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Solid-contact Potentiometric Sensor for the Determination of Total Ammonia Nitrogen in Seawater

Lan Ding[1,2,†], *Jiawang Ding*[2,†], *Baojun Ding*[1,*], *Wei Qin*[2,*]

[1] School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, P.R. China.
[2] Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong 264003, P.R. China.
†The two authors contributed equally to this work
[*]E-mail: dingbj@dlut.edu.cn (B.J. Ding); wqin@yic.ac.cn (W. Qin)

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A solid-contact potentiometric sensor for in situ detection of total ammonia nitrogen (TAN, free ammonia plus the ammonium ion) in seawater is described. In the compact system, an all-solid-state polymeric membrane ammonium-seletive electrode is integrated with a polyvinyl alcohol hydrogel buffer film of pH 7.0 and a gas-permeable membrane. The gaseous NH_3 in seawater diffuses through the gas-permeable membrane and is converted to NH_4^+ in the hydrogel buffer, which can be potentiometrically sensed by the solid-contact ammonium-sensitive membrane electrode. The electrode configuration facilitates the alteration of NH_3 to NH_4^+ in the hydrogel buffer film and improves the sensitivity for the detection of TAN by the buffer trap effect. The gas-permeable membrane effectively eliminates the ion interferences from the seawater sample matrixes. The proposed sensor shows a stable potentiometric response in the concentration range of 10^{-6} - 10^{-4} M with a detection limit of 6.4×10^{-7} M, and has been successfully applied to the detection of TAN in seawater.

Keywords: Ammonia, Hydrogel, Gas permeable membrane, Solid-contact ion-selective electrode, Seawater

1. INTRODUCTION

Total ammonia nitrogen (TAN) refers to unionized ammonia (NH_3) plus the ammonium ion (NH_4^+), which plays an important role in the nitrogen cycle of the natural ecosystems [1-3]. Moreover, TAN is an important criterion for evaluating the contamination of marine ecosystem [4].The determination of TAN in seawater is of great importance for marine environment, fisheries and aquaculture. Unfortunately, the low TAN concentrations, the variable salinities and the matrix complexity of the estuarine and marine waters make TAN monitoring a real challenge [5].

Current methods for TAN analysis include spectrophotometry, fluorometry, and electrochemical detection [6,7]. Spectrophotometric measurements based on the Berthelot reactions are commonly employed for the determination of TAN using phenol, salicylate and 1-naphthol to form an indophenol blue or its derivatives [3,6,8]. The fluorimetric measurements are usually based on the orthophthaldialdehyde-sulfite chemistry [9-11]. In recent years, TAN in estuarine and marine waters has been determined automatically by integration of flow analysis with the optical modes. However, these methods suffer from problems of complex procedures, and interferences from the matrixes [3]. Moreover, these methods are unsuitable for on-site monitoring.

Electrochemical detection techniques offer an effective way for TAN detection [12]. Catalytic cathodic stripping voltammetry using hanging mercury drop electrode was developed for detection of low levels of ammonia in seawater [6]. Carbon nanotube based field effect transistors for the detection of NH_4^+ in artificial seawater was also reported [13]. Indirect electrochemical method based on the reaction of HBrO with NH_4^+ was employed for the determination of NH_4^+ in environmental water samples [14]. However, these methods still need additional reagents and complicated processes, which would restrict their practical applications.

With the demand for in situ monitoring and field analysis, gas-diffusion potentiometric method based on an internal glass membrane pH electrode was employed for the detection of TAN [15-17]. However, this method suffers from problems of from volatile amines, poor sensitivity and difficulty in miniaturization [15,18]. Moreover, current pH-based electrodes are mainly used for the determination of TAN in freshwater [19]. Meyerhoff's group later adopted the polymeric membrane ammonium-selective electrode that possesses attractive features such as simplicity, low cost, and high sensitivity as an internal probe in the design of potentiometric sensors capable of selectively and sensitively sensing ammonia in various samples [15,20-22].

In recent years, potentiometry based on polymeric membrane ion-selective electrodes (ISEs) has gone through a renaissance [12,23]. In particular, solid-contact ISEs with their durability, ease of miniaturization and low maintenance are regarded as the most promising generation of potentiometric ion sensors [24,25]. In addition, solid-contact ISEs are more robust, easy to store and not sensitive to high pressures as compared to the conventional ISEs with an inner filling solution, which makes them suitable for in situ measurements [12,26-28]. However, it is unfortunate that the applications of solid-contact ISEs for determination of TAN in seawater have not been investigated.

