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Preparation and characterization of a novel Co(II) optode based on polymer inclusion membrane

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ABSTRACT

A greener analytical procedure based on automated flow through system with an optical sensor is proposed for determination of Co(II). The flow through system consisted of polymer inclusion membrane (PIM) containing potassium thiocyanate (KSCN) that was placed between the measuring cell and fixed with optical sensor probe as an optical sensor for monitoring of Co(II) at 625 nm. In the presence of Co(II) ions, the colourless membrane changes to blue. The sensing membrane was prepared by incorporating SCN into a non plasticized PIM. The prepared PIM were found to be homogenous, transparent and mechanically stable. The optode shows reversible optical response in the range of $1.00 \times 10^{-6} - 1.00 \times 10^{-3}$ mol L^{-1} with detection limit of 6.10×10^{-7} mol L^{-1}. The optode can be regenerated by using 0.1 mol L^{-1} of ethylenediaminetetraacetic acid (EDTA). The main parameters of the computer controlled flow system incorporating the flow-through optode, a multi-port selection valve and peristaltic pump were optimized too. The calculated Relative Standard Deviation (R.S.D) of the repeatability and reproducibility of the method are 0.76% and 4.73%, respectively. This green system has been applied to the determination of Co(II) in wastewater samples with reduced reagents and samples consumption and minimum waste generation.

1. Introduction

Green analytical chemistry, which evolved from the green chemistry concept has the goal to develop analytical processes that reduce consumption of reagents, replace toxic substances, minimize waste generation and decontamination of analytical waste to guarantee operator safety and preserve the environment [1]. To achieve the goal, several strategies can be implemented, as recommended by Armenta et al. [2]. The strategies are to employ a remote sensing approach if possible, use non-invasive methods of analysis, use the chemometrics approach for data treatment, miniaturization and/or automation of analytical methods and online decontamination of analytical waste. These basic strategies can be used to enhance existing analytical methods or develop a new method. In developing a new method, the amount and toxicity of reagents and solvents used and wastes generated are as important as other analytical parameters, such as accuracy, sensitivity and selectivity. From this point of view, the most suitable strategy available to develop a new method is by using an automation method (flow-through system). This is due to the fact that reagent consumption and waste production in this method are generally low [3].

In recent years, there has been growing interest in the development of optical chemical sensors (optodes) as viable alternatives to other types of chemical sensors, namely electrochemical sensors and potentiometric sensors. Optodes can be based on various optical principles (reflectance, absorbance, fluorescence, luminescence) covering different regions of the spectrum (ultra-violet, visible, infrared, near infrared). Optodes are compact and perfectly suited to miniaturization, and at the same time they are unaffected by electrical interferences and use the simplicity of photometric measurements. In addition to the advantages of the low cost of materials and ease of miniaturization, a wide variety of sensor designs is made possible [4–10].

In the field of analytical chemistry, several types of membranes, such as bulk liquid membranes (BLMs), supported liquid membranes (SLMs), emulsion liquid membranes (ELMs), polymeric plasticized membranes (PPMs) and polymer inclusion membrane (PIM) have been produced and studied for the past three decades [11–23]. Most of these membranes are used for separation, concentration and purification of chemical species in the laboratory.

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Among the fabricated membranes, PIM have shown superior versatility and stability compared with other types of membranes. PIM are much better in terms of interfacial surface areas, high mass transfer rates, high fluxes, minimum use of hazardous chemicals, flexibility in membrane composition, good selectivity, high separation efficiency as well as ease of operation.

PIM is not only used in the separation and transport of chemical species, but also in a variety of chemical sensors, such as ion-selective electrodes (ISEs) [24,25], optodes [26–29], fluorescent sensor [30], biosensor [31], membrane sensor [32] and electrochemical sensor [33]. However, the exploitation of these membranes is totally different, and depends on their application. For chemical sensing, the membranes are used as the mechanical support for the reagent and as an interface for the analyte and reagent to react. But in separation, the membranes act as the medium for the mass transport process of ions from the source to the receiving phase. Due to its advantages, interest in utilizing PIM in optodes has increased rapidly [15,17,34,35]. The feasibility and stability of the membranes are the main reasons behind this. These membranes are prepared by physical immobilization of the reagent and carrier in a plasticized polymer matrix. In this context, the term physical immobilization refers to the entrapment of dyes in a bulk matrix, which they cannot leave because of their lipophilicity [36–40].

