PHOTOCAT

Documentation of Photocatalytic Activity Following ISO 22197-1 Removal of NOx

Thomas Betong

Trial Samples

Report #223

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Photocat A/S, Langebjerg 4, DK-4000 Roskilde, Denmark
www.photocat.net info@photocat.net +45 7022 5055

Received materials

2 samples were received from Thomas Betong:

Fig.1 Front of received samples

Fig.2 Back of received samples

Sample description

The samples were coated with Concrete Dry 200 - 2012.

Sample 1: ca. 80 g/m^2 Dry 200

Sample 2: ca. 80 g/m^2 Dry 200

Sample preparation

The test material were cut in 0.049m x 0.099m samples on a wet circular saw and was cleaned with de-ionized water and dried in an oven at 110 ºC for 12 hrs before testing, following the procedure proposed by Prof. Brouwers (Hüsken et al., Building and Environment 44 (2009) 2463-2474), which agrees with the ISO 22197-1 standard that specifies that the sample "may be dried within a temperature range that does not cause physical or chemical changes to the test piece (max of 110 ºC)". Dryness is confirmed when a constant mass is reached.

The coating was done on the dried and cured samples, by manual application using a pressurized spray set-up. The samples were then allowed to dry at ambient lab conditions overnight.

The samples were then activated in UV at 1 mW/cm2 for 12 hours and then analyzed following ISO 22197-1. The samples are pre-activated with UVA fluorescent light. According to the ISO 22197-1 standard paragraph 8.1.1 the pre-activation is used to remove organic matter on the surface of the tested samples, such as fingerprints pollution etc. It is stated in the ISO standard that the pre-activation should be at least 5 hrs with an UV irradiance that is high enough to secure complete decomposition of organic matter. This means that if the organic matter is not fully decomposed in 5 hrs. the pre-activation needs to be longer. The pre-activation continues only no organic matter on the surface interfere with the results. Often accepted pre-activation times are up to 5 days.

Test conditions according to ISO 22197-1

The photoreactor is manufactured by Prof. Bahnemann Leibniz Universität Hannover, and is fittet with an UV transparent quartz lid and 5.0 mm laminar flow air gap above the sample.

The ISO 22197-1 test set-up at Photocat was validated by a Round-Robin test between the Photocat Lab, the Lab of Leibniz Universität Hannover and Laboratoire Centre de recherché routières, Sterrebeek.

Inlet concentration	1.0 ppm NO, 3 L/min.
Temperature	20 ºC ± 5 ºC
Relative humidity	50 ± 15 % RH
Light source	UVA-340 fluorescent tubes from Q-Lab. See Appendix A for more details.
Light intensity	1.0 mW/cm2 UVA (320-400 nm) calibrated by light detector.
Light detector	PMA2100 from Solar Light with UV-A detector PMA2110 (320-400nm) External calibrated June 20, 2017.
NOx analyzer	Horiba APNA 370 NOx analyzer with a detection limit of 1 ppb External calibrated Mar. 14, 2022.

Test summary

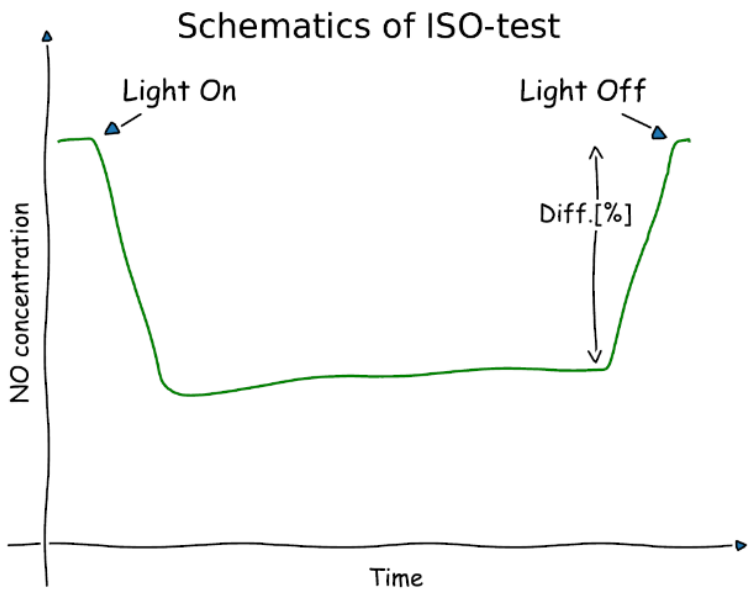
Date	2022-06-16
Product	Concrete Dry 200 - 2012
Samples	2
Location	Photocat Lab, Roskilde, Denmark
Test method	Photocatalytic Activity Test – ISO 22197-1 (removal of NOx)
Light intensity at start	1.0 mW/cm2 UVA (320-400 nm)
Light intensity at end	1.0 mW/cm2 UVA (320-400 nm)
Duration of analysis	30 min. *
Person in charge of test	SØ

