



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



Faiz Bukhari Mohd Suah

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia

## ARTICLE INFO

### Article history:

Received 18 November 2016

Received in revised form

7 February 2017

Accepted 7 February 2017

Available online 9 February 2017

### Keywords:

Optode

Flow through system

Polymer inclusion membrane

Aliquat 336

Cobalt(II)

Green analytical chemistry

## 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<sup>-1</sup> with detection limit of  $6.10 \times 10^{-7}$  mol L<sup>-1</sup>. The optode can be regenerated by using 0.1 mol L<sup>-1</sup> 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.

© 2017 The Author. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 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 on-line 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.

E-mail address: [fsuah@usm.my](mailto:fsuah@usm.my).

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  $\mu\text{g L}^{-1}$  in seawater and up to 100  $\mu\text{g L}^{-1}$  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 tricaprilmethylammonium 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  $\text{mg L}^{-1}$  Co(II) (0.4770 g  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (BDH) was prepared in deionized water. The stock solutions of 1.0  $\text{mol L}^{-1}$  thiocyanate (SCN), 1.0  $\text{mol L}^{-1}$  hydrochloric acid (HCl) (BDH), 1.0  $\text{mol L}^{-1}$  sulphuric acid ( $\text{H}_2\text{SO}_4$ ) (Ajax), 1.0  $\text{mol L}^{-1}$  nitric acid ( $\text{HNO}_3$ ) (BDH) and 0.5  $\text{mol L}^{-1}$  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

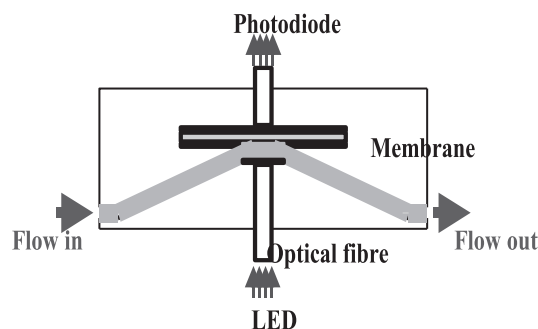


Fig. 1. Flow-through measuring cell.

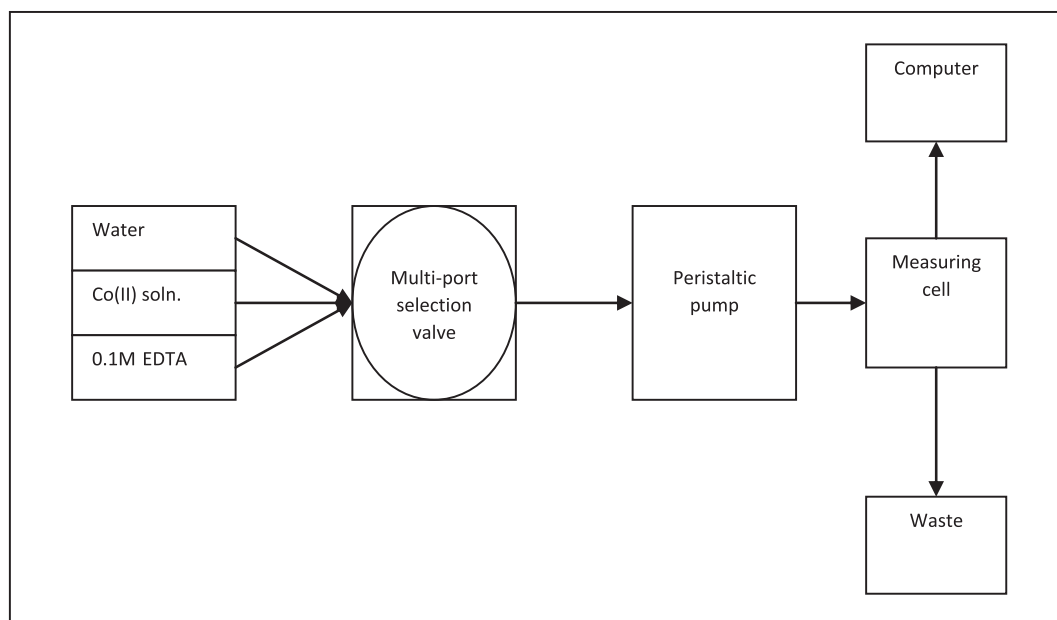


Fig. 2. Schematic diagram of the flow system.

intervals at  $1.0 \text{ mL min}^{-1}$ . The light source used was a red light emitting diode (LED) (625 nm, RS Components, Australia), which corresponds to the maximum absorbance of the membrane after it is exposed to the Co(II) solution. The light intensity was measured by an enhanced photodiode (400–700 nm) coupled with an optical fibre cable. Signal processing was performed using an analog to digital data acquisition card (PCL318, Advantech, Taiwan) and computer software in Microsoft C. UV–Vis spectra were recorded in 10 mm quartz cells using a Libra S12 UV–Visible Spectrophotometer (Biochrom Ltd, USA). The homogeneity of the membrane inspected using a Nikon Labophot 2, type 104 microscope and its thickness measured with a light optical microscope model Leica DM LM, (Leica Camera, Japan).

