

Removal of nitric oxide - ISO 22197-1:2007

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Please find attached the results of NO_x removal capability, determined in accordance with ISO 22197-1:2007, on 4 samples of photocatalytic cement (Sample KNO_xOUT A clear over silicone, B clear over acrylic, C acrylic and D silicone), supplied by Johnson Ongking from Boysen KNO_xOUT in a form of a cast samples 10x5x0.5 cm. Comparison is made to 2 examples of other photocatalytic materials (example two data are in the appendix and tables only).

All samples were pretreated in order to decompose any residual organic matter by irradiating with an ultraviolet lamp (1 mW/cm²) for 16 h, under a flow of zero-calibration gas at 3 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 1 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 3 L/min ± 0.15 L/min, for 30 min whilst the change in the volume fraction of NO and NO₂ were recorded. After 30 minutes, the gas flow was maintained and irradiation of the sample commenced. The NO and NO₂ 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, NO₂ 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 pieces 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) – example 2 data are available in the appendix.

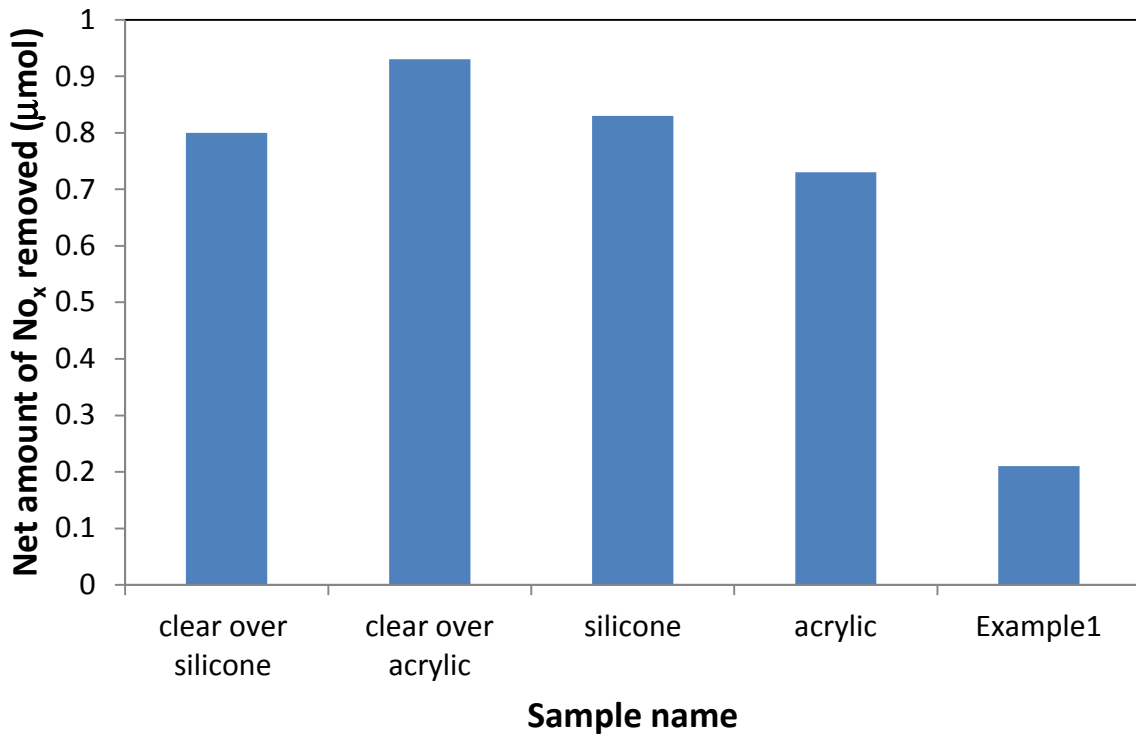


Figure 1 – Histogram illustrating the ability of supplied test pieces, and 1 example test piece, to remove NO_x from an air stream containing 1 ppm NO over a 5 hour period (units: μmol). All supplied samples are photocatalytic cements, whilst example 1 is a sample of TiO_2 paste dipcoated onto glass.

