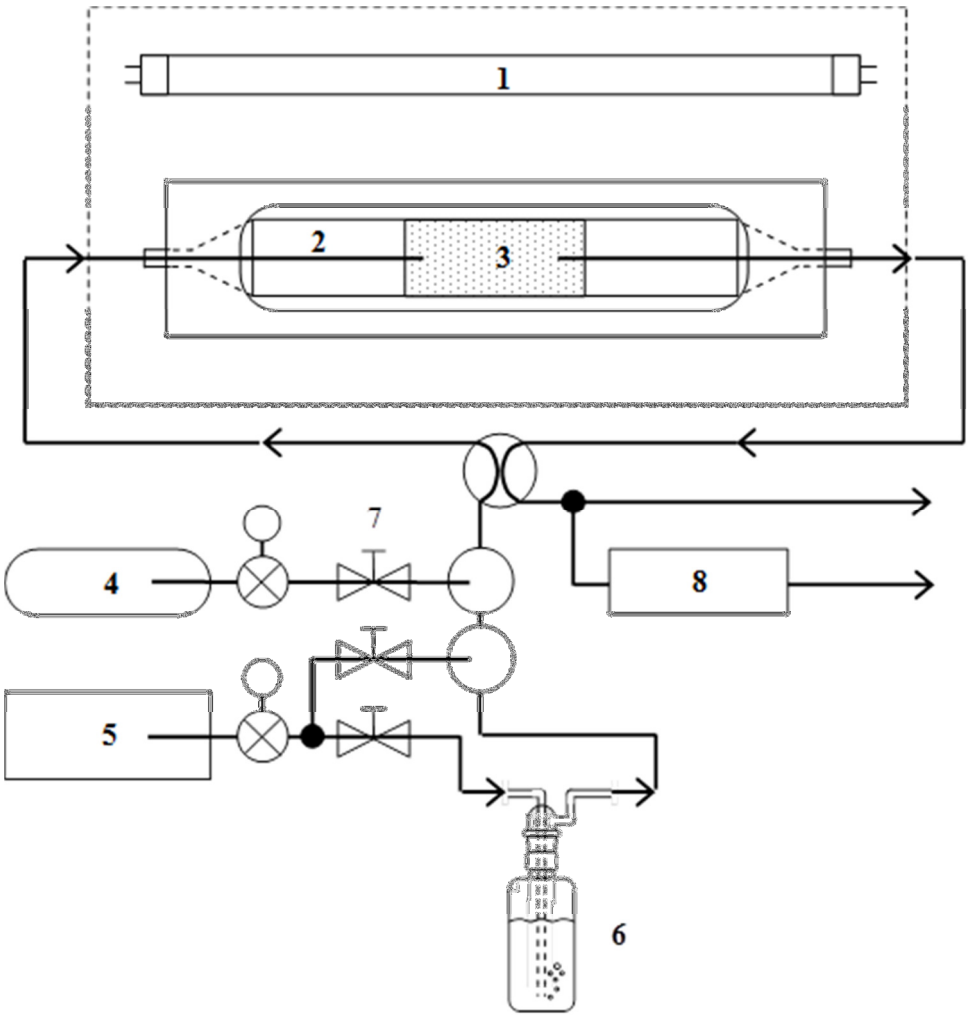

Figure 4 – Irradiation set up for the air purification ISO standards, comprising: (1) UV light source, (2) glass cover, (3) sample under test, (4) standard gas (i.e. test pollutant), (5) purified air source, (60 humidifier, (7) mass-flow controllers and (8) pollutant gas analyser.

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Thus, a UVA light (1) is used to illuminate, through a quartz or borosilicate glass window (2), the sample (3) under test (a 5 cm x 10 cm rectangle, typically ca. 5 mm thick). The test pollutant (4) is mixed with air (5), and humidified (RH = 50% at 25°C) using a water-filled Drechsel bottle (6). The flow rate of the different gas streams are managed by mass-flow rate controllers (7) and the inlet and outlet gas streams are sampled by a gas sampling valve attached to a suitable analytical system (8). The reactor is built out of material that is inert with regard to the test pollutant and UV, such as stainless steel, Perspex, or PTFE. Figure provides a side view illustration of the photoreaction cell for a solid sample; the gas stream (2) flows through the narrow (5 mm) gap between the glass window (1) and the sample (3), which is on a height-adjustable plate (4).

