

Ammonium Ion Sensor Based on SiO₂/ZrO₂/phosphate-NH₄⁺ Composite for Quantification of Ammonium Ions in Natural Waters

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Um eletrodo íon seletivo foi construído e avaliado para determinação de íons amônio em águas naturais. O eletrodo consiste de uma pasta de carbono com o compósito SiO₂/ZrO₂/fosfato-NH₄⁺ obtido pelo processo de sol-gel. O eletrodo exibe uma resposta sub-Nernstiana para concentrações entre 7,7×10⁻⁷ e 4,0×10⁻² mol L⁻¹ e um limite de detecção de 1,58×10⁻⁷ mol L⁻¹ (8,5×10⁻³ ppm). A resposta do eletrodo foi rápida (1 minuto). Os coeficientes de seletividade K^{pot}_{A,B} para os diversos íons geralmente presentes em águas naturais foram determinados pela aplicação do *matched potential method*. O método potenciométrico com o eletrodo íon seletivo foi validado pelo método de Berthelot (método padrão) pela determinação de íons amônio em águas naturais. O eletrodo íon seletivo provou ser satisfatório para o controle de qualidade de águas naturais.

Ion selective-electrode was constructed and evaluated for determination of ammonium ions in natural waters. The electrode consists of paste carbon with the composite SiO₂/ZrO₂/phosphate-NH₄⁺ obtained through sol-gel process. The electrode exhibits a sub-Nernstian response for ammonium concentrations between 7.7×10⁻⁷ and 4.0×10⁻² mol L⁻¹ and a detection limit of 1.58×10⁻⁷ mol L⁻¹ (8.5×10⁻³ ppm). The electrode response for ammonium was fast (1 minute). The selectivity coefficients K^{pot}_{A,B} for several ions usually present in natural waters were determined applying the matched potential method. The potentiometric method with the ion selective electrode was validated by the Berthelot method (standard method), through the determination of ammonium ions in natural waters. The ion selective-electrode proved suitable for routine quality control of natural waters by potentiometry.

Keywords: ammonium ion sensor, potentiometric sensor, natural waters

Introduction

The presence of ammonium ions in rivers and lakes can be associated in most cases to pollution caused by livestock, intensive agriculture and mainly, nowadays, to liberation of domestic sewage in courses of superficial waters in an indiscriminate way and in larger and larger amounts.

Ammonium ion sensor is a useful tool in environmental pollution control,¹ food and clinical analysis²⁻⁴ and other industrial applications.⁵ Among the ion sensors, ammonium sensor is also used more frequently as potentiometric biosensor in which enzymes or microbial cells are immobilized on the surface of the sensor.^{6,7} Due to the many applications of the ammonium ion sensors,

design of solid-state sensor for ammonium and its fabrication through simple procedure are desirable.⁸

Inorganic ion exchangers are characterized by high thermal stability and resistivity towards strong oxidizing agents and mineral acids. Recently the SiO₂/ZrO₂/phosphate composite was prepared by the sol-gel process,⁹ which allies the good properties of ionic exchange of the zirconium(IV) phosphate^{10,11} in a matrix of mixed oxide, SiO₂/ZrO₂ high and homogeneously dispersed. This composite presents high superficial area, phosphate groups on the surface of the same species and determined as H₂PO₄⁻, a high thermal stability, a high proton exchange capacity and a great affinity for ammonia gas with the formation of NH₄⁺ ions on the solid's surface.⁹

In the present study, we used the SiO₂/ZrO₂/phosphate ion exchanger as a sensing material for the construction

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of a novel solid state ammonium ion sensor. This sensor offers the advantages of thermal stability, simplicity, sensitivity, reliability, low cost, fast response time and long life.