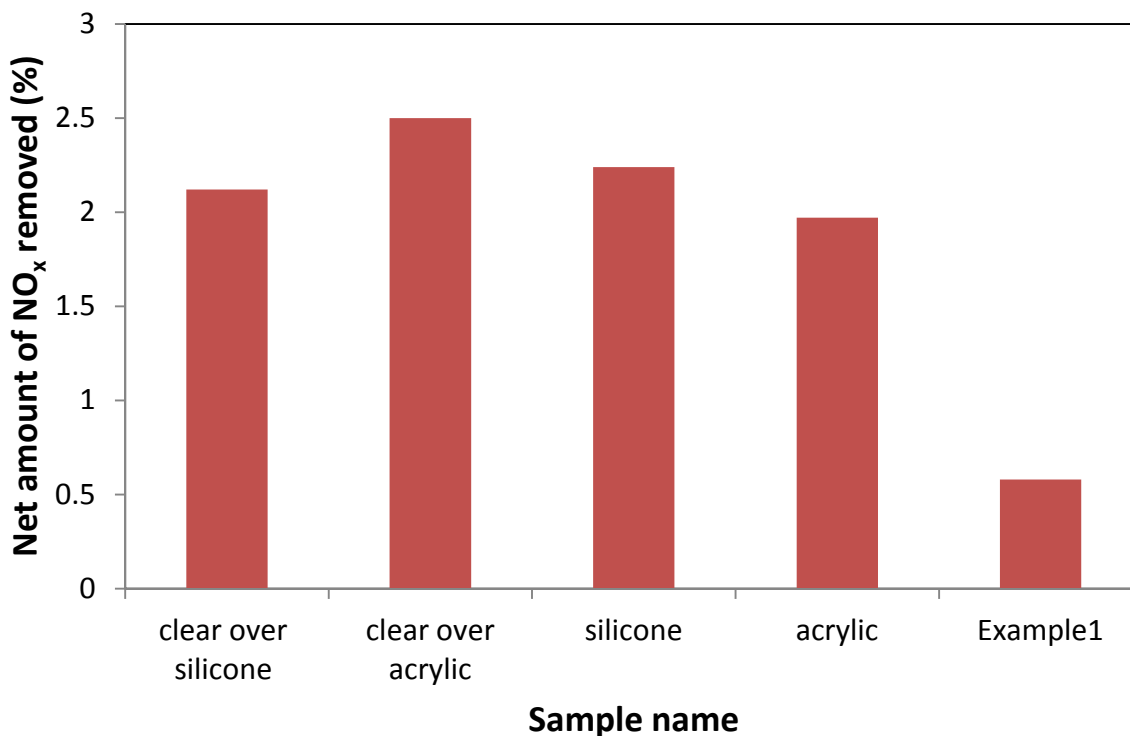


Figure 2 – Histogram illustrating the ability of supplied test pieces, and 1 example test piece, to remove NO_x from an air stream containing 1 ppm NO over a 5 hour period (units: % of NO supplied to the reactor). All supplied samples are of photocatalytic cements, whilst example 1 is a sample of TiO₂ paste dipcoated onto glass.

Table 1 summarises (i) NO supplied to the reactor (ii) NO removed by the test piece (iii) total NO unreacted (iv) amount of NO₂ generated by the test piece and (v) net amount of NO_x removed by the test piece = ((ii)-(iv)) for each of the supplied samples, and for the one example test piece, 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 TiO₂ paste on glass and of photocatalytic paper, for your comparison.

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Sample number (and name)	Units: μmol				
	(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))
Clear over silicone	37.53	8.10	29.43	7.30	0.80
Clear over acrylic	37.04	9.42	27.62	8.50	0.93
Silicone	36.92	11.60	25.32	10.77	0.83
Acrylic	37.23	8.92	28.30	8.19	0.73
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 NO₂ generated by the test piece and (v) net amount of NO_x removed by the test piece = ((ii)-(iv)) for each of the tested samples, and example test pieces, in units μmol .

Sample number (and name)	Units: % of NO supplied to the reactor				
	(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))
Clear over silicone	100.00	21.58	78.42	19.46	2.12
Clear over acrylic	100.00	25.44	74.56	22.94	2.50
Silicone	100.00	31.42	68.58	29.18	2.24
Acrylic	100.00	23.97	76.03	21.99	1.97
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 NO₂ generated by the test piece and (v) net amount of NO_x removed by the test piece = ((ii)-(iv)) for each of the tested samples, and example test pieces, as a % of NO supplied to the reactor.

