LIFE 08 ENV/F/000487

Deliverable IV: Action P2

Protocols and techniques for evaluation of the use and efficiency of photo-catalytic depollution materials on air quality

Introduction

Urban environments provide huge surface area that can interact with the gaseous pollutants which may be transformed in less harmful chemical substances following this interaction. The use of simulation chamber to assess the chemical impact of massive solid surfaces on air quality is fairly new and very challenging. The chambers are the best tools to investigate these systems in detail and in realistic conditions. It is of primary importance to work on the definition of suitable tests to allow the chamber experiments efficiently characterize new atmospheric urban air chemistry. Methods for the identification of the surface processes and assessment of their impact are essential for the successful development and use of materials with the potential to affect the ambient air quality.

This report presents the test protocols developed within Photopaq Project for testing the interaction between air pollutants and material surfaces at atmospherically relevant conditions. The partners involved in action 2 possess different types of facilities which allow them to test the effectiveness and the impact of the wide use of materials.

Test protocol

PARIS12 and CNRS-ICARE have investigated the protocol for the determination of the uptake of a number of important air pollutants such as NO_2, O_3 and some VOCs. They have also conducted a series of tests on the effective formation rates of potential radical sources (e.g. HONO, OH, NO_3 or peroxyacyl nitrates). To determine these parameters, low concentrations of the studied pollutants have been introduced in the chamber in the presence and absence of material plates (doped or not with Titanium dioxide, TiO_2) and the gas phase composition was continuously analysed. A number of experiments were conducted in order to evaluate the effectiveness of the *reduction of the NOx concentration* in air when exposed to TiO_2 doped surfaces. The chambers used this work are described briefly in this report.

- *Investigation protocol*

Simulation chambers are probably the most direct way for investigating the effectiveness of photocatalytic material on de-pollution, the potential feedback from surface chemistry to air

composition and to draw mechanisms for modelling purpose. Nevertheless, the smog chamber approach is not artefact-free as the chamber themselves exhibit surfaces with potential chemical reactivity (the walls).
To deconvolve the studied effect from the chamber dependent mechanism a double dual strategy is recommended. This strategy involves the use of various chambers - ideally with very different wall effects (material, coating, surface-to-volume ratio…). Furthermore, for each infrastructure, it is necessary to carry out two set of experiments: in the presence and in the absence of the studied materials. The first set aim at defining the chamber auxiliary mechanism while the second allow investigating properly the effect of the studied surfaces.

- *CESAM chamber (LISA)*
The experiments were carried out using the Multiphase Atmospheric Simulation Environmental Chamber (CESAM, Figure 1). It consists of a 4.2 m^3 stainless steel vessel which can be roughly described as a vertical cylinder in which 6 glass plates (120 cm × 40 cm) are vertically hung offering a geometrical surface of 2.88 m^2. A set of stainless steel magnetic torque mixing fans are installed inside the chamber reactor which allows to mix the gas phase compounds in less than 100 s. The chamber is equipped with a powerful solar simulator system which comprises 3 xenon arc lamps of 4 kW each. This set-up provides an irradiation inside the chamber very close to the sun spectrum at the ground level. The lamps are symmetrically located above the chamber on one large movable and rigid framework. By optimizing the focal point of the light beam, it is possible to obtain a converging or diverging light beam with a maximum intensity inside the reactor; meanwhile the light spots projected at bottom level are as large as possible for minimizing the local overheating effects. Photolysis frequencies of NO_2 and O_3 in the chamber radiation have been determined using the chemical actinometry method (in the NOx/air/light system), the mean values of J_{NO2} ($3.0x10^{-3}$ s^{-1}) and J_{O1D} ($1.02x10^{-5}$ s^{-1}) are roughly one fourth of those measured in the boundary layer on a sunny day at mid latitude, in June at noon.

The chamber was evacuated to 10^{-3} mbar before each experiment. Synthetic air was produced from the mixture of ca. 200 mbar of O_2 (AIRLIQUIDE, ALPHAGAZ™ class 1) and ca. 800 mbar of N_2 produced from the evaporation of a pressurized liquid N_2 tank. NO was purchase from AIRLIQUIDE (ALPHAGAZ™ purity Class 2 UN1956). Experiments were carried out at atmospheric pressure and a temperature of 293±2 K. The simulation chamber is equipped with in-situ long path FITR system (192 m) and with environmental analyzer. A Horiba™ APOA® 370 monitor was used for O_3 detection by means of a cross flow modulated ultraviolet absorption method while NOx measurements were performed using a Horiba™ APNA® chemiluminescence monitor. Nitrous acid was quantified using the NitroMac instrument[3] with a detection limit of 3 ppt for a time period of 10 minutes. Several experiments were performed in the absence of glass, in the presence of non treated surfaces and with TiO_2 treated surfaces inside the chamber. NO initial concentration ranged from 20 to 100 ppb and relative humidity was varied from 0 to 40%.

