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Test report

Determination of the photocatalytic activity with the tangential flow method - reduction of nitric oxide

(UNI 11484 simplified method, in accordance with CEN / TS 16980-1: 2016)

on materials - Rondine ceramica, Advance Rondine Collections 3D series

for

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Torino, June 8, 2020

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1. GENERAL TEST CONDITIONS

The photocatalytic NO/NO_x abatement tests were carried out using the method described in UNI 11484 (Determination of photocatalytic activity with a tangential continuous flow method - Abatement of nitric oxide - March 2013). The method follows the European Union technical specification CEN/TS 16980-1:2016 "Continuous flow methods – Part 1: Determination of NO in the air by photocatalytic materials". The tests were carried out with a simplified procedure, i.e. when the condition of stability of the concentrations measured under irradiation was reached or the maximum irradiation time was reached (according to the UNI 11484 180 minutes), the flow rate was not changed within the reactor, thus ending the test under these conditions. The irradiance was in UV 10 W m^{-2} from 290 to 400 nm), e in deroga sotto irraggiamento visibile.

The determination of the NO/NO_2 content in the flow was carried out using an APNA 370 chemiluminescence detector (serial number WWSBNNW6). The measuring reactor had an internal volume of 3.6 dm^3. The mixing inside the reactor was guaranteed by a compact axial fan EBMPAPST 612 JH (dimensions 60×60×32 mm) that provides a nominal flow equal to 70 m^3 h^{-1}.

The irradiation took place with two different irradiation systems. In the first case, according to the indications of the UNI 11484 standard, the sample was irradiated in the UV by means of a set of two Philips PL-S 9W/2P BLB fluorescent lamps whose emission spectrum is shown in **Figure 1**. The intensity of the radiation incident on the sample was **10 W m^{-2}** between 290 and 400 nm.

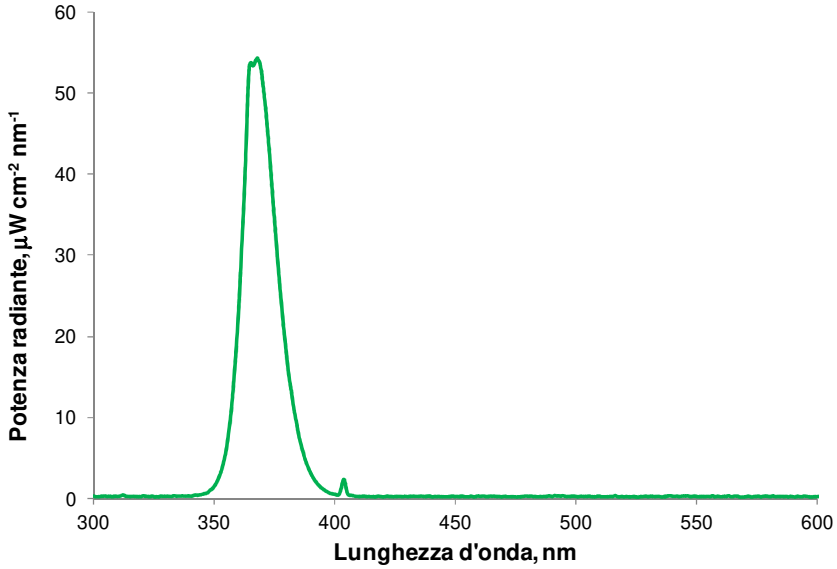

Figure 1. Emission spectrum of the Philips PL-S 9W / 2P BLB lamp. The radiant power was measured in the same position in which the sample is housed by placing the Pyrex glass cover for closing the measuring reactor between the lamp and the sample.

In the case of Visible irradiation, at variance with the standard UNI 11484, it was used a LED illuminator (6500 K color temperature), assembled at the laboratories of the Department of Chemistry of the University of Turin, devoid of UV emission. The spectrum of this source (**Figure 2**) was characterized as shown below. The irradiance on the sample surface was **250 W m^{-2} between 400 and 800 nm.**