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Customer Name: Johnson Ongking
 Customer contact: johnson@boysen.com.ph
 Sample name: KNOxOUT clear over silicone
 Sample description: Cast cement block

Testing conditions

Date (dd/mm/yy) 30/09/2015
 T (°C) = 25.5
 RH (%) = 50
 STP flow (L/min) = 3.01
 irradiance (mW/cm²) = 1
 NO supply conc. (ppm) = 1.00

	Amount (μmol)	Area (%)
(i) NO supplied to the reactor	37.53	100.00
(ii) NO removed by the test piece	8.10	21.58
(iii) total NO unreacted	29.43	78.42
(iv) amount of NO ₂ generated by the test piece	7.30	19.46
(v) net amount of NO _x removed by the test piece = ((ii)-(iv))	0.80	2.12

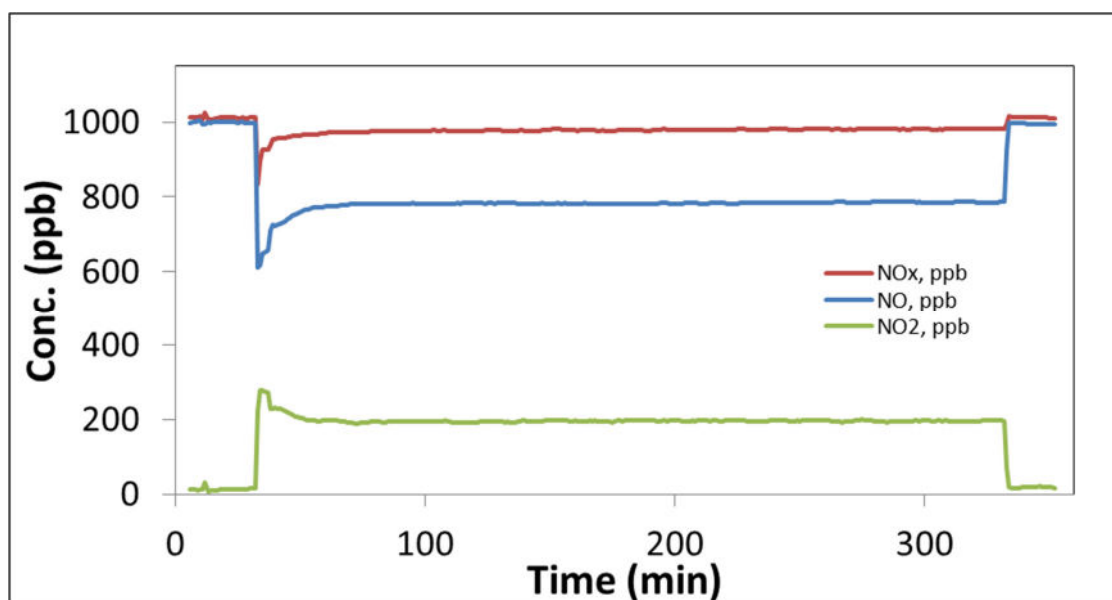


Figure 3 – Trace of NO/NO_x/NO₂ concentration during the ISO test for sample KNOxOUT clear over silicone.

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Customer Name: Johnson Ongking
 Customer contact: johnson@boysen.com.ph
 Sample name: KNOxOUT clear over acrylic
 Sample description: Cast cement block

Testing conditions

Date (dd/mm/yy) 01/10/2015
 T (°C) = 26
 RH (%) = 50
 STP flow (L/min) = 3.048
 irradiance (mW/cm²) = 1
 NO supply conc. (ppm) = 1.00

Results

	Amount (μmol)	Area (%)
(i) NO supplied to the reactor	37.04	100.00
(ii) NO removed by the test piece	9.42	25.44
(iii) total NO unreacted	27.62	74.56
(iv) amount of NO ₂ generated by the test piece	8.50	22.94
(v) net amount of NO _x removed by the test piece = ((ii)-(iv))	0.93	2.50

