



Application of a new potentiometric method for determination of phosphate based on a surfactant-modified zeolite carbon-paste electrode (SMZ-CPE)

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ABSTRACT

A phosphate-selective electrode based on surfactant-modified zeolite (SMZ) particles into carbon-paste has been proposed (SMZ-CPE). The electrode was fully characterized in terms of composition, response time, ionic strength, thermal stability and usable pH range. The electrode containing 20% SMZ exhibited linear response range to phosphate species in the range of 1.58×10^{-5} to 1.00×10^{-2} M with a detection limit of 1.28×10^{-5} M and a Nernstian slope of 29.9 ± 0.9 mV per decade of phosphate concentration. The electrode response to phosphate remains constant in the pH range of 4–12 and in the presence of 1×10^{-4} to 4×10^{-3} M NaNO₃. The response of the electrode reaches equilibrium within several seconds after immersing the electrode in phosphate solution. Common anions such as Cl⁻, Br⁻, I⁻, NO₃⁻, SO₄²⁻ and Cr₂O₇²⁻ have little effect on the determination of phosphate but AsO₄³⁻ shows some interference. A successful application of the electrode for determination of phosphate in a fertilizer, using direct potentiometry, is presented. The electrode was also used for the potentiometric titration of phosphate. The validation of the obtained results in each case was proved by statistical methods.

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1. Introduction

Phosphorus, and specifically orthophosphate, is an essential nutrient used by plants and animals for growth and energy transport. However, excessive phosphorus concentration leads to eutrophication of natural waters which can result in algal bloom formation [1]. The rapid growth of aquatic vegetation in turn causes the death and decay of vegetation and aquatic life due to decrease of dissolved oxygen levels. The resulting eutrophication of natural waters is a subject of utmost concern, and has been recognized by the European Union through legislation that stipulates $0.1 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ as an indicator level for possible problematic algal growth in rivers [2]. Already many different methods have been reported for phosphate determination [3–5].

Liu et al. determined phosphate using a PVC membrane electrode based on Ferrocence-bearing macrocyclic amide compound. The electrode showed a Nernstian slope of 29.8 mV per decade and a detection limit of 2.2×10^{-6} M [6]. Phosphate-selective electrodes containing immobilized ionophores have been constructed by Goff with a detection limit of 1.0×10^{-6} M [7]. A dynamic range of

1×10^{-5} to 1×10^{-1} M with a calibration slope of about –19 mV per decade of phosphate has been reported by Tanaka and co-workers on their lead ion-selective electrode [8]. Furthermore, in recent years, there have been several reports on phosphate-selective electrodes [9–14].

Zeolites possess permanent negative charges in their crystal structures making them suitable cation exchangers. This negative charge is also suitable for surface modification of zeolites using cationic surfactants such as hexadecyltrimethyl ammonium (HDTMA) ion. At surfactant concentrations greater than the critical micelle concentration (CMC) and when sufficient surfactant is present, the sorbed surfactant molecules primarily form a bilayer on the zeolite external surfaces [15]. This bilayer formation results in a charge reversal on the external zeolite surface, providing sites where anions will be retained and cations repelled, while neutral species can partition into the hydrophobic cores. Recent studies indicate that surfactant-modified zeolites (SMZ) are effective sorbents for multiple types of contaminants, such as chromate, arsenate, antimonate, nitrite, nitrate and some other anionic and organic pollutants [16,17]. A review in this matter was published by Bowman [18].

The carbon-paste electrode (CPE) was introduced by Adams [19] in 1958. CPE and chemically modified carbon-paste electrodes (CMCPEs) are widely used in various fields of electrochemistry [20,21]. In comparison with ion-selective electrodes based on polymeric membranes, CMCPEs possess advantages such as ease of preparation and regeneration, stable response and very low Ohmic

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resistance [22]. CPEs have been used for potentiometric determination of various cations, anions, organic and pharmaceutical species [23–28]. One of the most important groups of CMEs is zeolite modified electrodes (ZMEs), which have been extensively reviewed by Rolison [29] and Walcarius [30].

In this work, Na–Y zeolite was modified with HDTMA and the resulting SMZ was used for modification of carbon-paste electrode (SMZ-CPE). The obtained electrode was used as a new potentiometric sensor for phosphate determination.

2. Experimental

2.1. Reagents and chemicals

The Na–Y zeolite (Cat. No. 33444-8) and spectroscopic grade mineral oil (Nujol) were purchased from Aldrich and used without further purification. Graphite powder, trisodium phosphate hexahydrate, potassium nitrate, potassium chloride, sodium arsenate, hexadecyltrimethyl ammonium bromide (HDTMA-Br) and all other chemicals of analytical reagent grade were from Merck. Triply distilled-deionized water was used throughout the experiments. The pH of solutions was adjusted with sodium hydroxide or hydrochloric acid solution as appropriate. For preparation of SMZ, the Na–Y zeolite (5 g) was mixed with 100 mL of 50, 100 and 200 mM HDTMA solutions in separate bottles, and stirred for 24 h on a magnetic stirrer. The mixture was then centrifuged at 5000 rpm for 20 min and the resulting SMZ was dried in air. The IR results showed adsorption of an appropriate amount of surfactant on the zeolite.