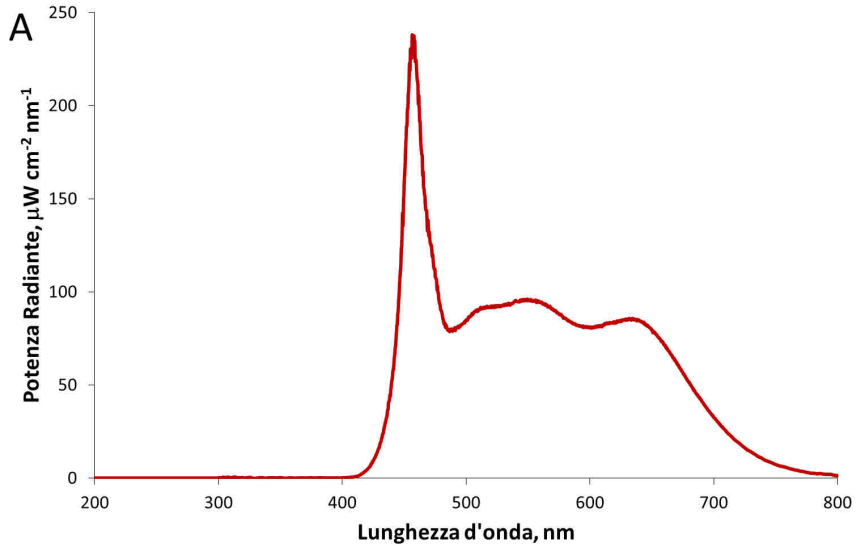

Figure 2. Emission spectrum of the LED lighting system (6500 K color temperature). The radiant power was measured in the same position in which the sample is housed by placing the Pyrex glass cover for closing the measurement reactor between the lamp and the sample.

The irradiance at the surface of the samples was evaluated spettroradiometrically with the two employed irradiation systems, through the use of an Ocean Optics USB2000 + UV-VIS spectrophotometer equipped with an optical fiber having a diameter of 400 µm and length equal to 30 cm, and a cosine corrector (Ocean Optics CC-3-UV-T, PTFE optical diffuser, spectral range 200-2500 nm, external diameter 6.35 mm, field of view 180 °). The spectroradiometer was calibrated with an Ocean Optics DH-2000-CAL Deuterium-Halogen Light Source for UV-Vis-NIR measurements, calibrated in turn in absolute irradiance by the seller (Radiometric Calibration Standard UV-NIR, calibration certificate # 2162).

2. SAMPLES

The samples (delivered directly by the client to UNITO on 21/05/2019) are 3 ceramic tiles (labeled AR, BR, CR, respectively, with dimensions 9.9 cm × 9.9 cm × 10 mm) with a potentially photoactive white paint deposited on one of the faces, whose photocatalytic properties are the subject of this document.

The tests in accordance with the UNI 11484 standard ("simplified" test) were performed on the samples as such **without any pretreatment**. The tests in accordance with the UNI 11484 standard, but with Visible radiation took place on the samples used for the test under UV radiation, but after washing with demineralized water and drying at 90 ° C.

The list of tested samples, with the respective irradiated surface area and an indication of the type of radiation used during the test, is reported in **Table 1**. The pictures of the tested samples are shown in **Figure 3**.

Table 1. Samples analyzed

Sample	Sample description	Irradiation	Test	Area, cm^2	Pretreatment
AR (UV)	Ceramic tile	UV	NO/NOx, UNI 11484:2013	98.0	NO
BR (UV)	Ceramic tile	UV	NO/NOx, UNI 11484:2013	98.0	NO
CR (UV)	Ceramic tile	UV	NO/NOx, UNI 11484:2013	98.0	NO
AR(Vis)	Ceramic tile	Visible	NO/NOx, UNI 11484:2013 (Visible)	98.0	Washing with water after test in UV
BR(Vis)	Ceramic tile	Visible	NO/NOx, UNI 11484:2013 (Visible)	98.0	Washing with water after test in UV
CR(Vis)	Ceramic tile	Visible	NO/NOx, UNI 11484:2013 (Visible)	98.0	Washing with water after test in UV

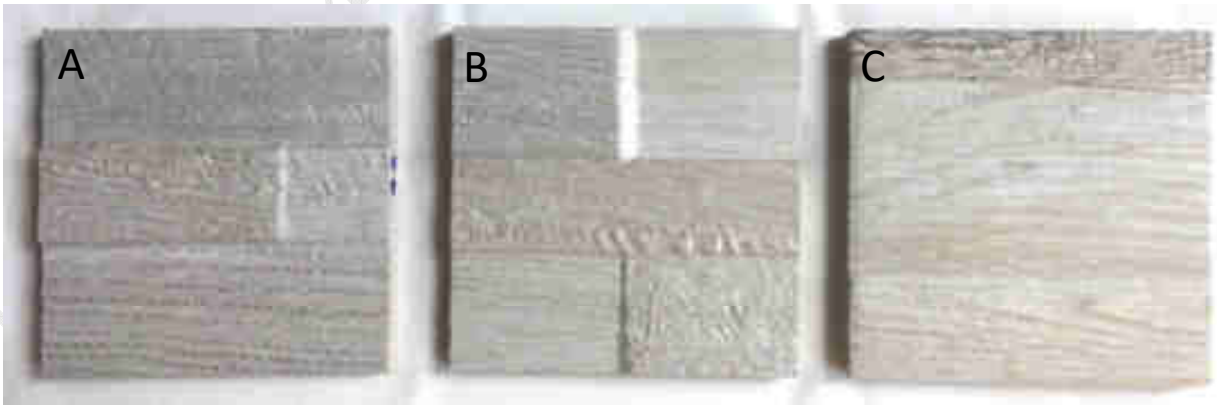

Figure 3. Pictures of the samples tested according to UNI 11484:2013: A = *AR*, B = *BR,* C = *CR* . The sample face reported is the irradiated one (UV and Visible irradiation) during the photocatalytic NO / NO_x abatement tests.

