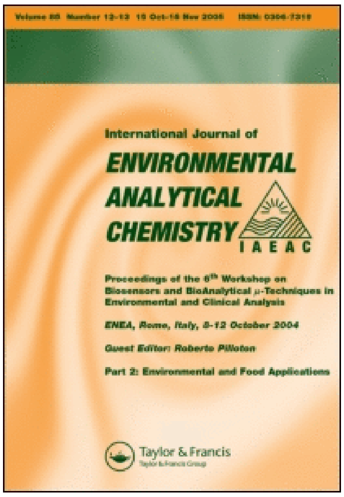

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OPTOCHEMICAL SENSOR FOR AMMONIA BASED ON A LIPOPHILIZED PH INDICATOR IN A HYDROPHOBIC MATRIX

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An optical sensor for the determination of ammonia in water based on ion pairing has been investigated. A pH-sensitive dye is immobilized as an ion pair in a silicone matrix. The colour of the dye changes from yellow to blue depending on the concentration of ammonia in the sample solution. This change is reversible. The concentration of ammonia can be determined by measuring the transmittance at a given wavelength.

All measurements were performed with a dual-beam optical meter. The measurement range was from 5.9×10^{-7} to 1×10^{-3} M (0.01 to 17 mg/l) in 0.1 M phosphate buffer of pH 8. The detection limit was 10 µg/l. The response times at a flow rate of 2.5 ml/min were 4 min for t_{90} and 10 min for t_{100} at a change from 41.9 to 82.5 µM ammonia and 12 min for t_{90} and 48 min for t_{100} at a change from 160 to 0 µM ammonia. The operational lifetime of the ammonia sensor was limited to a period of a few days only. A continuous decrease in baseline signal and relative signal change was observed over the whole measurement. The storage stability was more than 10 months (dry). With respect to possible application of the ammonia sensor to environmental analysis, the influence of pH, typical interferences, such as amines and various detergents on the sensor response was investigated. No interference due to pH was observed in the range from pH 5 to pH 9. With methyl- and ethylamine the response was not completely reversible. The sensor was affected by cationic detergents, but not by anionic or neutral detergents.

Keywords: Optochemical sensor; ammonia; ion pairs; transmittance measurements

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INTRODUCTION

In order to obtain real-time information on environmental monitoring, methods for on-line determination of ammonia are of increasing interest. The measurement of ammonia is important in discharge water, in sewage treatment works, in surface water and in ground water. The upper limit for ammonium ions in drinking water is 2.8×10^{-2} mM. The ratio of ammonium and free ammonia depends on pH, temperature and salinity of the water. Continuous determination of ammonia is important since ammonia is toxic to lower organisms, especially to fish, at concentrations as low as 1.5×10^{-3} mM [1]. The determination of ammonia in air is also important over a wide range of concentrations. Its concentration at ground level averages 2×10^{-3}– 1×10^{-2} mg/l and decreases monotonically with increasing altitude. It is the only significant alkaline gas in the atmosphere, where the average residence time is only 7–14 days due to aerosol formation and neutralization by more acidic species. For this reason, the measurement of ammonia is of interest for studies of smog and acid rain formation [2]. Bacterial activities are natural sources of ammonia. Anthropogenic sources of ammonia are animal breeding, fertilizer and purification plants. Ammonium ions and ammonia can reach the ground water from fertilizers containing urea and ammonium salt [3]. The annual emissions of ammonia in Europe amount to 6.4 million tons, of which 81 % come from animal breeding. Communal purification plants must not exceed the limit of 0.7 mM ammonium nitrogen in the processed sewage. Like other gases such as ozone, carbon dioxide and nitrogen oxides, ammonia is discussed in connection with the greenhouse effect in the atmosphere and its influence on the world climate [3].