### 2.3. Preparation of the PIM

The membrane was prepared by dissolving about 60 mg of PVC and 40 mg of Aliquat 336 in 10 mL of 2-MeTHF. The composition of the polymeric membrane prepared is PVC (60%): Aliquat 336 (40%). Once dissolved, the solution was poured directly into a 7.5 cm diameter glass rings on a glass plate, covered with filter paper to ensure slow evaporation and to protect the membrane from dust. The membrane was allowed to sit overnight to allow the 2-MeTHF to evaporate, which formed colourless, transparent and flexible membranes. Then, the membrane was treated with 30 mL of  $1.0 \text{ mol L}^{-1}$  SCN solution for overnight at ambient temperature. Later, it was washed with deionized water to remove the additional reagent. The membrane was stored in a sealed plastic bag when not in use.

### 2.4. Spectrophotometric measurements of the PIM

The sensing membrane was immersed in 10 mL of  $1.00 \times 10^{-5} \text{ mol L}^{-1}$  Co(II) buffered at pH 5.0 and the solution was stirred for 5 min. Then the membrane was cut into strips ( $1 \times 2 \text{ cm}$ ) and placed between two glass slides. The absorbance spectrum of the membrane was recorded between 500 and 700 nm.

### 2.5. Flow-through measurements of Co(II)

Initially, the carrier solution (deionized water) was pumped through the system for  $t = t_{\text{carrier}}$ , to establish a baseline. This was followed by the injection of the Co(II) solution (sample solution) for  $t = t_{\text{sample}}$ , which allowed the membrane to extract the Co(II) and gave a corresponding absorbance reading. For the final 30 s of  $t_{\text{sample}}$ , the pump was stopped to give a better precision of the absorbance reading. Then  $0.1 \text{ mol L}^{-1}$  of EDTA (stripping solution) was introduced to the system, which complexed Co(II), released from the membrane and allowed the membrane to be reused. Finally carrier solution was passed again through the measuring cell for  $t = t'_{\text{carrier}}$  to condition the membrane prior to sample injection. The operation parameters (e.g.  $t_{\text{carrier}}$ ,  $t_{\text{sample}}$ ,  $t_{\text{stripping}}$  and  $t'_{\text{carrier}}$ ) that influence the sensitivity, reproducibility and repeatability in the experimental flow system are interrelated with the flow rate and to simplify their study, the flow rate was set at  $1.0 \text{ mL min}^{-1}$ . Table 1 shows the range studied and the optimal values found. In screening the efficiency of various stripping reagents in removing Co(II) from the sensing membrane, a  $1.00 \times 10^{-5} \text{ mol L}^{-1}$  Co(II) solution was used and  $t_{\text{carrier}}$ ,  $t_{\text{sample}}$ ,  $t_{\text{stripping}}$  and  $t'_{\text{carrier}}$  were selected at 60, 90, 240 and 60 s, respectively.

### 2.6. Determination of Co(II) in real sample

Vitamin B12 tablet (Malaysia) was placed in a flask and nitric acid (2–3 mL) were added. The solution later transferred into 100 mL calibrated flask and was diluted with distilled water. Finally the sample was taken for analysis by the recommended procedure.

Table 1  
Physical parameter optimized in the flow system.

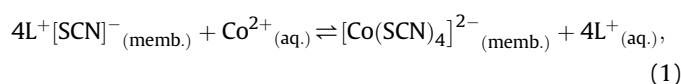
Parameter	Range studied (time, s)	Optimal value (time, s)
$t_{\text{carrier}}$	30–300	60
$t_{\text{sample}}$	30–600	90
$t'_{\text{carrier}}$	30–300	60
$t_{\text{stripping}}$	90–600	240

### 3. Results and discussion

Numerous combinations of the matrix-forming polymer (PVC), plasticizer (1-dodecanol), extractant (Aliquat 336) and  $\text{SCN}^-$  were studied to optimize Co(II) uptake in the PIM at a pH of 5.0. Table 2 lists the different PIM compositions and their absorption at 625 nm. The proportion of the PIM was optimized to increase their absorption and uniformity. To determine the optimum composition, each PIM was prepared by fixing its mass to 100 mg and varying the mass composition of the different components (PVC, Aliquat 336 and 1-dodecanol). A comparison of the absorbance of the different PIM after loading them with fixed amounts of Co(II) at pH 5.0 proved that PIM IV, with a composition of PVC = 60 wt% (m/m), Aliquat 336 = 40 wt% (m/m), produced the highest absorbance at 625 nm (Table 2). Therefore, this membrane was selected for further experiments. The wavelength of maximum absorbance for the Co–SCN complex in the membrane is 625 nm. Thus a red LED, which corresponds to this wavelength, was chosen as the light source for the flow-through optode system. The average thickness for 100 mg membrane used in this study is 15  $\mu\text{m}$ . The PIM produced in this study was homogeneous, transparent and self-supporting.