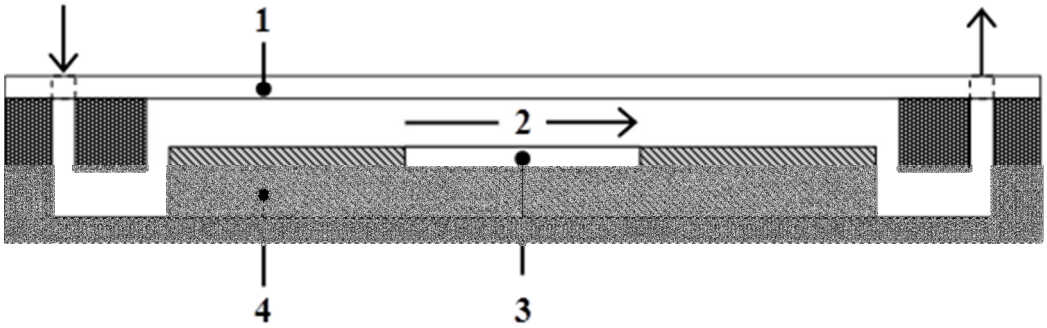

Figure 5 – Cross-sectional view of the photoreactor illustrated in Figure for solid, flat test pieces. The components are: (1) glass cover, (2) test gas flow, (3) flat test sample, and (4) height-adjusting plate.

Before carrying out the test each sample is cleaned photocatalytically by exposing it to UV light for 16 hours. All test pieces are tested immediately after cleaning. Note: in all these air-pollution tests the flow rate is normalised for STP and dry gas conditions, and *f* corrected for the water vapour present (by multiplying by 1.016).

After placing the cleaned test piece in the photoreactor and adjusting the space between the detachable window and the sample so that it is ca. 5 mm, the test gas (50 ppmv NO in N_2,

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mixed with air to produce the reaction test stream of 1 ppmv of NO and 21% O_2) is allowed to flow into the photoreactor without illumination for 30 min before the light is switched on. The concentration(s) of the analyte(s) of interest are monitored regularly during this 'dark' absorption time, and subsequently, *i.e.* when the system is illuminated and 30 min after the light has been switched off. The concentration versus time data profile(s) are then processed so as to provide one or more measures of the efficiency of the test piece to remove photocatalytically the air-pollutant under test.

Under the conditions specified in the standard, typical plots of the observed temporal variations in [NO] and [NO_2] generated by the test for a titania sample are illustrated in Figure .