Experimental

Preparation of the SiO₂/ZrO₂/phosphate, SZP

The SiO₂/ZrO₂/phosphate composite was prepared by the sol-gel method according to the following procedure: 15.5 mL of 3.0 mol L⁻¹ HCl solution were added to 250 mL of TEOS-ethanol solution in 1:1 (v/v) proportion (solution A), and the mixture was refluxed for 2.5 h. About 80 mL of 1.77 mol L⁻¹ zirconium(IV) butoxide-ethanol solution were slowly added to solution A, and the mixture was stirred for 3 h at room temperature. Finally, a solution containing a mixture of 75 mL of ethanol and 7.8 mL of 3.0 mol L⁻¹ HCl solution was added, and the resulting mixture was stirred for two hours at room temperature. The temperature of reaction flask was raised to 333 K to promote the complete gelation of the mixture. The solvent was evaporated by heating the resulting xerogel at 383 K for 24 h, and the solid was ground and sieved in order to obtain particles of a size between 0.15 and 0.25 mm. In 50 mL of 0.4 mol L⁻¹ phosphoric acid solution 4 g xerogel was dispersed. The mixture was shaken for 24 h, and the solid was filtered, washed, and dried at 353 K. The resulting solid was designated as SiO₂/ZrO₂/phosphate composite, SZP.

Preparation of the SiO₂/ZrO₂/phosphate-NH₄⁺

About 500 mg of SZP was dispersed in 0.50 mol L⁻¹ NH₄Cl solution and left for 3 h in room temperature. The solid was filtered, washed with water and let dry in room temperature, obtaining the SiO₂/ZrO₂/phosphate-NH₄⁺, SZPA.

Chemical analyses

The SiO₂/ZrO₂/phosphate-NH₄⁺ was treated with 40 wt. % HF solution until complete dissolution of the sample. The resulting solution was diluted with 100 mL of water, and concentrated NH₄OH was added until the hydrous zirconium oxide precipitated. The precipitate was allowed to stand for 3 h, filtered and washed with water. The solid phase was heated at 1073 K for 8 h and weighed as ZrO₂. The solution phase was acidified with sulfuric acid, and the volume was adjusted. The quantity of phosphorus was determined spectrophotometrically using the molybdenum blue method.

Specific surface area and average pore volume

The specific surface area, S_{BET} , was determined by the BET multipoint technique on a Micromeritics Flowsorb II 2300 connected to a flow controller. The average pore volumes, V_p , were determined by the mercury intrusion technique on a Micromeritics Pore Size 9320 equipment.

Scanning Electron Microscopy

The scanning electron microscopy (SEM) images of the samples were obtained by dispersing the powders on a double face conducting tape fixed on a brass support. The sample was coated with graphite by using the sputtering technique on a LVC 76 of Plasma Science Inc. equipment. The microscope used was a JEOL JSM T-300 connected to a secondary electron detector and an X-ray dispersive energy analyzer from Northern.

High power decoupling-magic angle spinning ³¹P NMR

The high power decoupling magic angle spinning (HPDEC-MAS) NMR spectra of the solids were obtained at room temperature on a Bruker AC300P spectrometer operating at 121 MHz. The conditions used were a sequential pulse with contact time of 5 ms and intervals between the pulses of 30 s. Phosphoric acid (85 wt.%) was used as reference.

Potentiometric measurements

All reagents used were of analytical grade. The water used was Milli-Q_{plus} quality with resistivity higher than 18 MΩ cm⁻¹.

The carbon paste electrode was prepared by intimately mixing 50 mg of graphite powder with 50 mg of SiO₂/ZrO₂/phosphate-NH₄⁺, SZPA, and a drop of mineral oil. This paste was then put into a cavity consisting of a platinum disk sealed into the extremity of a glass tube. The cavity's depth was 1 mm and it is important to reproduce the quality of the paste and the platinum disk to provide a good electrical contact.

The interference on the electrode response for most common components found in natural waters was evaluated by determining the potentiometric selectivity coefficient $K_{A,B}^{\text{pot}}$ of the membrane using the matched potential method which is independent of the Nicolsky-Eisenman equation and is recommended by IUPAC.¹²⁻¹⁴

The ammonium chloride stock solution was prepared by dissolving 2.6740 g of the salt in 500 mL water at pH 6.6 (KH₂PO₄/KOH buffer). Working solutions were freshly

prepared by appropriate dilution of the stock solution with water at pH 6.6.