This interesting result proved that the best PIM (in terms of sensitivity, homogeneity and transparency) can be prepared without the use of a plasticizer. Here, Aliquat 336 also acts as a plasticizer in addition to its major function as an extractant. This observation can be explained by the structure and features of Aliquat 336, which has a polar group that is able to reduce attractive intermolecular forces among chains in the polymer systems, which allows the entrapment of reagent and the formation of a self-supporting membrane.

The membrane extracts a coloured complex of the analyte, and absorbance at the appropriate wavelength is related to the concentration of the analyte in the sample. The absorbance measurements can be made manually, using spectrophotometry or the procedure can be automated by incorporating the membrane into a flow injection analysis system. It is observed that the otherwise colourless membrane becomes blue upon contact with the Co(II) solution. A blue complex with the formula  $[\text{Co}(\text{SCN})_4]^{2-}$  is formed between Co(II) and  $\text{SCN}^-$  ions, which fades when the solution is diluted with water. The extraction process can be described by the following equation:



where L is Aliquat 336 chloride, *aq.* refers to the aqueous phase and

*memb.* refers to the membrane phase.

The extractant used in this study, Aliquat 336, is a water-insoluble quaternary ammonium salt that is widely used to extract and transport metal ions and small organic compounds [14]. In this study, Aliquat 336 reacts as an ion-exchanger forming an ion-pair with the Co(II) complex from the aqueous phase. Aliquat 336 immobilized in PVC membrane shows an excellent ability to extract  $[\text{Co}(\text{SCN})_4]^{2-}$  by forming an ion-pair, which causes the colourless membrane to change to blue. The introduction of Aliquat 336 enhances the extraction of Co(II) into the membrane compared with the PVC:1-dodecanol based membrane with an up to threefold increase in the absorption intensity, as shown in Fig. 3. This behaviour can be explained by a strong ionic interaction between the  $[\text{Co}(\text{SCN})_4]^{2-}$  and the Aliquat 336 because of the ion-pairing between the negative charge of the complex and the positive charge of the Aliquat 336. In addition, Aliquat 336 also provides extra solubility because of its superior solubilisation ability, which also allows hydrophobic interaction to take place. When these two interactions (electrostatic and hydrophobic) occur concurrently, a maximum enhancement of the absorption is obtained because of the achievement of a more rigid structure [26]. It is also known that this membrane is mechanically stable, and suitable for use as an optode.

The effect of the pH of the Co(II) solution over the range 2.0–10.0 on the absorbance of the membrane for a solution containing  $1.00 \times 10^{-6} \text{ mol L}^{-1}$  Co(II) was also studied (Fig. 4). It was observed that the maximum response was attained at pH 5.0. In another experiment, the effect of  $\text{SCN}^-$  concentration on the

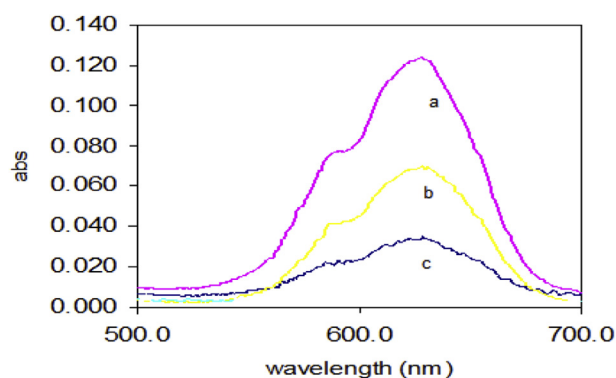


Fig. 3. Absorption spectra of different type of membranes: (a) PVC = 60 wt%: Aliquat 336 = 40 wt%, (b) PVC = 50 wt%: Aliquat 336 = 30 wt%: 1-dodecanol = 20 wt%, and (c) PVC = 60 wt%: 1-dodecanol = 40 wt%. Conditions:  $[\text{SCN}^-] = 1.0 \text{ mol L}^{-1}$ ,  $[\text{Co(II)}] = 1.00 \times 10^{-5} \text{ mol L}^{-1}$ , pH = 6.0.

Table 2

The PIMs compositions prepared in this study.