Herein, we design an integrated potentiometric sensor based on a solid-contact ammonia-selective electrode and investigate its applicability for determination of TAN in seawater. The use of a solid-contact ammonia-selective electrode offers an effective way for developing a robust miniaturized sensor with a micromolar detection limit. The buffered hydrogel of polyvinyl alcohol (PVA) with good adsorption capacities for both the ammonia gas and NH_4^+ ions is used as an internal electrolyte to convert gaseous NH_3 to NH_4^+ [29-31]. The gas-permeable membrane can effectively eliminate the ion interferences from the seawater sample matrixes. To the best of our knowledge, this is the first attempt to apply the solid-contact potentiometric sensor for detection of TAN in seawater.

2. EXPERIMENTAL

2.1. Regents and materials

Poly(3-octylthiophene) (POT), high molecular weight poly(vinyl chloride) (PVC), the ammonium ionophore (nonactin), Trizma base (Tris), 2-nitrophenyl octyl ether (*o*-NPOE), and 1,3-[bis-tris(hydroxymethyl)-methylamino] propane were obtained from the Sigma-Aldrich. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) was a product of Alfa Aesar. Poly(vinyl alcohol) (PVA) and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals used in this study were of analytical grade. THF was freshly distilled prior to use. Aqueous solutions were prepared with freshly deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system. Hydrophobic gas-permeable membranes were obtained from Dongguan PUW EPTFE Material Co., Ltd. (Dongguan, China), including PUW302W, PUW576 and PUW876 (air-permeabilities: 2900-3400, 1450-1750, and 300-600 ml/cm2/min@7kpa, respectively; thicknesses: 0.01-0.02, 0.11-0.22, and 0.09-0.15 mm, respectively). A continuous flow analyzer obtained from SEAL Analytical (Germany) was used as reference method for comparison. Seawater samples were collected from the Gulf of Bohai, China.

2.2. Electrode preparation

The ammonium ion-sensitive membrane contained 32.8 wt% PVC, 65.9 wt% *o*-NPOE, 0.3 wt% NaTFPB and 1.0 wt% nonactin [32,33]. The membrane cocktail was prepared by dissolving 200 mg of the components in 1.0 mL THF. The POT solution (25 mM) was prepared by dissolving POT in trichloromethane. An amount of 10 µL of the POT solution was drop-cast onto a glassy carbon (GC) electrode and left to dry to form the ion-to-electron transducer layer. Then, 80 µL of the cocktail solution was drop-cast onto the POT layer on the GC electrode. All the membrane electrodes were conditioned in 10^{-3} and 10^{-6} M NH_4Cl for 12h, respectively. The hydrogel mixtures were prepared by dissolving PVA in 1.0 mM pH 7.0 Tris buffer containing 8.3 mM chloride. The polymeric membrane was first covered with a thin layer of the PVA hydrogel and then a gas-permeable membrane. The micrographs of the gas-permeable membranes were characterized by scanning electron microscopy (SEM, JSM-6700F, operating at 5.0 kV).

2.3. EMF measurements

All measurements of the electromotive force (EMF) were performed on a PXSJ-216 pH meter (Leici, Shanghai). The solid-contact ammonium-selective membrane electrode and the Ag/AgCl wire were used as indicator and reference electrodes, respectively. The activities of NH_4^+ were calculated by the Debye-Hückel equation [34]. Experiments were performed in a 30 mL polytetrafluoroethylene beaker with a stir bar. The temperatures in the range of 15-35 °C were controlled using a water bath. When not in use, the potentiometric sensor was placed in 0.01 M Tris buffer of pH 8.0.

2.4. Continuous flow analysis

Continuous flow analysis (CFA) was carried out using a continuous flow analyzer. The experimental temperature was kept at 37°C and the mobile phase flow rate was set at 1.2 mL/min. After the injection column was washed with deionized water for 40 s, 800 μL of the sample solution was auto-injected into the column for the detection of the total ammonia nitrogen. Data acquisition and processing were obtained by the AACE 7.02 software.

3. RESULTS AND DISCUSSION

3.1. Sensor design

Compared to the conventional glass membrane pH electrode used as indicator electrode for potentiometric detection of ammonia, the polymeric membrane ammonium-selective electrode shows the improved response characteristics in terms of selectivity and sensitivity [20-22]. In addition, the use of the solid-contact membrane electrode rather than the conventional electrode configuration using the inner filling solution offers advantages of good durability, ease of miniaturization and convenient maintenance [25,27,35].