For the evaluation of interferents normally found along with ammonium in natural waters (Fe^{3+} , Mg^{2+} , Mn^{2+} , Ca^{2+} , Na^+ , Li^+ and K^+), were prepared solutions of interferents and ammonium chloride at concentrations in the range of 9.0×10^{-2} to 9.0×10^{-3} mol L^{-1} in water at pH 6.6.

In the study on the effects of $[\text{H}^+]$ on the electrode response the solution pH was adjusted by adding H_2SO_4 or KOH .

The potentiometric measurements were carried out on a Hanna Instruments HI 9321 microprocessor pHmeter (sensitivity of 0.1 mV), using a reference saturated calomel electrode (SCE) with a saturated KNO_3 salt bridge. All measurements were made in a thermostated cell at 298 ± 1 K.

Natural waters samples

Samples of natural waters were collected in points of the river Tibagi next to water treatment station and in the lakes Igapó I, II and III of the Londrina city in Brazil.

All samples were filtered in quantitative filters and buffered to pH = 6.6. The determinations of the quantity of ammonium ions in the samples were accomplished immediately after the collection by the standard method (Berthelot)¹⁵ and for the potentiometric method. When necessary, dilutions of the samples were accomplished with water buffered at pH = 6.6.

Results and Discussion

$\text{SiO}_2/\text{ZrO}_2/\text{phosphate-NH}_4^+$, SZPA, with the following characteristics were obtained: Zr = 32.4 wt.%, P = 4.5 wt.%, NH_4^+ = 5.2 wt.%, specific surface area $S_{\text{BET}} = 432$ $\text{m}^2 \text{g}^{-1}$ and average pore volume of 0.29 mL g^{-1} .

Figure 1a shows the SEM image of a SZPA particle, and Figure 1b shows the corresponding EDS image. The white points in Figure 1b are emission lines of ZrK_α at 2.05 keV.¹⁶ Within the magnification used ($\times 1000$), it is very clear that the oxide particles are highly dispersed and no evidence of metal oxide island formation is detected.

Important information for the phosphate structures is given by the ^{31}P NMR spectra for SZP as show in Figure 2. The main peak at -22.1 ppm is assigned to the H_2PO_4^- species and the other two with weak intensities at -13.7 and -27.8 ppm to the same species in different environments.¹⁷

The potential E generated at the electrode surface is the result of the summation of the potentials¹⁸

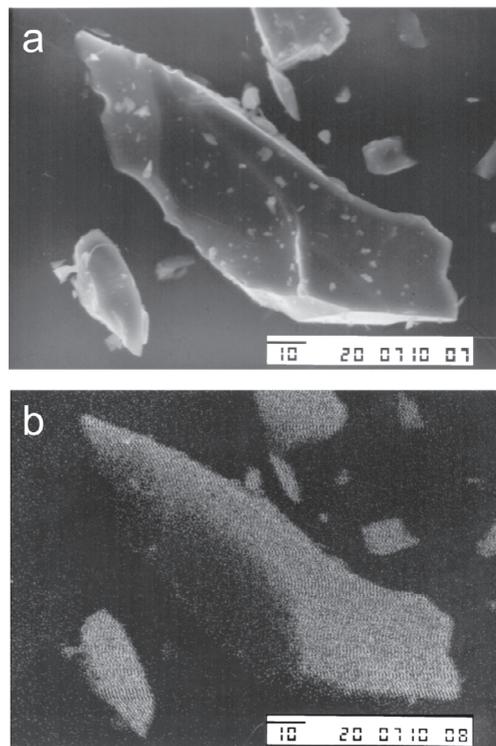


Figure 1. (a) Scanning electron microscopy image of SZP and (b) the corresponding energy-dispersive scanning (EDS) Zr and P mapping images.

$$E = E_m + \Sigma E_j + \Delta E, \quad (1)$$

where E_m is the potential due to the matrix resistance, ΣE_j is the summation of the liquid junction potentials, and ΔE is the potential difference between the internal and external membrane. In the present case E_m and ΣE_j are constant during the measurements, so the above equation is reduced to,

$$E = E' + \Delta E, \quad (2)$$

where $E' = E_m + \Sigma E_j$.

