

Photolysis for Enhancing the Specificity of NO_x Electrochemical Sensors

Reinoud F. Wolffenbuttel¹, David Bilby², Jacobus H. Visser²

¹ *Laboratory for Electronic Instrumentation, Department of Microelectronics, Delft University of Technology, 2628 CD Delft, The Netherlands,*

² *Research and Advanced Engineering, Ford Motor Company, Dearborn, MI 48121, USA*

Corresponding Author's e-mail address: R.F.Wolffenbuttel@TUDelft.NL

Summary:

Operation of the electrochemical NO_x gas sensor lacks specificity between NO and NO₂ detection. Radiation of a NO_x-containing exhaust gas mixture by UV light of 370 nm wavelength is investigated for photodecomposition of NO₂ into NO and atomic oxygen. The objective is to achieve sufficient modulation of the NO/NO₂ composition for significantly improving specificity of a commercially available sensor in a dynamic operating mode. A sufficient photolysis conversion efficiency is demonstrated using a 100 sccm flow in a quartz tube and commercially available LEDs for enabling NO/NO₂ selective detection.

Keywords: automotive sensor, exhaust sensor, electrochemical sensor, sensor specificity, photolysis

Background, Motivation and Objective

The increased emphasis by regulatory agencies on exhaust gas management has called for automotive gas sensors for a range of gases, each with demanding specifications and at low-unit costs for commercial viability in the automotive application. The electrochemical NO_x sensor is a proven concept and satisfies these constraints. However, satisfying the tightening in levels of acceptable emission and the need for selectively monitoring other gases in the reduction chain from NO₂ to N₂, for instance N₂O, requires an NO_x sensor for selectively measuring these constituents.

Photolysis of NO₂ in the atmosphere by UV light is well documented and is used here as a solution within the framework of the mantra 'learning from nature' for providing specificity in the measurement of the NO and NO₂ compositions in an exhaust gas, using an industrially available NO_x electrochemical sensor in combination with gas illumination by UV light in a pulsed mode [1].

Description of the Approach

Photo-dissociation of NO₂ into NO is maximum at 370 nm wavelength [2, 3]. The absorption coefficient at ppm-level concentrations is sufficient for an absorption depth of several cm, which implies that an efficient conversion can be achieved using a gas flow in a quartz tube of practical dimensions (see Fig. 1). The NO_x sensor is placed downstream the flow.

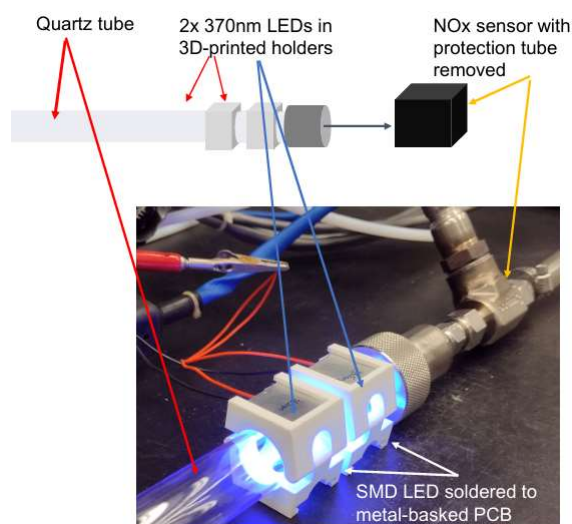


Fig. 1. Set-up for validating photo-dissociation of NO₂ at 370 nm and for measuring photolysis efficiency.

The generic effect is validated using the quartz tube in the transmission path of a spectrometer set-up (Ocean Optics Flame-S spectrometer-see Fig. 2). The spectral absorption is consistent with literature on NO₂ [4], while the NO generation results in relatively small spectral absorption peaks in the 200-230 nm band [5].

Gas mixtures are applied with the LEDs operated in a pulsed mode (see Fig. 3). The response lags the LED cycle, because of the relatively low flow rate of 100 ppm. The NO₂ concentration is indeed reduced during an illumination phase and

recovers during the dark phase in between. The incomplete recovery results in a time dependent response, which can be circumvented by adding a purging phase.

