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Solid-contact Hg(II)-selective electrode based on a carbon-epoxy composite containing a new dithiophosphate-based ionophore

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ABSTRACT

The experimental results herein concern a novel ion-selective electrode manufactured with an inner solid contact based on a new ligand O,O′-(2,2′-biphenylene)dithiophosphate pentyl (PenDTF). This electrode displays high selectivity toward the Hg(II) ion even in the presence of different divalent ions. The electrode also exhibited a good Nernstian response to Hg(II) (33.7 ± 1.0 mV decade^{-1}) over an ample concentration range (5.3×10^{-7}–1.0×10^{-2} mol L^{-1}), with a detection limit of $(6.1 \pm 1.7) \times 10^{-7}$ mol L^{-1}. As a result of design, the electrode can be used for many experiments, simply renewing its contact surface with emery paper, without giving rise to a significant response deviation, exhibiting a variation coefficient of 3%, capable of being tested within the 0–5 pH interval. The electrode was used satisfactorily as indicating electrode during the potentiometric titration of Hg(II) ions with EDTA.

1. Introduction

Mercury is generally found at very low concentrations in the environment and can be easily absorbed by the human being and other living organisms [1,2], where its bioaccumulation is highly toxic for the kidneys, causing also neurological damages, paralysis and even problems during pregnancy. Further, it can be found in diverse chemical forms, although the elemental and the inorganic forms can be transformed through biological systems in the organic form in short-chained alkyl compounds, which are well known to be responsible of damages to the central nervous system [3]. From the middle ages, mercury salts have been widely used for various human activities. For instance in medicine, they have been used as ointments for skin and eyes. More recently, mercury compounds are used in diuretics, dental amalgams, antiseptics etc. [4–6].

Due to the considerable impact that the ion has on the environment and on human health, there exists an imperative necessity to develop new chemical methods for accurate determination [7,8] and effective removal [9,10] of small mercury concentrations.

There have been classical spectroscopy methods used for the determination of mercury, characterized for having a low detection limit, like atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS) and capillary electrophoresis, among others, although they are costly techniques that cannot be readily used in field analysis [11,12].

Among the different techniques within the analytical field for metal ions, electroanalysis is considered one of the most powerful ones; however, the use of conventional electrochemical cells and several voluminous electrodes, poses a problem for recording measurements in part due to a fairly large electrolyte solution volume required [13].

The potentiometric sensors offer several advantages such as: low cost, ease of fabrication, low detection limits, wide response range, reasonable selectivity, among others [14,15]. Diverse reports can be found in the literature concerning ion-selective electrodes (ISE) that used neutral ligands for Hg(II) detection, from which it becomes obvious that the contact surface configuration varies [16–19], as in some cases the ligand is encapsulated within a polymer membrane, to decrease its loss in the electrode. However, it has been found also that the surface undergoes irreversible damages when Hg(II) is added to the solution, which induces the wrong responses after each experiment [19].

From the first Hg(II) ion-selective electrode that was based on 1,4-dithio-12-crown-4 reported by Lai and Shih [20], other

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different ionophores have been synthesized and used for Hg(II) selective detection, ligands such as thiols [21], Schiff's bases [22], thioureas [23], and calixarene's derivatives [24], among others have been used under conditions where the nitrate ion (NO_3^-) was the predominant anionic species, due to the low solubility of the mercury species with counter ions different to nitrate.

It is known that Hg(II) shows significant affinity toward ligands containing sulfur atoms, which explains their successful use as ionophores for this metal; such affinity has been corroborated using DFT (Density Functional Theory) calculations [25,26].

This research work presents the potentiometric studies for Hg(II) detection with a new ion-selective electrode with an inner solid contact; the composite for its construction was a 1:1 epoxy resin/graphite mix, into which the ionophore O,O′-(2,2′-biphenylene)dithiophosphate pentyl (PenDTF) was mixed in. The electrode can be put to use immediately after every experiment during a given sequence, simply renewing its contact surface through controlled-grit size abrasive traditional treatment.