Membrane	PVC (mg) ( $\pm 0.2$ )	Aliquat 336 (mg) ( $\pm 2.0$ )	1-dodecanol (mg) ( $\pm 0.5$ )	Composition (wt%)	Maximum absorption <sup>a</sup>
I	70	30	–	70:30:00	0.120
II	70	20	10	70:20:10	0.086
III	70	10	20	70:10:20	0.080
IV	60	40	–	60:40:0	0.133
V	60	30	10	60:30:10	0.112
VI	60	20	20	60:20:20	0.108
VII	60	10	30	60:10:30	0.106
VIII	60	–	40	60:0:40	0.042
IX	50	50	–	50:50:0	0.060
X	50	40	10	50:40:10	0.058
XI	50	30	20	50:30:20	0.072
XII	50	20	30	50:20:30	0.068
XIII	50	10	40	50:10:40	Non forming membrane

<sup>a</sup> Absorption measured at 625 nm,  $[\text{Co(II)}] = 1.00 \times 10^{-5} \text{ mol L}^{-1}$ ,  $[\text{SCN}^-] = 1.0 \text{ mol L}^{-1}$ , pH = 5.0.

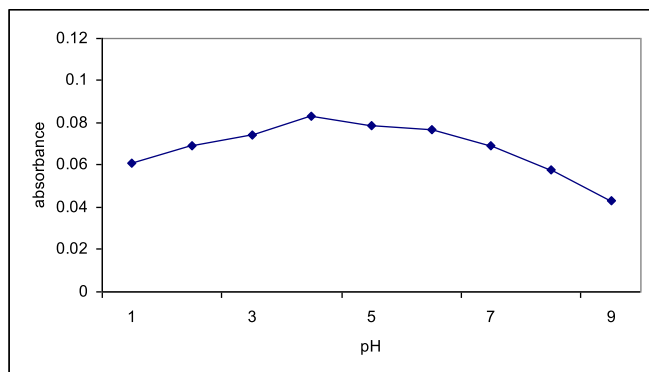


Fig. 4. Effect of pH on the membrane response for a solution containing  $1.00 \times 10^{-6} \text{ mol L}^{-1}$  of Co(II).

membrane response was investigated in the concentration range  $0.1\text{--}2.0 \text{ mol L}^{-1} \text{ SCN}^-$ . It was found that a concentration of  $1.0 \text{ mol L}^{-1} \text{ SCN}^-$  produces the highest response for a solution containing  $1.00 \times 10^{-6} \text{ mol L}^{-1} \text{ Co(II)}$  buffered at pH 5.0. Thus, this was chosen as the optimum concentration of  $\text{SCN}^-$  for the treatment of the prepared membrane.

Fig. 5 shows the system response during one operation cycle with  $0.1 \text{ mol L}^{-1}$  of EDTA used as a stripping reagent. Deionized water used as the carrier solution ( $t_{\text{carrier}}$ ) was pumped through the measuring cell. When the multi-port selection valve switched to a  $1.00 \times 10^{-6} \text{ mol L}^{-1} \text{ Co(II)}$  solution, the absorbance started to increase as the result of formation of the Co–SCN complex in the sensing membrane. After the sample introduction time ( $t_{\text{sample}}$ ) has been chosen, the multi-port selection valve was switched back to the carrier solution ( $t'_{\text{carrier}}$ ), which resulted in the formation of an absorbance plateau, the height of which compared with the original baseline was named the signal (Fig. 5). When  $0.1 \text{ mol L}^{-1}$  EDTA was pumped through the measuring cell, the Co–SCN complex dissociated. The EDTA solution was preselected to flow longer ( $t_{\text{stripping}}$ ) than the  $t_{\text{sample}}$  to ensure that the Co–SCN complex dissociated completely. Finally, the multi-port selection valve was switched back to the carrier solution and it flowed through the system for a predetermined period of time. This is to permit restoration of the sensing membrane composition prior to the next

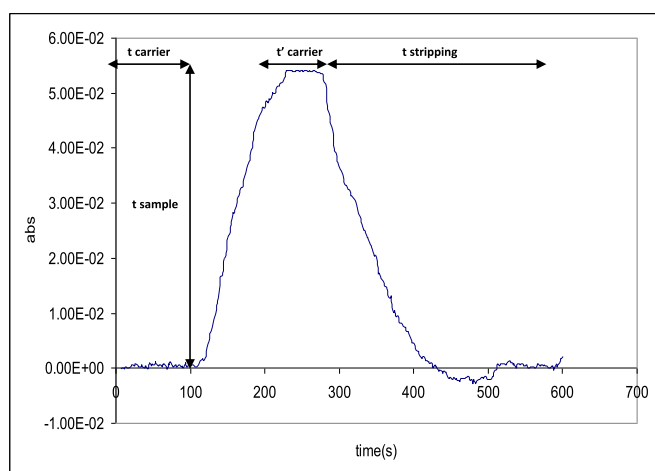


Fig. 5. System response during one operation cycle of the flow system (sample  $1.00 \times 10^{-6} \text{ mol L}^{-1} \text{ Co(II)}$ ); with  $t_{\text{carrier}} 60 \text{ s}$ ,  $t_{\text{sample}} 90 \text{ s}$ ,  $t'_{\text{carrier}} 60 \text{ s}$ ,  $t_{\text{stripping}} 240 \text{ s}$  and flow rate of  $1.0 \text{ mL min}^{-1}$ .

sample introduction. In addition, the optimization of the system was also carried out with respect to the sensitivity. The optimal values of the operation parameters are shown in Table 1.

