

## Standard Operating Procedure (SOP): Air Pollution Simulation Chamber for the Assessment of Photocatalytic Coatings for NO<sub>x</sub> Oxidation

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Date of approval:		Date for review:	

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### 1. Justifying the hazards

Can the substance or process be substituted or modified with a less hazardous version? Can the volume be decreased?

Identify hazards with specific risk assessments and a College or a departmental approval process			
<a href="#">Ionising radiation sources</a>	<input type="checkbox"/>	<a href="#">Biological sources</a> (microorganisms, human/animal tissues, plants)	<input type="checkbox"/>
<a href="#">Class 3R, 3B or 4 Lasers</a>	<input type="checkbox"/>	<a href="#">Offsite work</a>	<input type="checkbox"/>
Confirm if <a href="#">Lone working</a> is permitted with this SOP? <input type="checkbox"/> If it is permitted, describe the control measures for lone workers:			

### 2. Preparing for the SOP

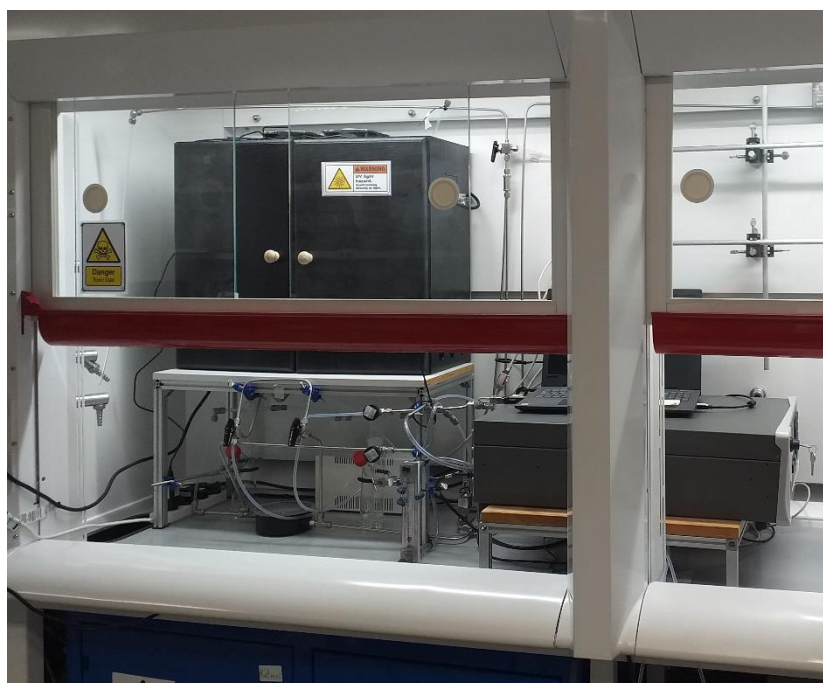
Specific Training

All users should be trained by a competent user before beginning any independent work on this reactor.

**NOTE: NO LONE WORKING, OUTSIDE OF REGULAR WORKING HOURS, IS PERMITTED.**

### 3. Initial checks

- 1) Ensure that the air flow in the fume hood has a face velocity of 0.35 m/s prior to starting work
- 2) Check that the special gas being used (NO and/ or NO<sub>2</sub>) is open (pressure ~2 bar)
- 3) Leak test the system weekly using an oxygen compatible leak detection fluid (e.g. snoop) at the joints



**Figure 1.** The Air Pollution Simulation Chamber for the Assessment of Photocatalytic Coatings for NO<sub>x</sub> Oxidation

#### 4. Setting up the apparatus

Turning the equipment on

##### *Chemiluminescence (CL) NO<sub>x</sub> analyser*

The CL NO<sub>x</sub> analyser (Figure 2, left) and pump (Figure 2, right) should be kept on continuously; however, if there will be a long break in work (e.g. at least a fortnight), the NO<sub>x</sub> analyser and pump should be switched off. If found off, the NO<sub>x</sub> analyser is turned on from a switch at the back of the device, and the pump from the plug. Once turned on, the catalyst inside the CL NO<sub>x</sub> analyser must reach an operating temperature of 325 °C before NO and NO<sub>2</sub> concentrations can be accurately measured. The catalyst temperature can be accessed from the front panel on the analyser.