The chemical compound used as ionophore (PenDTF, see Fig. 1) was dithiophosphate-type, which has displayed, during extraction and transport studies, high selectivity to Hg(II) before different metal ions [27]. Chemically, the PenDTF ligand is a neutral compound bearing donating atoms like sulfur, with free electron pairs that can be coordinated to the metal ions; also this is a hydrophobic ligand, which favors the potentiometric studies in aqueous media. In view of the aforementioned, in this work a novel ISE electrode for the selective and quantitative determination of Hg(II) is presented.

2. Experimental

2.1. Reagents and solutions

All substances used were analytical grade reagents. The PenDTF compound was synthesized following the method reported in [28]. 2,2′-biphenol, toluene, 2-propanol anhydrous, phosphorus pentasulfide and 1-bromopentane were all from Sigma-Aldrich. Deionized water with 18 MΩ resistivity from a Milli-Q Millipore equipment was used to prepare all solutions. The support electrolyte solution was 1.0 mol L^{-1} $HClO_4$ (J.T. Baker) along with $Hg(NO_3)_2 \cdot H_2O$ (Merck) to prepare the corresponding ions solutions.

2.2. Electrode design and its potential measurements

Araldite M resin and hardener HY 5162 (Ciba–Geigy) were mixed in a small glass container, along with graphite and PenDTF ligand as indicated in Table 1; after mixing thoroughly all constituents until a homogeneous paste was achieved, a small portion was inserted in a PVC tube with an approximate 7 mm ID. A copper contact bar was placed centered in the paste to provide electrical connection, subsequently the device, Hg(II)-ISE-PenDTF, was left to rest for 24 h at 40 °C. Thereafter, the resulting electrode was immerse-conditioned in 1.0×10^{-3} mol L^{-1} $Hg(NO_3)_2$ for 5 min prior running each test.

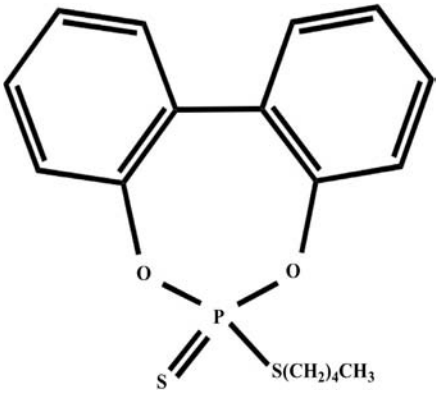

Fig. 1. Ligand structure O,O′-(2,2′-bifenilen)dithiophosphate pentyl (PenDTF).

The Hg(II) analysis was undertaken by means of chronopotentiometry at the null current potential using an Epsilon BASi EW-8111 potentiostat. A two-electrode set-up was used where the working electrode was that obtained mixing in the ligand PenDTF while a saturated Ag/AgCl (Metrohm 6.0736.110) worked as reference. All experiments were carried out with the aid of a conventional glass electrochemical cell holding 10 mL of 1.0 mol L^{-1} $HClO_4$ (J.T. Baker).

2.3. Potentiometric titration

Titrations of Hg(II) with ethylenediaminetetraacetic acid, EDTA (Sigma), were carried out using as working electrode a mercury cup electrode (M221Hg-9, Radiometer analytical) or the Hg(II)-ISE-PenDTF in acetate buffer prepared with acetic acid and sodium acetate (Baker Analyzed), along a reference electrode of Ag/AgCl (Metrohm 6.0736.110).

3. Results and discussion

3.1. Synthesis

PenDTF compound was synthesized following the method reported in [28], Fig. 2 shows the nuclear magnetic resonance spectrum (NMR) of ^1H in $CDCl_3$ at 25 °C: a NMR spectrometer Bruker DMX500 of 500 MHz was used to perform the characterization. The chemical shifts for the aliphatic part below; δ(ppm): 3.10 (dt, 2H, $^3J_{H-P}=$ 19.25 Hz), 1.78 (quintet, 2H, $CH_2{}^a$), 1.38 (m, 2H, $CH_2{}^b$), 1.38 (m, 2H, $CH_2{}^c$), and 0.89 (t, 3H, CH_3).