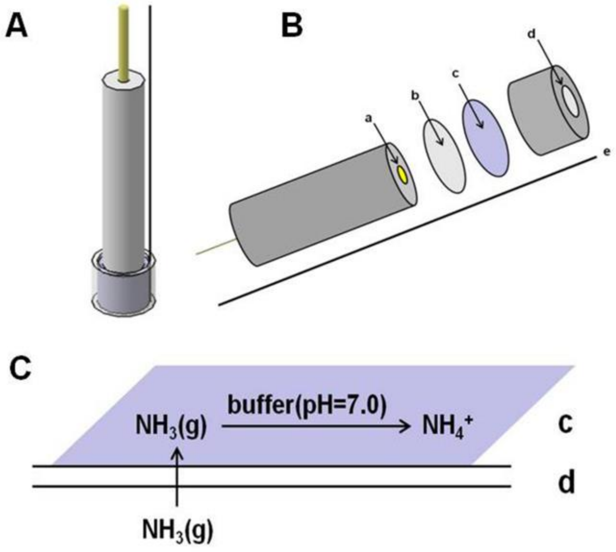

Figure 1. (A) Schematic diagram of the solid-contact potentiometric sensor for TAN. (B) Components of the sensing system. (C) Processes occurring at the sample-membrane interface and in the thin film of PVA hydrogel. In the diagrams of (B) and (C), a, b, c, d and e refer to the hydrophobic conductive polymer POT coated on the GC electrode, ammonium-selective polymeric membrane, buffered PVA hydrogel film of pH 7.0, outer hydrophobic gas-permeable membrane and Ag/AgCl electrode, respectively.

Figure 1 shows the design of the integrated solid-contact potentiometric sensor system (Figure 1A and 1B) and indicates the diffusion and chemical processes that occur at the sample-membrane interface and in the thin film of PVA hydrogel, respectively (Figure 1C). As can be seen, the outer hydrophobic gas-permeable membrane is covered tightly on the PVA hydrogel film, which is coated on the polymeric ISE membrane. An Ag/AgCl wire electrode is inserted into the PVA hydrogel film and used as reference electrode. Gaseous NH_3 in seawater (pH 8.0) diffuses through the gas-permeable membrane into the buffered hydrogel film (pH 7.0) in which the gaseous NH_3 is converted into its ionic form (NH_4^+). The generated NH_4^+ in the hydrogel film can be potentiometrically sensed by the solid contact ammonium-selective polymeric membrane electrode using POT as the ion-to-electron transducer.

3.2. Characteristics of the solid-contact NH_4^+-selective polymeric membrane electrode

In this work, the solid-contact ammonia-selective polymeric membrane electrode is used as the indicator electrode, for which the hydrophobic conducting polymer POT works as ion-to-electron transducer [36]. The stability of the solid-contact ISEs can be greatly improved by the use of POT without influencing membrane selectivity [37-39]. The selectivity of the polymeric membrane electrodes was determined by using Bakker's method [40]. The logarithmic Nikolskii coefficients of NH_4^+ over K^+, Na^+ and Ca^{2+} are -0.90 (±0.01), -2.75 (±0.01) and -5.33 (±0.16), respectively, which agree well with those reported in the earlier literature [41]. Figure 2 shows the time-dependent potentiometric response trace of the all-solid-contact NH_4^+-selective electrode. It can be seen that the dynamic response time is less than 5 s for the NH_4^+ activities tested. The electrode exhibits a Nernstian response over the range of 1×10^{-6} to 1×10^{-3} M with a slope of 59.5 ± 2.9 mV, and the detection limit is 3.2×10^{-7} M.

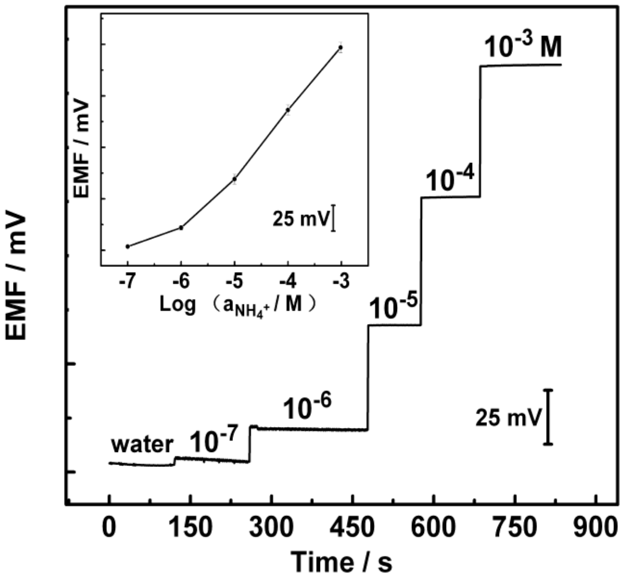

Figure 2. Time-dependent potentiometric response trace of the all-solid-state NH_4^+-ISE for measuring NH_4Cl solutions. Inset shows the calibration curve.

3.3. Optimization of polyvinyl alcohol hydrogel

PVA is a water-soluble polymer with hydrophilic and hydrogen bonding properties. It possesses long term thermal and pH stabilities and an excellent thin film forming capability [42-45]. Moreover, hydrogels based on PVA have been proved to exhibit good adsorption capacities for both the gaseous NH_3 and the ammonium ions [29-31]. However, the PVA hydrogels have not been used in the ammonia gas sensing systems. In this work, the internal buffer solution used for trapping ammonia in the conventional ammonia sensor configuration is replaced by the buffered PVA hydrogel. The PVA hydrogel can load the buffer solution and enhance the stability of the sensor, which makes the sensor fabrication and experimental operation much convenient.