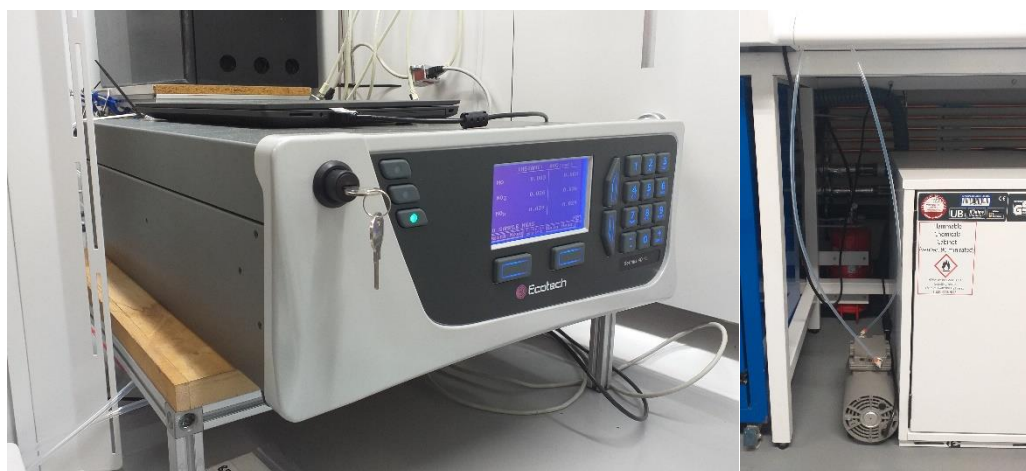


Figure 2. The CL NO<sub>x</sub> analyser (left) and pump (right)

NOTE: ONCE TURNED ON, THE CL NO<sub>x</sub> ANALYSER AUTOMATICALLY AND CONTINUOUSLY MEASURES CHANGES IN NO<sub>x</sub> CONCENTRATION EVERY 10 SECONDS. THIS DATA, WHICH CAN AMOUNT TO SEVERAL YEARS WORTH OF MEASUREMENTS, IS AUTOMATICALLY STORED IN THE CL NO<sub>x</sub> ANALYSER. THIS INFORMATION CAN BE ACCESSED USING THE AIRODIS SOFTWARE ON THE CONNECTED LAPTOP (LOCATED ON TOP OF THE CL NO<sub>x</sub> ANALYSER).

##### *House air and NO/ NO<sub>2</sub> special gases*

The NO (40 ppm) and NO<sub>2</sub> (100 ppm) special gases are stored inside the gas cylinder cabinet. These special gases are toxic and should only be turned on when used. To turn the special gas on, first turn the knob on at the top/ neck of the cylinder (Figure 3, left (a)). You then need to ensure that the safety valve is open (Figure 3, left (b)) to allow the gas to flow from the cylinder into the gas regulator. You then have to turn on the main gas regulator valve to allow the gas to flow into the regulator (Figure 3, left (c)). When using these gases, the pressure should be maintained between just over ~1 bar and up to ~2 bar. You can see the pressure in the cylinder on the left gauge (Figure 3, left (1)) and the pressure exiting the cylinder into your reaction on the right gauge (Figure 3, left (2)). If you want to flush the gas out of the regulator, close all valves and then open the flush valve (Figure 3, left (d)). Only do this if you have good reason to do so (e.g. the set-up hasn't been used in weeks and the gas in the pipes is stale); otherwise this will waste a costly gas. Each cylinder costs in the region of £350 to replace, so use sparingly.

**NOTE: IF THE PRESSURE EXITING THE CYLINDER INCREASES SUBSTANTIALLY OVER TIME, THIS MAY DUE TO A FAILURE IN THE REGULATOR. IF THE PRESSURE INCREASES BEYOND ~5 BAR, THIS IS UNSAFE, AND THE GAS CYLINDERS SHOULD BE TURNED OFF IMMEDIATELY AT THE NECK.**

The NO/ NO<sub>2</sub> special gases have pipelines that go from the gas cabinet to all fume hoods on the right side of lab B01 (Figure 3, right). To turn these gas lines on, the special gas knobs should be turned on (a half turn clockwise is normally sufficient). If the gas line has not been used in a while, then remove the gas pipe from the outlet in the fumehood and allow the NO/ NO<sub>2</sub> gas to flow for a few minutes to clear the gas line of stale gas.

**NOTE: DO NOT OPEN THE SPECIAL GAS LINES IN ANY FUME HOOD OTHER THAN WHERE THE NO<sub>x</sub> REACTOR IS STORED.**

The house air is turned on at the fume hood by turning house air knob (a half turn clockwise is sufficient), and the regulators inside the fume hood should be turned on and maintained at ~2 bar.