3. EXPERIMENTAL RESULTS AND MEASURING CONDITIONS

3.1. *Sample "AR" (UNI 11484, UV)*

The following table shows the operating conditions used in the test and its results.

Initial concentration of nitrogen oxides before entering the reactor	C_{NO}^{IN} **= 0.515 ppmv** $C_{NO_2}^{IN}$ **= 0.000 ppmv**
Gas flow	***F* = 1.608 dm³ min⁻¹**
Temperature inside the reactor	***T* = 29.2 °C**
Relative humidity inside the reactor	***HR%* = 45.1**
Irradiance of the lamp to the sample surface (290-400 nm)	***I* = 10 W m⁻²**
Time elapsed between the time the UV lamp is switched on and the start of the concentration recording	**31.5 min**
Conversion in the absence of sample	$C_{NO}^{OUT,BUIO}$ **= 0.5036 ppmv** $C_{NO_2}^{OUT,BUIO}$ **= 0.016 ppmv** $C_{NO}^{OUT,LUCE}$ **= 0.4972 ppmv** $\eta_{NO,lamp}^{foto}$ **= 1.3 %**
Conversion in the dark in the presence of a sample	η_{NO}^{buio} **= 2.0 %** $\eta_{NO_2}^{buio}$ **= -0.2 %**
Conversion under radiation in the presence of a sample	The graph showing the evolution of the concentrations during the various test steps is shown in **Figure 4.**
Observed rate of photocatalytic degradation	**See Table 2**
Remarks	***none***

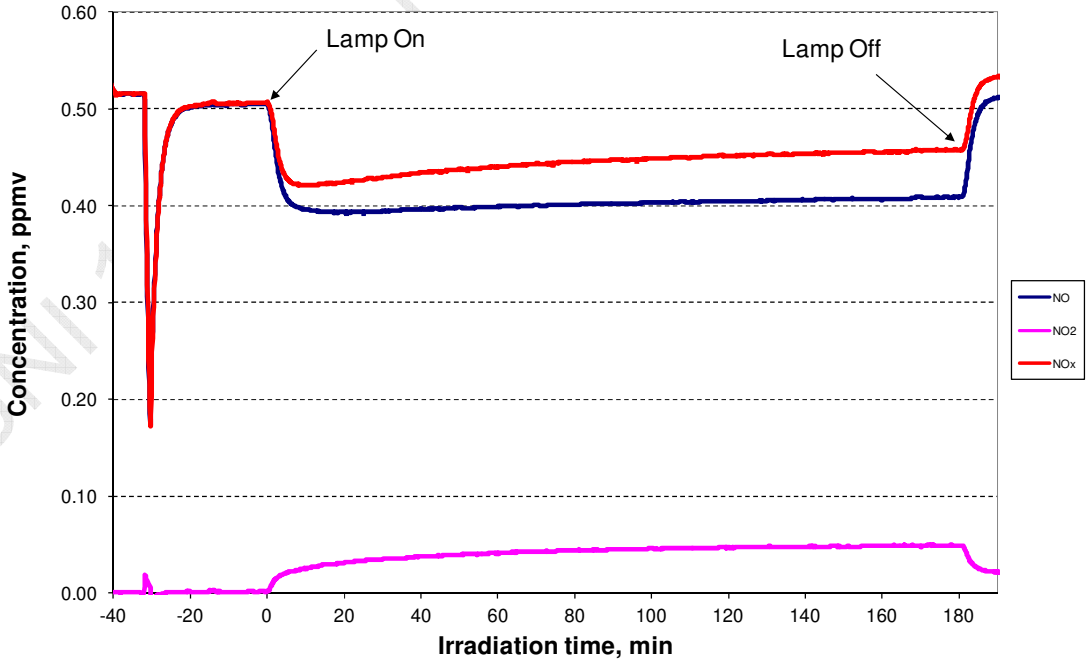

Figure 4. Concentration vs time for NO, NO_2 and NO_x during the photocatalytic test on *AR (UV)* sample. Test dated 29-05-2020 and performed with UV irradiation in accordance with UNI 11484 (simplified).

3.2. *Sample "BR" (UNI 11484, UV)*

The following table shows the operating conditions used in the test and its results.