Since the conversion of NH_3 to NH_4^+ occurs in the PVA hydrogel film, the PVA hydrogel was optimized. The influence of the amount of PVA hydrogel dissolved in Tris-HCl (pH 7.0, 10^{-3} M) was examined. Figure 3A shows the potentiometric responses of the electrode with different amounts of the

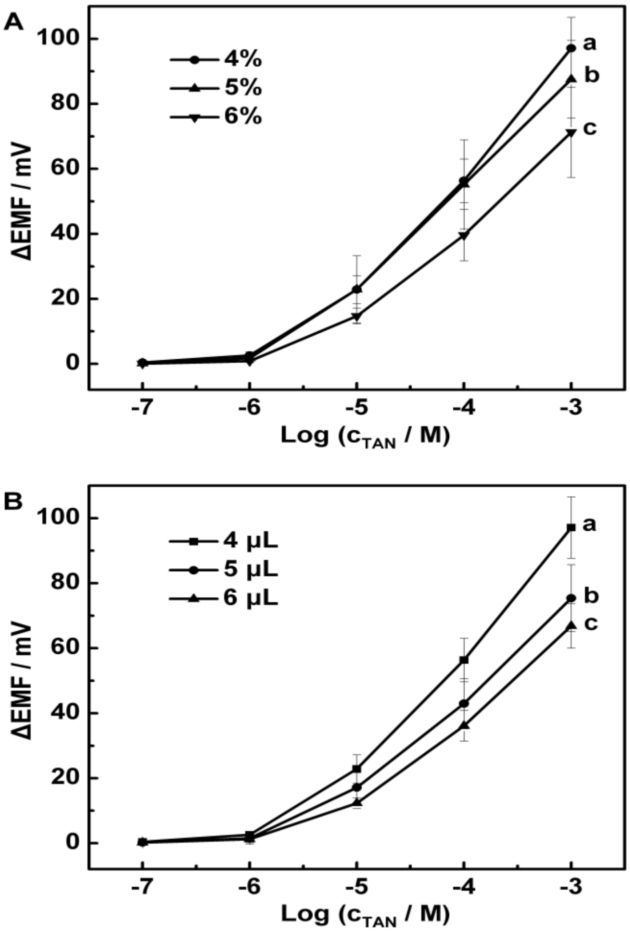

Figure 3. (A) Potentiometric responses to ammonia nitrogen using different concentrations of the polyvinyl alcohol hydrogel: (a) 4, (b) 5, and (c) 6 wt %. (B) Potentiometric responses to ammonia nitrogen using different volumes of the poly(vinyl alcohol) hydrogel: (a) 4, (b) 5, and (c) 6 μL. Unless noted otherwise, the measurements were done in Tris-HCl (pH 8.0, 0.01M) by using 4 μL of 4 % PVA hydrogel (pH 7.0). Each error bar represents the standard deviation of three measurements (n = 3).

PVA hydrogel in the range of 4 - 6 wt %. It can be seen that higher PVA concentrations result in lower potentiometric responses, which is probably due to the lower diffusion rate of gas ammonia in the hydrogel layer. However, when the concentration is less than 4%, the high mobility of the hydrogel could cause the instability in the response of the potentiometric sensor. Therefore, 4 wt % of hydrogel was used for the further experiments.

The volume of the PVA hydrogel was also a key factor for the experiments. Different amounts of the PVA hydrogel have different thickness, which could influence the diffusion rates of NH_3 and NH_4^+ in the hydrogel film. Potentiometric responses of the electrode with 4, 5, 6 μL of the hydrogel (corresponding to the thicknesses of 141, 177 and 212 μm, respectively) were measured and the results are shown in Figure 3B. It can be seen that the potentiometric response increases with decrease in the hydrogel volume. Experiments also showed that the amount of less than 4 μL was not enough to cover the electrode surface completely. Therefore, 4 μL of the PVA hydrogel was selected for the present sensor.