3.2. Optimization of the electrode's composition

It is paramount for ion selective electrodes, ISE, that the recognition element is included in their composition, as well as to control precisely the additives used to build them because most of the relevant analytic parameters, like sensitivity and selectivity, depend largely on their nature. Therefore, different aspects of their composition were optimized, like the influence of the composite composition over the potentiometric response of the electrode, which was analyzed by means of factorial design type 2^3 (two levels, three factors): the three factors analyzed were the resin, the hardener amount and the ionophore's concentration; the high level for each factor was 250, 100 and 20 mg whereas the low level per factor was 200, 50 and 10 mg, respectively, thus keeping constant the graphite amount in the composite. Table 1 shows the composition of the different electrodes built along with their analytic parameters. The potentiometric response of the sensors was tested within a wide Hg(II) concentrations range from 1.0×10^{-9} to 1.0×10^{-2} mol L^{-1} in 1.0 mol L^{-1} $HClO_4$. Each test was performed quintuplicate to ensure reproducible results; a variation ($n=5$).

From the data presented in Table 1 concerning the different electrodes for the Hg(II)-ISE-PenDTF, it becomes clear that electrode 1 is the best sensor since it exhibits the best analytic features, like the best Nernstian behavior, the best sensitivity and an ample linearity range (see Fig. 3), which constitute the main reasons for choosing it as the working electrode for subsequent experiments.

A comparison of the influence of individual factors on the response levels of the sensors, through the proposed factorial

Table 1
Factorial design applied to the electrode's composition.

Hg(II)-ISE-PenDTF[a]	Composition of the electrode (mg)				Slope (mV $decade^{-1}$)	LOD (mol L^{-1})	Linear interval (mol L^{-1})
	Graphite	**Resin**	**Hardener**	**Ionophore**			
1	350	250	100	20	**33.7 ± 1.0**	**$6.1 \times 10^{-7} \pm 1.7 \times 10^{-7}$**	**5.3×10^{-7}–1.0×10^{-2}**
2	350	250	50	20	146 ± 27	$2.4 \times 10^{-5} \pm 5.5 \times 10^{-6}$	5.0×10^{-5}–1.0×10^{-2}
3	350	200	50	20	100 ± 11	$6.7 \times 10^{-5} \pm 1.1 \times 10^{-5}$	9.2×10^{-5}–1.0×10^{-2}
4	350	200	50	10	71.0 ± 8.0	$2.3 \times 10^{-5} \pm 3.5 \times 10^{-6}$	5.0×10^{-5}–1.0×10^{-2}
5	350	200	100	10	32.0 ± 0.8	$1.9 \times 10^{-6} \pm 8.5 \times 10^{-7}$	3.6×10^{-6}–1.0×10^{-2}
6	350	250	100	10	38.0 ± 2.5	$1.6 \times 10^{-4} \pm 4.1 \times 10^{-5}$	1.8×10^{-4}–1.0×10^{-2}
7	350	200	100	20	21.4 ± 1.6	$1.0 \times 10^{-5} \pm 8.2 \times 10^{-7}$	1.6×10^{-5}–1.0×10^{-2}
8	350	250	50	10	94.5 ± 7.1	$2.0 \times 10^{-5} \pm 6.5 \times 10^{-6}$	5.0×10^{-5}–1.0×10^{-2}

[a] Hg(II)-ISE-PenDTF (ion- selective electrode Hg(II) based on PenDTF).