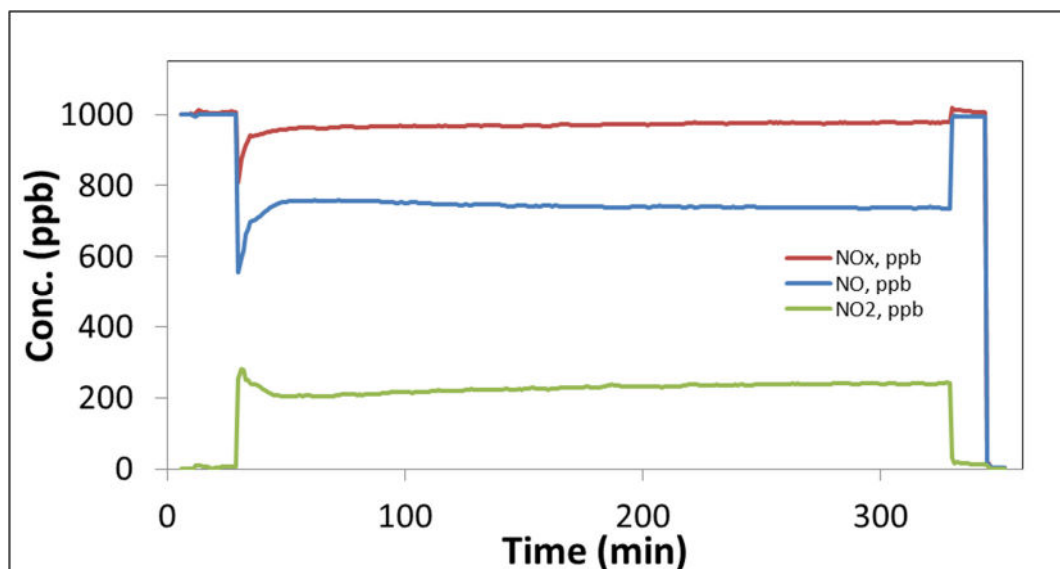


Figure 4 – Trace of NO/NO_x/NO₂ concentration during the ISO test for sample KNOxOUT clear over acrylic.

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Customer Name: Johnson Ongking

Customer contact: johnson@boysen.com.ph

Sample name: KNO_xOUT silicone

Sample description: Cast cement block

Testing conditions

Date (dd/mm/yy) 02/10/2015

T (°C) = 24

RH (%) = 50

STP flow (L/min) = 2.98

irradiance (mW/cm²) = 1

NO supply conc. (ppm) = 1.01

Results

	Amount (μ mol)	Area (%)
(i) NO supplied to the reactor	36.92	100.00
(ii) NO removed by the test piece	11.60	31.42
(iii) total NO unreacted	25.32	68.58
(iv) amount of NO ₂ generated by the test piece	10.77	29.18
(v) net amount of NO _x removed by the test piece = ((ii)-(iv))	0.83	2.24

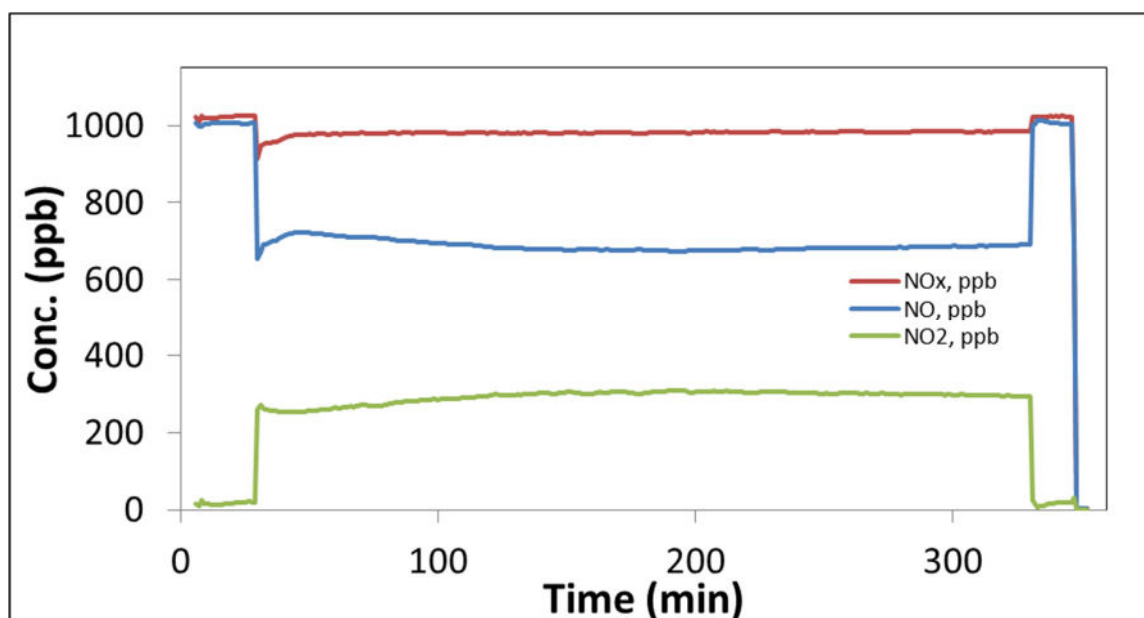


Figure 5 – Trace of NO/NO_x/NO₂ concentration during the ISO test for sample KNO_xOUT silicone.