Effective stripping of the membrane is necessary for the system to be used in practical situations. Therefore, the possibilities of using several reagents (e.g. HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and EDTA) as stripping reagents were also investigated. Incomplete stripping and increasing baseline occurred in the cases of HCl,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . The best result was obtained with the use of EDTA. A solution of  $0.1 \text{ mol L}^{-1}$  EDTA provided complete regeneration of the membrane. EDTA complexes with the Co(II) ions preferentially, thus liberating them from the membrane. This feature allows multiple measurements to be taken with the same membrane. The EDTA strips the membrane relatively quickly and  $t_{\text{stripping}}$  was determined by testing how long it took for the absorbance reading to return to the baseline. A longer stripping time did not affect the baseline shift, indicating that as the membrane becomes loaded, the cobalt moves further into the membrane and would require a much longer stripping time than is practical. As higher EDTA concentrations did not produce any extra improvement,  $0.1 \text{ mol L}^{-1}$  EDTA was used as the stripping solution in subsequent experiments.

The relationship between the signal and the Co(II) concentration was found to be linear over the concentration range  $1.00 \times 10^{-6}$  to  $1.00 \times 10^{-3} \text{ mol L}^{-1}$  with  $y = 0.0613x + 0.4493$  and correlation coefficient,  $R^2 = 0.9832$  (Fig. 6). It was noticed that by increasing the  $t_{\text{sample}}$ , the sensitivity increased at the expense of sample throughput. However, by introducing a longer  $t_{\text{sample}}$  to the measuring cell, the time needed to strip the membrane was also increased. For example, by increasing the  $t_{\text{sample}}$  from 90 s to 180 s, the  $t_{\text{stripping}}$  increased from 240 s to 360 s. Therefore, it was found that the duration required to complete one cycle of operation increased when a longer  $t_{\text{sample}}$  was used. To compromise between the need for sensitivity and reproducibility of the membrane, a  $t_{\text{sample}}$  of 90 s was chosen.

The continuous regeneration of the optode was studied for  $1.00 \times 10^{-6} \text{ mol L}^{-1} \text{ Co(II)}$  ion. As observed in Fig. 7, the optode was able to complete 10 repetitions continuously, with the relative standard deviation (R.S.D.) of 3.80%. However, further studies must be carried out to extend the regeneration of the optode up to at least 20 cycles.

The calculated limit of detection, based on three times the standard deviation of a blank, was  $6.10 \times 10^{-7} \text{ mol L}^{-1}$ . The precision using a single membrane was tested by performing eight replicate measurements for  $1.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Co(II)}$  solutions. The R.S.D. for this determination was 0.76%. Reproducibility was evaluated by carrying out the same procedure with eight different membranes; the R.S.D. for the same concentration of Co(II) was 4.73%. Sensing membranes were used for up to two weeks and no

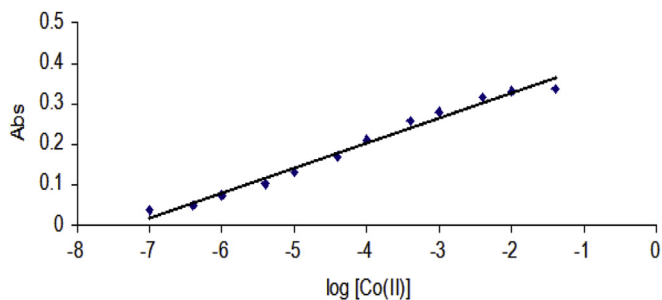


Fig. 6. The absorbance vs.  $\log[\text{Co(II)}]$  in the Co(II) solutions, buffered at pH 5.0 with the experimental conditions were as in Table 1.