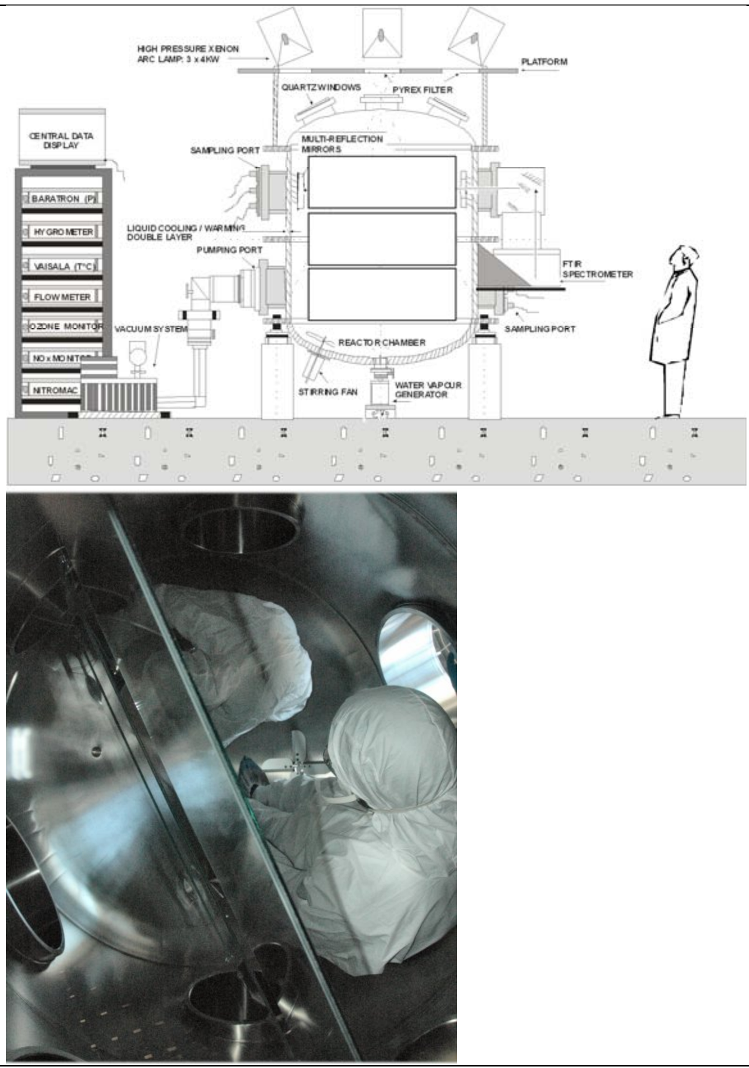


Figure 1. Scheme of the CESAM reactor. The three rectangles in bold represent the 6 plates of material set back to back in the chamber.

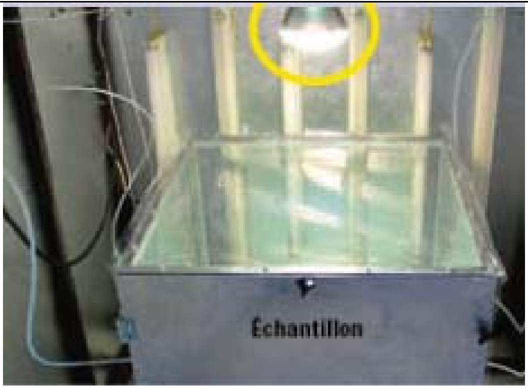
ICARE Chambers:

The tests were performed using three different chambers:

(i) 275 L indoor Atmospheric Simulation Chamber made of Teflon with a cubic shape (Figure 5.5.2a). It is equipped with a number of inlets and outlets for the gas injection (air, NO-NO_2, O_3 …) and analysis (NO-NO_2, O_3 …). The chamber is placed in a box with internal faces covered with aluminium and equipped with a ventilation system which allows homogenization of the internal temperature. An ULTRA-VITALUX 300W (® OSRAM) is used to simulate solar radiations.