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Customer Name: Johnson Ongking
 Customer contact: johnson@boysen.com.ph
 Sample name: KNOxOUT acrylic
 Sample description: Cast cement block

Testing conditions

Date (dd/mm/yy) 02/10/2015
 T (°C) = 24.7
 RH (%) = 49
 STP flow (L/min) = 3.053
 irradiance (mW/cm²) = 1
 NO supply conc. (ppm) = 1.00

Results

	<u>Amount</u> (μmol)	<u>Area</u> (%)
(i) NO supplied to the reactor	37.23	100.00
(ii) NO removed by the test piece	8.92	23.97
(iii) total NO unreacted	28.30	76.03
(iv) amount of NO ₂ generated by the test piece	8.19	21.99
(v) net amount of NO _x removed by the test piece = ((ii)-(iv))	0.73	1.97

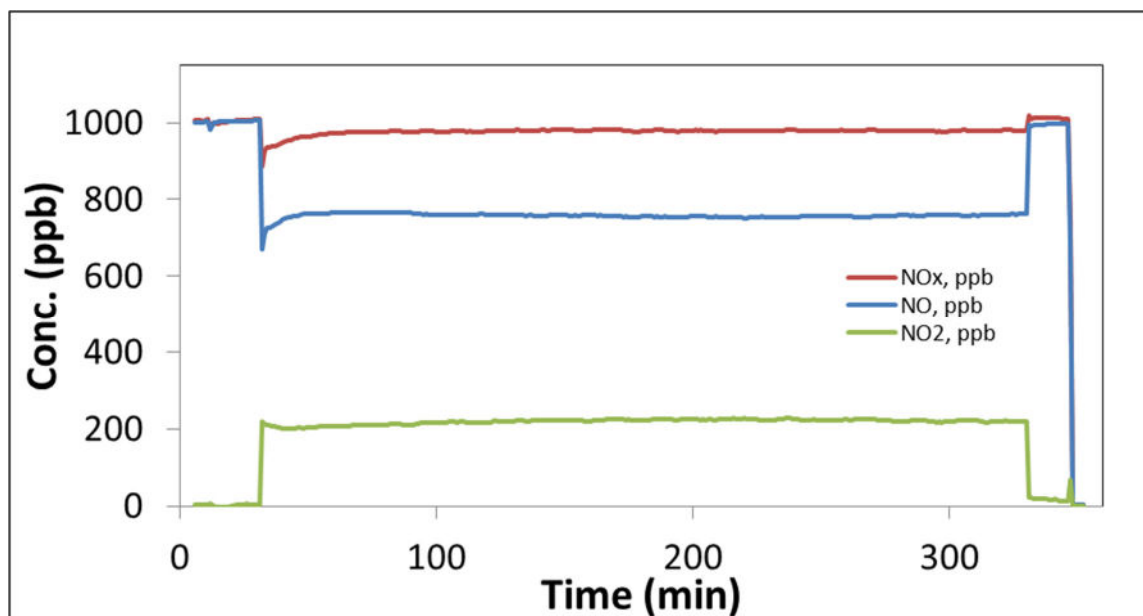


Figure 6 – Trace of NO/NO_x/NO₂ concentration during the ISO test for sample KNOxOUT acrylic.

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 (CH₃CHO), ISO 222197-2: 2011 [2] and toluene (CH₃C₆H₅), 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 automobiles and fossil fuels in power stations. In the absence of a catalyst NO is oxidised relatively slowly to nitric oxide by oxygen ($t_{1/2} \sim 70$ 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 NO₂, 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, NO₂, 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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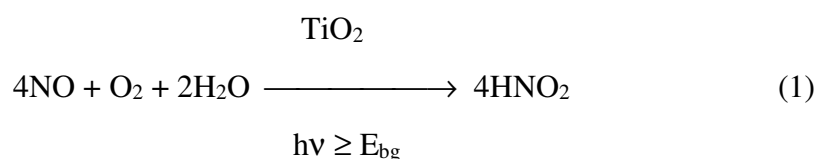
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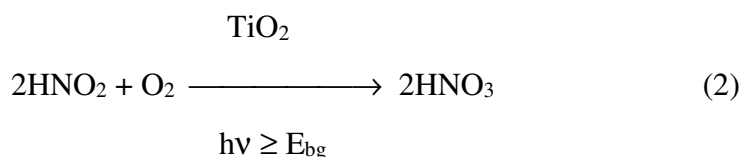
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Key reactions