Dissolved cobalt occurs in the environment at concentrations ranging from 0.5 to 12.0 μg L^{-1} in seawater and up to 100 μg L^{-1} in wastewater [41]. At high concentrations, dissolved cobalt is toxic and has been reported to produce increased blood pressure, pulmonary disorders, vomiting and diarrhoea [42]. Thus, there is an urgent need for specific monitoring and detection of Co(II) in many industrial, environmental and food samples. The detection of Co(II) at low concentrations is usually carried out by relatively expensive spectroscopic techniques, such as graphite furnace atomic absorption spectrometry (GFAAS) [43] and inductively coupled plasma–emission spectroscopy (ICP-ES) [44]. However, these techniques involve the risk of sample contamination and analyte loss because of sample preparation and preconcentration steps. In addition, spectrophotometric [45–47] and spectrofluorometric [48] techniques have also been widely used. Most of the reagents are either not selective, with Fe(II) and Ni(II) being the main interferences, or the products are water insoluble and require extraction and separation [46,47] or even a computational approach to determine each species [49]. The potentiometric ISE techniques appear to overcome most problems, being very useful at low levels of Co(II) [50]. However, most of these ISEs suffer from interferences from many cations present in real samples that are co-oxidized at the applied potential [51,52].

To date, only a few studies have been carried out to detect and quantify traces of Co(II) by optodes. Malcik et al. [53] have developed a multi-ion optode including Co(II) based on several reagents. However, the Co(II) optode has a low regeneration time and is not fully reversible. In 2002, two reports were published by Yusof et al. [54] and Paleologos et al. [55] on the construction of an optode for the determination of Co(II). The former method is based on the immobilization of 2-(4-pyridylazo)resorcinol (PAR) in chitosan membrane as a transducer. Despite the fact that this optode has a wide linear range and short regeneration time, the sensor is prone to leaching and not selective. A Co(II) optode based on spectrophotometric measurement of the complex of pyrogallol red with Co(II) immobilized on a cellulose acetate membrane has been reported [56]. However, the drawbacks of this optode are that it is not based on a flow-through method, which means continuous monitoring and determination of Co(II) are not feasible. Another multi-ion optode that also comprised Co(II) as one of the analytes has been developed by Benounis et al. [57]. However, the physical parameters of the optode, such as selectivity, reproducibility and repeatability have not been discussed. A flow-through optode for the determination of Co(II) at the trace level has been reported by Yusof et al. [58]. The set-up of this optode is similar to the previously reported one [54], but this time the PAR reagent is physically adsorbed onto XAD-7. The only fluorescence-based optode for the determination of Co(II) has been reported by Shamsipur et al. [59]. Unfortunately, the response time of the optode is quite slow and continuous measurement of the Co(II) is not possible because the measurement was carried out in a batch mode.

The present paper reports the development of a novel flow-through optode based on the immobilization of Aliquat 336 into a PVC membrane and its application for the determination of Co(II) in aqueous solutions. Numerous experimental conditions have been investigated to achieve the desired output.

2. Experimental

2.1. Reagents and solutions

Poly(vinyl) chloride (PVC), and tricaprylmethylammonium chloride (Aliquat 336) and 2-methyltetrahydrofuran (2-MeTHF) were purchased from Sigma-Aldrich. While 1-dodecanol and potassium thiocyanate (KSCN) were purchased from Merck. All chemicals were analytical reagent grade. A 200 mL stock solution of 500 mg L^{-1} Co(II) (0.4770 g $CoSO_4 \cdot 7H_2O$ (BDH) was prepared in deionized water. The stock solutions of 1.0 mol L^{-1} thiocyanate (SCN), 1.0 mol L^{-1} hydrochloric acid (HCl) (BDH), 1.0 mol L^{-1} sulphuric acid (H_2SO_4) (Ajax), 1.0 mol L^{-1} nitric acid (HNO_3) (BDH) and 0.5 mol L^{-1} ethylenediaminetetraacetic acid (EDTA) (disodium salt) (Aldrich) were prepared by dissolving the appropriate amount of the corresponding reagent in deionized water. Working standard solutions of lower concentrations were prepared by suitable dilution of the stock solutions with deionized water. Buffer solutions were prepared according to methods from Handbook of Basic Tables for Chemical Analysis [60]. All solutions were prepared using analytical reagent grade chemicals and distilled water, purified through a MilliQ Plus system (Millipore).

2.2. Apparatus

The flow injection system incorporated a membrane, cast onto a small glass slide into a flow cell (Fig. 1). The flow system (Fig. 2) was controlled by a computer, running a C (MS) program. The system consisting of a peristaltic pump (C-4V, Alitea, Sweden), a multi-position valve injector (DCSD10P, Valco Instruments, USA), the flow-through measuring cell and connecting PTFE (Teflon) tubing (inner diameter = 0.75 mm) was used for flowing different solutions through the flow-through measuring cell for preselect time

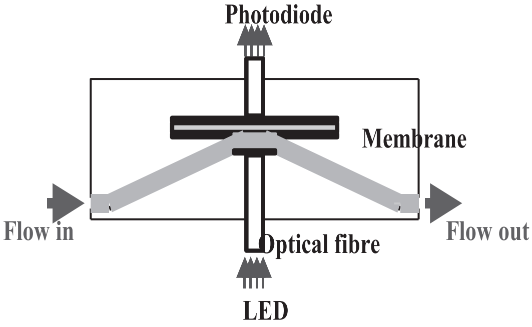

Fig. 1. Flow-through measuring cell.