Initial concentration of nitrogen oxides before entering the reactor	C_{NO}^{IN} **= 0.509 ppmv** $C_{NO_2}^{IN}$ **= -0.002 ppmv**
Gas flow	***F* = 1.608 dm³ min⁻¹**
Temperature inside the reactor	***T* = 28.4 °C**
Relative humidity inside the reactor	***HR%* = 44.1**
Irradiance of the lamp to the sample surface (290-400 nm)	***I* = 10 W m⁻²**
Time elapsed between the time the UV lamp is switched on and the start of the concentration recording	**31.5 min**
Conversion in the absence of sample	$C_{NO}^{OUT,BUIO}$ **= 0.5036 ppmv** $C_{NO_2}^{OUT,BUIO}$ **= 0.016 ppmv** $C_{NO}^{OUT,LUCE}$ **= 0.4972 ppmv** $\eta_{NO,lamp}^{foto}$ **= 1.3 %**
Conversion in the dark in the presence of a sample	η_{NO}^{buio} **= -1.0 %** $\eta_{NO_2}^{buio}$ **= 0.1 %**
Conversion under radiation in the presence of a sample	The graph showing the evolution of the concentrations during the various test steps is shown in **Figure 5.**
Observed rate of photocatalytic degradation	**See Table 2**
Remarks	***none***

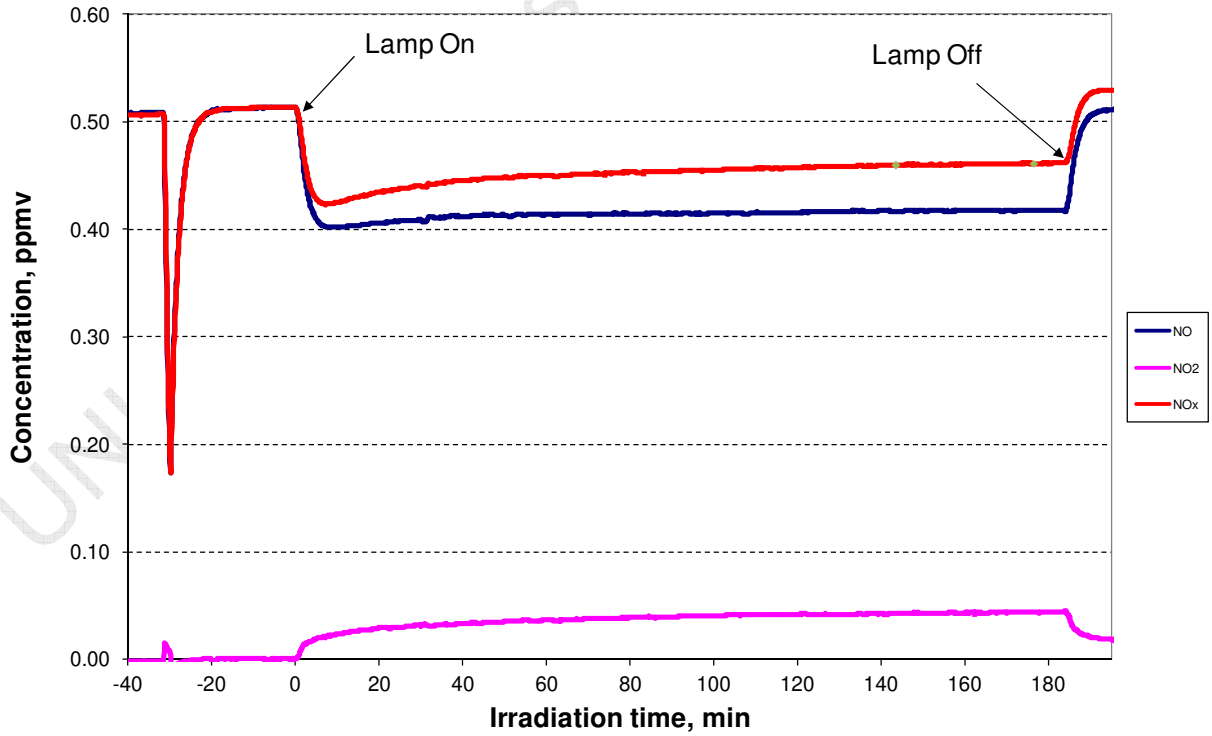

Figure 5. Concentration vs time for NO, NO_2 and NO_x during the photocatalytic test on *BR (UV)* sample. Test dated 01/062020 and performed with UV irradiation in accordance with UNI 11484 (simplified).

3.3. *Sample "CR" (UNI 11484, UV)*

The following table shows the operating conditions used in the test and its results.