3.4. Effect of temperature

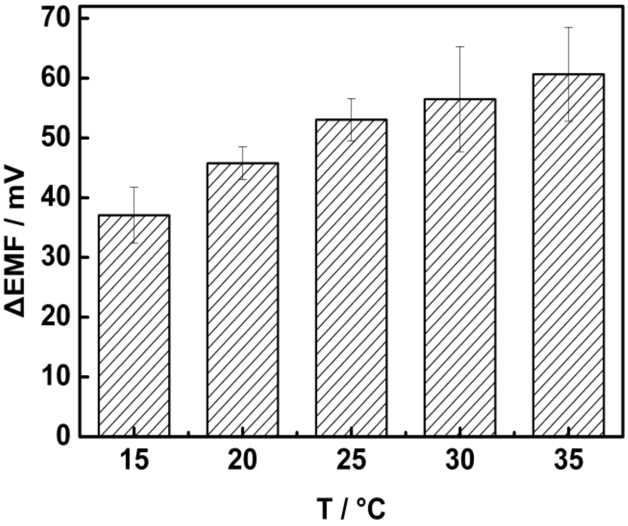

Figure 4. Potentiometric response of the sensor to 10^{-4} M NH_4Cl at different temperatures. Each error bar represents the standard deviation of three measurements (n = 3).

Since the conversion of NH_4^+ to NH_3 can be largely influenced by temperature [46,47], the effect of temperature on the sensor response was tested. The results are shown in Figure 4. It can be seen that the potential response of the present sensor to 10^{-4} M NH_4Cl in Tris buffer of pH 8.0 increases with increase in temperature. Previous studies show that the percent un-ionized ammonia increases with increase in temperature [47]. In addition, according to the Nernst equation, higher temperatures can induce higher potential responses of an ISE [48]. However, experiments also showed that the higher noise levels could be observed at temperatures higher than 25 °C. Therefore, the following experiments were carried out at 25 °C.

3.5. Optimization of the gas-permeable membrane

Since the amount of gaseous species passing through the gas-permeable membrane has a great influence on the response of the sensor, the gas-permeable membrane was optimized in terms of air-permeability and thickness. Three different kinds of hydrophobic polytetrafluroethylene gas-permeable membranes were investigated, including PUW302W, PUW576 and PUW876. Compared to PUW576 and PUW876, PUW302W membrane has the maximum air-permeability (2900-3400, mL/cm^2/min@7kpa) and the thinnest thickness (0.01-0.02 mm). Experiments revealed that the sensor using PUW302W membrane showed more rapid and stable potentiometric response (Figure 5A) than those using PUW576 and PUW876 membranes. It can be seen that the response time is less than 30 s and recovery time is about 10 minutes. Moreover, the SEM image shows that PUW302W is composed of a relatively uniform porous structure (Figure 5B). Therefore, PUW302W membrane was selected for the present work.

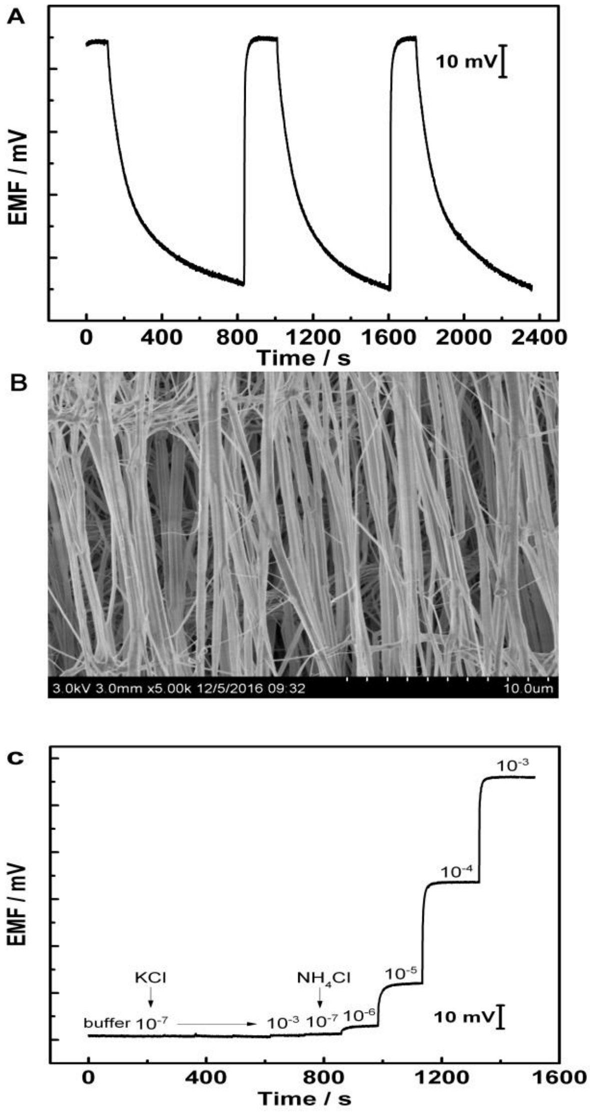

Figure 5. (A) Recycle response profiles for 10^{-3} M NH_4Cl and the blank solutions. (B) SEM image of PUW302W. (C) Potentiometric response of the sensor in Tris-HCl buffer.