* The samples were tested in the ISO 22197-1 for 30 min. from the light was turned on until the light was turned off. The standard ISO 22197-1 specifies 5 hrs. of testing from the light is turned on until the light is turned off. For evaluation of many samples and for comparing samples between each other, Photocat often uses 35 min. or the time when the system is stable and in equilibrium. The activity results can vary compared to a full 5 hour test.

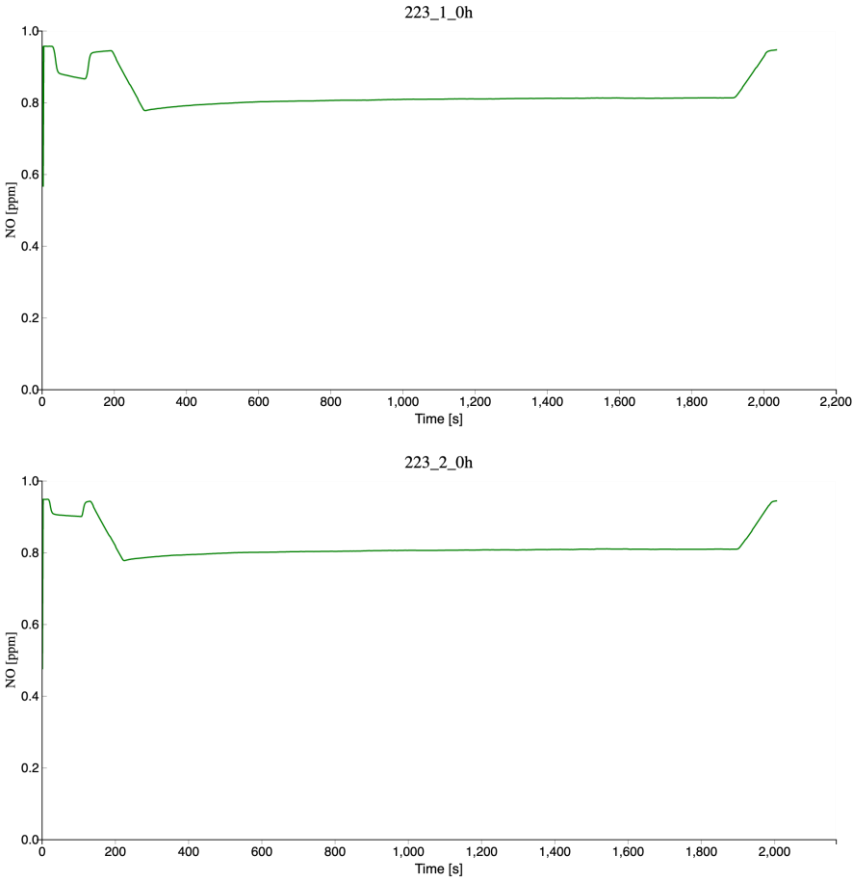
Evaluation of results

The activity of the tested sample is expressed as the percentage difference of the NO level* at the end of the test with UV light turned on and the NOx level after the UV light is turned off and the NO level is stable.

* See Appendix B for further information.



Results


223_1_0h
NO [ppm]
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1,000
1,200
1,400
1,600
1,800
2,000
2,200
Time [s]
223_2_0h
NO [ppm]
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1,000
1,200
1,400
1,600
1,800
2,000
Time [s]

Results summary

Sample	Name	NO-Degradation [%]	Photon eff. [%]	NO [mg/m2/hour]
1	223_1_0h	14.17	0.2	6.8
2	223_2_0h	14.29	0.2	6.9

Summary

The Thomas Betong NOxOFF Samples are Highly active with a maximum activity of 14.29% analyzed by ISO 22197-1.