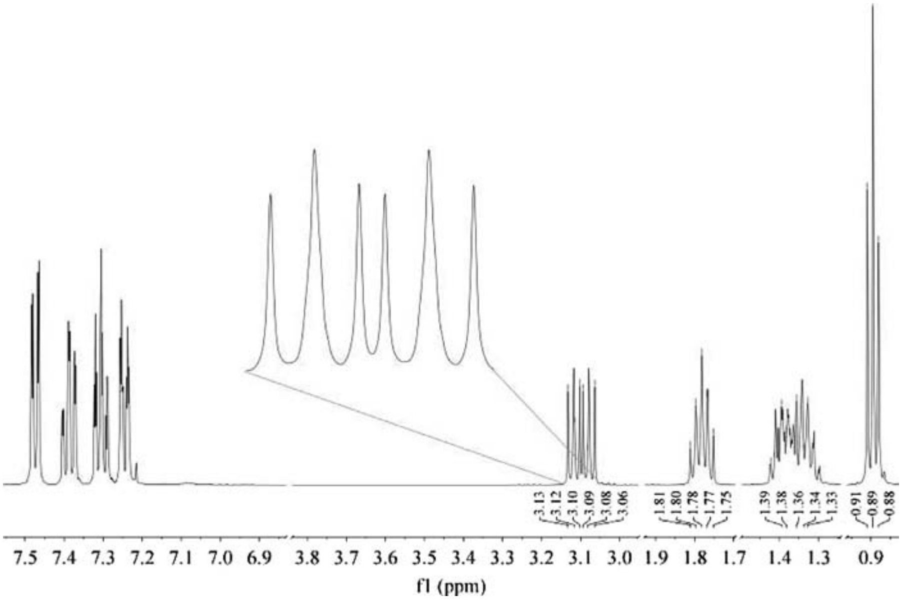

Fig. 2. ^{1}H NMR spectrum in $CDCl_3$ for PenDTF.

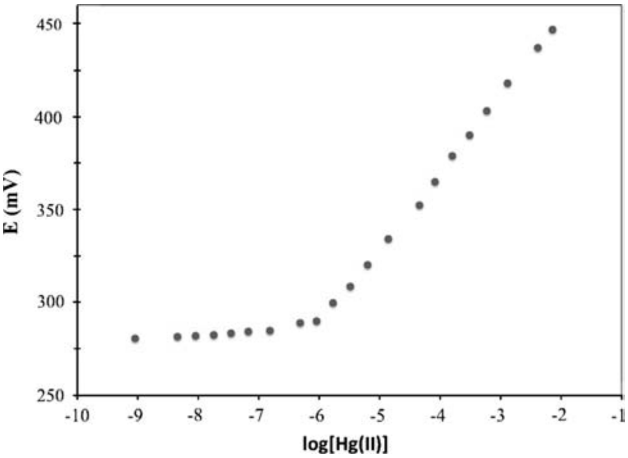

Fig. 3. Calibration curve of electrode Hg(II)-ISE-PenDTF 1.

design shows that for compositions 6 and 7, the ionophore is an important factor because the low level yields a concentration limit of detection (LOD, [29]) a decade lower with respect to the higher level. When comparing compositions 2, 3 and 8 a steep climb can be seen above those expected from the Nernst equation, that coincides with the low hardener level, focusing on the ionophore; meanwhile, the design shows that the lost slope level obtained is smaller than for the case of composition 8. Now, when comparing the sensors 1 and 5 that is where one gets the best analytical parameters; namely, that both ionophore levels have similar slopes, but with a decade fold the LOD concentration at the lowest level.

3.3. Effect of pH on potential response of electrode

The pH influence on the Hg(II)-ISE-PenDTF was determined using a 1.0×10^{-3} mol L^{-1} $Hg(NO_3)_2$ solution; the pH study was carried out in the 0–7 interval, adjusting the pH values required by adding a 1.0 mol L^{-1} HNO_3 solution along with 1.0 mol L^{-1} KOH: the results are shown in Fig. 4. As can be observed, the potential remained constant at low pH with a behavior similar to that observed with other types of ISEs [30,31]. The potential change at pH's above 5 can be due to formation of Hg(II) hydroxo complexes, see below. Thus, the 0–5 interval can be taken to be the working pH interval of the sensor propounded, as in this interval the sensor does not respond to H^+ ions, which agrees closely with previous studies [27], where the empirical tests showed formation of the Hg (II)-PenDTF complex at acid pHs.

