

TOWARDS A MINIATURIZED AMBIENT AMMONIA DETECTION SYSTEM

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Abstract — The development of a miniaturized ammonia sensor is described. First, gas is sampled into an acid sample solution using a miniaturized gas sampler. Subsequently, the solution is pumped into a selector, comprising two channels separated by a gas permeable, water repellent polypropylene membrane, while adding an alkaline solution to dissociate all acid gasses and neutralize the alkaline gasses. The resulting gaseous ammonia can diffuse through the membrane into a purified water stream where an electrolyte conductivity sensor quantifies the resulting ammonium concentration. The realized system has a detection limit for ammonia below 1 ppm and is shown to be selective with respect to normal ambient carbon dioxide concentrations.

Keywords: ammonia detector, micro fluidics, gas sensor

INTRODUCTION

In the medical community, there is a considerable interest in breath analyzers that can be applied to measure ammonia levels in exhaled air for the diagnosis of certain diseases, like a disturbed urea balance, e.g. due to kidney disorder [1] or H. pylori bacterial stomach infection [2, 3]. Often only a small volume of exhaled air is available and, today, no suitable miniaturized ammonia breath analyzer exists [4]. The ammonia analyzer should be extremely selective because the levels of exhaled ammonia, 0.05 - 2 ppm [3], are very low compared to that of interfering gasses, such as CO₂, up to 30000 ppm.

At the Energy research Centre of the Netherlands, ECN, an ammonia detector has been developed for measuring ambient ammonia levels for environmental monitoring [5]. To make the system suitable for breath analysis, miniaturization is necessary to reduce the required sample volumes. Moreover, this leads to reduced reagent consumption and potentially a reduced cost.

The ammonia analyzer comprises a gas sampler, a selector and a detector, shown in figure 1. The key components have been realized on chip. This paper presents first measurement results with a hybrid integrated, miniaturized system.

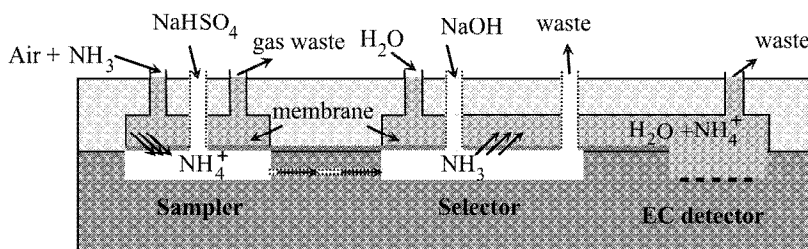
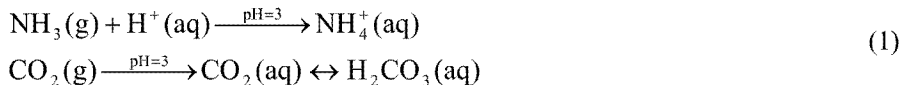


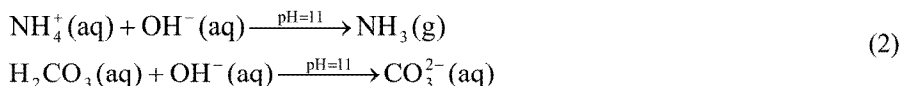
Fig. 1 Schematic of the micro-fluidic air ammonia analyzer comprising a gas sampler, a selector and an electrolyte conductivity detector [5].

THEORY

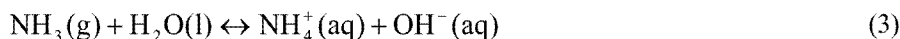
Ammonia is the main alkaline ambient gas. The detection principle is based on this fact. First, gas is sampled into an acid sample solution where ammonia dissociates and weak acid gasses stay neutral, as is described by equation 1:



The resulting solution is pumped into the selector where its pH is increased by adding a strong alkaline solution, converting the ammonium ions back to gaseous ammonia and dissociating sampled acid gasses like CO_2 , as described by equation 2:



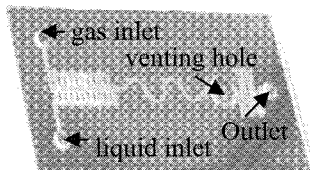
The selector is formed by two opposite channels separated by a gas permeable, water repellent polypropylene membrane. The opposite channel is flushed with purified water. The dissolved gaseous ammonia can pass the membrane into the purified water where they will partly ionize due to the dissociation equilibrium, as described in equation 3.



All remaining ionized acid gasses are flushed out of the system as waste. The formed ammonium ions in the water stream are quantified using an electrolyte conductivity detector.

EXPERIMENTAL

A miniaturized gas sampler for small volumes has been realized in previous research [6]. A picture of the sampler is shown in figure 2. The selector part has been realized by epoxy gluing a micro porous polypropylene membrane over 15 μm deep channels etched into glass chips using epoxy resin. The selector is shown in figure 3. An interdigitated electrolyte conductivity sensor with 165 fingers, 1200 μm long, 20 μm wide and 10 μm spacing is used to quantify the resulting ion concentration. A picture of this sensor is shown in figure 4. These elements have been interconnected using 0.8 mm ID PTFE tubing.