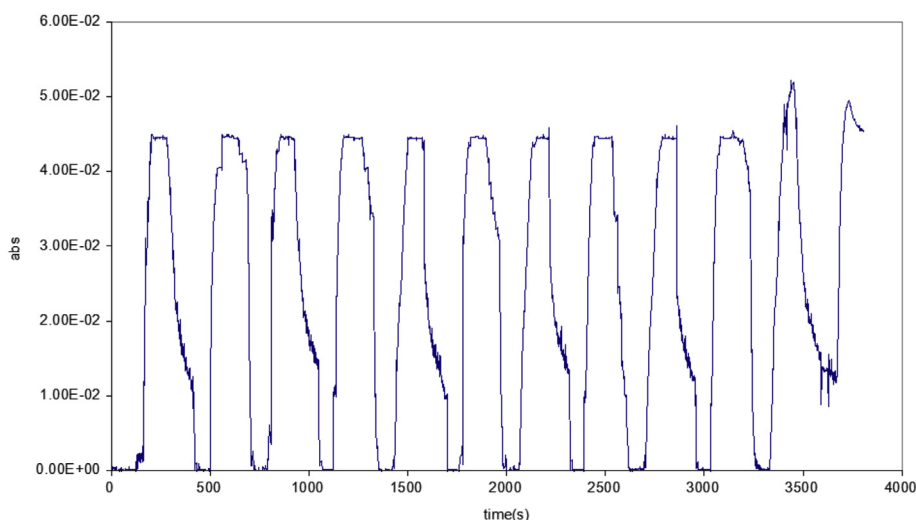


Fig. 7. The typical response of the optode after regeneration of the Co(II) optode using 0.1 mol L<sup>-1</sup> EDTA.

**Table 3**

The degree of interference in Co(II) determination.

Ions	Mole ratio (Co(II): ion)	% Abs. error
Al(III)	1:1	8.70
	1:100	8.95
Cd(II)	1:1	7.92
	1:100	8.32
Cr(III)	1:1	7.32
	1:100	17.92
Cu(II)	1:1	8.10
	1:100	33.48
Fe(II)	1:1	9.31
	1:100	31.20
Fe(III)	1:1	9.45
	1:100	29.30
Mg(II)	1:1	4.81
	1:100	n
Mn(II)	1:1	6.90
	1:100	8.05
Ni(II)	1:1	4.14
	1:100	9.30
Pb(II)	1:1	5.30
	1:100	6.56
Zn(II)	1:1	8.28
	1:100	18.33

Note: Interference (%) =  $((x-y)/y) \times 100$ , where  $x$  is the average of three absorbance value for mixed solution of Co(II) and foreign ions,  $y$  is average absorbance value for Co(II) solution only. n = no interference.  $[Co(II)] = 1.00 \times 10^{-5}$  mol L<sup>-1</sup>.

leaching or any changes in their chemical or physical properties were observed.

The degree of interference measured from some foreign ion at 1:1 and 1:100 mol ratio of Co(II):ion is summarized in Table 3. The experiments were carried out by fixing the concentration of Co(II) at  $5.00 \times 10^{-5}$  mol L<sup>-1</sup> and then measuring the change in absorbance before and after adding the interference ion to the Co(II) solution buffered at pH 5.0. The tolerance ratio of each foreign ion

**Table 4**

Determination of Co(II) in vitamin B12 sample using the optode.

Sample	Cobalt found ( $\mu\text{g mL}^{-1}$ )		Recovery (%) (n = 3)
	Proposed method (n = 3)	AAS found	
Vitamin B 12	9.50 ± 0.12	9.98 ± 0.05	103.2

was taken as the largest amount yielding an error below  $\pm 10\%$ . It was observed that only Cu(II), Fe(II), Fe(III) and Zn(II) seem to interfere at high ratio molar ratio.

However, these ions are not expected to be found in real water samples except for fluoride ion and Fe(III) ions. Fe(III) ions are present in the water sample due to natural occurrence, while fluoride ions originate from the salt used for water treatment. The possibility of having a very high concentration of these ions compared with Co(II) in the water sample is very low. However, these interferences could be eliminated with the addition of a suitable masking agent.

The interference of foreign ions were minimal. These interfering ions can be eliminated by the use of conventional methods, such as application of a masking agent, or a more practical method, such as synchronous derivative spectrometry.

Finally, to validate the applicability of the constructed automated flow-through system with an optical sensor, this flow system was applied to determine Co(II) in vitamin B 12 sample and wastewater samples by the standard-addition method (Tables 4 and 5). In this experiment, the tolerance limit was set at  $\pm 5\%$  of error. As can be seen, the results acquired are satisfactory and comparable to the atomic absorption spectrometry (AAS) method. The proposed automated flow-through system with an optical sensor is selective, simple, inexpensive, requires low reagent use and chemical consumption and minimum waste is generated.

#### 4. Conclusion

A flow-through optode based on a PIM that can be used for the selective determination of Co(II) was developed and integrated into a computer-controlled flow system. The membrane showed no evidence of leaching and was mechanically stable. The main parameters of the experimental flow system, such as composition of the membrane, solutions used and timing sequence in the operation of the system were also optimized. The optode shows a useful and reversible optical response in the range of  $1.00 \times 10^{-6}$  to  $1.00 \times 10^{-3}$  mol L<sup>-1</sup>. Moreover, the optode exhibits good Co(II) selectivity over other ions. Thus, the feasibility of using the developed automated flow-through system with an optical sensor for analytical purposes has been demonstrated. This system can be relatively easy to miniaturize and this will allow the manufacture of portable instruments for Co(II) analysis. In addition, this system is superior to the batch-wise method because it offers an inexpensive

**Table 5**  
Determination of Co(II) in wastewater samples using the optode.

Sample	Spiked Co(II) ( $\mu\text{g mL}^{-1}$ )	AAS found ( $\mu\text{g mL}^{-1}$ )	Proposed method ( $\mu\text{g mL}^{-1}$ ) (n = 3)	Recovery (%) (n = 3)
Sewage water <sup>a</sup>	3	3.05 $\pm$ 0.02	3.16 $\pm$ 0.04	110.5
Sewage water <sup>b</sup>	5	5.08 $\pm$ 0.02	5.20 $\pm$ 0.04	103.2
Washing water	10	10.19 $\pm$ 0.04	9.37 $\pm$ 0.06	95.1

<sup>a</sup> Municipal drain.