Initial concentration of nitrogen oxides before entering the reactor	C_{NO}^{IN} **= 0.513 ppmv** $C_{NO_2}^{IN}$ **= 0.000 ppmv**
Gas flow	***F* = 1.608 dm³ min⁻¹**
Temperature inside the reactor	***T* = 28.7 °C**
Relative humidity inside the reactor	***HR%* = 43.4**
Irradiance of the lamp to the sample surface (290-400 nm)	***I* = 10 W m⁻²**
Time elapsed between the time the UV lamp is switched on and the start of the concentration recording	**30.5 min**
Conversion in the absence of sample	$C_{NO}^{OUT,BUIO}$ **= 0.5036 ppmv** $C_{NO_2}^{OUT,BUIO}$ **= 0.016 ppmv** $C_{NO}^{OUT,LUCE}$ **= 0.4972 ppmv** $\eta_{NO,lamp}^{foto}$ **= 1.3 %**
Conversion in the dark in the presence of a sample	η_{NO}^{buio} **= 2.1 %** $\eta_{NO_2}^{buio}$ **= 1.5 %**
Conversion under radiation in the presence of a sample	The graph showing the evolution of the concentrations during the various test steps is shown in **Figure 6.**
Observed rate of photocatalytic degradation	**See Table 2**
Remarks	***none***

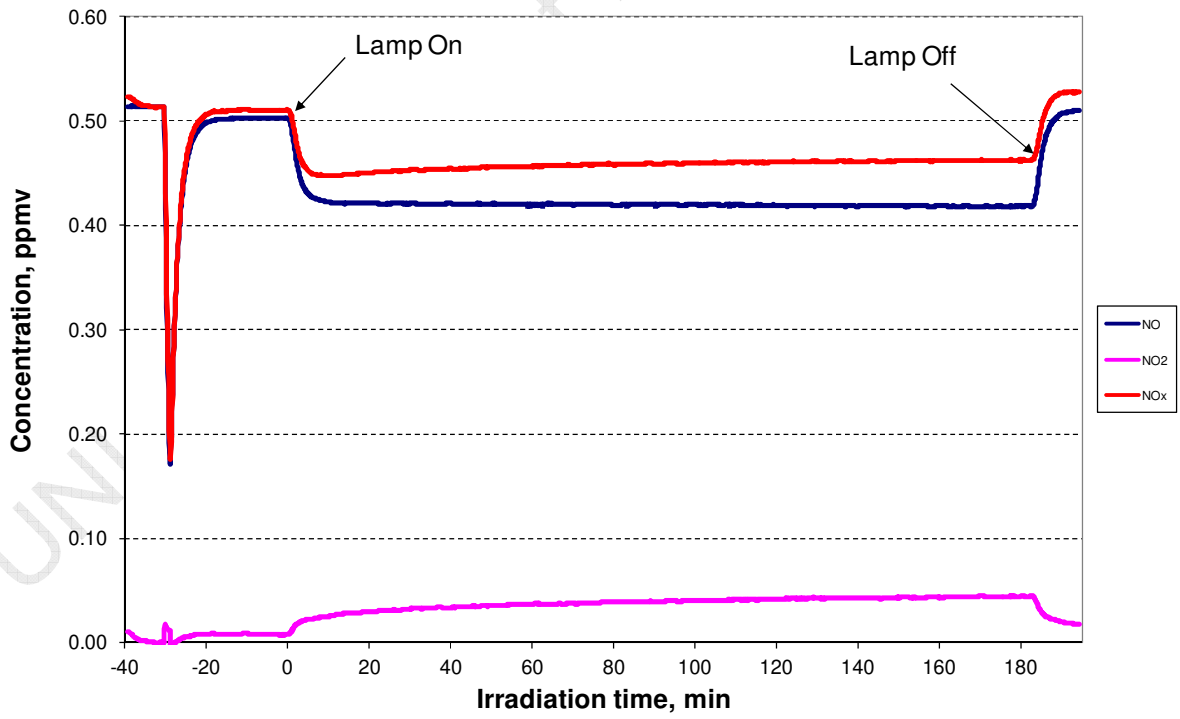

Figure 6. Concentration vs time for NO, NO_2 and NO_x during the photocatalytic test on *CR (UV)* sample. Test dated 01/06/2020 and performed with UV irradiation in accordance with UNI 11484 (simplified).

3.4. *Sample "AR" (UNI 11484, Visible)*

The following table shows the operating conditions used in the test and its results.

Initial concentration of nitrogen oxides before entering the reactor	C_{NO}^{IN} **= 0.506 ppmv** $C_{NO_2}^{IN}$ **= 0.001 ppmv**
Gas flow	***F* = 1.608 dm³ min⁻¹**
Temperature inside the reactor	***T* = 33.3 °C**
Relative humidity inside the reactor	***HR%* = 37.3**
Irradiance of the lamp to the sample surface (in the VISIBLE range 400-800 nm)	***I* = 250 W m⁻²**
Time elapsed between the time the VIS lamp is switched on and the start of the concentration recording	**32 min**
Conversion in the absence of sample	$C_{NO}^{OUT,BUIO}$ **= 0.5036 ppmv** $C_{NO_2}^{OUT,BUIO}$ **= 0.016 ppmv** $C_{NO}^{OUT,LUCE}$ **= 0.4972 ppmv** $\eta_{NO,lamp}^{foto}$ **= 1.3 %**
Conversion in the dark in the presence of a sample	η_{NO}^{buio} **= -1.5 %** $\eta_{NO_2}^{buio}$ **= 0.4 %**
Conversion under radiation in the presence of a sample	The graph showing the evolution of the concentrations during the various test steps is shown in **Figure 7.**
Observed rate of photocatalytic degradation	**See Table 2**
Remarks	***none***