Figure 3. The regulator inside the gas cylinder cabinet (left), and the regulators and knobs in the fume hood (right)

### ***Bronkhurst mass flow controllers***

The flow meters are digitally controlled. The white power supply box should first be turned on (Figure 4, left), and then the laptop (Bit Recovery = 00390872, password = Imperial345). Open the software FLOW DDE, click on “communication” and then “open communication”. After a few seconds, the software will say “server is ready and active for any client”. Then open the software FLOW PLOT. A window, “select parameters” will pop up. This has been pre-set, so simply click on “OK”. Then click on “instrument settings”. On “set point controller” select the channel and flow rate you require in percent. The house air, NO and NO<sub>2</sub> gas lines correspond to the mass flow controllers 3, 2 and 1, which have the maximum flow rates of 5000, 100 and 100 sccm respectively. To achieve ISO conditions, the mass flow

controller for air should be set to 58.5% (2925 sccm) and the mass flow controller for NO (40 ppm) should be set to 75% (75 sccm) to achieve a total flow of 3000 sccm and NO level of 1 ppm. To see these flows live, click on the “start” button on the FLOW PLOT software to see live changes in gas flows (Figure 4, right).

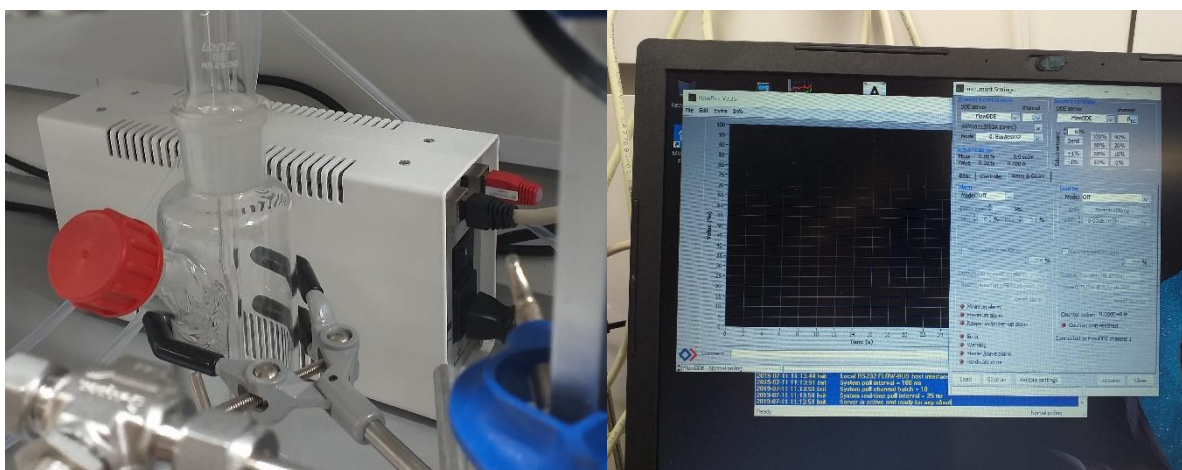


Figure 4. The white power box (left), and the FLOW PLOT software for controlling the mass flow controllers for house air, NO and NO<sub>2</sub> gases (right)

NOTE: ONCE THIS HAS BEEN SET, CHECK THE LIVE PANEL READINGS ON THE CL NO<sub>x</sub> ANALYSER AND THAT A NO CONCENTRATION OF ~1 PPM IS REACHED. NOTE: AN ADDITIONAL CHECK THAT SHOULD BE PERFORMED IS TO MEASURE THE LEVEL OF NO<sub>x</sub> PRESENT INSIDE THE HOUSE AIR. THIS CAN BE DONE BY TURNING THE NO AND NO<sub>2</sub> GAS FLOW METERS TO 0% FLOW, AND LEAVING THE HOUSE AIR ON. IF THE AMBIENT NO<sub>x</sub> CONTENT IS ABOVE ~0.03 PPM, CONSIDER REPLACING/RECHARGING THE FILTERS (Figure 5a).