Test responsible

Director of Technology

Appendix A - Light sources

The samples are tested with an UVA fluorescent light source simulating the UV spectrum of the sun light with a maximum peak at 340 nm. It is known that different light sources even though they are within the specification of the ISO standard yields different result. Photocat choose to use a light source with a spectrum similar to sunlight, in which the product will be used. Different labs use different light sources which can yield different activity results.

All the different photocatalytic ISO tests refer to the use of a suitable UV light source. However, typically 3 different types are recommended – two types of BLB (black light blue lamp) and a xenon arc lamp.

The specifications and explanation of the 3 different types of light sources for the photocatalytic ISO tests are described in 'ISO 10677:2011 – Ultraviolet light source for testing semiconducting photocatalytic materials'. The spectra for the 3 types of UVA light that can be used in the ISO 22197-1 standard are shown below.

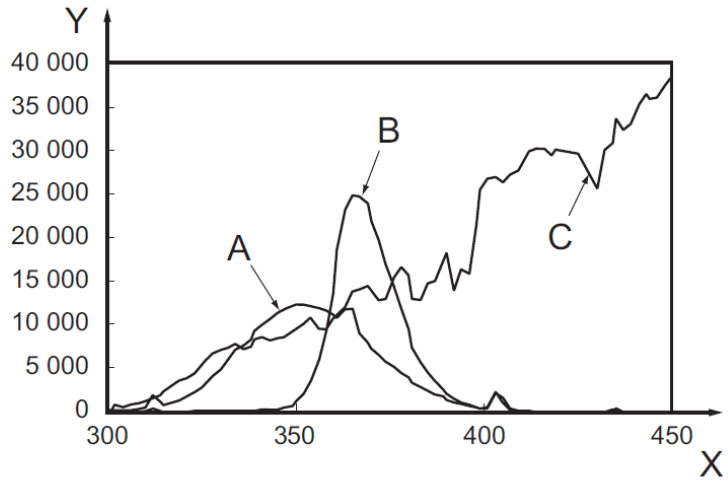


Figure A1. Y: Relative irradiance, X: wavelength (nm), A: Light source BLB max 351 nm, B: Light source BLB max 368 nm, C: sunlight.

According to and stated in ISO 10677:2011: 'the UV irradiance can differ depending upon the location, it is preferable that the irradiance of the UV light source used for the test should be representative of the actual irradiance where the photocatalytic material will be used'.

Furthermore ISO 10677:201 states: 'Considering the wavelength distribution, stability of irradiance and ability to produce a continuous spectrum, a fluorescent UV lamp and xenon arc lamp shall be used for testing photocatalytic materials'.

Light source used at Photocat Lab.

At Photocat we use UVA 340 nm fluorescent tubes as standard light source in the ISO 22197-1 set-up. The UVA 340 nm fluorescent tubes are purchased from Q-Lab Corporation (www.q-lab.com). The UVA-340 provides the best possible simulation of sunlight in the critical short wavelength region from 365 nm down to the solar cutoff of 295 nm. Its peak emission is at 340 nm. Below is the spectrum for the UVA 340 nm fluorescent tubes shown in comparison with sunlight.

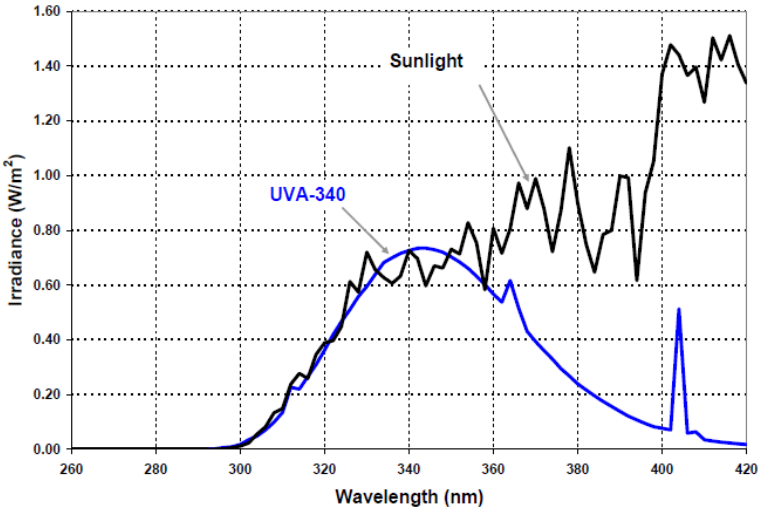


Figure 2 - Noon Summer Sunlight vs UVA-340 Irradiance

UVA-340 lamps provide the best available simulation of sunlight in the critical short-wave UV region.