3.4. Effect of renewal of the electrode surfaces by mechanical polishing

Due to the electrode design, see Section 2.2, its surface can be renewed by lightly abrading with emery paper; therefore, it becomes important to compare the calibration plots before and

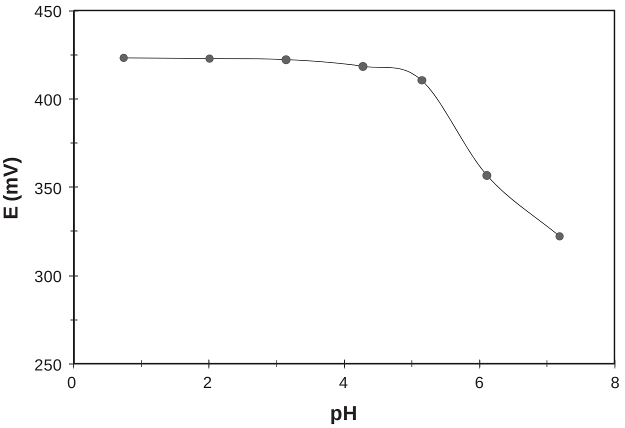

Fig. 4. Effect of pH on the electrode Hg(II)-ISE-PenDTF 1.

Table 2
Reproducibility of the electrode Hg(II)-ISE-PenDTF 1, as a function of the number of times that its surfaces was renewed by mechanical polishing, obtained from the calibration plots in Fig. 5.

Times that the surfaces was renewed	Slope (mV decade^{-1})	10^7 LOD (mol L^{-1})	Linear interval (mol L^{-1})
0	32.6 ± 0.5	6.9 ± 3.5	5.3×10^{-7}–0.01
1	34.5 ± 0.7	7.9 ± 3.4	5.3×10^{-7}–0.01
2	32.2 ± 0.4	6.8 ± 1.5	5.3×10^{-7}–0.01
3	34.6 ± 0.4	7.0 ± 3.5	5.3×10^{-7}–0.01
4	34.1 ± 0.5	4.2 ± 3.1	5.3×10^{-7}–0.01

after electrode renewal by abrasion. The potentiometric response of the sensors was tested within 1.0×10^{-9} to 1.0×10^{-2} mol L^{-1} Hg (II) concentrations range in 1.0 mol L^{-1} $HClO_4$, after several consecutive surface renewals. Table 2 summarizes the results found regarding the analytical features displayed by electrode Hg(II)-ISE-PenDTF 1. From these data it is possible to note that the average slope was 33.7 ± 1.0 mV decade^{-1} while the variation coefficient obtained was 3% for the linear part of the plots, see Fig. 5. From these results one may conclude that it is very recommendable to abrade the electrode previous to perform a Hg(II) quantification.

3.5. Selectivity

The most important characteristic of an ISE is its selective response capacity to a primary ion in the presence of other ions. This parameter is directly related to the thermodynamic equilibrium at the surface/solution interphase. The selectivity of the electrode containing the ligand PenDTF was tested by potentiometry with different divalent cations like: Ca(II), Ni(II), Cd(II), Mg (II), Cu(II), Co(II), Ba(II) and Hg(II), the slope assessment for the majority of cations tested showed values much lower than expected from Nernstian behavior; however, for the Hg(II) a linear potentiometric response was observed with a value closer to such behavior, within a wide concentration range and a low detectionc limit.