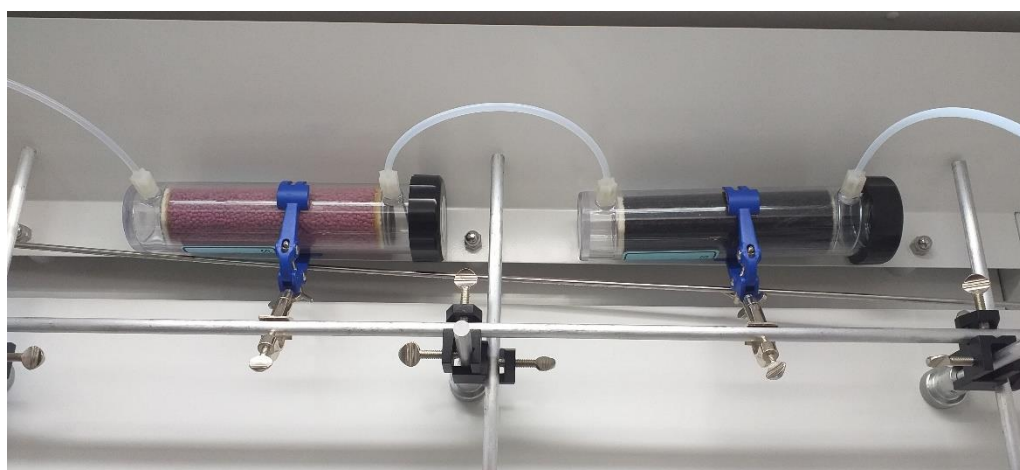


Figure 5a. Filters for house air

#### *Alicat gas flow meter*

This flow meter is stationed just before the CL NO<sub>x</sub> analyser (Figure 5b). It is primarily used to check gas losses that can occur due to leakage in the sample chamber (or elsewhere). It can be turned

on at the plug (and should be turned off at the end of the day). To more readily see the gas flow rate press the Alicat logo and this turns on a background light on the device



Figure 5b. Alicat gas flow meter

NOTE: IF AN UNUSUAL/ UNEXPECTED READING IS SHOWN, TURN OFF ALL GAS FLOWS AND PRESS THE TARE BUTTON IN THE TOP RIGHT TO ZERO CALLIBRATE THE DEVICE.

Putting the sample into the reactor

The reactor (a.k.a. the air pollution simulation chamber) is stored inside the black cupboard (Figure 6).

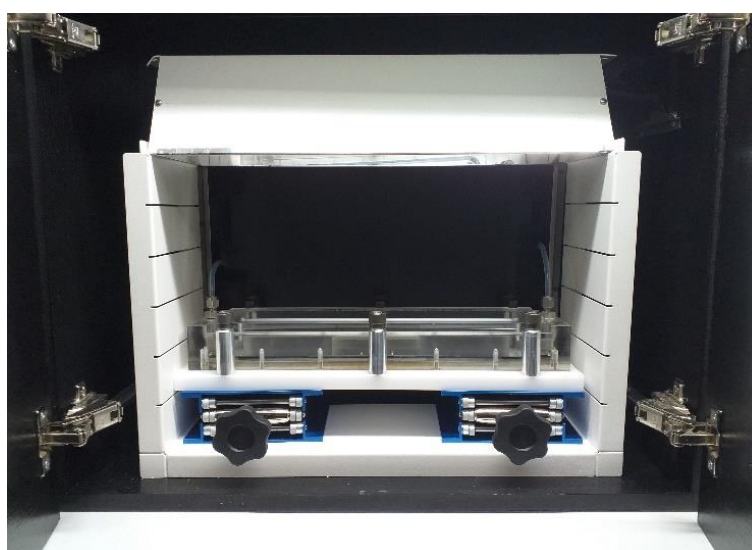


Figure 6. The reactor/ air pollution simulation chamber

**NOTE: WHENEVER OPENING THE BLACK CUPBOARD, PLEASE ENSURE THAT THE UVA LIGHT SOURCE IS TURNED OFF (THIS APPLIES IF UVA PROTECTIVE SPECS ARE NOT WORN).**

To allow easy sample change, the two gas lines going to the reactor can be taken off using an adjustable spanner (Figure 7, left). Samples should be changed inside of the fume hood, in case any unreacted  $\text{NO}_x$  is present inside the reactor. The top Perspex lid can be removed by loosening the bolts using an alum key. For the ISO test, the sample placed inside the reactor should be 5 cm x 10 cm in size. Replace the top Perspex lid and tighten the screws very loosely. Place the reactor back inside the cupboard and re-attach the two gas lines tightly using a wrench. Redirect the gas flow through the reactor by turning both by-pass valves simultaneously  $180^\circ$  (Figure 7, right).

**NOTE: DO NOT TURN THESE VALVES LESS THAN  $180^\circ$  OR YOU WILL CAUSE PRESSURE TO BUILD UP INSIDE THE HUMIDITY LOOP. THIS CAN RESULT IN A BUILD OF PRESSURE AND FOR THE DRESCNEL FLASK TO CRACK/ EXPLODE.**

Whilst monitoring the gas flow at the Mesa Labs gas flow meter, tighten the screws on the Perspex lid until there are little to no losses.



**Figure 7.** How to remove the reactor from the black cupboard (left), and the by-pass valves (right)

**NOTE: CHECK THE DIFFERENCE IN GAS FLOW RATE, BETWEEN GOING THROUGH THE REACTOR, AND BY-PASSING IT, BY SWITCHING THE TWO BY-PASS VALVES SIMULTANEOUSLY, ON AND OFF (Figure 7, right). WHEN THE REACTOR IS GAS TIGHT, TURN THE VALVES TO BY-PASS THE REACTOR, UNTIL YOU ARE READY TO START THE TEST.**

Setting the humidity

**NOTE: THIS SHOULD ONLY BE CARRIED OUT WITH THE HOUSE AIR FLOWING, IDEALLY AT AROUND 3000 SCCM.**

The two dreschel bottles (one dry; one filled with distilled water just above the inlet), hygrometer and two needle valves (Figure 8) can be used to set the humidity level. Adjust the needle valves to achieve the desired humidity level (open the needle valve closest to the wet dreschel flask, and close the needle valve closest to the dry dreschel flask, to increase the humidity and *vice-versa*). ISO protocol requires a humidity of 50%.