Figure A2. Spectra of UVA 340 nm fluorescent tubes and sunlight.

The light intensity is measured before and after test using a PMA2100 from Solar light, UV-A detector PMA 2110, which is calibrated against this type of light source.

Appendix B - Determination of photocatalytic activity

The photocatalytic activity following ISO 22197-1 standard tests is in this report reported as the removal of NO. The removal of NO is defined as the percentage removal at the end of the test defined as the final NO concentration with the Light on ($c_{NO,\,t}$) related to the NO concentration after end experiment ($c_{NO,\,t(light\ off)}$). This is also referred to as the NO-Degradation (final). This is illustrated in the figure below.

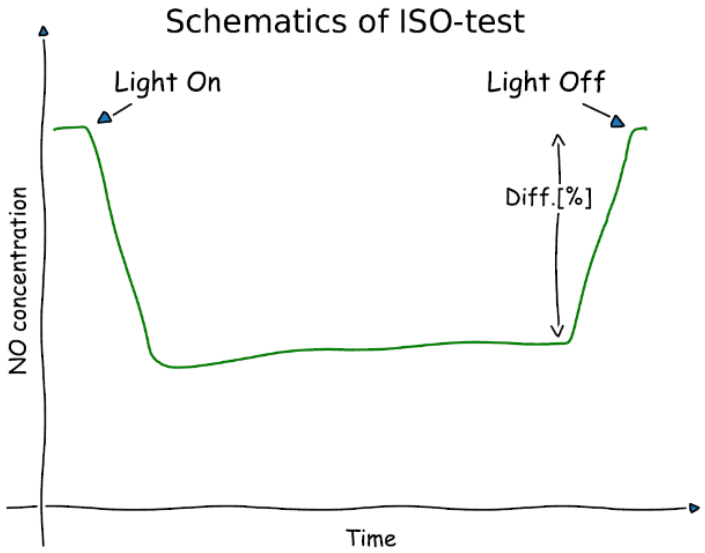


Figure A3. Schematic illustration of definition of NO-Degradation (final)

The NO-Degradation (final) is used to determine the photon efficiency, which is defined as the photons used by the sample divided with the number of photons available.

The NO-Degradation (final) is also used to determine the amount of NO removed in µmol, which is then used to calculate the NO removal in mg NO/m^2/hr.

Samples tested at Photocat following the ISO 22197-1 are ranked according to the following scheme.

Table A1. Ranking at Photocat after ISO 22197-1.

Photocat Ranking	**Photon Eff. NO [%]**	**NO-Degradation (final) [%]**
Active	0.029 % < ζ < 0.072 %	2.0 % < NO % < 5.0 %
Medium Active	0.072 % < ζ < 0.143 %	5.0 % < NO % < 10 %
Highly Active	0.143 % < ζ < 0.215 %	10 % < NO % < 15 %
Very Active	ζ > 0.215 %	NO % > 15 %

which is related to the evaluation by D-TOX, see below table.

Table A2. Ranking at D-TOX/Prof. Bahnemann after ISO 22197-1.

D-TOX Ranking	**Photon Eff. NO [%]**	**NO-Degradation (final) [%]**
Sufficient	0.01 % < ζ < 0.05 %	0.7 % < NO % < 3.5 %
Satisfying	0.05 % < ζ < 0.1 %	3.5 % < NO % < 7.0 %
Good	0.1 % < ζ < 0.2 %	7.0 % < NO % < 14 %
Very Good	0.2 % < ζ < 0.5 %	14 % < NO % < 35 %
Excellent	ζ > 0.5 %	NO % > 35 %

Some labs use the removal of NOx to determine and rank the photocatalytic activity. However, using the NOx removal as ranking parameter is questionable if the lab is using a chemoluminescent (CLD) NO-NOx analyzer using a catalytic converter (as employed at Photocat Lab). This is due to the fact that using a CLD NOx analyzer the NO_2 removal rates will only be lower limts and highly underestimated according to the issues with the CLD analyzer to detect and measure NO_2 (Engel et al., 2015).