(ii) The outdoor sunlight irradiated chamber (3.4 m^3 volume; Figure 2b) made of Teflon. The chemical analysis were preformed using commercial monitors (O_3, NO, NO_2 and NO_x). The physical parameters (pressure, temperature, relative humidity, light intensity (J_{NO2})) were continuously monitored using specific captors. A Teflon fan inside the chamber ensures the homogenisation of the gas mixture in less than 1 minute. Along the experiment, a slight air stream flowing into the chamber enables to compensate due to sampling volumes and maintains a slight overpressure to prevent any possible contamination from outside air. A series of tests has been performed on the setup to ensure its reliability, such as leak and homogenisation tests. The experiments were performed at a temperature of 293-301 K with a variation of 7 to 8 °C over the course of the run.

(ii) The large indoor chamber (7.3 m^3 volume; Figure 3b) made of Teflon of ICARE has been also used for these tests. The chamber is equipped with a wide range of analytical instrumentation and techniques to derive kinetic and mechanistic information. For photooxidation experiments, the gas mixture can be irradiated by UV-Vis lamps (centred on 254 nm (x 14) and 365 nm (x 28) and ORSAM ULTRA-VITALUX (x 12)). A multi-reflection White type mirrors system is mounted inside the reactor and interfaced to an FT-IR spectrometer (Nicolet Magna 5700), which allows in situ monitoring of reactants and oxidation products in the ppm-ppb range.
Analyses are also accomplished using different types of gas chromatographs equipped with, photo ionisation detector (PID) and mass spectrometry (ATD-GC-MS PerkinElmer Clarus 600) at ppb level measurement. A number of atmospheric key species are analyzed using specific monitors in the ppt-ppb range (e.g. O3 (HORIBA, APOA-360 and 370), NOx (HORIBA, APNA-360 and Thermo Environment 42i TL), HONO (LOPAP, QUMA-O3) and HCHO (Aerolaser AL 4021)).
The chamber is also equipped with instrumentation for particle analysis. Particles size distributions can be measured by a SMPS (TSI3080/CPC3022A). Particles can be also collected on filters and then analysed by different techniques including GC-MS, HPLC (UV and fluorimetric detections) and ionic chromatography.



(2a)


(2b)

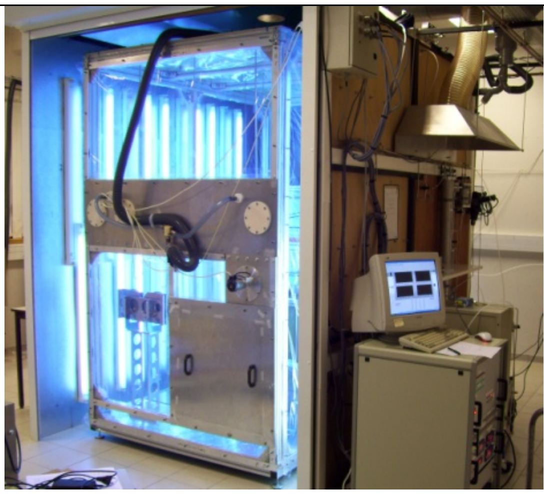

(2c)

Figure 2. ICARE chambers

<u>Example of Results and Conclusions</u>

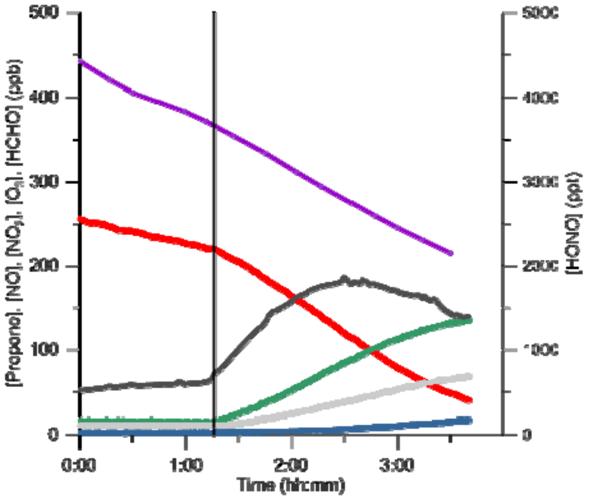
Several tests were performed with the empty chamber, with non-treated surfaces inside the chamber and in the presence of surfaces treated with TiO_2. Different types of surfaces were also used such as Glass and Concrete. The figures given below show examples of results from wide range of tests conducted in various chambers and under different conditions and different pollutants.