Several years ago, ammonia was most commonly determined by the indophenol method or the Nessler method, which are based on the irreversible change in colour occuring in a chemical reaction. This change in colour can be detected spectroscopically [4,5]. A large variety of optical ammonia sensors and probes have been described in the literature. Ammonia can be determined directly by measuring its intrinsic absorption of infrared light [6]. At present, this method is limited to ammonia in the gasphase only. Another generation of optical ammonia sensors is based on the principle of pH measurement. A solution of a pH indicator is entrapped by means of a gas-permeable membrane e.g. at the end of an optical fibre. Free ammonia, which penetrates the membrane, causes a change in pH in the indicator solution and, consequently, a reversible change in colour or fluorescence of the indicator dye. However, difficulties in sensor handling and manufacture, influences from sample ionic strength, osmolarity and slow response times belong to the main features of this type of gas sensor [7,8,9,10,11]. More selective membranes can be obtained by means of ionophore-based optical sensors for ammonia. The optodes are realized by using a plasticised PVC-membrane as the gas permeable membrane, which incorporates ammonium-ion selective ionophores (e.g. nonactin, valinomycin) and a chromophore which changes its absorption spectrum upon deprotonation. The resulting sensor membranes show a reversible response to ammonium ions, but are limited by the selectivity of the ion carrier. Interferences by other ions (e.g. potassium) are observed. Furthermore, leaching of the dye, ion carrier and plasticizer affect the sensor response characteristics and sensor stability [2,12].

Mills *et al.* [13] have shown that dissolving an indicator dye homogeneously in a polymer can be achieved through the formation of ion pairs, i.e. the pH indicator forms an ion pair e.g. with a lipophilic quarternized ammonium salt. These ion pairs can easily be dissolved in polymers, such as ethylcellulose or PVC, and have been successfully applied to the preparation of optical carbon dioxide sensors [13]. Recently, Werner *et al.* [1] demonstrated the feasibility of an ammonia sensor which is based on a lipophilized indicator dye homogenously dissolved in a silicone polymer layer. The lipophilic ion pair can be obtained from the indicator dye (bromophenol blue) and cetyltrimethyl-ammonium bromide (CTABr) via the following reaction:

$$\text{Indicator} - SO_3^-Na^+ + CTA^+Br^- \;--->\; \underset{\text{lipophilic ion pair}}{\text{Indicator} - SO_3^-CTA^+} + NaBr \quad (1)$$

In contact with gaseous or dissolved ammonia, the membranes change their colour reversibly e.g. from yellow to blue, and ammonia can be detected by measuring the absorbance of the membrane.

$$\underset{\textit{yellow}}{\text{Indicator} - OH + NH_3} <===> \underset{\textit{blue}}{\text{Indicator} - O^- + NH_4^+} \quad (2)$$

This type of ammonia sensor shows features such as easy manufacture, good mechanical and chemical stability, and a high ammonia sensitivity.

In this report, the properties of this new type of sensor material were investigated in more detail for possible application in environmental analysis. Effects resulting from varying membrane composition and membrane thickness, as well as measurement and storage stabilities, typical interferences from amines, varying pH or detergents, which are expected to appear e.g. in sewage water, were examined. Furthermore, the response of the optical sensor was compared with that of a commercially available ammonia electrode for flow-through measurements. The blue base form of bromophenol blue in silicone has an absorption maximum at 608 nm, the yellow acidic form at 426 nm. All measurements were performed with an instrument which was specially designed for absorbance based measurement with sensor foils under continuous flow [14].

EXPERIMENTAL

Preparation of the pH Indicator Ion Pair

Cetyltrimethyl-ammonium salt from bromophenol blue was prepared by dissolving 335.0 mg (0.5 mM) bromophenol blue (Fluka Chemie AG, Buchs, Switzerland; "standard for microscopy") in 35 ml distilled water. Five ml of 0.1 M sodium hydroxide solution were added. This solution was stirred for about 1.5 hours, the insoluble part was filtered by suction. One ml of 0.1 M hydrochloric acid was added and then 181.1 mg (0.5 mM) of cetyltrimethyl-ammonium bromide (Merck, Darmstadt, Germany) dissolved in 30 ml distilled water. The ion pair was stirred for 1 hour and filtered by suction with a G4 frit, washed with 40 ml distilled water and dried in a desiccator over $CaCl_2$.

3',3",5',5"-Tetrabromo-phenol-sulfonaphtalein cetyltrimethyl-ammonium salt: elemental analysis: (calc./found) for $C_{38}H_{51}NSO_5Br_4$: C (47.87/47.05); H (5.39/5.28); N (1.47/1.39). *Yield:* 97%.

