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Nathalie Redon, Caroline Duc, Sabine Crunaire, Nadine Locoge, Florian

Promonet, Jean-François Béguin

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A NEW PERFORMING SENSING SYSTEM TO MONITOR NH₃ CONCENTRATIONS FOR LIVESTOCK APPLICATIONS

N. REDON¹, C. DUC¹, F. PROMONET¹, J.F. BEGUIN¹, S. CRUNAIRE¹, N. LOCOGE¹

¹IMT Nord Europe, Institut Mines-Télécom, Univ. Lille, Centre for Energy and Environment, F-59000 Lille, France.

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INTRODUCTION

In the framework of QuantiAGREMI project, one of the main objectives aims to develop new measurement techniques *i*/ to quantify NH₃ emission fluxes from livestock housings, with a target uncertainty between 20 % to 40% for naturally or mechanically ventilated housing, and *ii*/ to monitor NH₃ concentrations in ambient air around livestock facilities to enhance spatiotemporal coverage in considering atmospheric conditions and sources. Recently many low-cost sensors for massive deployment have been developed and may have the potential to densify measurements on several farms and thus increase the representativeness of measurement data. With regard to NH₃ sensors, previous work has highlighted the need for accurate calibration and validation. In addition, measurements under livestock housing conditions for low-cost NH₃ sensors show that the results compared to the EMEP reference denuder method appear promising in the range >1 µmol/mol, but so far do not have the required accuracy for concentrations below. Thus, they cannot be used in naturally ventilated cattle housings with very low concentrations.

For several years, IMT Nord Europe has been interested in the development of surfaces sensitive to gaseous NH₃. The transduction is based on a conducting polymer layer showing a resistive variation in presence of this pollutant. In contrast with the majority of commercial sensors based on electrochemical or chemoresistive (MOX) techniques, the sensitive material developed at IMT Nord Europe enables a detection limit around few nmol/mol of NH₃, shows low interferences for other gases found around livestock buildings such as H₂S or NO₂. As a partner in the project, we are responsible for integrating this sensitive element to propose an autonomous measurement system and to optimise it to meet QuantiAGREMI requirements in all expected conditions (i.e. inside vs. outside buildings; emission vs. immission monitoring).

METHODS

The sensitive surface developed by IMT Nord Europe in previous work is prepared as follow: a conducting polymer, polyaniline (PANI), is doped with Camphor Sulfonic Acid (CSA), and dissolved in Dichloroacetic Acid (DCAA). Polyurethane (PU) is added to the mixture, bringing mechanical properties and limiting humidity influence. The ratio between PANI and PU is 70% wt-30% wt. The solution is mixed during 7 days, then undergoes a final sonication stage under ultrasound before being deposited by drop-casting on polyimide substrate covered by interdigitated gold electrodes. The surface is dried in a vacuum oven at 100°C during 7 days. The reaction between NH₃ and this sensitive surface (fig.1-a) induces a variation of conductivity inside the material, leading to variations of the resistance between the two electrodes in presence of ammonia. The phenomenon is totally reversible.

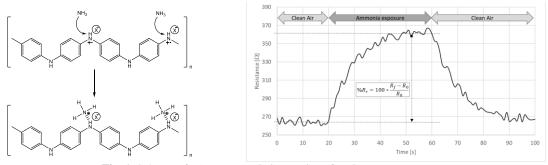


Fig. 1. Scheme of PANI-ammonia interactions forming sensor response.

The response is determined by calculating the instantaneous percentage of relative response under exposure $\[\%R_r\]$ (fig1-b). The experimental set-up used to qualify metrological performances under ammonia exposure consists of *i*/ a gas generation bench, with a calibrated cylinder of NH₃ at 10ppm, a zero air generator and an OMICRON dilution system to control flow rates from 0 to 20L/min and relative humidity from 0 to 90%RH; *ii*/ an exposure chamber [volume 0,5L or 5L], *iii*/an automated acquisition system based on a multimeter Keysight 34970A for sensors under tests, *iv*/ a ammonia reference analyser (LGR or PICARRO), used to established the correlation curve with $\[\%R_r\]$ and concentration levels of NH₃.

RESULTS

The sensitive surface is integrated into a prototype module made up of two parts: *i*/a flow management box, including a fan with controlled speed, a flow channel with a specific shape especially modelized to optimize gas-surface interactions, and a temperature and relative humidity sensor, and *ii*/a signal conversion box, including a Wheatstone bridge accepting resistance range from 200Ω to $2k\Omega$, an adjustable amplification stage (tuneable gain and offset) and a microprocessor able to convert the voltage into a standard I2C signal. Both parts of the module are easy to connect and to maintain, it is lightweight, compact, and low cost.

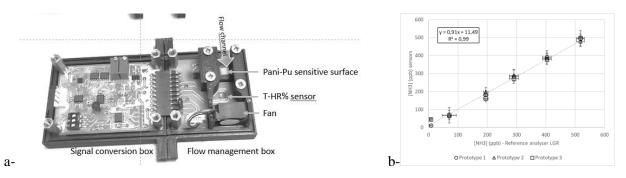


Fig. 2. a- photo of the prototype ammonia sensor developed, b-correlation curves of 3 triplicates of prototype

In lab-conditions and under 50% of RH, the performances obtained are as follows: the limit of detection is 2ppb, the sensitivity is 0,15%/ppb with a dispersion lower than 3% between different batch of sensors (Da Silva, 2023). When integrated into the prototype, an automatic correction algorithm based on the derivative/integral/acceleration of the response was defined in order to compensate drift and RH influence, and to improve the response time. Figure show correlation curves obtained in laboratory-controlled conditions.

CONCLUSIONS

We have developed an ammonia measurement module able to meet the main requirements of QuantiAGREMI project. This module must now be integrated into a measurement system enabling data recording and remote communication. This system called LAMMOS (Low AMmoniac MOdular Sensor), is under development, and will be deployed on field to determine its metrological performances under real conditions.

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