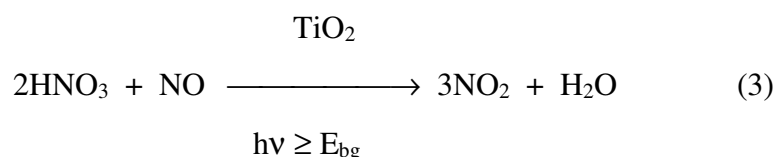
The titania-sensitised, photocatalytic oxidation of NO proceeds to nitric acid, via nitrous acid and a radical based mechanism.[4-8] The two key photocatalytic reactions are:



and



Recent work [4] reveals that the accumulation of nitric acid on the surface promotes its photocatalysed reaction with NO that generates the toxic product NO₂, i.e.



This can lead to an eventual steady state where the rate of NO removal is matched by the rate of NO₂ production; which is clearly highly undesirable. It follows that for any NO_x-removing photocatalyst product to work effectively it is necessary that the HNO₃ 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 NO₂ generated (n_{NO_2}) 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 1A.

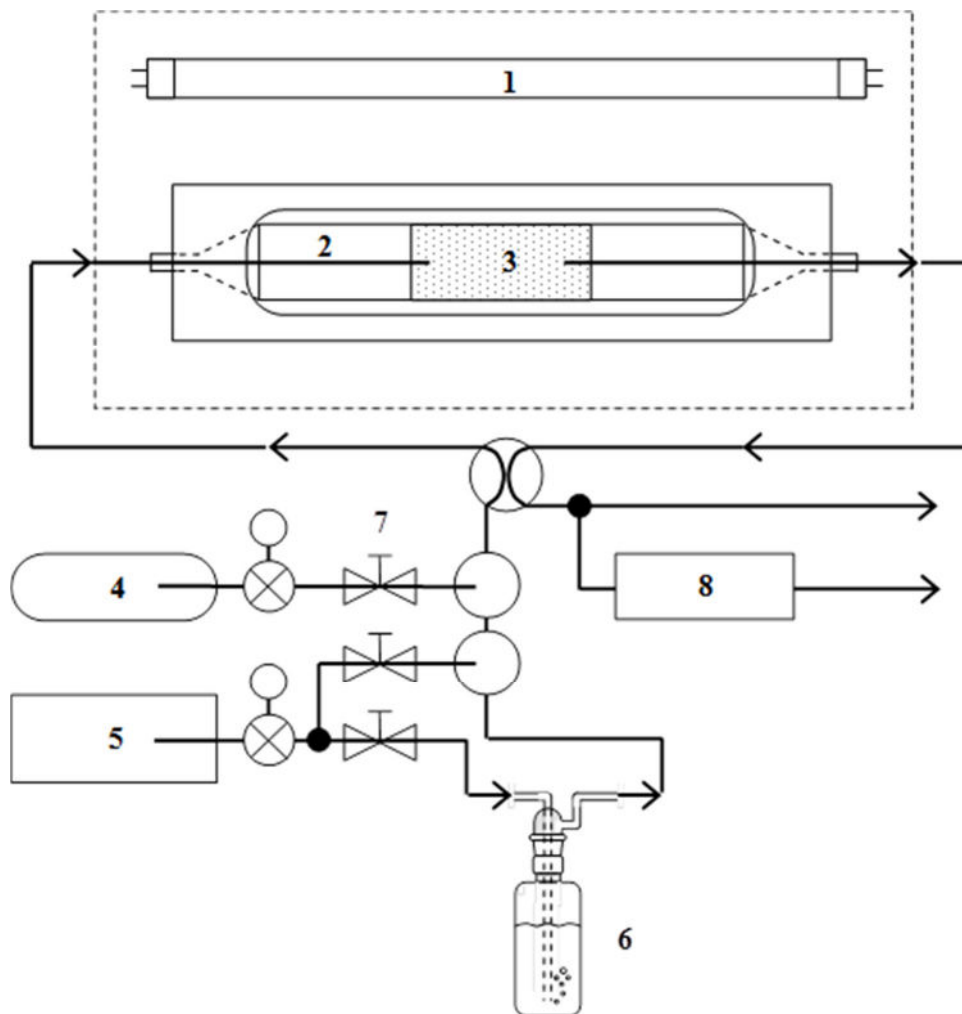


Figure 1A – Irradiation set up for the air purification ISO standards, comprising: (1) UV light source, (2) glass cover, (3) sample under test, (4) standard gas (i.e. test pollutant), (5) purified air source, (6) humidifier, (7) mass-flow controllers and (8) pollutant gas analyser.