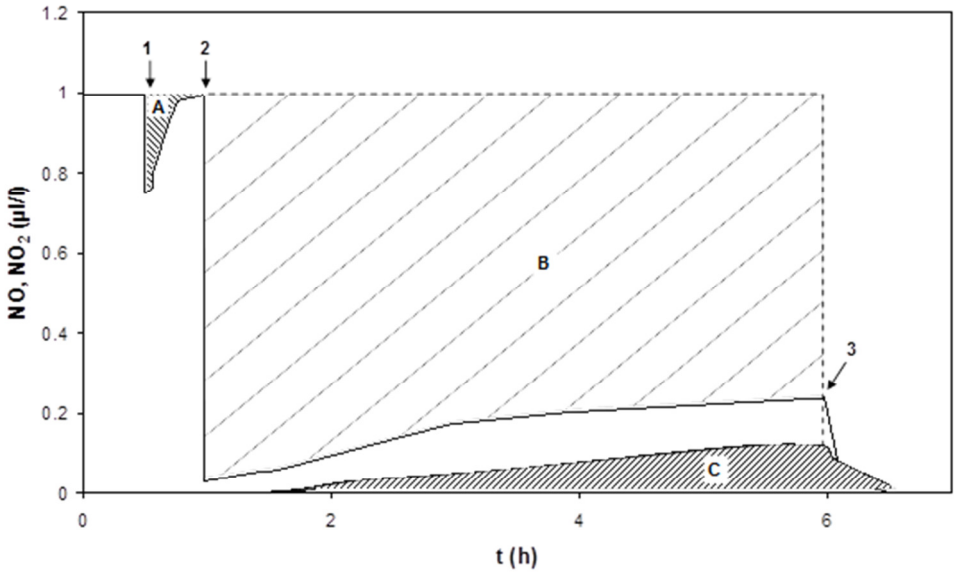

Figure 6 –Typical data set generated, i.e. NO removed and nitric acid generated, in the NO ISO standard, for which the feed stream [NO] is 1 ppmv. The hatched areas 'A' and 'B' are proportional to the amounts of NO adsorbed and photo-oxidised/removed, respectively. Hatched area 'C' is proportional to the amount of nitric acid generated. The key points are: (1) start of contact with NO-containing feed, (2) UV lights on and (3) UV lights off, feed gas changed to zero calibration gas (i.e. air).

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The hatched area 'A' is *proportional* to the amount of NO adsorbed by the test piece in the dark, n_{ads}, whereas marked areas 'B' and 'C' are *proportional* to n_{NO} and n_{NO2}, respectively; the latter three parameters have units: µmol, whereas the units of the hatched areas are: (µl/L).h. The standard suggests that the integrated areas due to (i) NO 'dark' adsorption ('A') and (ii) NO 'dark' desorption (the area under the [NO] decay curve after the light is switched off, *i.e.* at point 3 in Figure and beyond, should be calculated. However, since these are approximately the same and these two values are then subtracted from each other, *i.e.* they roughly cancel each other out and hence these values were not used to calculate the net amount NO_x removed by the test piece, n_{NOx}, as follows:

$$n_{NOx} = (f/22.4)(B-C) \qquad (4)$$

given f is in units: L min^{-1}.

Further examples are given below for the photocatalytic activity of TiO_2 paste coated on glass, and for a typical photocatalytic paper.

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Customer Name:	n/a
Customer contact:	n/a
Sample name:	**Example 1**
Sample description:	TiO_2 paste dip coated onto glass

Testing conditions

Date (dd/mm/yyyy)	16/04/2012
T (°C)	23.4
RH (%)	50
STP flow (L/min)	2.9456
Irradiance (mW/cm⁻²)	0.98
NO supply conc. (ppm)	0.993

Results	Amount (µmol)	Area (%)
(i) NO supplied to the reactor	36.86	100.00
(ii) NO removed by the test piece	5.59	15.18
(iii) total NO unreacted	31.26	84.82
(iv) amount of NO_2 generated by the test piece	5.38	14.60
(v) net amount of NO_x removed by the test piece = ((ii)-(iv))	**0.21**	**0.58**