Sensor Preparation

Mixtures for the preparation of ammonia-sensitive membranes were made by dissolving different amounts of the lipophilic indicator dye in various amounts of chloroform and mixing the solution with 1 g silicone prepolymer Elastosil E4 (Wacker, Munich, Germany) (Table I). These mixtures were cast on Mylar GA–10 polyester films (thickness 200 µm; Du Pont, Bad Homburg, Germany) with a thickness of 10 or 20 µm. Chloroform was evaporated at room temperature for 15 minutes. Then the membranes were dried in a drying oven at 90°C for 4–7 days (the length of the period depended on the amount of indicator used: the higher the amount of the indicator, the longer took the drying procedure). The actual thickness of the indicator layer after drying was a few µm only. Because of the release of acetic acid by the silicone prepolymer this procedure made sure that the indicator was in its protonated form after sensor preparation. The silicone E4 is chemically and mechanically stable and adheres well on the Mylar foils. The sensor membranes were yellow and transparent without any visible inhomogenities. The silicone layer was applied over one half of the polyester support only, since the second half served as a reference for the measurement (see below!).

TABLE I Mixtures for the preparation of various types of ammonia-sensitive membranes

Sensor type	*Ion pair [mg]*	*$CHCl_3$ [ml]*	*Silicone [g]*
I	4 mg	1.6 ml	1.0 g
II	6.4 mg	1.6 ml	1.0 g
III	8.6 mg	1.6 ml	1.0 g
IV	8.6 mg	3.0 ml	1.0 g
V	12.9 mg	4.0 ml	1.0 g
VI	24.9 mg	4.0 ml	1.0 g

Standard Solutions for Ammonia and Amines

Standard solutions of ammonia were prepared by diluting an aqueous solution of 0.05 M NH_4Cl with 0.1 M phosphate buffer of pH 8.0. Solutions of methyl- and ethyl amine were prepared by diluting 0.05 M standard solutions with 0.1 M phosphate buffer of pH 8.0. A correction of the pK_a of ammonia to compensate temperature changes during the measurement [1] was not taken into consideration. The pK_a value of ammonia is also affected by ionic strength [15]. One way to overcome this problem is to choose the buffer solution in such a concentration that small fluctuations of the ionic strength will be negligable. As a result, the ionic strength is virtually constant. For this reason, all the measurements were performed with 0.1 M phosphate buffer [15].

Instrumentation

For absorbance spectra and measurements over the whole visible range a UV–2101-PC spectrophotometer from Shimadzu (Kyoto, Japan) was used. For testing the response of the sensors, all measurements were performed with the dual-beam meter from Joanneum Research, which has been specially designed for flow through measurements. This optical meter is based on semiconducter devices, a light-emitting diode (LED) as the light source, photodiodes and analogue and digital components. The cell geometry is compact and robust. A yellow LED with an emission maximum at 592 nm was chosen as light source, because its emission band overlaps with the absorption spectrum of the ammonia sensitive membrane. The LED is intensive (1 cd at peak of the spatial radiation) and has a spectral halfwidth of 15 nm. The ammonia-sensitive dye is immobilized only on one half of the support layer. The light from the LED is split into two beams. One of them passes the sensing layer and the second one serves as a reference. Both light beams pass the sample solution. The light intensity of each beam is measured with a photodiode. The ratio of the measured intensities is proportional to the absorption of the sensor and can be related to the ammonia concentration of the sample solution. Associated electronics convert the photo current into a digital representation. The cell design and a block diagram of the electronic system of the Joanneum Research dual beam optical meter are shown in Figure 1.