**Figure 8.** The two dreschel bottles (one dry; one filled with distilled water just above the inlet), hygrometer and two needle valves for creating humidity inside the reactor

**NOTE: THE CHANGES IN HUMIDITY MEASURED BY THE HYGROMETER ARE NOT IMMEDIATELY RESPONSIVE, SO BE PATIENT IN ADJUSTING THE NEEDLE VALVES AND DO NOT TURN ON/OFF TOO DRAMATICALLY.**

Achieving the required light intensity

**NOTE: FOR THIS STEP, USE THE UV SAFETY SPECS PROVIDED.**

The light meter is stored in lab B01 on the shelf (Figure 9). Set the measurement wavelength to that of the light source being used (standard light source are black UVA bulbs,  $\lambda_{\max} = 352 \text{ nm}$ , 2 x 15 W). Measure the light power incident at the surface of the reactor (use a Perspex filter). You can adjust the incident power by adjusting the height of the reactor using the lab-jacks and shelves (Figure 6). For the ISO test, the height should be adjusted to achieve an incident UVA power of  $1.0 \text{ mW.cm}^{-2}$ .

**NOTE: THE ACTIVE AREA OF THE DETECTOR IS  $0.739 \text{ cm}^2$ . THE VALUE MEASURED SHOULD THEREFORE BE  $0.739 \text{ mW}$  TO ACHIEVE A POWER OF  $1.0 \text{ mW.cm}^{-2}$  [UNLIKE THE PHOTO BELOW, WHICH IS NOT AT THE ISO POWER LEVEL, AND IS INSTEAD AT  $1.43 \text{ mW.cm}^{-2}$  WHEN TAKING THE AREA OF THE DETECTOR INTO ACCOUNT].**



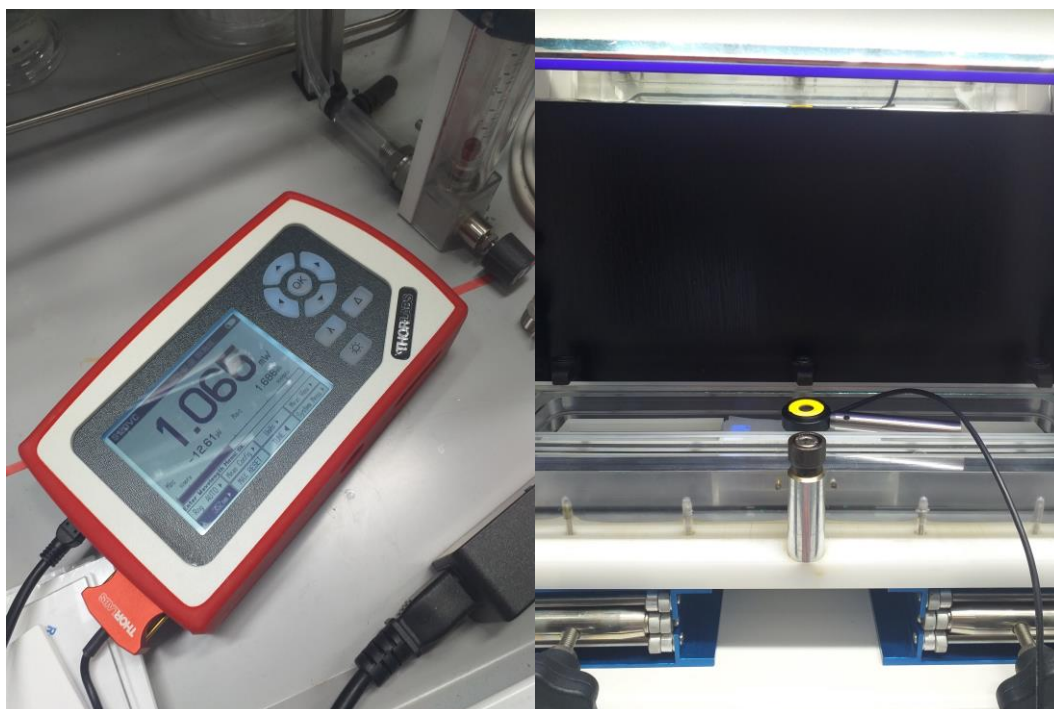


Figure 9. The light power meter, stored on the shelf in lab B01

**NOTE: TURN THE LIGHT SOURCE OFF, ONCE THE DESIRED LIGHT INTENSITY HAS BEEN ACHIEVED. THIS WILL BE TUNED ON AGAIN ONCE WHEN YOU ARE READY TO START THE PHOTOCATALYSIS EXPERIMENT.**

