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Supplementary Materials

Methodology for Simultaneous Analysis of Photocatalytic deNO$_x$ Products

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Abstract: The ISO standard 22197-1:2016 used for the evaluation of the photocatalytic nitric oxide removal has a main drawback, which allows only the decrease of nitric oxide to be determined specifically. The remaining amount, expressed as "NO_2", is considered as a sum of HNO_3, HONO NO_2, and other nitrogen-containing species, which can be potentially formed during the photocatalytic reaction. Therefore, we developed a new methodology combining our custom-made analyzers, which can accurately determine the true NO_2 and HONO species, with the conventional NO one. Their function was validated via a photocatalytic experiment in which 100 ppbv of either NO or NO_2 dispersed in air passed over (3 L min^{-1}) an Aeroxide© TiO_2 P25 surface. The gas-phase analysis was complemented with the spectrophotometric determination of nitrates (NO_3^-) and/or nitrites (NO_2^-) deposited on the P25 layer. Importantly, an almost perfect mass balance (94%) of the photocatalytic NOx abatement was achieved. The use of custom-made analyzers enables to obtain (i) no interference, (ii) high sensitivity, (iii) good linearity in the relevant concentration range, (iv) rapid response, and (v) long-term stability. Therefore, our approach enables to reveal the reaction complexity and is highly recommended for the photocatalytic NOx testing.

Keywords: photocatalysis; air purification; NOx; HONO; NO_2; mass balance

Citation: Suchanek, J.; Vaneckova, E.; Dostal, M.; Mikyskova, E.; Brabec, L.; Zouzelka, R.; Rathousky, J. Methodology for Simultaneous Analysis of Photocatalytic deNO$_x$ Products. *Catalysts* **2022**, *12*, 661. https://doi.org/10.3390/catal12060661

Academic Editor: Gassan Hodaifa

Received: 9 May 2022
Accepted: 14 June 2022
Published: 16 June 2022

Table S1. Overview of the analytical methodologies used for detection of gaseous nitrogen-based species and ozone.

Analyte	Method	LOD	Detection range
NO, NOx	APNA 370 (Horiba)	0.5 ppbv	1 % of whole range
N_2O	GC-MS@cryotrapping (Lu et al. 2016, see in manuscript)	<0.5 ppbv	-
NO_2	CLAD-FIA (Mikuska et al. 2008)	0.5 ppbv	3.0-655.0 ppbv
HONO	CWEDD-FIA (Mikuska et al. 2008, see in manuscript)	15 pptv	0.045-450.0 ppbv
HONO	FTIR – gas analyzer (ThermoFisher Scientific)	50–200 ppb	-
NO_2^-, NO_3^-	HPIC (ThermoFisher Scientific)	10, 50 ug L^{-1}	-
O_3	CLAD-FIA (Mikuska et al. 2008, see in manuscript)	0.3 ppbv	1.4-349 ppbv

Gaseous HONO analyzer

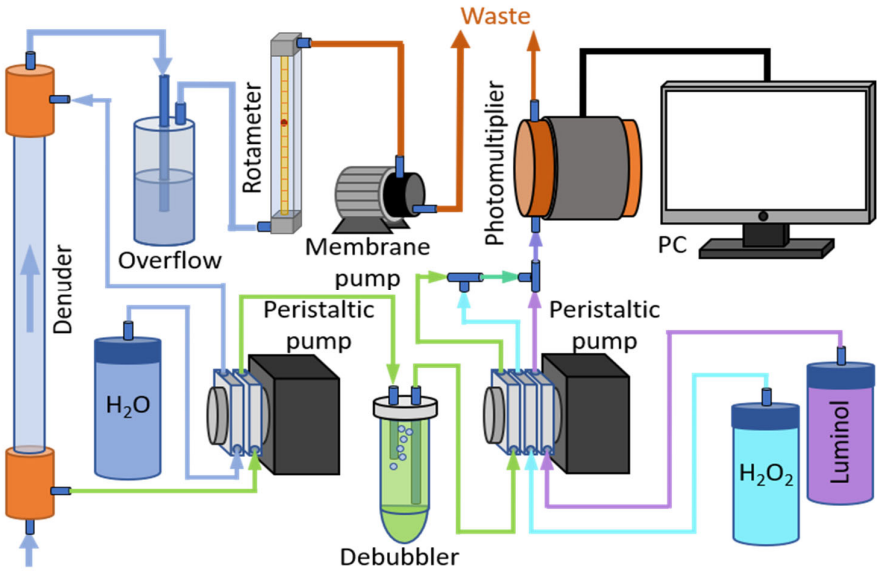

Figure S1. Custom-made analytical system for HONO detection in air, designed and assembled by Mikuska and co-workers [1].