The hydrophobic gas-permeable membrane can effectively eliminate the ion interferences from the sample matrixes. As shown in Figure 5C, there is negligible potentiometric response when 10^{-3} M KCl is added into the buffer solution, while an obvious potentiometric response can be observed when 10^{-6} M NH_4Cl is added. These results confirm that only gaseous species can pass through the hydrophobic gas-permeable membrane while ionic species can be effectively excluded by the gas-permeable membrane.

3.6. Effect of salinity

Since there is a high salinity background in seawater, the effect of salinity on the response of the proposed potentiometric sensor was investigated. The potential responses to 10^{-4} M NH_4Cl in 0.01 M Tris buffer of pH 8.0 with different concentrations of NaCl were tested. As shown in Figure 6, the response decreases with increase in the concentration of NaCl. Such inhibition effect of salinity is probably due to the fact that salinity can decrease the percent of unionized ammonia [47] and may also influence the diffusion coefficient of ammonia in the sample solution.

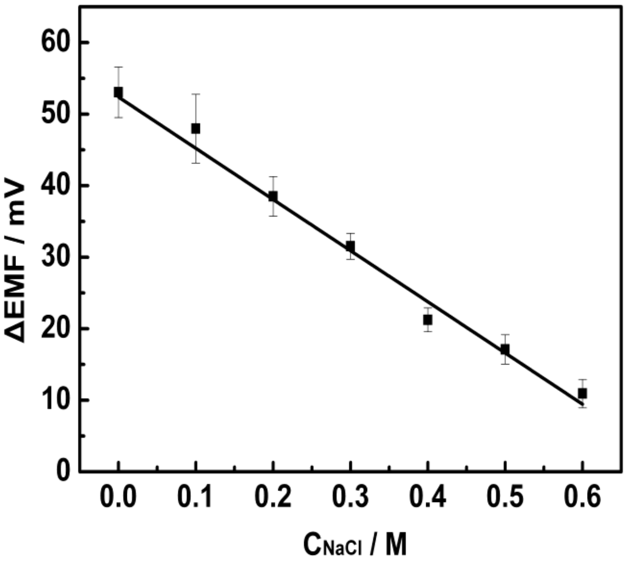

Figure 6. Potentiometric responses of the solid-contact potentiometric sensor to 10^{-4} M NH_4Cl in 0.01 M Tris buffer of pH 8.0 in the presence of NaCl at different concentrations. Each error bar represents one standard deviation of three measurements.

3.7. Precision of the sensor

The precision of the potentiometric sensor was evaluated by determining the inter- and intra-assay variations of 0.1 mM NH_4Cl in 0.01 M Tris buffer of pH 8.0. The coefficient of variation of the inter-assay was calculated to be 5.4% by determining the responses at five different electrodes. The intra-assay precision was estimated by assaying one sensor for five replicate determinations, and the RSD was 4.9%. These results indicate that the solid-contact potentiometric sensor shows an acceptable fabrication reproducibility.

3.8. Practical applications

The proposed solid-contact potentiometric sensor was applied for the detection of TAN in the seawater background (0.5 M NaCl, pH 8.0). As shown in Figure 7, the sensor shows a stable potentiometric response to TAN over the concentration range of 10^{-6} - 10^{-4} M, and the detection limit is 6.4×10^{-7} M. The comparison of the present sensor with other methods used for the detection of the ammonia nitrogen is listed in Table 1. It should be noted that the proposed solid-contact potentiometric sensor does not need any additional reagent or enrichment procedure in the measurements. It provides a simple and rapid way for the *in-situ* detection of ammonia nitrogen in seawater.

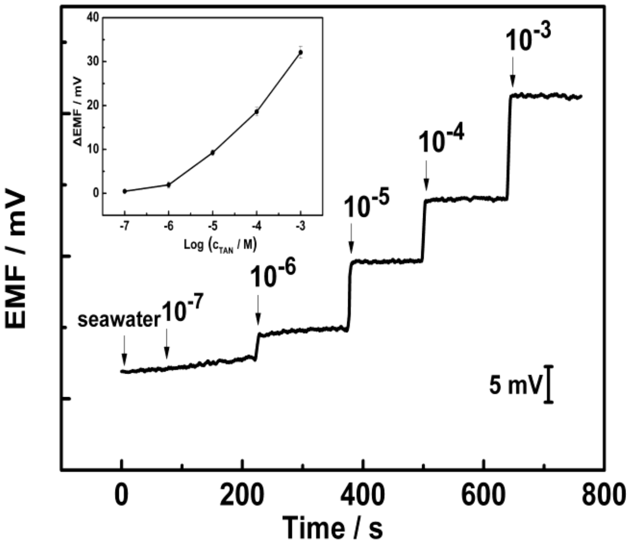

Figure 7. Potentiometric response of the solid-contact potentiometric sensor to TAN in the seawater background (0.5 M NaCl, pH 8.0). The inset shows the calibration curve.