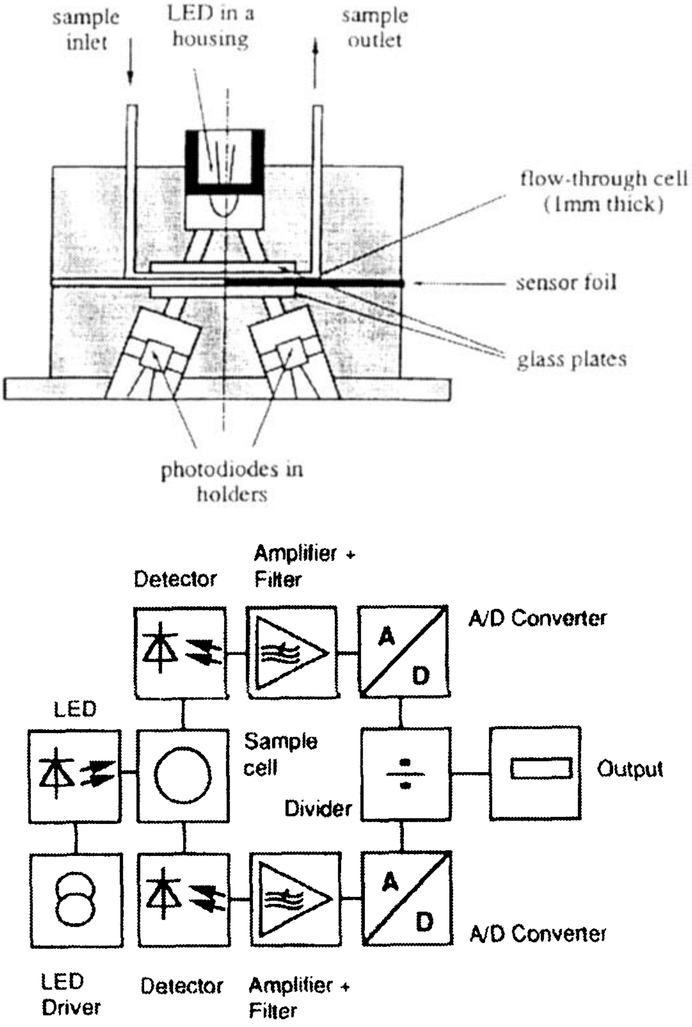

FIGURE 1 a) Design of the flow-through cell and the optical arrangement of the dual-beam optical pH meter, b) block diagram of the electronic system

A micro flow through ammonia electrode (Mikroelectrodes, Inc., Londonderry, NH, USA) was used for reference measurements to obtain a comparison of the optical sensor properties with those of the ammonia electrode.

A Besta motorvalve (Wilhelmsfeld, FRG) with 12 channels was used as autosampler. It was used for liquid samples, containing varying concentrations of ammonia. The sample solutions were pumped to the membrane in the flow-through cell of the instrument with a peristaltic pump Minipuls 3 (Gilson, Villier, France). The sample cell was not thermostatted, but a temperature sensor for measuring the solution temperature was placed inside. All measurements were performed at ambient temperature (25 ± 1°C) and pressure.

RESULTS

Investigations on Membrane Composition and Membrane Thickness

To compare the sensor membranes prepared with varying compositions and membrane thicknesses, measurements were performed in a concentration range of 0 to 160 μM (0 to 2.72 mg/l) ammonia in 0.1 M phosphate buffer of pH 8.0 at a flow rate of 0.1 ml/min. Before measurements, the sensor membranes were conditioned with 0.1 M phosphate buffer of pH 8.0 for 30 minutes, then with a solution of 160 μM ammonia in 0.1 M phosphate buffer of pH 8.0 for 1 hour and finally, with 0.1 M phosphate buffer of pH 8.0 for 1 hour at a flow rate of 0.1 ml/min. The conditioning procedure is important to obtain a stable baseline signal. When the sensor membranes were conditioned only with phosphate buffer of pH 8.0, it took more than one day to reach a stable signal of the baseline.

Three parameters were investigated to describe the membrane properties of the sensors. The relative signal change between 0 and 160 μM ammonia in 0.1 M phosphate of pH 8.0 at time $t = 0$ hours and at $t = 30$ hours, the decrease of the baseline signal in % after 30 hours (as a result of a drift) and the response times (t_{90} and t_{100}) at a change from 41.9 to 82.5 μM (0.7 to 1.4 mg/l) ammonia. The results are summarized in Table II.

