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Improvement Methods for Colorimetric Gas Sensor for Use in Indoor Livestock Farming †

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Abstract: Different published colorimetric sensors were investigated with the ultimate goal to develop a colorimetric sensor for a closed livestock farm, applicable in a rough environment. The methods were investigated to improve the lack of sensitivity, roughness, and reproduction of colorimetric sensors. The methods investigated varied from changing matrices, changing substrates, treatment of the substrates, and investigation of the distribution by camera of the chemical thin layer and investigation on temperature, water and cross interference of several other gases in the livestock gas matrix. Results showed that with changing several important parameters, other than only the choice of a color indicator results in a serious improvement of the sensor specification and an improved performance necessary for the rough circumstances in livestock farming.

Keywords: ammonia; colorimetric; livestock farming; halochromic

1. Introduction

Ammonia is an important air quality and health parameter component for livestock in indoor farming. Ammonia can cause severe infections in the lung and respiratory system of livestock causing environmental effects. Reducing ammonia through proper ventilation systems and robust ammonia sensors is therefore important. Many investigations describe ways to produce colorimetric gas sensors based on a halochromic material [1,2]. All these sensors work on the principle that the halochromic material changes the color if it comes into contact with ammonia (Figure 1). To detect this change in color three basic components are needed: a light source, the halochromic material and a light sensor.

Schematic overview:

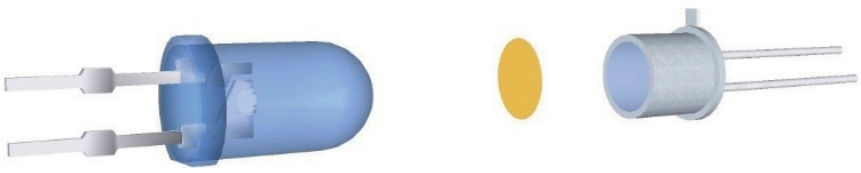

Figure 1. Schematic overview of the colorimetric sensor. The halochromic material exposed to ammonia results in color changes.

Many investigations describe ways to produce colorimetric gas sensors based on the above-mentioned method, but in most references, lack of sensitivity, robustness, and reproducibility are limiting practice implementation [3]. Traditional dip or spin coating shows inhomogeneous surface coverage of the substrate, resulting in poor reproducibility. Also drift, mostly caused by migration of the chemical matrix due to water or photo degradation by UV is an issue. The aim is to design a sensor that is robust, sensitive and reproducible, without the cross interference of gases present in livestock farming.

2. Materials and Methods

2.1. Dye

There are many different halochromic materials that can be used to detect ammonia. After testing a few different materials, we discovered that if the dye is more intense in blue color, it will degrade rapidly over time also known as photo bleaching by UV. We have chosen Bromocresol purple as core dye material. Bromocresol purple will become blue if it comes into contact with high amounts of ammonia but between 0–25 ppm the dye will not become blue and is therefore suitable for measuring ammonia in livestock farms.

2.2. Substrate

In the first tests we used microscope glass slides as substrate which were single or double- sided coated. Although it was suitable for measuring ammonia it came with some drawbacks. To get an accurate measurement the whole glass slide must be exposed evenly to the gas stream. In practice, we ended always up with a coated glass slide that produced relatively small electronic signals with high amounts of noise. Therefore, we have chosen a porous PTFE filter disc witch a hydrophilic surface. Due to the porous structure of the disc we can force sample gas through the disc.

2.3. Coating

Traditional dip or spin coating shows inhomogeneous surface coverage of the substrate. This was discovered when we replaced the light sensor with a digital camera. Due to the inhomogeneous surface the dye has certain spots that behave differently than other areas on the dye, resulting in poor reproducibility (and a nonlinear signal). We found that if we sprayed the halochromic material on the substrate we get a very reproducible and homogeneous layer.

2.4. Reference

After all the improvements, there are still certain factors that influence the measurement. Therefore, we have made a second sensor acting as reference sensor that is identical to the sensing sensor with the difference that the sample gas goes first through a platinum catalyst removing the ammonia without affecting all other gas compounds.

2.5. Platinum (Pt) Catalyst

The platinum catalyst was introduced in the system due to the fact that many chemical filter media showed disadvantages such as forming byproducts, limited use due to aging or pollution and water buffering effects resulting in unstable sensor signals. The idea of introducing a platinum catalyst was that it could be a reliable filter to ammonia and a very small capacity of water buffer, resulting in fast sensor reaction.

3. Results

The novelty is that a PTFE transmittance substrate, with a new chemical matrix, a correct applied wavelength (no UV) and a platinum catalyst are used. Several chemical color indicators are selected, investigated and tested. The results show that the chemical layer with a spray technique has very

reproducible properties for production. The spray dyes coated by spray technique were more stable and reliable than the dyes produced with dip coating. With the spray technique to produce colorimetric sensors, no sensitive material migration was found after long-term test runs with exposure of different concentrations of ammonia, resulting in an excellent baseline and reproducibility (Figure 2). Investigation of the drift results in a solution where a reference channel connected to a miniature platinum catalytic converter acts as a zero or sensor baseline reference which removes ammonia out of the gas stream without affecting all other gas compounds. With the addition of a catalytic converter also, the water influence is disappeared showing from results this water interference acts as an offset interference. The lowest detection limit (LOD) was investigated showing that the LOD improved 10 times according to previous research. A detection limit of 0.1 ppmv ammonia was reached under laboratory conditions. An investigation of cross sensitivity was performed by exposing several gas compositions to the sensor system, showing no cross interference towards hydrogen disulfide and carbon dioxide. During the practice tests, the colorimetric sensor system with Pt catalyst was tested in a simulated environment where real feces of animals formed ammonia (Figure 3). The sensor was compared with an ammonia analyzer based on a photoacoustic laser system (Figure 4). Results showed that the sensor range of the ammonia sensors was equivalent and that span and offset of the colorimetric sensor were in line with the photoacoustic laser (Figure 5).