A CLD analyzer is measuring the NO and the sum of NO and nitrogen-containing compounds from which NO can be subtracted, and is calculating the difference which is assumed to be NO_2 (Engel et., 2015). The CLD analyzer quantifies NO concentrations with high accuracy but has a significant uncertainty of measurements of NOx (NO + NO_2) resulting in a large uncertainty of the concentration of NO_2 (Engel et al. 2015).

Dunlea et al. were one of the first studies to quantify the uncertainties of determining the concentration of NO_2 by CLD analyzers. Dunlea et al. 2007 investigated the NOx pollution in Mexico City and they found a significant interference in the CLD analyzer measurement of NO_2. They found that up to 50 % of the ambient measured NO_2 was related to interference, meaning that they showed that the CLD analyzer overestimated the NO_2 concentration by a factor of 2 (Dunlea et al. 2007).

Dunlea et al. also found that the reason to the interference was mainly caused by HNO_3 in the air and they estimated that 60 % of the interference was related to HNO_3 (Dunlea et al. 2007). HNO_3 is the final product in the photocatalytic reaction, where NO and NO_2 is oxidized to HNO_3. HNO_3 is normally transformed from a gas into a solid by dry deposition on the substrate, but in the ISO 22197-1 standard test the gas is analyzed just after the reaction and it is therefore a possible cause to the uncertainties in establishing the NO_2 concentrations.

Villena et al. conformed the study by Dunlea et al. when the investigated the NOx pollution in Santiago de Chile (Vilena et al., 2012). Vilena et al. showed a positive interference of NO_2 of up to 25 ppb, which meant that the CLD analyzer overestimated the NO_2 concentration by up to a factor of 4. The conclusion by Vilena et al. is that the CLD techniques should not be used for selective NO_2 detection but only for detecting NO (Vilena et al. 2012).

Since the CLD analyzer is the most dominant and still recommended analyzer in the ISO 22197-1 standard test it is important only to quantify the effect from the NO removal data, as the concentration of NO_2 is overestimated as shown in the studies by Dunlea et al. and Vilena et al. If the NOx or NO_2 data are displayed in the ISO report and a CLD analyzer is used it is important to emphasize that the photocatalytic activity related to NOx/NO_2 is the lower estimated and in real life it will be higher.

If the ISO standard test is used for Air Quality Models (AQM) the NOx/NO_2 data is not valid to use if obtained by a CLD analyzer according to McClenny et al. who recommend that NO_2 data for AQM models requires uncertainties of less that ± 10 % and with the observed interferences of 50% or more for the CLD analyzer this is not acceptable (McClenny et al. 2002 and Dunlea et al. 2007). Therefore for AQM the NO removal data should be used.

References

Dunlea, E.J. , Herndon, S.C. , Nelson, D.D. , Volkamer, R.M. , San Martini, F. , Sheehy, P.M., Zahniser, M.S. , Shorter, J.H., Wormhoudt, J.C., Lamb, B.K., Allwine, E.J., Gaffney, J.S., Marley, N.A., Grutter, M., Marquez, C., Blanco, S., Cardenas, B., Retama, A., Ramos Villegas, C.R., Kolb, C.E., Molina, L.T., Molina, M.J. (2007), Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment, Atmos. Chem. Phys. 7 2691–2704.

Engel, A., Glyk, A., Hülsewig, A., Große, J., Dillert, R., Bahnemann, D. (2015). Determination of the photocatalytic deposition velocity. Chemical Engineering Journal. 261. 88-94. 10.1016.

McClenny, W. A., Williams, E. J., Cohen, R. C., and Stutz, J. (2002), Preparing to Measure the Effects of the NOx SIP Call – Methods for Ambient Air Monitoring of NO, NO2, NOy , and Individual NOz Species, J. Air Waste Manage. Assoc., 52, 542–562.

Villena, G., Bejan, I., Kurtenbach, R., Wiesen, P., Kleffmann, J. (2012) Interferences of commercial NO2 instruments in the urban atmosphere and in a smog chamber, Atmos. Meas. Tech. 5, 149–159.