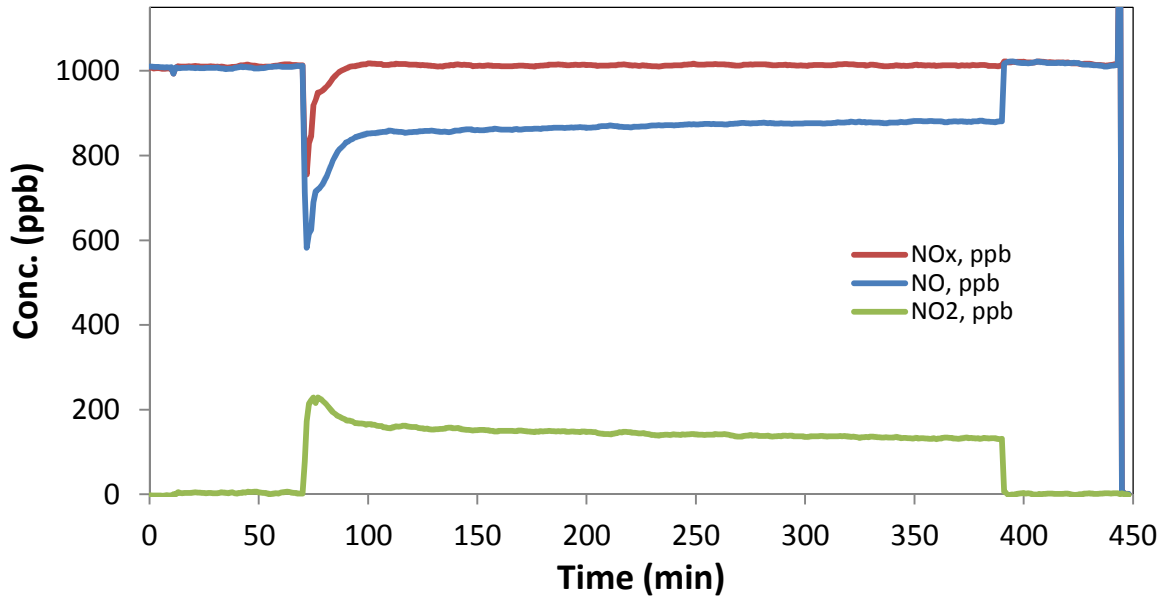

Figure 3 – Trace of NO/NO_x/NO_2 concentration during the ISO test for TiO_2 paste dip coated onto glass.

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Customer Name:	n/a
Customer contact:	n/a
Sample name:	**Example 2**
Sample description:	Photocatalytic paper

Testing conditions

Date (dd/mm/yyyy)	05/09/2012
T (°C)	21.1
RH (%)	51
STP flow (L/min)	2.8676
Irradiance (mW/cm^{-2})	0.98
NO supply conc. (ppm)	0.977

Results	Amount (µmol)	Area (%)
(i) NO supplied to the reactor	35.69	100.00
(ii) NO removed by the test piece	23.85	66.82
(iii) total NO unreacted	11.84	33.18
(iv) amount of NO_2 generated by the test piece	10.02	28.07
(v) net amount of NO_x removed by the test piece = ((ii)-(iv))	**13.83**	**38.76**

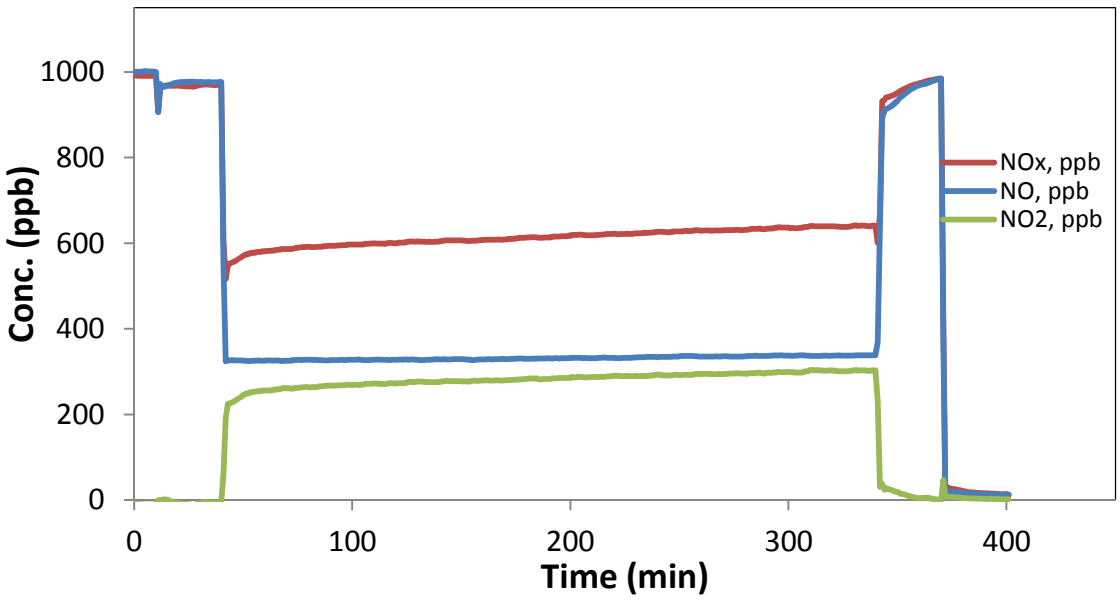

Figure 8 – Trace of NO/NO_x/NO_2 concentration during the ISO test for a typical photocatalytic paper.

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References

[1] ISO 22197-1: 2007, 'Fine ceramics, advanced technical ceramics) – Test method for air-purification performance of semiconducting photocatalytic materials – part 1: Removal of nitric oxide', ISO, Geneva, 2007.

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