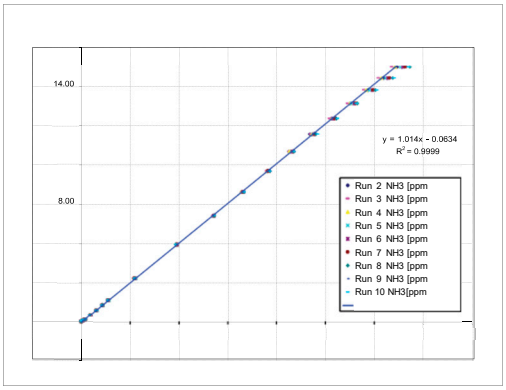

Figure 2. Comparison of 10 runs from 0–12 ppm Ammonia in steps of 0.1, 0.2, 0.4 0.6, 0.8, 1. 2, 4, 6, 8, 10 and 12 ppm.

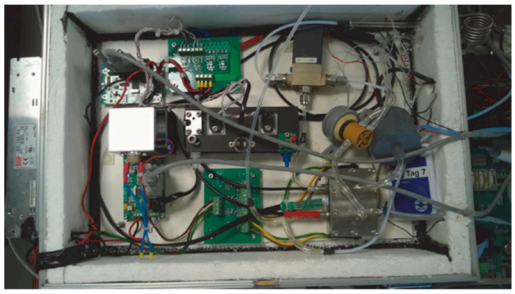

Figure 3. Colorimetric prototype with Pt catalytic filter to remove ammonia.

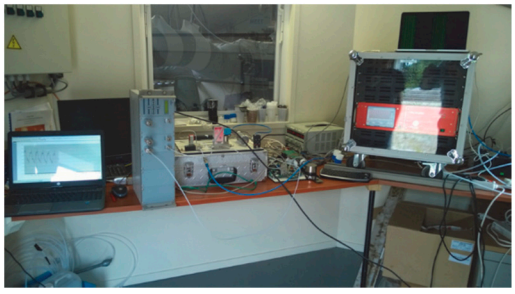

Figure 4. Setup in practice test with a comparison of the colorimetric gas sensor against a photoacoustic laser.

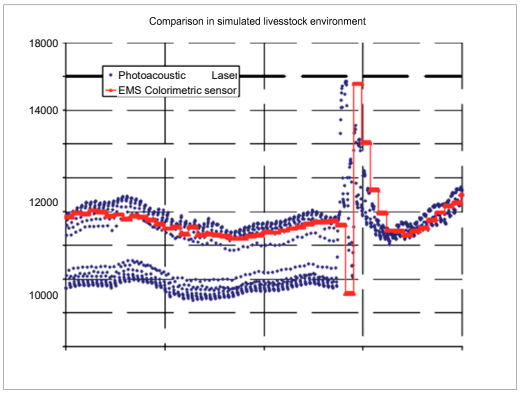

Figure 5. Result practice test comparison of measurements with photoacoustic laser and colorimetric gas sensor in simulated closed livestock farming.

4. Discussion and Conclusions

We developed a reliable ammonia sensor capable of measuring ammonia in the rough conditions of livestock farming. The halochromic sprayed dyes were resistant to the harsh environment and showed no permanent damage in contrast to the dip coated dyes. Due to the porous structure of the disc, sample gas is forced through the disc resulting in an even contact and exposure and very high reaction rates. All sample gas molecules are forced to flow through the halochromic dye, resulting in very high reaction rates and no chemical unused halochromic media on the PTFE substrate. The Pt catalyst acts as a stable reference for ammonia, resulting in a full removal of ammonia from the gas stream. The negative side effects of a possible water buffer measured with a relative humidity sensor behind the gas stream from the Pt catalyst showed that these unwanted distortion of signals resulting in negative side effects were completely removed, so that the colorimetric sensor showed relatively high speed measurements. Typical recovery times from ammonia exposure of 12 ppm to a full recovery of the signal, showed a recovery time of 7.5 min. Further development must be done to make this proof of concept a real product that is affordable enough for farmers. A way to do this is miniaturizing this product by MEMS technology.

References

1. Courbat, J.; Briand, D.; Wöllenstein, J.; de Rooij, N.F. Polymeric foil optical waveguide with inkjet printed gas sensitive film for colorimetric sensing. *Sens. Actuators B Chem.* **2011**, doi:10.1016/j.snb.2011.09.001.
2. Courbat, J.; Briand, D.; Damon-Lacoste, J.; Wöllenstein, J.; de Rooij, N.F. Evaluation of pH indicator-based colorimetric films for ammonia detection using optical waveguides. *Sens. Actuators B Chem.* **2009**, doi:10.1016/j.snb.2009.08.049.
3. Sjepherd, R.L.; Yerazunis, W.S. Low-Cost Surface Mount LED Gas Sensor. *Sensors* **2005**, *6*, 861–866.