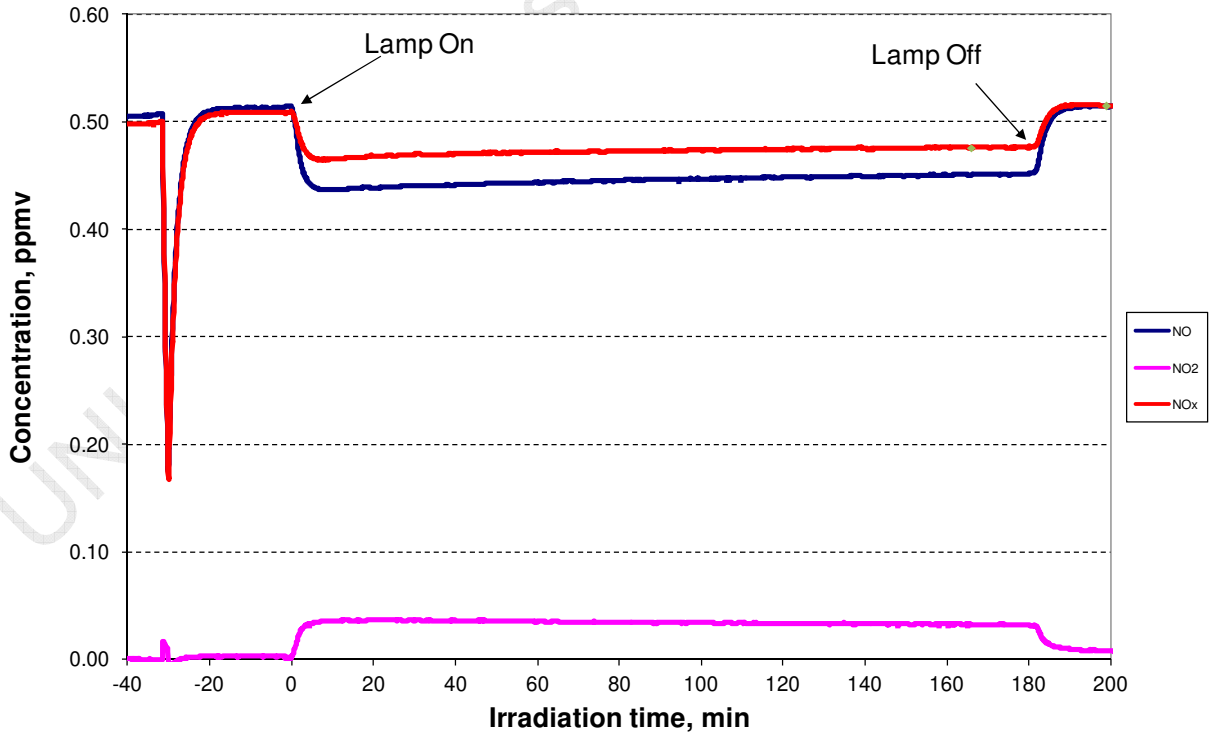

Figure 7. Concentration vs time for NO, NO_2 and NO_x during the photocatalytic test on *AR (Vis)* sample. Test dated 03/06/2020 and performed in accordance with UNI 11484 (simplified) with VIS irradiation.

3.5. *Sample "BR" (UNI 11484, Visible)*

The following table shows the operating conditions used in the test and its results.

Initial concentration of nitrogen oxides before entering the reactor	C_{NO}^{IN} **= 0.513 ppmv** $C_{NO_2}^{IN}$ **= 0.001 ppmv**
Gas flow	***F* = 1.608 dm³ min⁻¹**
Temperature inside the reactor	***T* = 33.4 °C**
Relative humidity inside the reactor	***HR%* = 36.6**
Irradiance of the lamp to the sample surface (in the VISIBLE range 400-800 nm)	**I = 250 W m⁻²**
Time elapsed between the time the VIS lamp is switched on and the start of the concentration recording	**45 min**
Conversion in the absence of sample	$C_{NO}^{OUT,BUIO}$ **= 0.5036 ppmv** $C_{NO_2}^{OUT,BUIO}$ **= 0.016 ppmv** $C_{NO}^{OUT,LUCE}$ **= 0.4972 ppmv** $\eta_{NO,lamp}^{foto}$ **= 1.3 %**
Conversion in the dark in the presence of a sample	η_{NO}^{buio} **= -0.3 %** $\eta_{NO_2}^{buio}$ **= -0.7 %**
Conversion under radiation in the presence of a sample	The graph showing the evolution of the concentrations during the various test steps is shown in **Figure 8.**
Observed rate of photocatalytic degradation	**See Table 2**
Remarks	***none***

