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Long-Term Monitoring of Gaseous Ammonia with a Semi-automatic Measuring Device

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Summary (max. 6 lines):

In the present paper the development of a semi-automated device for long-term monitoring of gaseous ammonia is described. A sensor material was produced that changes its optical properties in the presence of low concentrations of ammonia in air. The implementation into an electronic device enables precise, simple, economic 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

It is known since years that low concentrations of ammonia in the air not only smell intensively but also can cause considerable damage to human health and ecosystems. Because most of this gas is emitted in the agriculture sector (up to approx. 95 %), the EU regulation on national emission maxima (NEC-Directive 2016/2284) involves a reduction of ammonia emissions by 29 % in 2030 compared to 2005. In addition, 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]. Hence, reliable and cost-effective sensors for gaseous ammonia with sensitivities in the lower ppm range are required for continuous monitoring of air quality. Besides being miniaturizable, the developed sensors should be usable on-site for in-the-field measurements by untrained personnel over long periods.

The present work contributes to the development of a more precise, less expensive, simpler and faster sensor for ammonia in air, that can be used, for instance, to monitor the climate in barns. The implementation of a developed chemical sensor material, changing its optical properties in the presence of gaseous ammonia, into an in-house-build electronic device usable directly in the field is described.

Chemical Sensor Material

To be able to produce a chemical sensor material that can change its optical properties in the presence of gaseous ammonia, the fluorescent signaling unit, 1,3,5,7-tetramethyl-2,6-diethyl-boron-dipyrromethene (BODIPY) or dye **1**, was used as basic component in the presented study (Fig. 1). This dye has unique properties like high fluorescence quantum yields and excitation and emission maxima at reasonably long wavelengths in the visible spectral range (529 nm and 545 nm respectively) and was thus already described for the development of ammonia and pH sensors [2-4].

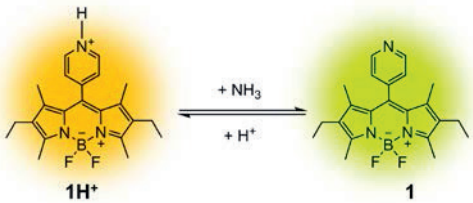

*Fig. 1. Scheme of sensor dye **1** and the fluorescence change (λ_{ex} 365 nm) in presence of ammonia.*

A detailed description of the preparation of the sensor material can be found elsewhere [2]. Briefly, 20 µL of a hydrogel-ethanol-water-mixture and 50 µL of **1H⁺** in ethanol (1 mM) were filled into the wells of a black 96-well microtiter plate with a transparent bottom and dried twice for 12 h. To avoid contamination

before the actual measurement, the plate was hermetically sealed with an aluminum foil.

Semi-automatic Measuring Device

A Fluorescence Spectrum Gas Injection Microtiter Plate Measuring Device (FS-GIMMD) being able to hold six 96-well microtiter plates has been developed (Fig. 2). Conclusively, one fully equipped device can be used to run up to 567 measurements. The easy replacement of the plates can be done by untrained personnel and allows the use of the setup for long term tracking of ammonia, for instance to monitor the air in barns. Each sensor material, being prepared in the wells as described before, can be illuminated by an excitation light (LED 500 nm) and the produced change in fluorescence signal in the presence of ammonia can be tracked by the optical head containing a C12666MA microspectrometer from Hamamatsu [2]. The validation was performed by generation of different concentrations of gaseous ammonia as well as varying relative humidity by an automated mechanical-electrical device. The gas mixing system is described in more detail elsewhere [2]. A typical measurement was performed by piercing the aluminum cover foil with two needles and passing a defined ammonia concentration over the sensor material for a defined time at a certain relative humidity. Afterwards, the identical procedure was carried out at the next position.

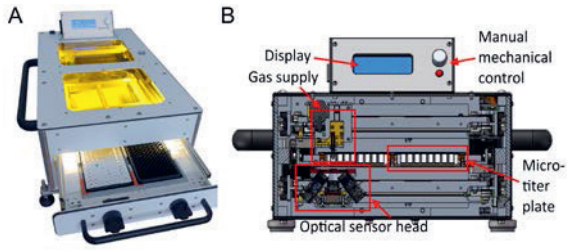

Fig. 2. Picture (A) and a scheme of the main mechanical parts (B) of the FS-GIMMD prototype.

Results and Discussion

As schematically shown in Fig. 1, dye **1** is highly fluorescent in the neutral state while protonation induces a change in emission [2]. A hydrogel matrix being polar and humid enough to accumulate gaseous ammonia was used to embed the protonated dye **1H$^+$**. Due to a pKa of 2.15 ammonia deprotonates **1H$^+$** leading to a fluorescence increase at 570 nm when excited at 500 nm. First tests with increasing concentrations of ammonia from 0 to 20 µmol mol^{-1} and at relative humidity of 0 %, 10 % and 25 % were performed with the developed FS-GIMMD. Measurements of the entire emission range (525 nm to 800 nm) over a time period of 60 minutes revealed that saturation is reached after 10 min. Fig. 3A exemplarily shows the emission spectra of one sensor material purged with 20 µmol mol^{-1} ammonia over 10 minutes and demonstrates the increase in fluorescence at 570 nm. Identical experiments were performed with increasing concentrations of ammonia (0, 1, 5, 10, 20 µmol mol^{-1}). The corresponding change in fluorescence at 570 nm plotted as a function of the concentration shows a linear increase (Fig. 3B). It was also observed that the calibration curve depends on the relative humidity and thus parallel tracking of the humidity is essential to determine real ammonia concentrations. In addition, the long-term stability of the sensor material in the microtiter plates has been validated over 1 year.

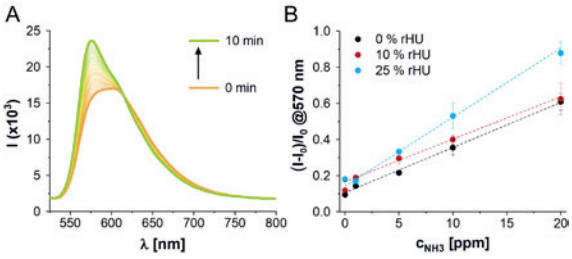

Fig. 3. Time dependent response in presence of 20 µmol mol^{-1} ammonia (A) and fluorescence change at 570 nm at different ammonia concentrations and relative humidity after 10 min (B) measured with the developed FS-GIMMD (λ_{ex} = 500 nm).

Conclusion

In conclusion, a semi-automated approach to long-term monitor low concentrations of gaseous ammonia in livestock housing, barns or stables, in a simple, precise, economic and fast manner has been developed. After implementation of the humidity dependent calibration curves, the sensor device could be easily adapted to other harmful gases which enables the use in a broad range of applications.

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