Table 1. Comparison of the proposed sensor with the other methods

Detection method	Linearity (nM)	Detection limit (nM)	Analysis time (min)	Reference
Colorimetry with solid phase extraction	0 - 428	3.5	>10	49
Fluorometry	0 - 600	1.1	>15	50
Cathodic stripping voltammetry	10 - 3000	4.0	>20	6
Cyclic and square-wave voltammetry	10^5 - 10^6	1.7×10^5	-	51
Ammonia gas-sensing electrode	2×10^2 - 10^4	2.0×10^2	2	52
Potentiometric sensor	10^3 - 10^5	6.4×10^2	0.5	This work

In order to evaluate the feasibility of the proposed method, the detection of TAN was carried out by direct potentiometry using the standard addition method. Table 2 shows the detection of TAN in seawater at 25°C. It can be seen that concentrations of TAN as determined by the proposed solid-contact potentiometric sensor are in good agreement with those obtained by the CFA method. These results indicate that the solid-contact potentiometric sensor is promising for application in the rapid on site detection of TAN in seawater.

Table 2. Determination of TAN in seawater

Samples	Proposed sensor (μM) [a]	CFA (μM) [a]
1	1.2 ± 0.1	2.7 ± 0.1
2	4.3 ± 0.1	3.8 ± 0.3
3	6.3 ± 0.7	5.7 ± 0.1
4	19.6 ± 1.6	19.0 ± 0.1

a. Average of three measurements ± standard deviation (n = 3).

4. CONCLUSIONS

In summary, a solid-contact potentiometric sensor for the detection of total ammonia nitrogen in seawater has been designed. Compared with these common methods based on spectrophotometry and fluorometry, the solid-contact potentiometric ion sensor eliminates the interferences from the matrix such as sample turbidity and volatile amines. In addition, the combination of both the PVA hydrogels and gas-permeable membranes greatly improves the performance of the sensor and provides a new method for rapid detection of TAN in seawater. Further studies on the optimizing the air-permeable membrane and further applications for in situ real-time monitoring of TAN in seawater are in progress in our laboratory.

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References

1 R. K. Larsen, J. C. Steinbacher and J. E. Baker, *Environ. Sci. Technol.*, 35 (2001) 4731.
2 L. Zhou and C. E. Boyd, *Aquaculture*, 450 (2016) 187.
3 Y. Zhu, D. X. Yuan, Y. M. Huang, J. Ma, S. C. Feng and K. N. Lin, *Mar. Chem.*, 162 (2014) 114
4 B. Han, L. Zheng, X. R. Wang and J. T. Wang, *Instrum. Sci. Technol.*, 43 (2015) 626.
5 K. Y. Chumbimuni-Torres, P. Calvo-Marzal, J. Wang and E. Bakker, *Anal. Chem.*, 80 (2008) 6114.
6 A. M. Harbin and C. M. G. Van Den Berg, *Anal. Chem.*, 65 (1993) 3411.
7 S. P. Basak, B. Kanjilal, P. Sarkar and A. P. F. Turner, *Synth. Met.*, 175 (2013) 127.