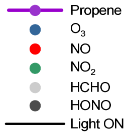
In summary:

- the tests indicate that there is a real effect on the NOx concentrations when exposed to surfaces containing TiO_2.
- there is also a production of HONO (a source of OH radicals in the atmosphere) when a gas mixture is exposed to surfaces containing TiO_2 and light.
- No effect on Pyrrole (a volatile organic compound) concentration,

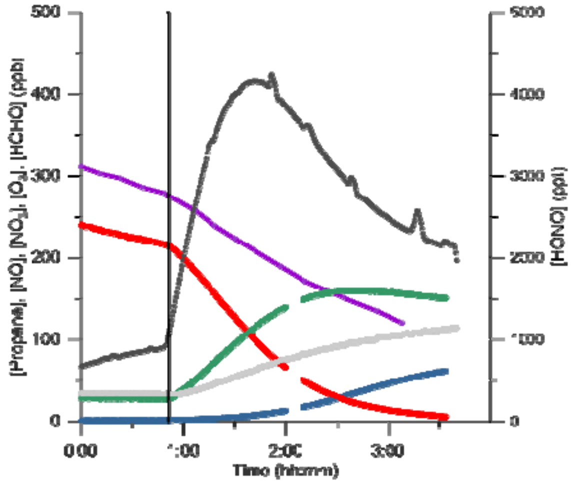
Surfaces without TiO_2 | Surfaces with TiO_2