The relative signal change of the sensor foils mainly depended on the dye concentration and on the membrane thickness. Relative signal changes of up to 50% could be obtained with high dye loading. No significant correlation could be found between the decrease in baseline signal over time and the membrane composition. However, thicker membranes showed a smaller drift in baseline signal. The response times of the sensor membranes increased with increasing membrane thickness. When choosing a type of membrane for all further investigations with the dual-beam optical meter, a compromise had to be made between relative signal change, response times and the drift in baseline. Sensor type V (Tables I and II) was chosen for this purpose, since it showed fast response times and a good relative signal change, although the drift in baseline intensity was rather high when compared with other sensor membranes.

TABLE II Comparison of relative signal changes, baseline drifts and response times (Table I) (0.1 M phosphate buffer pH 8.0; flow rate: 0.1 ml/min)

Sensor type	*Membrane thickness* [µm]*	*Relative signal change between 0.0 and 160 µM NH_3 [%]*		*Decrease of the baseline signal after 30 h [%]*	*Response times at a change from 41.9 to 82.5 µM NH_3 [min]*	
		t= 0 h	t = 30 h		t_{90}	t_{100}
I	10	9.5	9.35	1.6	15	36
I	20	12.0	11.9	0.4	30	72
II	10	39.7	38.0	4.3	30	60
III	10	50.8	49.4	2.8		>90
IV	10	12.7	11.6	8.8	12	24
V	10	23.8	21.3	10.5	10	29
VI	10	50.0	48.4	3.2	33	65

* Before solvent evaporation and curing of the membrane.

All sensor membranes could be stored dry for more than eight months without any visible changes in colour, polymer or adhesion of the polymer on the Mylar support. However, no quantitative tests were performed to check changes in ammonia sensitivity or relative signal change.

"Conditioning" and Response to Ammonia

Ammonia sensor membranes of type V (Table I) were placed in the flow-through cell and ammonia measurements were performed immediately after conditioning of the sensor. At a flow rate of 2.5 ml/min the conditioning procedure lasted only 40 minutes. The sensor membrane was treated for 10 min with phosphate buffer of pH 8.0, 10 minutes with a solution of 160 µM ammonia in 0.1 M phosphate buffer of pH 8.0 and for 20 minutes with 0.1 M phosphate buffer of pH 8.0.