HONO was continuously monitored using non-commercial instrumentation (Figure S1), whose principle is described by Mikuska and co-workers [1]. A thin film of deionized water flows down the inner wall of the cylindrical wet effluent denuder 50 cm in length and internal diameter of 1 cm. The inflow and outflow of liquid is provided by a peristaltic pump (ISM 847, Ismatec). The inner wall of the denuder tube is specially roughed to ensure a wettable surface. The gas to be analyzed is sucked in the opposite direction to the liquid flow (0.5 mL.min^{-1}) by a pump (HAILEA aco-328), the gas flow of 1.05 L.min^{-1} being controlled by a rotameter (FL-5541SA, Omega). Liquid running down the wall

quantitatively absorbs HONO from the gas phase. Collected HONO is transported by a peristaltic pump (ISM 852, Ismatec) into a debubbler and further to an on-line detection system. HONO is detected as nitrite employing a continuous flow system where HONO is first mixed with H_2O_2 reagent (consists of 1 mM H_2O_2, 0.3 M sulfuric acid, 1 mM EDTA, flow rate 0.14 mL.min^{-1}). H_2O_2 in acid solution oxidizes nitrous acid to peroxynitrous acid, followed by a merge with an alkaline luminol solution (2 mM luminol, 0.6 M KOH, 3 mM EDTA, flow rate 0.2 mL.min^{-1}). Chemiluminescent light emitted during the reaction of peroxynitrite with luminol is detected by a photomultiplier (65 PK 518, Tesla Praha). The required constant flow is ensured by a suitable combination of peristaltic pumps and tubing (LMT 55, Tygon) of suitable inner diameter. For the transport of all liquids and gases tetrafluoroethylene tubes were employed.

NO_2 analyzer

The NO_2 concentration was monitored using a custom-made analyzer (Figure S2) consisting of a peristaltic pump, reaction cell and measuring electronics. The principle of NO_2 detection is described elsewhere [2–4]. The analyzed gas was sucked into the reaction cell by membrane pump (ANR 70110035, Thomas), the flow rate of 0.46 L.min^{-1} being controlled by a 0.3 mm nozzle. A solution of luminol (97%, Sigma Aldrich) is introduced to the reaction vessel by a peristaltic pump (ISM 852, Ismatec) with flow rate 0.2 mL min^{-1} and afterwards goes down along the polyester wick. The continuous monitoring of NO_2 in the air operates by detecting the chemiluminescence produced when NO_2 encounters a wick wetted with a solution containing luminol. Intensity of emitted light is detected by photomultiplier (Hamamatsu R6094, maximum at 420 nm) operated at 600 V at the laboratory temperature of 22–25 °C.

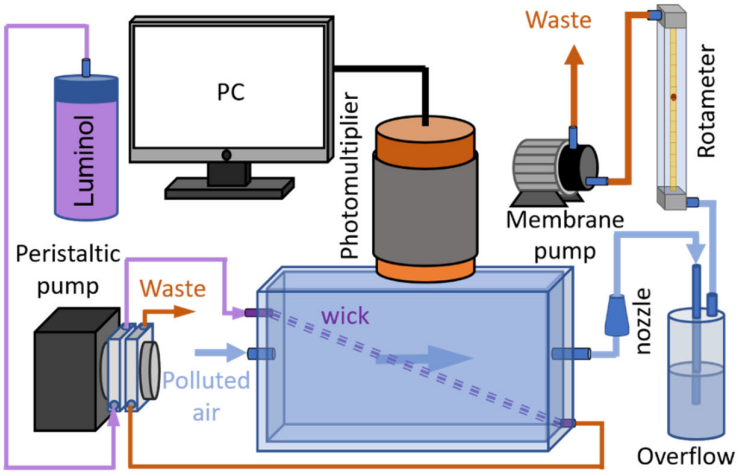

Figure S2. Custom-made analytical system for NO_2 detection in air, designed and assembled by Mikuška and co-workers [3].

NO/NO_2 analyzer

Commercial NO_x analyzer APNA-370 (Horiba) was employed to monitor NO and $NO+NO_2$ concentrations in the gas stream. Measuring principle is based on the cross modulation chemiluminescence method. NO is measured directly by its oxidation with O_3 and subsequent detection of luminescence from the NO_2* excited state, whereas NO_2 is first converted into NO. Also reduction of gaseous HONO and HNO_3 to NO cannot be excluded. Then the analyser would show either NO or the sum of NO_x concentrations except for N_2O.

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