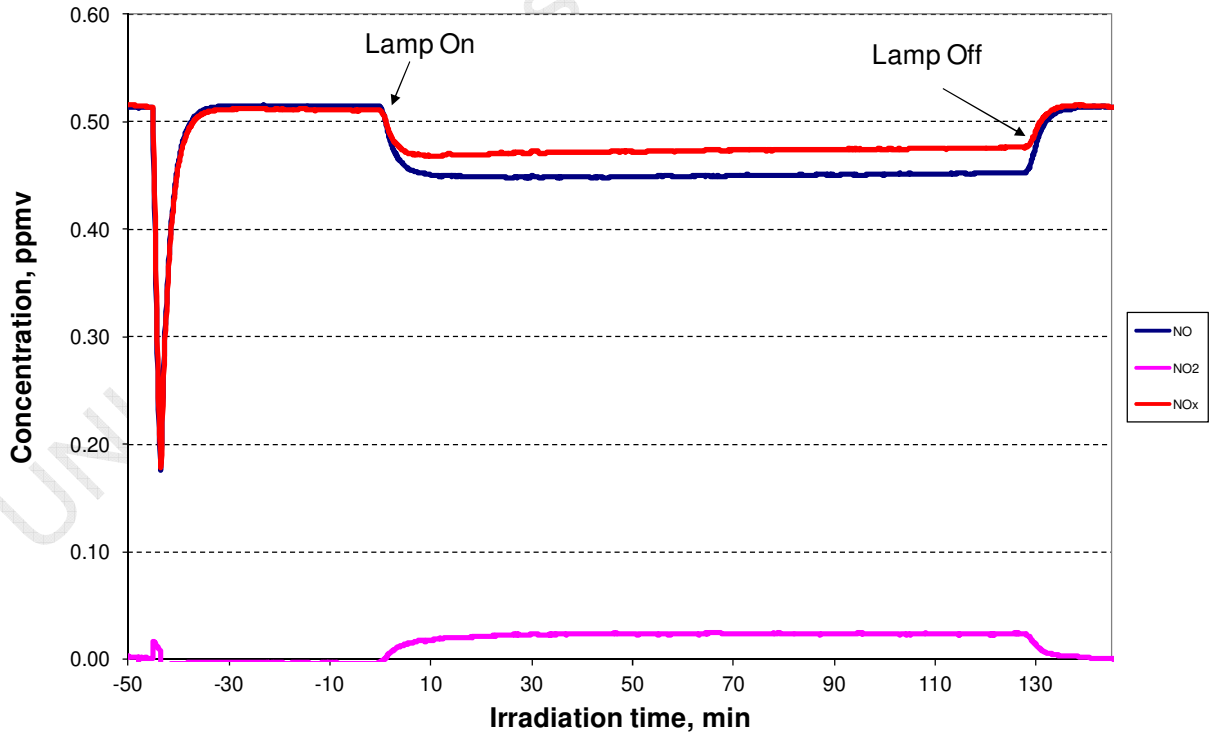

Figure 8. Concentration vs time for NO, NO_2 and NO_x during the photocatalytic test on *BR (Vis)* sample. Test dated 03/06/2020 and performed in accordance with UNI 11484 (simplified) with VIS irradiation.

3.6. *Sample "CR" (UNI 11484, Visible)*

The following table shows the operating conditions used in the test and its results.

Initial concentration of nitrogen oxides before entering the reactor	C_{NO}^{IN} **= 0.506 ppmv** $C_{NO_2}^{IN}$ **= -0.001 ppmv**
Gas flow	***F* = 1.608 dm³ min⁻¹**
Temperature inside the reactor	***T* = 32.5 °C**
Relative humidity inside the reactor	***HR%* = 37.1**
Irradiance of the lamp to the sample surface (in the VISIBLE range 400-800 nm)	***I* = 250 W m⁻²**
Time elapsed between the time the VIS lamp is switched on and the start of the concentration recording	**31 min**
Conversion in the absence of sample	$C_{NO}^{OUT,BUIO}$ **= 0.5036 ppmv** $C_{NO_2}^{OUT,BUIO}$ **= 0.016 ppmv** $C_{NO}^{OUT,LUCE}$ **= 0.4972 ppmv** $\eta_{NO,lamp}^{foto}$ **= 1.3 %**
Conversion in the dark in the presence of a sample	η_{NO}^{buio} **= -1.1 %** $\eta_{NO_2}^{buio}$ **= -0.5 %**
Conversion under radiation in the presence of a sample	The graph showing the evolution of the concentrations during the various test steps is shown in **Figure 9.**
Observed rate of photocatalytic degradation	**See Table 2**
Remarks	***none***