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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 2A 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).

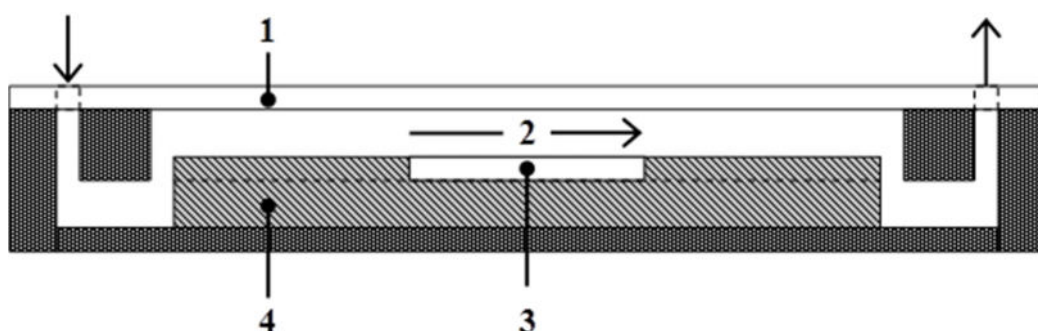


Figure 2A. – Cross-sectional view of the photoreactor illustrated in Figure for solid, flat test pieces. The components are: (1) glass cover, (2) test gas flow, (3) flat test sample, and (4) height-adjusting plate.

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 N₂,

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mixed with air to produce the reaction test stream of 1 ppmv of NO and 21% O₂) 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 [NO₂] generated by the test for a titania sample are illustrated in Figure 3A.

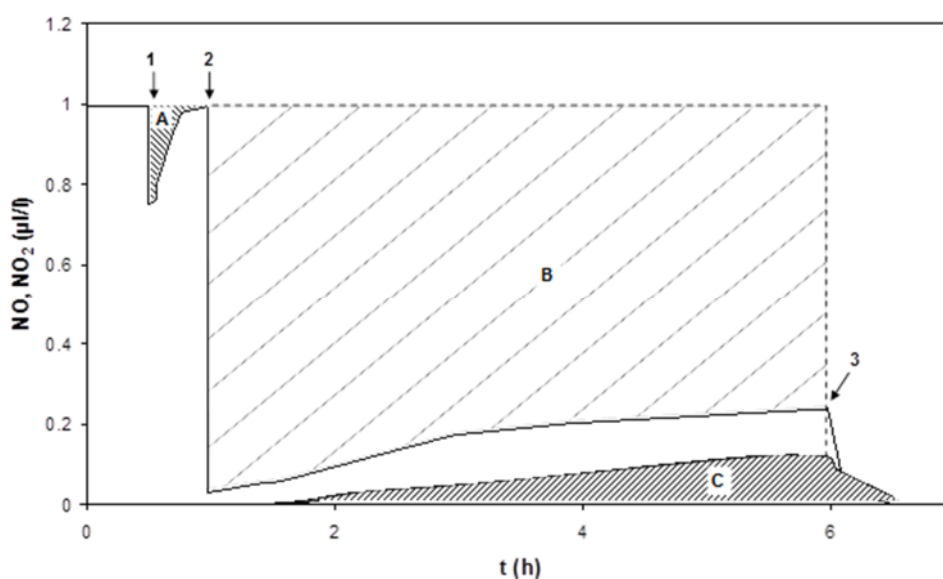


Figure 3A. –Typical data set generated, *i.e.* NO removed and nitric acid generated, in the NO ISO standard, for which the feed stream [NO] is 1 ppmv. The hatched areas 'A' and 'B' are proportional to the amounts of NO adsorbed and photo-oxidised/removed, respectively. Hatched area 'C' is proportional 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_{NO_2} , respectively; the latter three parameters have units: μmol , whereas the units of the hatched areas are: $(\mu\text{l/L})\cdot\text{h}$. 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_{NO_x} , as follows:

$$n_{\text{NO}_x} = (f/22.4)(B-C) \quad (4)$$

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: TiO₂ 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

	<u>Amount (μmol)</u>	<u>Area (%)</u>
(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

