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Highly selective optical-sensing film for lead(II) determination in water samples

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ABSTRACT

An optical sensor is described for a sensitive and selective spectrophotometric determination of Pb(II) ions in aqueous solution. A sensor membrane based on 4-hydroxy salophen has been developed for the determination of Pb(II) ions that displays excellent performance. The membrane responds to lead(II) ions, giving a color change from colorless to yellow in a buffer solution (pH 3.1). The optode has a linear range of 1.0×10^{-3}–1.0×10^{-7} mol L^{-1} Pb(II) ions with a detection limit of 8.6×10^{-8} mol L^{-1} Pb(II). The response time is within 10 min depending on the concentration of Pb(II) ions such that it can quantitatively detect Pb(II) even at concentration levels of 8.6×10^{-8} mol L^{-1} Pb(II) (0.018 ppm). The optode developed here is found to be stable, cost effective, easy to prepare, and efficient for direct determination of Pb(II) in a variety of aqueous samples using spectrophotometry. However, it is for one time use only as the reaction of Pb(II) with 4-hydroxy salophen is irreversible. The optode was successfully used for measuring Pb(II) ions in different water samples and in SRM sample.

1. Introduction

The determination of lead is becoming increasingly important. Lead is widely distributed in nature and found in many ores including galena, anglesite, and cerrosite. It has found wide applications in storage batteries, cable sheath, solders, and radiating shielding. The major source of lead in the environment is the use of lead as a petrol additive. Atmospheric pollution by lead has caused considerable concern in the past and many countries have phased-out the use of lead in petrol. However, lead already in the environment is cycled through the biogeochemical cycle, and lead originally released into the atmosphere has ended up in surface and ground waters [1]. Lead can cause damage to the nervous system and the kidneys and is a suspected carcinogen [2]. Lead in the environment is generally present as inorganic Pb(II).

The number of reagents available for the spectrophotometric determination of lead is relatively small. The main reagents are dithizone [3], diethyldithiocarbamate [4], 4-(2-pyridilazo)resorcinol [5], diphenylthiocarbazone [6], and potassium hexacyanoferrate(III)-sodium tetrahydroborate [7]. In addition, several preconcentration methods based on spectrophotometric detection have been reported for lead(II) determination at trace levels [8–17].

Although each chromogenic system has its own advantages and disadvantages with respect to sensitivity, selectivity, and rapidity depending on the chromogenic reagent used, most of them require extraction using an organic solvent, surfactant, or even toxic cyanide as a masking agent to increase the sensitivity or selectivity. Cation detection in chemical, clinical, biological, environmental, and industrial samples is of vital importance. Instrumental methods available for this purpose, including flame photometry, atomic absorption spectrometry, electron microscope analysis, and neutron activation analysis, often suffer from high cost, large sample sizes required, and their inability to be used for continuous monitoring. Thus, over the past two decades, an increasing interest has been focused on the development of sensors which offer distinct advantages in terms of sensitivity, selectivity, response time, and remote sensing. Optical sensors are suited to this type of application as they may easily be incorporated into low-cost, easy-to-use kits while also offering the selectivity and sensitivity necessary for environmental monitoring [1].

Immobilization of dyes into or onto a solid support is a key issue for their application in optical sensing [18]. In general the ideal immobilization techniques should produce a highly stable assembly of molecules that remain strictly accessible to dissolved dye. Covalent attachment to a functionalized support [19] and physical entrapment [20] are two commonly employed techniques. Entrapment is the technically simpler technique, but the response is often relatively long.

A few papers have been published on optical sensors for lead(II) determination using hexamethine–hemicyanine dyes [21] and 3,3′,5,5′-tetramethyl-*N*-(9-anthrylmethyl)benzidine [22] as a fluorescence sensor, xylenol orange [23], dithizone [24], nile blue [25], gallocyanine [26], and oxodiamide derivative [27] as an absorbance/reflectance sensor, and quinolinesulphonic acid

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derivatives as a phosphorescence sensor [28]. The enzyme is also used as a biosensor [29]. The reported methods suffer from low sensitivity and/or poor selectivity. The bio-detection system needs expensive materials and/or complicated instrumentation [29]. Many of the reported optical sensors named above [21–27] are based on blending of the ligand with a plasticizer and fixing them in a holder such as polyvinyl chloride. A common weak point of many of these optical sensors is the leakage of the reagent into aqueous solutions on contact with them. Recently, He et al. [30], Chen et al. [31] and Rivera et al. [21] have introduced a new type of fluorescent probes for lead(II) ions determination using dicarboxylate pseudocrown receptor [28], and DNA probe [30]. These probes can be limited by interfering background fluorescence or non-specific quenching from competing metal ions [30,31] and/or has not enough sensitivity [21]. However, a main shortcoming of most of the reported lead ion optical sensors is their long response time. Thus, sensitive and simple lead optode with relatively short response times are still being sought for.