<sup>b</sup> Industry drain.

system, full automation, rapidity, low reagent consumption and minimum waste generation.

## Acknowledgements

This work was partly supported by Universiti Sains Malaysia (304/PKIMIA/6313225). Author would also want to thank Professor Spas Kolev and Professor Robert Cattrall, both from The University of Melbourne, Australia for their constructive discussions and assistances.

## References

- [1] M. de la Guardia, S. Garrigues, Challenges in Green Analytical Chemistry, Royal Society of Chemistry, Cambridge, UK, 2011.
- [2] S. Armenta, S. Garrues, M. de la Guardia, Trends. Anal. Chem. 27 (2008) 497–511.
- [3] M. Koel, M. Kaljurand, Green Analytical Chemistry, Royal Society of Chemistry, Cambridge, UK, 2010.
- [4] P.C.A. Jeronimo, A.N. Araujo, M.C.B.S.M. Montenegro, C. Pasquini, I.M. Raimundo Jr., Anal. Bioanal. Chem. 380 (2004) 108–114.
- [5] S.A. El-Safty, D. Prabhakaran, A.A. Ismail, H. Matsunaga, F. Mizukami, Adv. Funct. Mater. 17 (2007) 3731–3745.
- [6] M.J.E. Resendiz, J.C. Noveron, H. Disteldorf, S. Fischer, P.J. Stang, Org. Lett. 6 (5) (2004) 651–653.
- [7] S. Tao, T.V.S. Sarma, Opt. Lett. 31 (10) (2006) 1423–1425.
- [8] B. Kuswandi, Anal. Bioanal. Chem. 376 (2003) 1104–1110.
- [9] H. Tsai, R. Doong, Biosens. Bioelectron. 20 (2005) 1796–1804.
- [10] O.S. Wolfbeis, Fiber Optic Chemical Sensors and Biosensors, CRC Press, Boca Raton, FL, 1991.
- [11] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Netherlands, 1991.
- [12] J. de Gyves, E. Rodriguez de San Miguel, Ind. Eng. Chem. Res. 38 (1999) 2182–2202.
- [13] E.L. Cussler, Facilitated transport, in: R.W. Baker, et al. (Eds.), Membrane Separation Systems: Recent Developments and Future Directions, Noyes Data Corporation, New Jersey, 1991.
- [14] L.D. Nghiem, P. Mornane, I.D. Potter, J.M. Perera, R.W. Cattrall, S.D. Kolev, J. Membr. Sci. 281 (2006) 7–41.
- [15] X.J. Yang, A.G. Fane, K. Soldenhoff, Ind. Eng. Chem. Res. 42 (2003) 392–403.
- [16] M. Cox, Solvent extraction in hydrometallurgy, in: J. Rydberg, et al. (Eds.), Solvent Extraction Principles and Practice, Marcel Dekker, Inc., New York, 2004.
- [17] R.W. Cattrall, Chemical sensors, in: R.G. Compton (Ed.), Oxford Chemistry Primers, vol. 52, Oxford University Press, New York, 1997.
- [18] A.M. Sastre, A. Kumar, J.P. Shukla, R.K. Singh, Sep. Purif. Meth. 27 (2) (1998) 213–298.
- [19] A.M. Neplenbroek, D. Bargeman, C.A. Smolders, J. Membr. Sci. 67 (2/3) (1992) 149–165.
- [20] M. Sugiura, M. Kikkawa, S. Urita, J. Membr. Sci. 42 (1/2) (1989) 47–55.
- [21] P.R. Danesi, Sep. Sci. Technol. 19 (11–1) (1984) 857–894.
- [22] A. Gherrou, H. Kerdjoudj, R. Molinari, P. Seta, Mater. Sci. Eng. C 25 (4) (2005) 436–443.
- [23] S. Sodaye, G. Suresh, A.K. Pandey, A. Goswami, J. Membr. Sci. 295 (2007) 108–113.
- [24] E. Bakker, P. Bühlmann, E. Pretsch, Chem. Rev. 97 (1997) 3083–3132.
- [25] A. Radu, A.J. Meir, E. Bakker, Anal. Chem. 74 (2004) 6402–6409.