## 5. Procedure

If carrying out an experiment in line with ISO protocol, a complete description is provided in the document “BS\_ISO\_22197-1\_2016: Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for air-purification performance of semiconducting photocatalytic materials, Part 1: Removal of nitric oxide”. Some requirements, to meet ISO protocol, have been described above. In brief: (i) a sample of size 5 x 10 cm (50 cm<sup>2</sup>), (ii) UVA light of intensity 1 mW.cm<sup>-2</sup>, (iii) a humidity of 50% at 25 °C, (iv) a total flow rate 3000 sccm with NO at 1 ppm in air, should be used.

**NOTE: ANY DEVIATION FROM THE ISO TEST SHOULD BE PRE-DETERMINED; HOWEVER, THE MINIMUM PERMISSIBLE TOTAL FLOW RATE TO THE CL NO<sub>x</sub> ANALYSER IS ~700 SCCM.**

Starting the test

**NOTE: THE CL NO<sub>x</sub> ANALYSER AUTOMATICALLY AND CONTINUOUSLY MEASURES CHANGES IN NO<sub>x</sub> CONCENTRATION EVERY 10 SECONDS. THE DATA CAN BE ACCESSED AFTER THE EXPERIMENT. PLEASE NOTE THE TIME AT WHICH CERTAIN KEY EVENTS OCCUR (E.G. THE START OF THE DARK EXPERIMENT, LIGHT EXPERIMENT).**

**NOTE: TO START THE TEST, THE GAS SHOULD BE FLOWED INTO THE REACTOR. THIS IS ACHIEVED BY TURNING THE TWO BY-PASS VALVES SIMULTANEOUSLY (Figure 7, right).**

**NOTE: DURING THE EXPERIMENT, KEEP AN EYE ON THE TOTAL GAS FLOW ON THE MESA LABS FLOW METER, AND THE LIVE MEASURED NO<sub>x</sub> CONCENTRATION ON THE CL NO<sub>x</sub> ANALYSER.**

### *Dark measurement*

According to ISO protocol, the gas (3000 sccm, NO at 1 ppm) should be flowed over the sample in the dark for 30 mins [NOTE THE TIME]. If after 30 mins, the concentration of NO<sub>x</sub> falls below 0.9 ppm, continue until it climbs above 0.9 ppm once more.

**NOTE: THIS DROP IS DUE TO THE ABSORPTION OF NO ONTO THE SAMPLE. HIGH SURFACE AREA SAMPLES CAN CAUSE THE NO<sub>x</sub> CONCENTRATION TO FALL BELOW 0.9 PPM, BUT ONCE SATURATED WITH NO, THE CONCENTRATION SHOULD START TO CLIMB.**

### *Light measurement*

Whilst maintaining the gas flow (3000 sccm, NO at 1 ppm), turn on the light source [NOTE THE TIME] and allow the photocatalytic reaction to occur over a period of 5 hrs.

**NOTE: IF LITTLE OR NO CHANGE IN NO<sub>x</sub> OCCURS AFTER 30 MINUTES OF EXAMINATION, IT IS LIKELY THE SAMPLE IS NOT PHOTOCATALYTICALLY ACTIVE. IN ORDER TO PRESERVE NO GAS, IT IS ADVISED THAT THE REACTION SHOULD BE STOPPED. IF SOME ACTIVITY WAS OBSERVED, BUT LOW (I.E. < 5% REMOVAL OF NO<sub>x</sub>), ISO PROTOCOL STATES THE SAMPLE CAN BE RE-MEASURED USING HALF THE FLOW RATE (1500 SCCM, NO AT 1 PPM) AND USING TWICE THE SURFACE AREA (2 SAMPLES OF 5 X 10 CM SHOULD BE USED). UNDER THESE CONDITIONS, QUADRUPLE THE NO REMOVAL ACTIVITY SHOULD BE OBSERVED.**

After 5 hrs, the light source should be turned off [NOTE THE TIME] for a period of 30 minutes. After this time, the feed gas should be changed to air (*i.e.* the NO gas stream should be turned off) [NOTE THE TIME] for a period of 30 minutes.

The reaction is now complete.