*Fig. 2 Image of the 2*3 cm miniaturized gas sampler.*

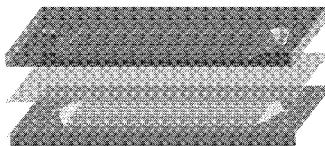


Fig. 3 Image of the selector, PP between glass chips.

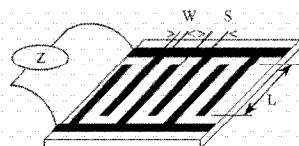


Fig. 4 EC detector: interdigitated electrodes

To show the selectivity and sensitivity of the analyzer, the system is first tested with 1.5 ml/min of pressurized air, containing 300 ppm CO_2 , then with nitrogen containing 10 ppm ammonia and finally with only purified nitrogen. Secondly, different ammonia concentrations in a nitrogen carrier flow are applied to the gas sampler. Gas flow is regulated with mass-flow controllers acquired from Bronckhorst, EL-flow F-110C. The gas is sampled into an 8 $\mu\text{l}/\text{min}$ NaHSO_4 , pH 3, sample flow. Liquid flow is regulated using a microdialysis syringe pump, CMA 102. The carrier gas is removed from the system through a venting hole sealed with a gas permeable, water repellent, membrane. Subsequently, the sample solution is made alkaline by adding 1.5 $\mu\text{l}/\text{min}$ 0.25 M NaOH. The solution flows into the selector where gaseous ammonia passes the membrane into a 10 $\mu\text{l}/\text{min}$ purified water stream in the opposite channel. The resulting ion concentration due to the dissociation reaction is measured using an electrolyte conductivity sensor [7].

RESULTS AND CONCLUSIONS

After purging the system using pressurized air containing 300 ppm CO_2 , the gas source is changed to nitrogen with ammonia. The conductivity increases strongly when 10 ppm ammonia is sampled instead of 300 ppm CO_2 , as can be seen in figure 5. After changing the gas source to pure nitrogen, the conductivity is decreased again. Although, from these results, it is hard to give a number for the selectivity, it is clear that the system is very selective to ammonia compared to CO_2 . When different ammonia concentrations are applied, it is shown that the conductivity decreases with lower ammonia concentrations, figure 6.

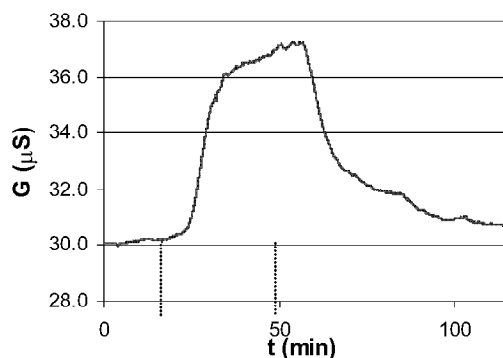


Fig. 5 **Selectivity** result showing a high selectivity to 10 ppm NH_3 over 300 ppm CO_2 .

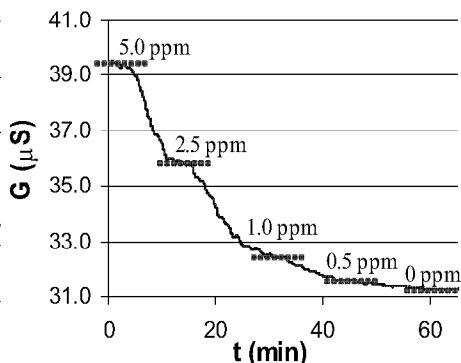


Fig. 6 **Sensitivity** result showing a detection limit below 500 ppb.

The presented system uses small volumes of reagents compared to the original system, e.g. the volume of the sample solution compartment is reduced more than hundred fold and the flow through time of the key elements is reduced significantly. In future research, the system can be made significantly faster by reducing the volume in the interconnecting tubing.

REFERENCES

- [1] L.R. Narasimhan, W. Goodman, C. Kumar, N. Patel, "Correlation of breath ammonia with blood urea nitrogen and creatine during hemodialysis", PNAS, vol. 98, no. 8, pp 4617-4621, 2001
- [2] J. C. E. Underwood, "General and Systematic Pathology", Churchill Livingstone Inc, 2nd edition, pp 414-415, 1996
- [3] D. J. Kearney, T. Hubbard, D. Putnam, "Breath ammonia measurement in Helicobacter pylori infection", Digestive diseases and sciences, vol. 47, No. 11, pp 2523-2530, 2002
- [4] E. Verpoorte, "Microfluidic chips for clinical and forensic analysis", Electrophoresis, 23, pp 677-712, 2002
- [5] J.W. Erisman, R. Otjes, A. Hensen, P. Jongejan, P. v.d. Bulk, A. Khlystov, H. Möls and S. Slanina, "Instrument development and application in studies and monitoring of ambient ammonia", Atm. Env. 35, pp 1913-1922, 2001
- [6] B.H. Timmer, W. Olthuis, P. Bergveld, A. v.d. Berg, "Miniaturization of an ammonia sampler" presented at Nanotech 2002 Montreux, Switzerland, 2002
- [7] B.H. Timmer, W. Sparreboom, W. Olthuis, P. Bergveld, A. v.d. Berg, "Optimization of an electrolyte conductivity detector for measuring low ion concentrations", Lab on chip, Volume 2, Issue 2, pp. 121-124, 2002