Propene/NOx/Sunlight

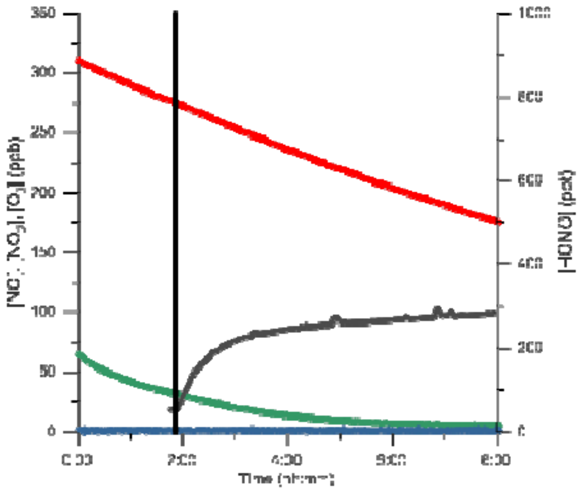


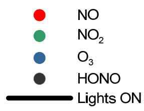


Glass

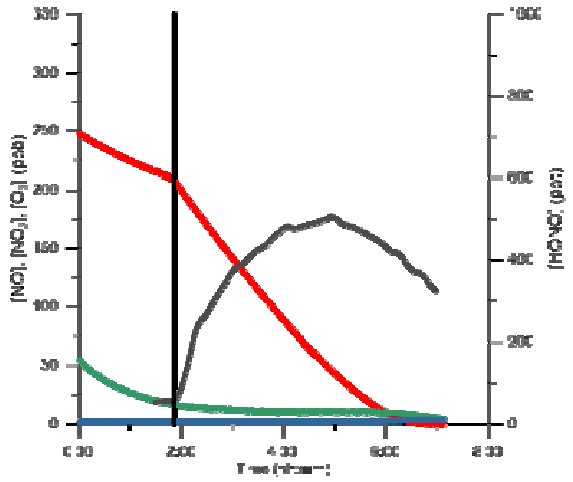


NOx/light

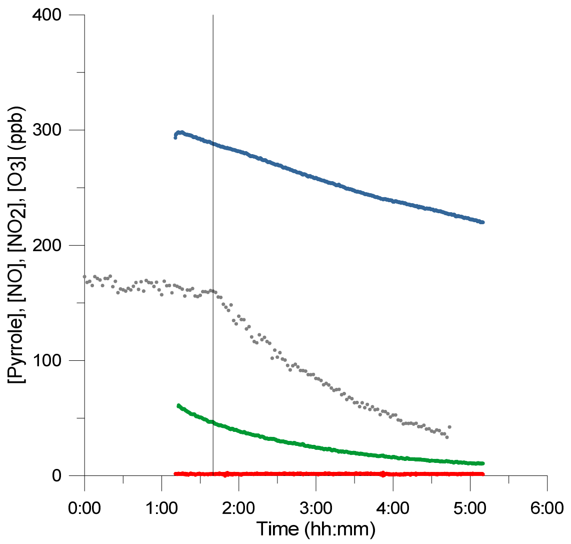


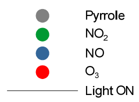


Concrete

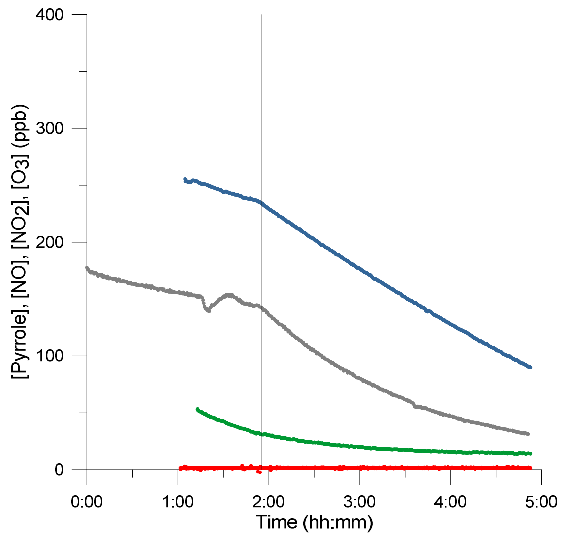


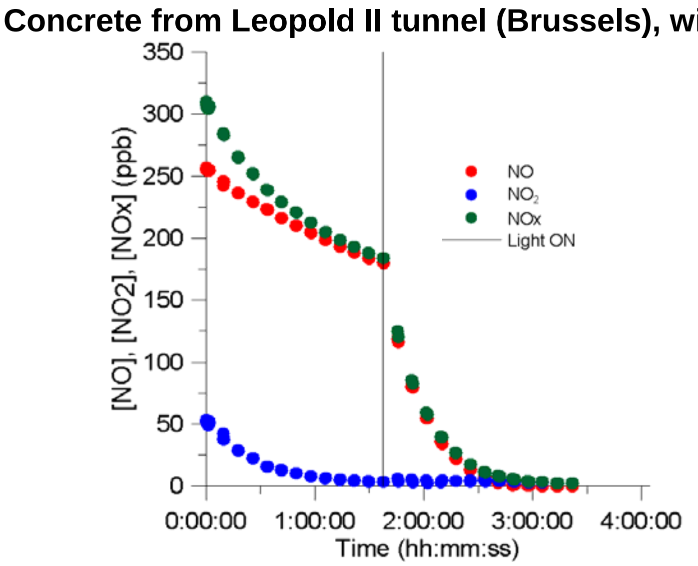
Pyrrole/NOx/light

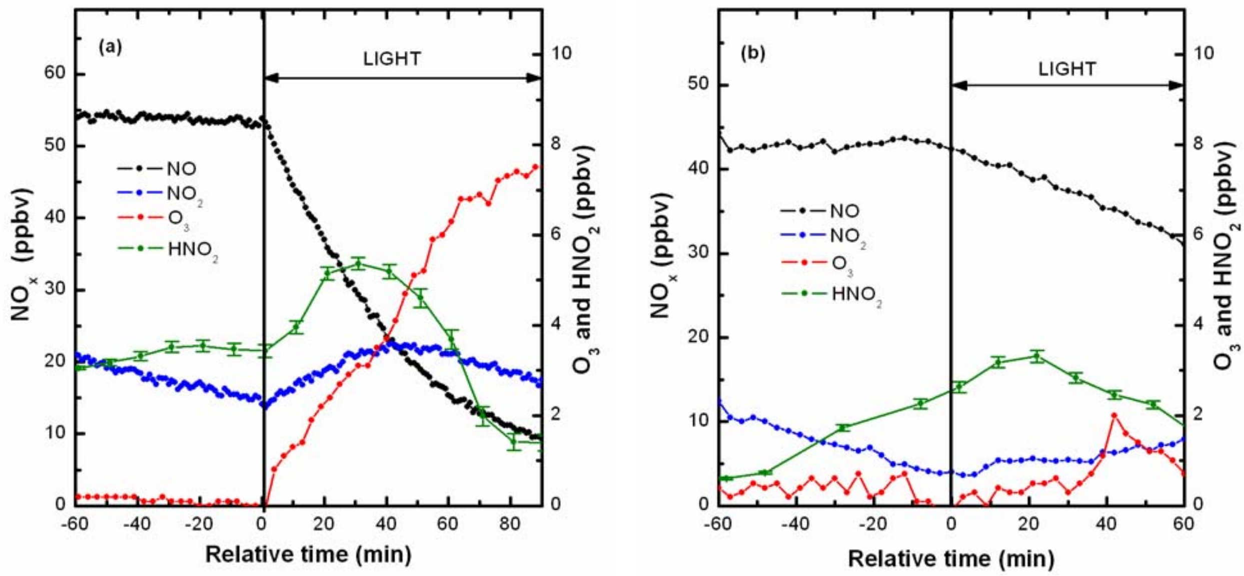




Concrete







NO, NO_2, HNO_2 and O_3 profiles recorded in the presence of (a) a TiO_2 coated glass and (b) a standard glass (TiO_2 free) in the CESAM chamber. The vertical line indicates the start of the irradiation.