### Getting the data

The data can be accessed using the laptop using the software Airodis. Open the software and click on "launch workspace". Once the workspace opens, click on the station "NO<sub>x</sub> analyser" and then the button "download". A new window opens, and after specifying the dates, click on "download" (Figure 10, left). For 12 hours of data, it can take a few minutes to download. After it has downloaded, click on the "data manager" tab to view. If happy with the data, click on the "Excel export" icon to export the data (Figure 10, right).

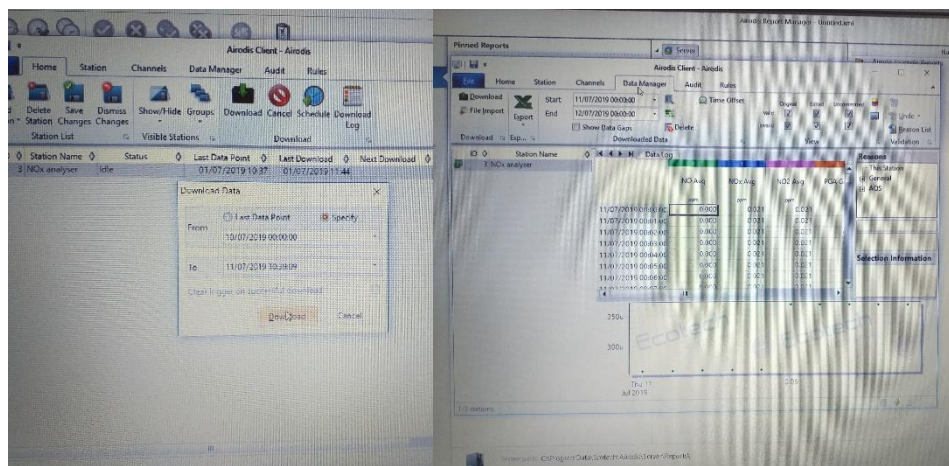
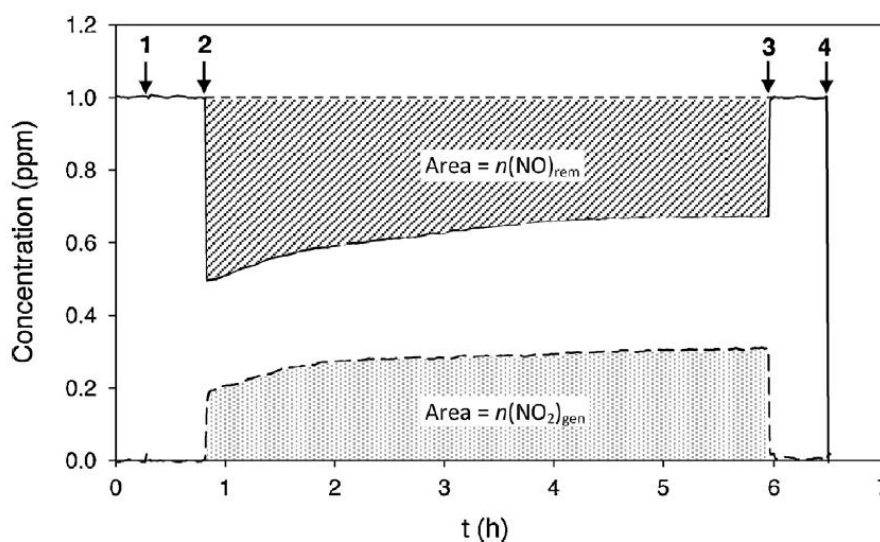


Figure 10. The Airodis software being used to download NO<sub>x</sub> data from the CL NO<sub>x</sub> analyser (left), and view & export this data (right)

Once plotted, a typical reaction profile is shown below:



**Fig. 1.** Typical data set generated, i.e., NO removed (solid line) and NO<sub>2</sub> generated (broken line), during an NO ISO standard test (inlet [NO] = 1 ppmv). The two shaded areas are equivalent to the number of moles of NO removed,  $n(\text{NO})_{\text{rem}}$ , and NO<sub>2</sub> generated,  $n(\text{NO}_2)_{\text{gen}}$ , by the sample, respectively. (1) Start of sample contact with NO-containing feed, (2) UV light on, (3) UV light off and (4) feed gas changed to zero calibration gas (i.e., air).

Shutting down the system

*If experiments will be performed within a fortnight*

Turn the house air and NO/NO<sub>2</sub> special gases off at the regulator in the fume hood (Figure 3, right), and then turn off the knobs for these gas supplies at the fume hood. Turn the mass flow controllers to 0% flow rate, then open release valve slowly to release built-up pressure (Figure 11). Turn the Bronkhurst mass flow controllers off at the white power supply box. Turn the Mesa Labs mass flow meter off. Remove the test sample from the reactor.