2.2. Modified electrode preparation

The SMZ-modified carbon-paste electrodes were prepared according to a previously reported method [31]. An appropriate amount of the SMZ (5–25 weight% with respect to graphite) was mixed with 100 mg graphite powder and then Nujol (24 weight%) was added. After thorough hand mixing in a mortar a fine paste was obtained. A portion of the resulting composite mixture was packed into the end of a polyethylene tube. The electrode body was made by drilling a bore of 2.5 mm diameter through 1/3 of a solid polyethylene rod of 3 cm length and 11 mm diameter. In the opposite end, a bore of 6 mm diameter was drilled. The modified carbon-paste was inserted from the wider side and pressed down using a rod of the same diameter. In this way the carbon-paste is packed into the short diameter side of the electrode. Electrical contact was made by forcing a copper wire of about 1 mm diameter, positioned into a glass tubing of 6 mm diameter, down the polyethylene tube and into the back of the paste. Unmodified electrodes were prepared in a similar way, using a carbon-paste with unmodified Na–Y zeolite. The electrode surface was polished on a soft paper and then rinsed with water.

2.3. Apparatus

Potentiometric experiments were carried out on a model 691 pH/Ion Meter (Metrohm). The measuring system comprised of the SMZ-modified carbon-paste as the indicator electrode and a saturated Ag/AgCl reference electrode. All potentials are reported versus this reference electrode. The pH measurements were performed using a corning model 125 pH-meter equipped with a combined electrode. Infrared spectra were recorded on a FT-IR Nicolet 400 instrument using Nujol mulls.

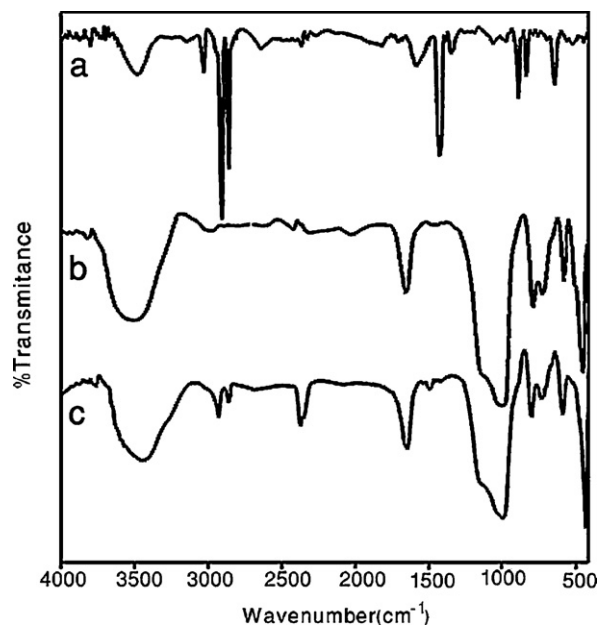


Fig. 1. FT-IR patterns for (a) HDTMA (b) Na–Y and (c) SMZ.

2.4. Procedure

The SMZ-modified carbon-paste electrode was polished on a soft paper and rinsed with water. This electrode was immersed into a 1×10^{-3} M phosphate solution and the solution stirred (150 rpm) until the response of the potentiometer with respect to the Ag/AgCl reference electrode became stable (10 min). After this conditioning time, the electrodes were rinsed with water and immersed into the measuring cell containing phosphate solution (at pH 10.0 adjusted by addition of HCl or NaOH solution, as appropriate) and the equilibrium potential was recorded (after 10 s). All potentiometric measurements were conducted at room temperature. The electrode was kept in open air when not in use. The activities of ions were calculated according to Debye–Huckel theory [32]. Potentiometric titration was conducted manually under convective mass transport provided by magnetic stirring. The end point was calculated by differentiation of the titration curve.

2.5. Preparation of fertilizer sample

Solid sample of ammonium phosphate fertilizer was ground in an agate mortar and a known amount of powder was dissolved in water by stirring for 5 min. The soluble excipient was filtered off with a filter paper. The filtrate was further diluted for standard addition or external standard methods to obtain concentrations in the range of 1.58×10^{-5} to 1.00×10^{-2} M of phosphate.

3. Results and discussion

3.1. Characterization of the SMZ

FT-IR spectra obtained using KBr pellets of HDTMA surfactant, Na–Y zeolite and SMZ-Y are shown in Fig. 1. The IR pattern of SMZ-Y shows characteristic peaks at 2919, 2840, 1420 and 714 cm^{-1} , which indicate the incorporation of HDTMA into the zeolite structure. There is a slight shift in peaks at each wavenumber, however, both of the patterns are nearly the same. Specially, the presence of peaks at 2919, 2840 and 1420 cm^{-1} in SMZ spectrum (related to C–H, C–C and N–C vibrations in the surfactants, respectively), that are absent in the Na–Y spectrum, confirm loading of HDTMA on zeo-

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