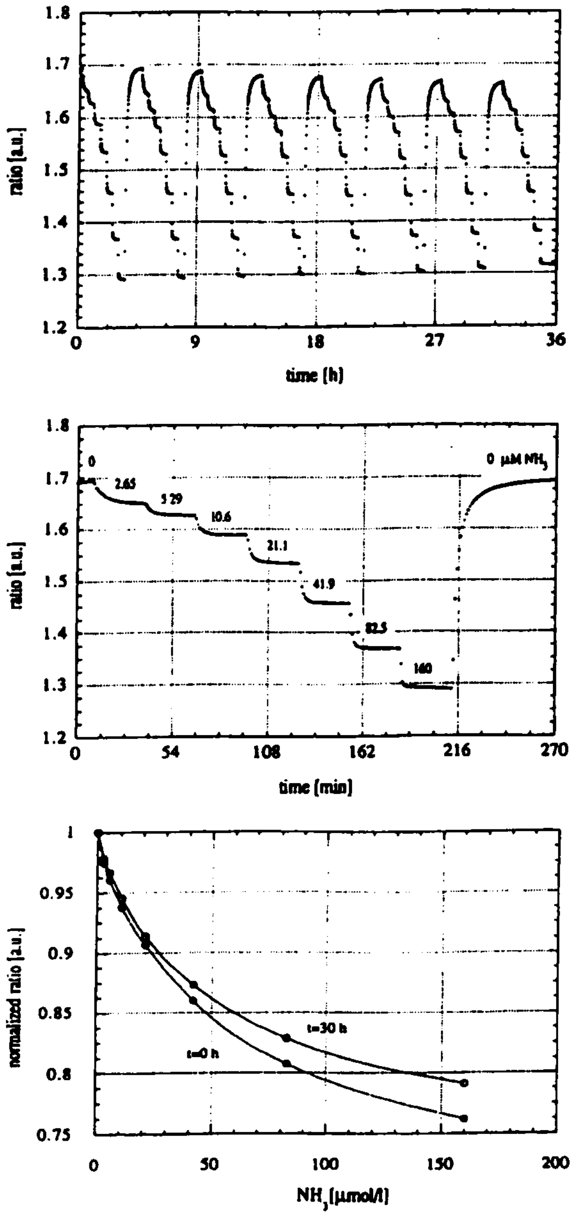

FIGURE 2 Ammonia measurement with a freshly-conditioned ammonia sensor type V (0.1 M phosphate buffer of pH 8.0 with varying ammonia concentration: 0.0, 2.65, 5.29, 10.6, 21.1, 41.9, 82.5, 160 μM; flow rate: 2.5 ml/min) over a period of 3 days: a) whole measurement; b) first measurement cycle; c) comparison of the calibration graphs obtained with the first and last cycle

The typical response of a freshly-conditioned sensor V membrane to solutions of 0 to 160 μM ammonia in 0.1 M phosphate buffer of pH 8.0 over a period of 3 days is shown in Figure 2. A comparison of the calibration graphs obtained from the first (measurement start) and last (30 h after measurement start) measurement cycle is also shown. The sensor showed a continuous decrease in both, baseline signal and ammonia sensitivity.

The response times (t_{90} and t_{100}) depended on the change in ammonia concentration and on the sample flow rate. Table III summarizes the response times (t_{90} and t_{100}) for changes in ammonia concentrations at flow rates of 0.1 and 2.5 ml/min. The response times were significantly (2 to 3 times) faster at the higher flow rate. No further reduction of the response time was observed at flow rates higher than 2.3 ml/min.

Possible Interferences and Cross-sensitivities in Environmental Application

The cross-sensitivity to pH was tested by pumping 0.1 M phosphate buffer solutions of varying pH over the membrane. There was no interference due to pH in the range of pH 5 to 9. This, of course, is of great importance when measuring ammonia in sewage water, where it is likely that pH changes over a wide range occur.

TABLE III Dependence of the response times t_{90} and t_{100} of sensor type V (Table I) on the flow rate and the change in ammonia concentration (0.1 M phosphate buffer of pH 8.0)

Change in concentration from x to y ammonia [μM]	*Response time at a flow rate of 0.1 ml/min*		*Response time at a flow rate of 2.5 ml/min*	
$x \to y$	t_{90} *[min]*	t_{100} *[min]*	t_{90} *[min]*	t_{100} *[min]*
0.0 → 2.65	22	44	10	20
2.65 → 5.29	20	40	9	15
5.29 → 10.6	18	38	7	13
10.6 → 21.1	17	34	6	12
21.1 → 41.9	16	32	5	10
41.9 → 82.5	10	29	4	8
82.5 → 160	6	22	2	6
160 → 0.0	25	120	12	48

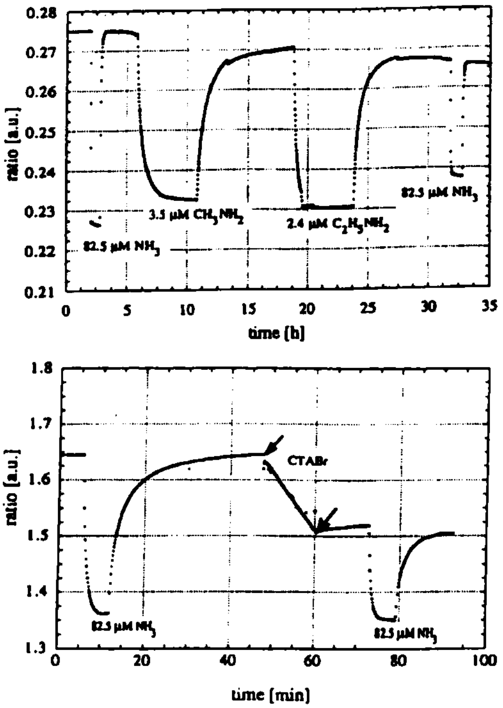

FIGURE 3 Interferences (0.1 M phosphate buffer of pH 8.0; flow rate: 0.1 ml/min): a) methylamine and ethylamine (sensor type V); b) 0.01 M cetyltrimethyl ammonium bromide (sensor type V)

