

Semi-automatic Measurement Device for Long-Term Monitoring of Ammonia in Gas Phase

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Summary (max. 6 lines):

The present paper describes the development of a sensor material that changes its fluorescence in the presence of gaseous ammonia in a relevant concentration range. The implementation into a semi-automatic gas measurement device enables low-cost, precise, simple and fast monitoring of low concentrations of harmful gases, like ammonia, and hence can help to improve the climate monitoring in livestock housing, barns or stables.

Keywords (max. 5): spectroscopy, embedded sensor, environment, air quality

Introduction

Extensive emission of ammonia into the air is known to be a crucial problem since years. Most of the emitted ammonia is generated in the agriculture sector (up to approx. 95 %). Even in the low concentration range does ammonia not only smell intensively but it also has a huge ecological and climatic relevance. In addition, the EU regulation on national emission maxima (NEC-Directive 2016/2284) involves a reduction of ammonia emissions by 29 % in 2030 compared to 2005, mainly to improve animal husbandry. The German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety specifies a limit concentration value in an exhaust gas of 30 mg m⁻³ equal to 41 μmol mol⁻¹ for ammonia [1].

The present work contributes to improve the determination of ammonia in air, for instance through monitoring barn climate, to become more precise, less expensive, simpler and faster. The production of a chemical sensor matrix changing its optical properties in the presence of gaseous ammonia and its implementation into an in-house-developed electronic device usable in the field is described.

Chemical Sensor Matrix

The basic component of the chemical sensor matrix is the fluorescent signaling unit, 1,3,5,7-tetramethyl-2,6-diethyl-boron-dipyrrromethene

(BODIPY) or dye **1**, used in the presented study (Fig. 1). This dye was already described in previous publications in which it has been used for the development of ammonia and pH sensors [2-4], especially due to its unique properties like high photostability, high fluorescence quantum yields and excitation and emission maxima at reasonably long wavelengths in the visible spectral range (529 nm and 545 nm respectively).

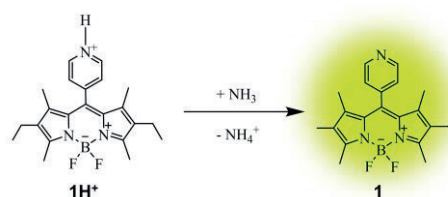


Fig. 1. Scheme of the sensor dye **1**.

The preparation of the sensor material is described in detail elsewhere [2]. Briefly, the wells of a black 96-well microtiter plate with a transparent bottom were filled with 20 μL of a hydrogel-ethanol-water-mixture and 50 μL of **1H⁺** in ethanol (1 mM) with a 12 h drying period in between and in the end. Finally, the plate was sealed with an aluminum foil to avoid contamination before the actual measurement.

Electronic, Mechanical and Optical System

The Fluorescence Spectrum Gas Injection Microtiter Plate Measuring Device (FS-GIMMD) (Fig. 2) was to hold 6 times 96-well microtiter

plates with a transparent bottom which are hermetically sealed with an aluminum foil cover. In total, 567 measurements can be performed with one fully equipped device. Since the prepared plates can be easily replaced by untrained personnel, the setup is suitable for long term tracking of the analyte, for instance to monitor the concentration of ammonia in barns. Each well contains the sensor material, embedded in a hydrogel matrix, being illuminated by an excitation light (LED 500 nm) to produce a fluorescence signal which changes when reacting to ammonia. An automated mechanical-electrical device initiates a given gas mixture and thus simulates different concentrations of gaseous ammonia and allows varying the defined relative humidity. A detailed description of the device and the gas mixing system can be found elsewhere [2]. The measurements were performed by piercing the aluminum cover foil with two needles and passing a defined ammonia concentration over the sensor material for a defined time before moving to the next position where the identical procedure was carried out.

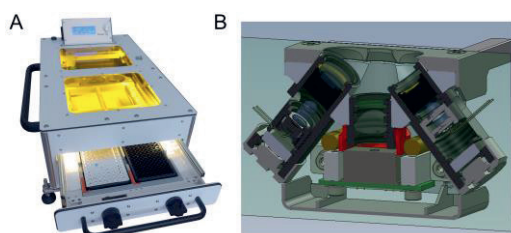


Fig. 2. FS-GIMMD prototype design (A) and a scheme of the optical head (B).

Results and Discussion

As already reported previously, dye **1** is highly fluorescent in the neutral state while protonation induces a quenching of the emission (Fig. 1) [2]. The protonated dye $1H^+$ was embedded in a suitable hydrogel matrix being polar and humid enough to accumulate gaseous ammonia. With a pKa of 2.15 ammonia deprotonates $1H^+$ leading to a fluorescence increase at 570 nm ($\lambda_{ex} = 500$ nm). First attempts with the FS-GIMMD and the optimized sensor material have been done with increasing concentrations of ammonia from 0 to 20 $\mu\text{mol mol}^{-1}$ and at relative humidity of 0 %, 10 % and 25 %. The entire emission range (525 nm to 800 nm) is registered for 10 minutes which was determined to be the optimum response time after performing several runs up to 60 minutes. Fig. 3A shows the course of the spectra measured with the FS-GIMMD for one sensor material purged with 20 $\mu\text{mol mol}^{-1}$ ammonia over 10 minutes. It is clearly visible that the fluorescence maximum at 570 nm increases when the gaseous ammonia is present. Performing the same experiment with increasing concentrations of ammonia (0,

1, 5, 10, 20 $\mu\text{mol mol}^{-1}$) followed by analyzing the change in fluorescence at 570 nm as a function of the concentration nicely demonstrates a linear increase (Fig. 3B). It is also shown that adjusting different relative humidity results in different calibration curves, indicating that the humidity needs to be tracked in parallel to determine real ammonia concentrations.

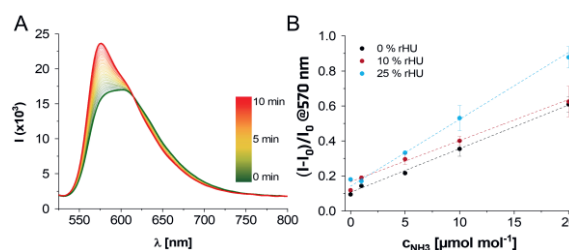


Fig. 3. Time dependent response of sensor material in presence of 20 $\mu\text{mol mol}^{-1}$ ammonia (A) and change in fluorescence at different ammonia molar fractions and relative humidity after 10 min (B) measured with the developed FS-GIMMD ($\lambda_{ex} = 500$ nm).

In addition, the microtiter plates have been stored for 6 months and showed unchanged performance to freshly prepared once, verifying the long-term stability in the applied format.

Conclusion

In conclusion, the foundation was laid for a semi-automated approach to long-term monitor and hence to regulate low concentrations of gaseous ammonia in livestock housing, barns or stables, in an economic, simple, precise and fast manner. After the planned implementation of the humidity dependent calibration curves, the sensor device can be adapted to other relevant harmful gases which enables the use in a broad range of applications.

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