For the development of the potentiometric method using ion-selective electrode SZPA some analytical parameters, such as stability of the electrode membrane, response time, life time, dependence of the potential as a function of the ammonium concentration and pH of the medium were studied. The selectivity and the detection limit of the electrode were evaluated.

The effect of the hydrogen ion concentration, in the pH range of 1.0 to 10.0, on the electrode response for ammonium concentrations of 1.0×10^{-3} , 1.0×10^{-4} and 1.0×10^{-5} was also evaluated. The results obtained are shown in Figure 3. In every case, the potential was constant in the pH range from 6.0 to 7.0. Below pH 3.0 a constant

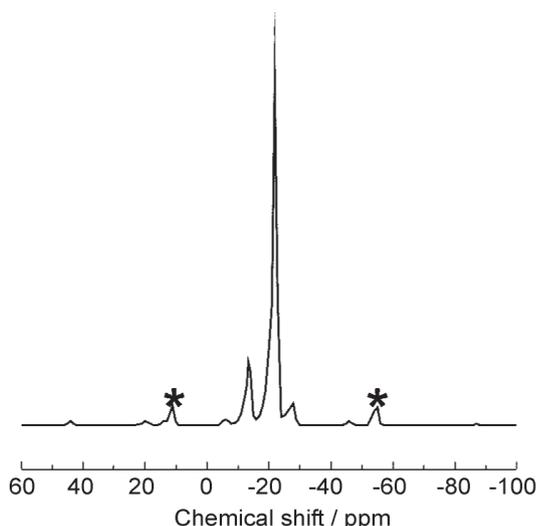


Figure 2. HPDEC MAS ³¹P NMR spectrum of SZP. Peaks marked (*) indicates the spinning sidebands.

potential was observed, which could be explained by total proton exchange of the phosphate groups of SZP composite. For solutions with pH in range from 3.0 to 6.0 a decrease of the potential was observed. In acid solutions the proton ions compete with the adsorbed NH₄⁺ ions by an ion exchange reaction and the latter can be leached off from the surface and released to the solution phase. For solutions with pH over 7.0, a decrease of the potential was also observed. In alkaline solutions the hydroxyl anion reacts with the acid proton of the group phosphate present in the surface of the composite SZPA. The proton exchange of SZP for ammonium ions in aqueous solution happens in a fast way. However, due to the pH 6.2 of the solution 5.0×10⁻¹ mol L⁻¹ NH₄Cl, the total exchange of the acid protons by ammonium ions is not expected, but it is expected that this happens in a partial way, as it can be observed in the Figure 4. Between pH 6.0 and 7.0, the potentiometric measurements can be done with buffering the solutions. In samples the pH correction is necessary.

The electrode response time, for ammonium solutions in concentrations range of 7.7×10⁻⁷ to 4.0×10⁻² mol L⁻¹ was of about one minute. No potential changes were obtained after 10-14 hours of continuous sampling of an ammonium solution. Also, no memory effect was observed for ten determinations of ammonium solutions alternating the concentrations between 1.0×10⁻⁶ and 1.0×10⁻² mol L⁻¹. The electrode showed a life-time of six months with 1000 determinations for each sensor membrane, with a decrease in potential of only 10% in relation to the initial response. The analytical curve (Figure 5) shows a linear relationship between the electrode potential and the logarithmic concentration of ammonium in the range of 7.7×10⁻⁷ and 4.0×10⁻² mol L⁻¹ with a sub-Nernstian response of 31.3 mV

decade⁻¹ and a correlation coefficient of 0.9999. The detection limit was calculated as 1.58×10⁻⁷ mol L⁻¹ (8.5×10⁻³ ppm), which is a detection limit value smaller in comparison with other potentiometric sensors reported.¹⁹⁻²¹