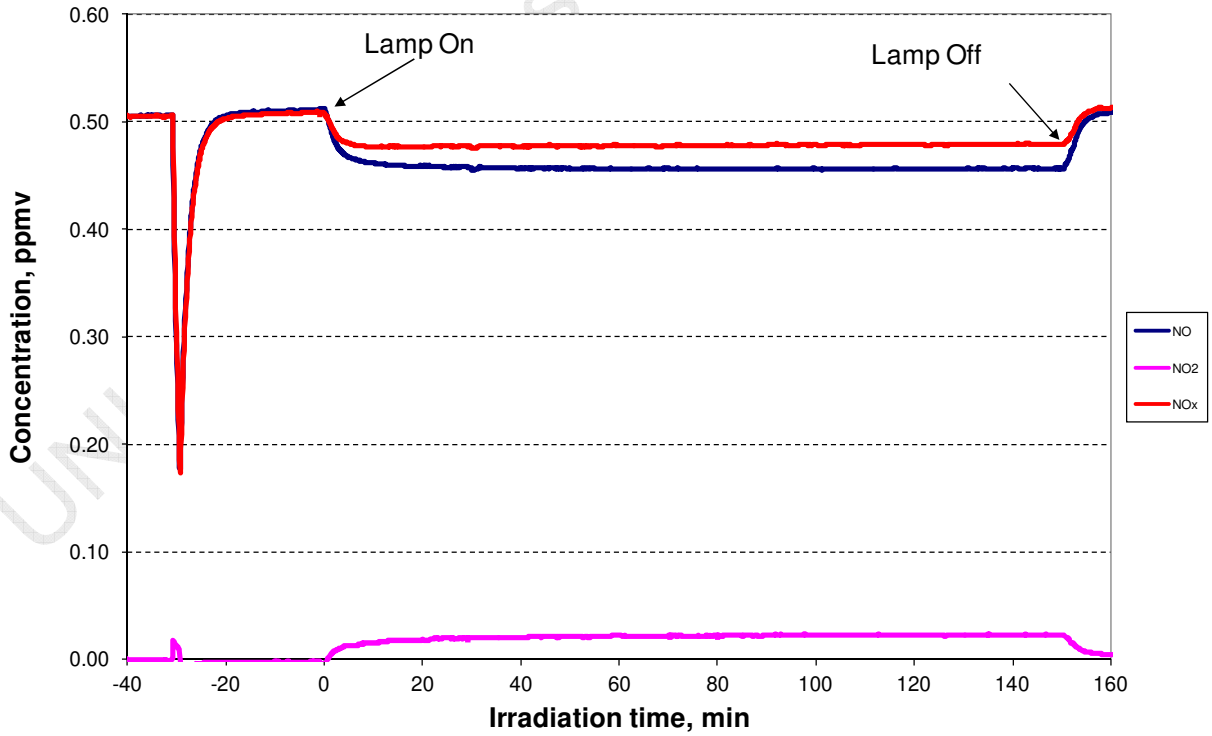

Figure 9. Concentration vs time for NO, NO_2 and NO_x during the photocatalytic test on *CR (Vis)* sample. Test dated 04/06/2020 and performed in accordance with UNI 11484 (simplified) with VIS irradiation.

4. SUMMARY OF RESULTS

The specimens showed a measurable NO abatement under UV and Visible irradiation. The results of measurements of the photocatalytic activity according to UNI 11484 under UV (no pretreatment) and Visible irradiation (after washing with water) of the 3 samples are summarized in Table 2 (for NO/NO_x). The conversions and rates are reported as average values calculated after 180 minutes of irradiation or when the stability of the conversion is attained in accordance with the UNI 11484.

Table 2. Measurement results. The conversions refer to the measured values after 180 minutes of irradiation

Sample	***Irradiation***	$\eta^{totale}_{NO,i}$ **, %**	$\eta^{totale}_{NO_x,i}$ **, %**	$r^{foto}_{NO,i}$ **,** **µg m^{-2} h^{-1}**	$r^{foto}_{NO_x,i}$ **,** **µg m^{-2} h^{-1} [*i*]**
AR(UV)	UV	20.7	11.2	1450	1130
BR(UV)	UV	17.9	9.3	1370	1140
CR(UV)	UV	18.5	9.9	1240	1060
AR(Vis)	Visible	10.9	4.7	820	640
BR(Vis)	Visible	11.8	7.2	830	720
CR(Vis)	Visible	9.8	5.3	720	590

[*i*] The photocatalytic NO_x conversion rate is expressed as µg equivalents of NO_2 converted per m^2 of sample in 1 hour.

Torino, June 8, 2020

Prof. Claudio Minero