In this work, a simple method is developed for detecting trace levels of lead(II). Spectrophotometric reagent, 4-hydroxy salophen, has been immobilized on triacetyl cellulose as the solid and transparent phase. 4-Hydroxy salophen is covalently bonded to a transparent triacetyl cellulose film. The sensitivity of the membrane in contact with lead(II) ions in a solution with pH 3.1 and its absorbance depend on Pb(II) concentration. Generally speaking, the optical sensing system developed provides a sensitive and selective method for lead(II) ion determination.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical-reagent grade and were purchased from Merck (Darmstadt, Germany) unless otherwise stated, and were used directly without further purification. Triply distilled water was used to prepare buffer and reagent solutions.

Stock solutions of Pb(II), 1.0×10^{-2} mol L^{-1}, was prepared by dissolving $Pb(NO_3)_2$ in 100 mL of distilled water. Working standard solutions of Pb(II) were prepared by appropriate dilution of the stock solution before used.

4-Hydroxy salophen was synthesized as reported elsewhere [32]. Solution of 5.7×10^{-4} mol L^{-1} 4-hydroxy salophen (0.020% w/v) was prepared daily by dissolving 0.020 g of the reagent in distilled water in a 100 mL standard flask.

Polyvinyl alcohol solution was prepared by dissolving 0.500 g of the reagent in 100 mL of water.

Thiourea solution was prepared by dissolving 0.600 g of the reagent in 100 mL water.

A buffer solution (containing boric acid, citric acid, acetic acid and sodium hydroxide, 0.1 mol L^{-1}) with different pH values were used for the study of the influence of pH.

2.2. Apparatus

A homemade cell holder [33] was used with a special frame with a size of 8.5 mm × 35 mm (Fig. 1).

UV–vis spectra were obtained with a UV/Vis/NIR Jasco spectrophotometer, Model V-570 (Tokyo, Japan), connected to a Pentium IV computer was used for getting the absorption spectra and absorbance measurements. The control sample was stretched in the same way inside the cuvette using a frame of the same size. The reference cell contained a membrane without any 4-hydroxy salophen reagent.

A Shimadzu, Model AA-680G (Kyoto, Japan), furnace atomic absorption spectrometer furnished with a Pb-hollow cathode lamp was used. The instrument was set at a wavelength of 283.3 nm operated at 20 mA and all of other parameters were adjusted according to the standard recommendation.

A Corning pH-meter, Model 140 (New York, USA) with a double junction glass electrode was used to check the pH of the solutions.

2.3. Membrane preparation

In order to increase the porosity of the membrane, the triacetyl cellulose film was hydrolyzed to de-esterify the acetyl groups. This was accomplished by treating the membrane with 0.1 mol L^{-1} KOH solution for 24 h. The film was then washed with distilled water. It was found that further activation processes were not necessary [19,33]. The cellulose membrane was immediately treated with a mixture of 0.60% (w/v) thiourea and 0.50% (w/v) polyvinyl alcohol solution for 24 h at 25 °C. Then, the cellulose membranes were treated with a 5.7×10^{-4} mol L^{-1} 4-hydroxy salophen solution at 25 °C and in the buffer solution (pH 6.2) for 5 h. The activated membranes were washed with distilled water and dried at room temperature.

2.4. Recommended procedure

The membranes with the immobilized indicator were placed vertically inside the cuvette using a specially designed frame with an opening size of 8.5 × 35 mm (Fig. 1). The control sample against which the measurement was performed consisted of a triacetyl cellulose film treated in the same way but without an indicator. It was also placed vertically inside the cuvette using a frame of the same size. The membrane was immersed into a Pb(II) solution in a buffer solution (pH 3.1) for 10 min, and subsequently washed with distilled water and dried. The absorbance of the membrane was measured spectrophotometrically at 434 nm. The Pb(II) con-

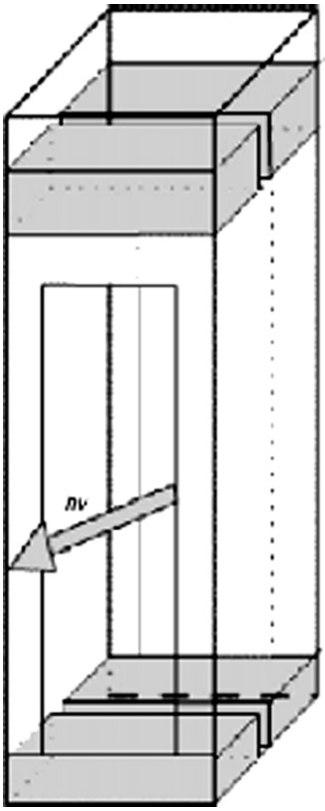

Fig. 1. Schematic diagram of the homemade cell.