The interference of ions which are normally found in natural waters such as Fe³⁺, Mg²⁺, Mn²⁺, Ca²⁺, Na⁺, Li⁺ and K⁺, which could interfere on the electrode response, was verified by determining the K_{A,B}^{pot} of the membrane

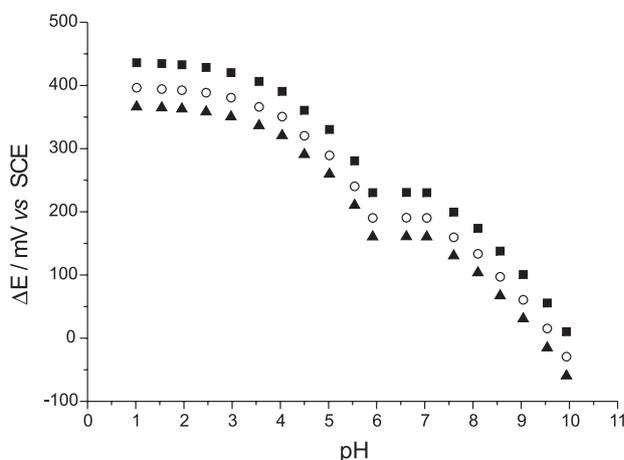


Figure 3. Effect of the solution pH on the response of the SZPA ion selective electrode. Ammonium concentrations: (■) 1.0×10⁻³ mol L⁻¹, (○) 1.0×10⁻⁴ mol L⁻¹ and (▲) 1.0×10⁻⁵ mol L⁻¹.

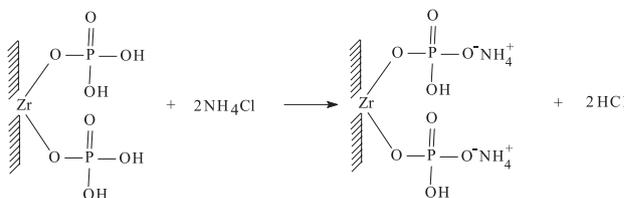


Figure 4. Schematic representation of the SZPA surface in the solution pH 6.6.

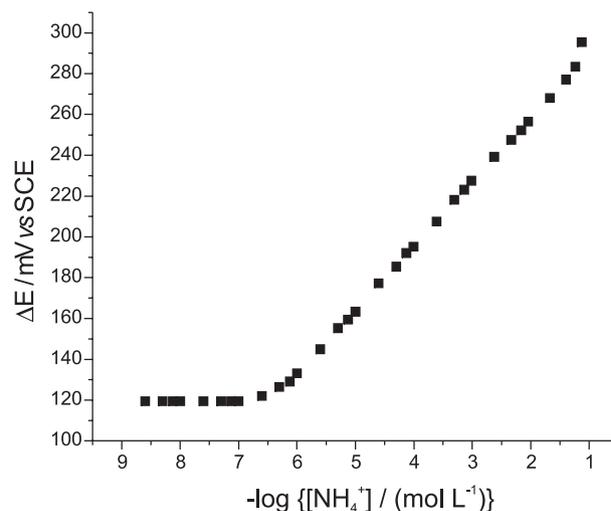


Figure 5. Calibration curve obtained with the SZPA ion selective electrode.