The ammonia-sensitive membranes were affected by amines. The influence of methylamine and ethylamine on the ammonia sensor response was investigated by comparing the response of the ammonia sensor to 1.55 mM solutions of ammonium, methyl ammonium and ethyl ammonium chloride in 0.1 M phosphate buffer of pH 8.0. The actual concentrations of ammonia, methylamine and ethylamine were 82.5, 3.5 and 2.4 μM, respectively. Although the amine concentration was much lower than the ammonia concentration, the change in transmittance measured was almost equally high (Figure 3a). Furthermore, the response to the amines was not completely reversible and the sensitivity to ammonia was decreased after contact of the sensor membrane with amines. The response time for methylamine was more than 4 hours while in presence of ethylamine a stable signal was reached after 2 hours at a flow rate of 0.1 ml/min. It was not possible to regenerate the sensor by treating it with 0.1 M phosphate buffer of pH 8.0 for 1 day or with 10% acetic acid.

The influence on the ammonia sensor of anionic, neutral and cationic detergents was also investigated. For this purpose, 0.01 M solutions of lauryl sulfate, Triton X–100 and cetyltrimethyl-ammonium bromide in 0.1 M phosphate buffer of pH 8.0 were used. To check the influence of the detergents on the ammonia sensitivity before and after treatment of the sensor with the detergents, the response towards 82.5 μM ammonia was checked. No influence was found with lauryl sulfate and Triton X–100. Cetyltrimethyl-ammonium bromide, which is also the counterion of the indicator in the polymer membrane, caused an extraction of the indicator dye from the polymer membrane. Figure 3b shows the irreversible decrease of the relative signal change from 18 to 11%. No influence on the response time before and after the treatment of the sensor with the detergent was observed.

Comparison of the Optical Ammonia Sensor with a Gas-Sensitive Ammonia Electrode

A comparison of a continuous ammonia measurement with the optical ammonia sensor and an ammonia electrode over a period of 15 h is shown in Figure 4. In contrast to the optical ammonia sensor (type V), the electrode showed a linear calibration graph in the range of 2.7 to 160 μM ammonia when plotting the potential difference vs. the negative logarithm of the ammonia concentration. Besides that, the electrode did not show substantial drifts over the measurement time. The average response times of the electrode at a flow rate of 0.5 ml/min were 2 to 5 min for t_{90} and 13 min for t_{100} over the range of 0 to 160 μM ammonia. However, when changing from 160 to 0 μM ammonia t_{90} increased to 13 min and t_{100} to 83 minutes. The response times of the optical sensor were slower at the same flow rate of 0.5 ml/min. Unfortunately, no experiments could be performed at higher flow rates, where the optical sensor is faster (Table III).

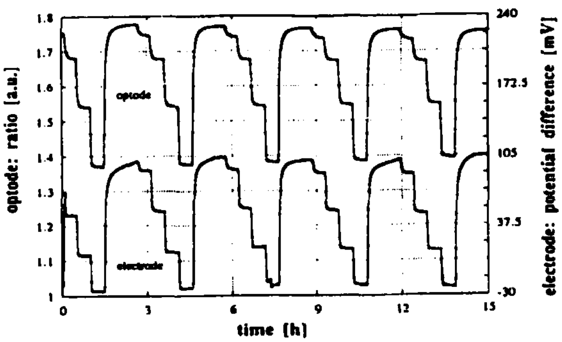

FIGURE 4 Comparison of an ammonia measurement with the optical sensor (type V, freshly inserted membrane) and a gas-sensitive ammonia electrode (0.1 M phosphate buffer of pH 8.0; ammonia concentrations: 0.0, 2.65, 10.6, 41.9, and 160 μM: flow rate: 0.5 ml/min)

No electrode response could be observed with our experimental set-up, when flow rates of higher than 0.6 ml/min were used. Furthermore, no measurements over periods of more than 15 h could be performed with the electrode, which was due to loss in electrolyte solution of the ammonia electrode.