Figure 11. The pressure release valve

*If experiments will be performed after a fortnight*

Carry out the shut down described above, with the addition of turning off the CL NO<sub>x</sub> analyser and pump.

### 6. Disposal & gas cylinder replacement

Used samples, that will not be further examined, should be disposed of in the yellow sharps waste bin. NO and NO<sub>2</sub> gas cylinders (both 40 ppm in N<sub>2</sub>) are 40 L in volume, held at 200 bar. This equates to ~8000 L of gas stored. Under ISO conditions, NO is carried at a flow rate of 75 sccm. An ISO test typically takes around 8 hrs to perform, and therefore requires ~36 L of NO gas. Therefore, one cylinder should cater for more than 200 experiments.

NOTE: A NO/ NO<sub>2</sub> CYLINDER COSTS ~£250 TO REPLACE, AND HAS A LEAD TIME OF ~2 WEEKS.

### 7. Personal Protective Equipment (PPE)

Given its location in a working laboratory, the user is required to wear safety specs and a lab jacket at all times when using this apparatus.

### 8. Risk Analysis of SOP and emergency procedures

(In addition to Dept. [Safe Lab Practice](#))

**Always remember to include fire associated risks and control measures where appropriate**

Hazard	Raw risks	Current control measures	Residual risk (Low/Med/High)
NO *PWE = 25 ppmv	ISO test requires 1 ppmv; however, stock NO gas housed in gas cylinder is 40 ppmv. Exposure before dilution, through <b>inhalation can cause:</b>  <u>Symptoms</u>	<b>ALL WORK MUST BE CARRIED OUT IN A FUME HOOD WITH THE SASH LOW</b>	low

	irritation to eyes, wet skin, nose, throat; drowsiness, unconsciousness; methemoglobinemia  <u>Target Organs</u> Eyes, skin, respiratory system, blood, central nervous system		
NO <sub>2</sub> *PWE = 1 ppmv	Stock NO <sub>2</sub> gas housed in gas cylinder is 40 ppmv. Exposure, before dilution, through <b>inhalation, skin/ eye contact can cause:</b>  <u>Symptoms</u> irritation to eyes, nose, throat; cough, mucoid frothy sputum, decreased pulmonary function, chronic bronchitis, dyspnea (breathing difficulty); chest pain; pulmonary edema, cyanosis, tachypnea, tachycardia  <u>Target Organs</u> Eyes, respiratory system, cardiovascular system	<b>ALL WORK MUST BE CARRIED OUT IN A FUME HOOD WITH THE SASH LOW</b>	low
UVA light ^PWE = 0.04 mW.cm <sup>-2</sup> for an 8 hour period	ISO test requires 1 mW.cm <sup>-2</sup> . Above the PWE, <b>exposure to eyes</b> can cause damage to the eye-lens and result in cataractogenesis	<b>USER MUST WEAR UVA PROTECTIVE SAFETY SPECS WHEN REQUIRED</b>	low

\* Permissible workplace exposure (PWE), according to The National Institute for Occupational Safety and Health (NIOSH)

^The European Optical Radiation 2006/25/EC Directive is based on exposure limit values defined by the International Commission on Non-Ionising Radiation Protection (ICNIRP); UVA light in the spectral region 315 nm – 400 nm (UVA), maximum permissible radiant exposure (HUV-A max), within an 8 hour period per day for the unprotected eye, is 10,000 J.m<sup>-2</sup>.

Additional control measures to minimise residual risks	Implementation date

Who may be harmed	
Staff / students	<input checked="" type="checkbox"/>
Cleaners / Engineers	<input type="checkbox"/>

Supporting staff <input type="checkbox"/>	Others (specify):
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**Emergency procedures – describe the response(s) required by the user and lab members**

No work should be carried out in this fume hood if the face velocity is below 0.35 m/s. If there is a fault with the fume hood, all work should be immediately stopped, and all gases should be turned off in the correct manner.

All pipework should be checked regularly using snoop leak detector. If there is a gas leak, the pipework should be repaired before starting any work. If a gas leak is suspected during operation, all work should be stopped immediately, all gases should be turned off in the correct manner, and the fault repaired before carrying out further work.

**Recommended trainings and records:**

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List of individuals competent to demonstrate safe work practice and train others (level 1 trainers):	Names of those that have been trained and can work unsupervised (level 2) and date training completed:
1. Andreas Kafizas	1. Andreas Kafizas
2.	2. Louise McGrath
3.	3. Zhipeng Lin
4.	4. Yuqi Chen 01/03/2022
5.	5. Oyelusi Olaifa (05/03/22)
6.	6. Shize Li 05/03/23
7.	7. Akshi 21/02/2023
8.	8. Paransa Alimard 27/02/2023
9.	9.
10.	10.
11.	11.