by applying the matched potential method which is independent of the Nicolsky-Eisenman (N-E) equation.¹² To determine the selectivity coefficient the change in potential was measured upon changing the primary ion concentration. The interfering ion was then added to an identical reference solution until the same potential change was obtained. The change in potential must be produced in a constant initial background of the primary ion and must be the same in both cases.^{12,13} Table 1 shows the average calculated values, from five determinations for each sample, by using this methodology. The Fe³⁺ ion presents a great affinity for the composite SZPA, although this is not very preoccupying because in samples of natural waters Fe³⁺ is usually found insoluble or metal-complex. The selectivity order obtained for the interferents of unitary charge was Na⁺ > Li⁺ > K⁺. This unexpected behavior was already observed in the literature²² for the zirconium(IV) phosphate. The selectivity coefficient values compared favorably not only with the commercial NH₄⁺ ion glass electrode,²³ but also with others of literature.^{20,24}

Table 1. Potentiometric selectivity coefficients for the ammonium ion-selective electrode K^{pot}_{A,B} determined by method recommended by IUPAC¹⁶

Interferent ion (B)	Selectivity coefficients (K ^{pot} _{A,B})
Fe ³⁺	0.58
Mg ²⁺	0.12
Fe ²⁺	0.11
Mn ²⁺	0.10
Ca ²⁺	0.09
Na ⁺	0.08
Li ⁺	0.07
K ⁺	0.06

Validation

The potentiometric method with the ammonium ion selective electrode developed was validated by comparison with the Berthelot method in the quantification of ammonium, in thirteen natural water samples.

The natural water samples were used in both methods (Berthelot and potentiometric) without previous treatment.

The analytical curve in the Berthelot method¹⁵ was linear in the concentration range of 4 to 40 μmol L⁻¹ of ammonium ions ($y = 0.00497 + 0.03641x$, where x is the concentration of ammonium ion in μmol L⁻¹ and y is the absorbance). The correlation coefficient of the regression equation was 0.9998.

The analytical curve in the potentiometric method was linear in the logarithmic concentration of ammonium

range of 7.7×10^{-7} and 4.0×10^{-2} mol L⁻¹ ($y = 320.9824 - 31.3469 \log[\text{NH}_4^+]$) and a correlation coefficient of 0.9999.

The results obtained for ammonium determination in natural water samples by potentiometry and standard method are shown in Table 2. The mean values obtained (Table 2) by the two methodologies do not differ significantly.

Table 2. Comparative results for ammonium ions content in natural waters by Berthelot and potentiometric methods

Samples	Ammonium ion ^a ± sd / (mmol L ⁻¹)	
	Berthelot method	Potentiometric method
1	1.278 ± 0.030	1.26 ± 0.02
2	1.099 ± 0.028	1.12 ± 0.01
3	14.232 ± 0.027	14.03 ± 0.03
4	1.265 ± 0.032	1.26 ± 0.02
5	1.140 ± 0.022	1.12 ± 0.01
6	1.593 ± 0.024	1.57 ± 0.01
7	1.278 ± 0.032	1.29 ± 0.02
8	10.285 ± 0.024	10.25 ± 0.03
9	4.179 ± 0.026	4.16 ± 0.01
10	6.602 ± 0.028	6.57 ± 0.02
11	4.034 ± 0.032	4.12 ± 0.02
12	6.806 ± 0.030	6.79 ± 0.02
13	1.675 ± 0.022	1.65 ± 0.01

^aAssay values represent average of ten (n=10) determinations; sd: standard deviation of the mean value (10 determinations) of the concentration of the ammonium ion.

Conclusions

The ion-selective electrode described in this paper, presents the following advantages: it can easily prepared, presents high chemical stability, it is highly selective to ammonium and has low fabrication cost. The response time was relatively short, approximately one minute, and the detection limit was 1.58×10^{-7} mol L⁻¹ (8.5×10^{-3} ppm). Detection of relatively high ammonium ion concentrations (4.0×10^{-2} mol L⁻¹) may be attributed to the high capacity of ion exchanger composite. The high stability of the SZPA and high affinity of the ammonium ion by the solid graphite/SZPA phase makes the electrode potentially useful in determining ammonium ion in natural waters. The potential electrode application in the determination of ammonium ion in natural waters is possible.

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