DISCUSSION

The immobilization of a pH-sensitive dye in a silicone polymer matrix resulted in an optical sensor for ammonia, which can be produced simply, at large scale and at low costs. Bromophenol blue was immobilized as an ion pair to achieve a homogeneous distribution of the dye within the polymer. The advantage of immobilization via ion pairs is that the dye does not crystallize [1] and dye leaching is minimized. Silicone was chosen as polymer because of its good permeability for ammonia [16] and its mechanical and chemical stability. Bromophenol blue shows good photostability and longwave absorption, which makes it possible to use a light-emitting diode as the light source. The principles and the feasibility of this type of ammonia sensor were already reported by Werner *et al.* [1]. The aim of this work was to investigate the possibility of application of this ammonia sensor for environmental analysis in combination with a low-cost instrument. For this reason, parameters, such as sensor matrix composition, long-term stability, interferences from amines, pH and various detergents were investigated.

The measurement range was from 0.01 to 17 mg/l (5.9×10^{-7} to 10^{-3} M) ammonia. The operational lifetime of the ammonia sensor, which was "optimized" for our instrumentation, was limited to a period of a few days. A continuous decrease in baseline signal and a decrease in ammonia sensitivity were observed. The first drift may be caused by a slow deprotonation of the dye in the membrane, although there was no visible influence of varying pH on the sensor. This drift could be prevented or reduced, for example, by using sample solution with lower pH (e.g. pH 7.0 instead of pH 8.0). An additional gas-permeable membrane (e.g. Teflon) may also help to resolve the drift problems. As a result of these phenomena, the sensor is not easy to calibrate and it is suitable for measurements over a period of a few days only. The response time of the sensor was found to decrease with increasing flow rate in our experimental set-up, but reached a stable level at approximately 2.3 ml/min (t_{90} ranged from 2 to 10 minutes). For practical purposes, this means that no problems may be expected in flowing waters (e.g. rivers) whereas in e.g. ground water it may be necessary to use an additional (e.g. magnetic) stirrer. Such stirrers are also used in combination with oxygen electrodes for e.g. borehole measurements.

With respect to possible application of the ammonia sensor to environmental analysis, the influence of pH, typical interferences, such as amines and various detergents on the sensor response was investigated. There was no interference due to pH, but the ammonia sensor was affected by amines. It was found that the response was not completely reversible when the ammonia-sensitive membrane got in contact with methyl- or ethylamines and the relative signal change for ammonia decreased. The ammonia sensor was also tested with anionic, neutral and cationic detergents. While the sensor was not affected by anionic and neutral surfactants, there existed an interference due to the cationic detergent cetyltrimethyl-ammonium bromide. It seems that dye was extracted out of the membrane. As a result the relative signal change for ammonia was reduced. This fact, of course, limits the application of the sensor in, e.g. sewage water, where it is likely that cationic detergents and also amines occur in high concentrations.

For practical purposes, free ammonia can only be measured directly with the ammonia sensor at high pH values, where free ammonia is present in the water. Of course, it would also be possible to determine the ammonium content (or total ammonia and ammonium) from e.g. neutral or acidic waters by adjusting the sample pH to an appropriate value. Ammonium is converted into ammonia which in turn can be detected with the sensor. However, this would require a high sample pH (e.g. pH 12) which may affect the sensor membrane and the sensor stability.

A comparison of the ammonia electrode with the ammonia optode showed that the electrode – in contrast to the optical sensor exhibited – a linear calibration graph (in the range of 2.65 to 160 μM ammonia), short response times at low flow rates (t_{90} ranged from 2 to 5 minutes at a flow rate of 0.5 ml/min) and a small drift at constant temperature. However, the electrode seemed to be affected by the sample flow rate itself: when the flow rate exceeded 0.6 ml/min, the ammonia electrode did not show any response anymore with our set-up. The potential remained unchanged even in presence of various concentrations of ammonia. Besides that it was not possible to carry out longterm measurements (e.g. over a period of a few days) with the electrode, because the inner electrolyte solution of the ammonia electrode disappeared after approximately 25 hours for reasons which are unknown at present. The main advantages of the optical ammonia sensor over the ammonia electrode are the following: no electrolyte solution is required, the sensor is insensitive to changes in the sample flow rate, the sensor shows good storage stability, ease of production and low price. The disadvantages of the optical ammonia sensor are its limited operational lifetime (< 1 week) and its relative high response times at low flow rates (t_{90} ranged from 5 to 18 minutes at a flow rate of 0.5 ml/min).

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