- [26] F.B.M. Suah, M. Ahmad, Anal. Chim. Acta 951 (2017) 133–139.
- [27] S. Sodaye, Y.M. Scindia, A.K. Pandey, A.V.R. Reddy, Sens. Actuators B 123 (2007) 50–58.
- [28] F.B.M. Suah, M. Ahmad, L.Y. Heng, Sens. Actuators B 201 (2014) 490–495.
- [29] F.B.M. Suah, M. Ahmad, L.Y. Heng, Spectrochim. Acta A 144 (2015) 81–87.
- [30] X. Wang, H. Zeng, Y. Wei, J.M. Lin, Sens. Actuators B 114 (2006) 565–572.
- [31] M. Zhu, S. Han, Z. Yuan, J. Electroanal. Chem. 480 (2000) 255–261.
- [32] M.Y. Abdelaal, J. Appl. Polym. Sci. 82 (2001) 2008–2015.
- [33] K. Prasad, K.P. Prathish, J.M. Gladis, G.R. Naidu, T.P. Rao, Electroanal 19 (2007) 1195–1200.
- [34] B. Adhikari, S. Majumdar, Prog. Polym. Sci. 29 (2004) 699–766.
- [35] T.S. Snowden, E. Anslyn, Curr. Opin. Chem. Biol. 3 (1999) 740–746.
- [36] I. Oehme, S. Prattes, O.S. Wolfbeis, G.J. Mohr, Talanta 47 (1998) 595–604.
- [37] Y.M. Scindia, A.K. Pandey, A.V.R. Reddy, S.B. Manohar, Anal. Chim. Acta 515 (2004) 311–321.
- [38] M. Lerchi, E. Bakker, B. Rusterholz, W. Simon, Anal. Chem. 64 (1992) 1534–1540.
- [39] I. Murkovic, I. Oehme, G.J. Mohr, T. Ferber, O.S. Wolfbeis, Mikrochim. Acta 121 (1995) 249–258.
- [40] I. Murkovic, O.S. Wolfbeis, Sens. Actuators B 38–39 (1997) 246–251.
- [41] G.A. Knauer, J.H. Martin, R.M. Gordon, Nature 297 (1982) 49–51.
- [42] B. Venugopal, T.D. Luckey, A Metal Toxicity in Mammals, vol. 2, Plenum Press, New York, 1979.
- [43] J. Chen, K.C. Teo, Anal. Chim. Acta 434 (2001) 325–330.
- [44] K. Wladyslaw, M. Zofia, J. Anal. At. Spectrom. 13 (5) (1998) 363–369.
- [45] J. Ghasemi, A. Niazi, Microchem. J. 68 (2001) 1–11.
- [46] J. Yun, H. Choi, Talanta 52 (2000) 893–902.
- [47] Z.L. Ma, Y.P. Wang, C.X. Wang, F.Z. Miao, W.X. Ma, Talanta 44 (1997) 743–748.
- [48] Q. Ma, Q.E. Cao, Y. Zhao, S. Wu, Z. Hu, Q. Xu, Food Chem. 71 (2000) 123–127.
- [49] B.D. Ozturk, H. Filik, E. Tutem, R. Apak, Talanta 53 (2000) 263–269.
- [50] V.K. Gupta, Ak. K. Jain, M. Al Khayat, S.K. Bhargava, J.R. Raioni, Electrochim. Acta 53 (2008) 5409–5414.
- [51] A.K. Singh, R.P. Singh, P. Saxena, Sens. Actuators B 114 (2006) 578–583.
- [52] A.K. Singh, S. Mehtab, P. Saxena, Sens. Actuators B 115 (2007) 455–461.
- [53] N. Malcik, O. Oktar, M.E. Ozser, P. Caglar, L. Bushby, A. Vaughan, B. Kuswandi, R. Narayanaswamy, Sens. Actuators B 53 (1998) 211–221.
- [54] N.A. Yusof, M. Ahmad, Sens. Actuators B 86 (2002) 127–133.
- [55] E.K. Paleologos, M.I. Prodromidis, D.L. Giokas, A.C. Pappas, M.I. Karayannis, Anal. Chim. Acta 467 (2002) 205–215.
- [56] A.A. Ensafi, A. Aboutalebi, Sens. Actuators B 105 (2005) 479–483.
- [57] M. Benounis, N. Jaffrezic-Renault, H. Halouani, R. Lamartine, I. Dumazet-Bonnamour, Mater. Sci. Eng. C 26 (2006) 364–368.
- [58] N.A. Yusof, M. Ahmad, Spectrochim. Acta A 69 (2008) 413–418.
- [59] M. Shamsipur, M. Sadeghi, K. Alizadeh, H. Sharghi, R. Khalifeh, Anal. Chim. Acta 630 (2008) 57–66.
- [60] T.J. Svoronos, P.D.N. Svoronos, CRC Handbook of Basic Tables for Chemical Analysis, CRC Press, Boca Raton, 1989.