8 T. Shoji and E. Nakamura, *J. Flow Injection Anal.*, 26 (2009) 37.
9 S. H. Xue, K. Uchiyama and H. F. Li, *J. Environ. Sci.*, 24 (2012) 564.
10 R. J. Watson, E. C. V Butler, L. A. Clementson and K. M. Berry, *J. Environ. Monit.*, 7 (2005) 37.
11 Y. Zhu, D. X. Yuan, H. Y. Lin and T. J. Zhou, *Anal. Lett.*, 49 (2016) 665.
12 J. Bobacka, A. Ivaska and A. Lewenstam, *Chem. Rev.*, 108 (2008) 329.
13 C. W. Jang, Y. T. Byun and Y. M. Jhon, *J. Nanosci. Nanotechnol.*, 12 (2012) 1765.
14 M. Takahashi, K. Nakamura and J. Jin, *Electroanalysis.*, 20 (2008) 2205.
15 Y. M. Fraticelli and M. E. Meyerhoff, *Anal. Chem.*, 53 (1981) 1857.
16 M. J. Beckett and A. L. Wilson, *Water Res.*, 8 (1974) 333.
17 G. K. Buckee, *J. Inst. Brew.*, 80 (1974) 291.
18 H. L. Lee and M. E. Meyerhoff, *Analyst*, 110 (1985) 371.
19 T. R. Gilbert and A. M. Clay, *Anal. Chem.*, 45 (1973) 1757.
20 M. E. Meyerhoff and R. H. Robins, *Anal. Chem.*, 52 (1980) 2383.
21 M. E. Meyerhoff, *Anal. Chem.*, 52 (1980) 1532.
22 M. E. Meyerhoff, Y. M. Fraticelli, J. A. Greenberg, J. Rosen, S. J. Parks and W. N. Opdycke, *Clin. Chem.*, 28 (1982) 1973.
23 E. Bakker and E. Pretsch, *Angew. Chem. Int. Ed.*, 46 (2007) 5660.
24 T. J. Yin and W. Qin, *TrAC- Trends Anal. Chem.*, 51 (2013) 79.
25 J. B. Hu, A. Stein and P. Bühlmann, *TrAC-Trends Anal. Chem.*, 76 (2016) 102.
26 R. Athavale, I. Kokorite, C. Dinkel, E. Bakker, B. Wehrli, G. A. Crespo and A. Brand, *Anal. Chem.*, 87 (2015) 11990.
27 E. Lindner and R. E. Gyurcsányi, *J. Solid State Electrochem.*, 13 (2009) 51.
28 A. Düzgün, G. A. Zelada-Guillén, G. A. Crespo, S. MacHo, J. Riu and F. X. Rius, *Anal. Bioanal. Chem.*, 399 (2011) 171.
29 S. Patachia, C. Croitoru, C. Florea, L. Dumitrescu and I. Scarneciu, *Annals of DAAAM & Proceedings*, (2008) 1039.
30 Y. Zheng, Y. Liu and A. Wang, *Chem. Eng. J.*, 171 (2011) 1201.
31 Y. Su, J. Liu, Q. Yue, Q. Li and B. Gao, *Environ. Technol.*, 35 (2014) 446.
32 W. Qin, T. Zwickl and E. Pretsch, *Anal. Chem.*, 72 (2000) 3236.
33 Q. Y. Zhang, J. W. Ding, L. J. Kou and W. Qin, *Sensors*, 13 (2013) 6936.
34 S. Kamata, A. Bhale, Y. Fukunaga and H. Murata, *Anal. Chem.*, 60 (1988) 2464.
35 T. J. Yin, D. W. Pan and W. Qin, *Anal. Chem.*, 86 (2014) 11038.
36 W. J. Song, X. W. Wang, J. W. Ding, J. Zhang, R. M. Zhang and W. Qin, *Chinese J. Anal. Chem.*, 40 (2012) 670.
37 J. Sutter, A. Radu, S. Peper, E. Bakker and E. Pretsch, *Anal. Chim. Acta.*, 523 (2004) 53.
38 K. Y. Chumbimuni-Torres, N. Rubinova, A. Radu, L. T. Kubota and E. Bakker, *Anal. Chem.*, 78 (2006) 1318.
39 J. P. Veder, R. De Marco, K. Patel, P. Si, E. Grygolowicz-pawlak, M. James, M. T. Alam, M. Sohail, J. Lee, E. Pretsch and E. Bakker, *Anal. Chem.*, 85 (2013) 10495.
40 E. Bakker, *J. Electrochem. Soc.*, 143 (1996) L83.
41 S. C. Ma, N. A. Chaniotakis and M. E. Meyerhoff, *Anal. Chem.*, 60 (1988) 2293.
42 O. M. Păduraru, C. Vasile, C. N. Cascaval and A. Stoleriu, *J. Optoelectron. Adv. Mater.*, 9 (2007) 1019.
43 O. M. Păduraru, D. Ciolacu, R. N. Darie and C. Vasile, *Mater. Sci. Eng. C*, 32 (2012) 2508.
44 S. Chakravarty, P. Dutta, S. Kalita and N. Sen Sarma, *Sens. Actuators B: Chem.*, 232 (2016) 243.
45 D. M. Sabara, J. S. Dunne, A. Q. H. Pedro, J. Trifunovic, I. L. O. Balogun, O. Kotlicic, A. Serrano and I. Kertesz, *Biotechnol. Food Sci.*, 75 (2011) 39.
46 R. P. Trussell, *J. Fish. Res. Bd. Can.*, 29 (1972) 1505.

47 K. Emerson, R. C. Russo, R. E. Lund and R. V. Thurston, *J. Fish. Res. Bd. Can.*, 32 (1975) 2379.
48 E. Bakker, P. Buehlmann and E. Pretsch, *Chem. Rev.*, 97 (1997) 3083.
49 G. H. Chen, M. Zhang, Z. Zhang, Y. M. Huang and D.X. Yuan, *Anal. Lett.*, 44 (2011) 310.
50 N. Amornthammarong and J. Z. Zhang, *Anal. Chem.*, 80 (2008) 1019.
51 R. C. Bianchi, E. R. Da Silva, L. H. Dall'Antonia, F. F. Ferreira and W.A. Alves, *Langmuir.*, 30 (2014) 11464.
52 C. Garside, G. Hull and S. Murray, *Limnol. Oceanogr.*, 23 (1978) 1073.