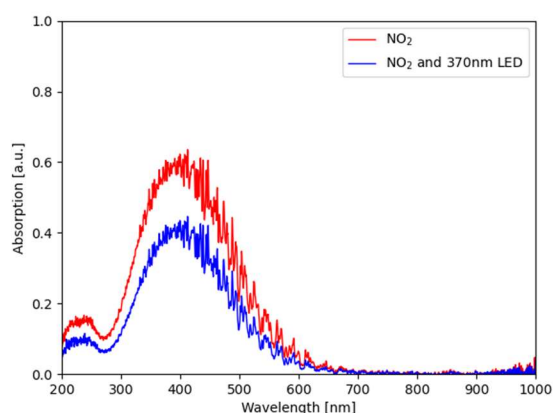


Fig. 2. Spectral absorption of NO_2 at 1000 ppm flow and without oxygen in the experiment, non-illuminated (red line) and radiated with LEDs at 370 nm wavelength (blue line)

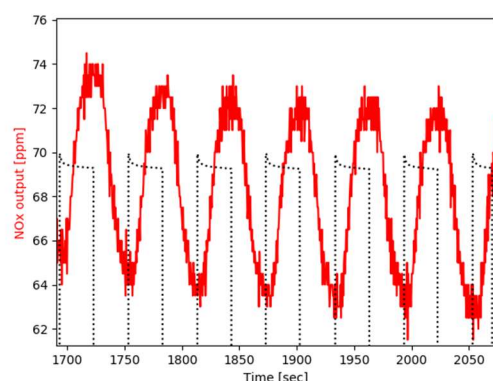


Fig. 3. Response of the NO_x sensor and the exit of the quartz tube to a 100 ppm NO_2 at the input, with the state of the LED indicated by the dotted line. The slow response is due to the relatively low flow rate.

The response to an NO_2/NO mixture is shown in Fig. 4. The NO_2 concentration changes between 100 ppm and 80 ppm. During NO_2 at 80 ppm, the NO concentration is changed between 100 ppm, 60 ppm and 20 ppm.

Although the NO_x sensor output signal for $\text{NO}_2=100$ ppm is overlapping with the signal for $\text{NO}_2=80/\text{NO}=20$ ppm, the individual NO_2 and NO concentrations can in principle be resolved due to the pulsed mode operation using the peak-to-peak signal fluctuations. Therefore, detection using lock-in techniques can be applied.

In the simple set-up used only a part of the wall area of the quartz tube is covered by LEDs and a more significant modulation depth can be expected from an optimized design.

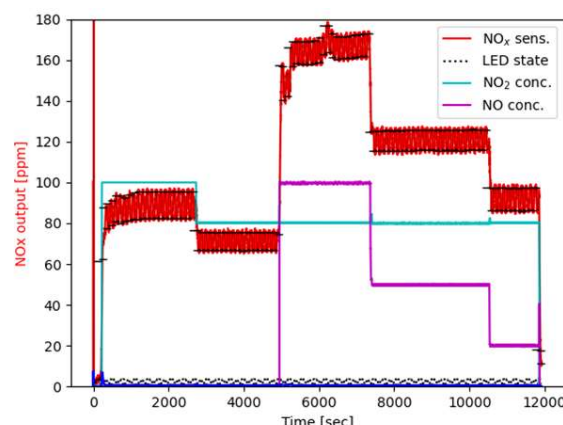


Fig. 4. Response of the NO_x sensor at the exit of the quartz tube to different concentrations of a NO_2/NO mixture entered at the input line (note that the LED pulse series is too compressed to be clearly visible in this long time series).

Ozone generally plays a role in the effectivity of UV photolysis [6]. The thermodynamics of the equilibration reaction indicates a recovery rate of NO_2 from NO oxidation with ozone, which makes the reaction depend on the NO and O_2 concentrations. Optimization of the set-up and investigation of these dependencies are topics of future work.

References

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