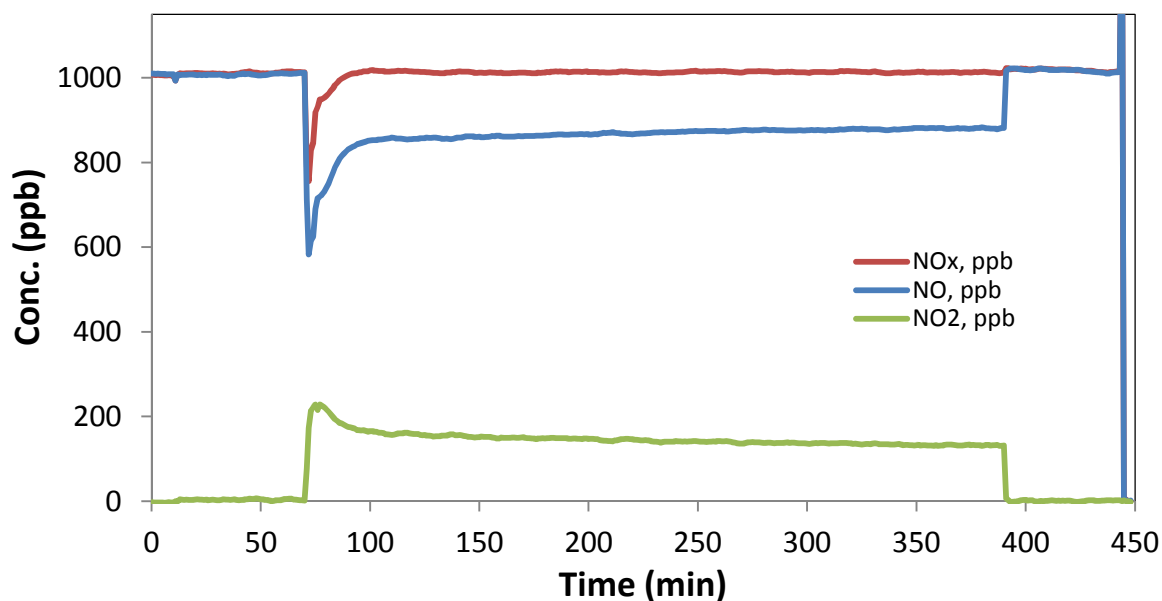


Figure 4A.— Trace of NO/NO_x/NO₂ concentration during the ISO test for TiO₂ paste dip coated onto glass.

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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

	<u>Amount (μmol)</u>	<u>Area (%)</u>
(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

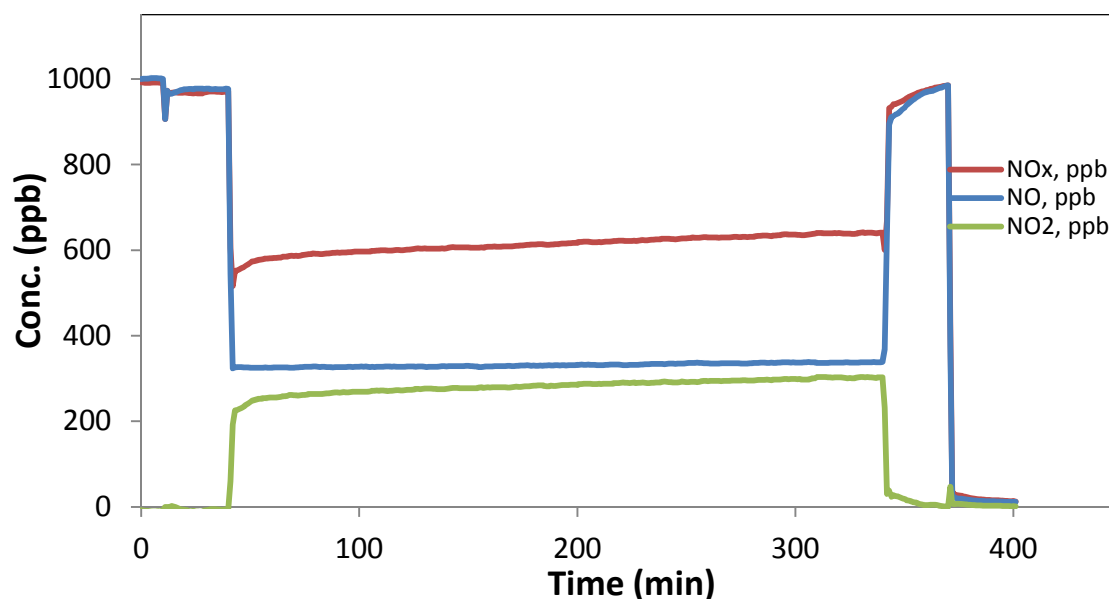


Figure 5A. – Trace of NO/NO_x/NO₂ concentration during the ISO test for a typical photocatalytic paper.

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