The potentiometric selectivity coefficient (as measured in terms of the potentiometric selectivity constant $K_{i,j}^{Pot}$) that describes the preference of the electrode suggested to an interfering ion in the presence of Hg(II), was determined by means of the fixed interference method, which is based on the Nikolsky-Eisenman semiempiric equation [29,32], as follows:

$$E_{\mathrm{ISE}} = E^0 + \frac{RT}{z_i F} \ln\left[a_i + \sum K_{i,j}^{Pot} a_j^{z_i/z_j}\right] \tag{1}$$

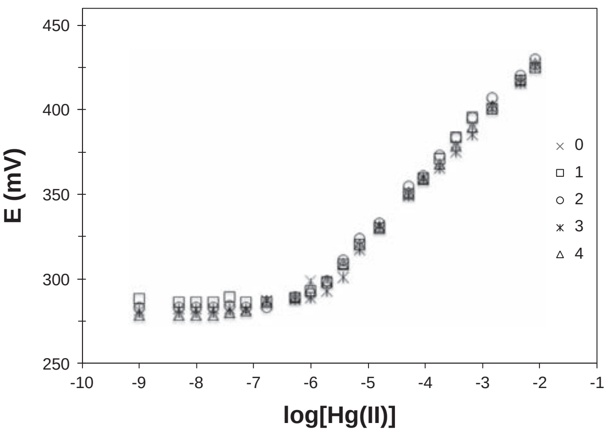

Fig. 5. Calibration curve of the electrode Hg(II)-ISE-PenDTF 1, as a function of the number of times, indicated in the Fig., that its surfaces was renewed by mechanical polishing.

Table 3
Potentiometric selectivity coefficient of various interfering ions $K_{\mathrm{Hg(II)},j}^{Pot}$.

Interfering ion	$K_{\mathrm{Hg(II)},j}^{Pot}$
Ba(II)	$2.6 \times 10^{-5} \pm 2.4 \times 10^{-6}$
Ca(II)	$6.3 \times 10^{-5} \pm 5.5 \times 10^{-6}$
Co(II)	$0.10 \times 10^{-5} \pm 1.5 \times 10^{-7}$
Mg(II)	$20 \times 10^{-5} \pm 2.7 \times 10^{-5}$
Cu(II)	$1.1 \times 10^{-5} \pm 8.4 \times 10^{-7}$
Cd(II)	$4.8 \times 10^{-5} \pm 2.9 \times 10^{-6}$
Ni(II)	$5.4 \times 10^{-5} \pm 5.3 \times 10^{-6}$

where E_{ISE} is the measured potential, E^0 the standard potential, a_i and a_j the activities of the primary and interfering ions, respectively, z_i the change of primary ion, z_j the change of the interfering ion, F the Faraday constant, R is the universal gas constant and T the absolute temperature. In this method, the primary ion concentration is varied in $HClO_4$ 1.0 mol L^{-1} solution whereas the secondary ion concentration is kept constant at 1.0×10^{-3} mol L^{-1}, the equations for each ion can be written as

$$E_i = E^0 + \frac{RT}{z_i F} \ln[a_i] \tag{2}$$

$$E_j = E^0 + \frac{RT}{z_i F} \ln\left[K_{i,j}^{Pot} a_j^{z_i/z_j}\right] \tag{3}$$

Equalizing the potentials one gets

$$K_{i,j}^{Pot} = \frac{a_i}{a_j^{z_i/z_j}} \tag{4}$$

Using the fixed interference method (FIM), the selectivity coefficients were calculated and are shown in Table 3.

From the $E_{\mathrm{Hg(II)\text{-}ISE\text{-}PenDTF}}$ vs. log[Hg(II)] plots and using the previous expression for $K_{i,j}^{Pot}$ the potentiometric selectivity coefficients were determined for various metal cations. As can be seen, for the majority of the cations used the selectivity coefficients values were smaller than 0.01, which indicate that the interference produced by these ions in the sensor's operation is negligible. The electrode's selectivity sequence with the ligand PenDTF with respect to different ions, follows the order Hg(II) > Mg(II) > Ca(II) > Ni(II) > Cd(II) > Ba(II) > Co(II) > Cu(II).

Electrodes formed by a carbon-epoxy matrix may display an anionic response due to the presence of anionic sites on its surface, which is undesirable for an ISE, thus, we examined the potentiometric response of the electrode Hg(II)-ISE-PenDTF 1 to different anions with different charges namely: COO^-, CO_3^{2-}, Cl^- and SO_4^{2-}. It was found that the electrode proposed here shows no change in potential at different concentrations of this sort of anions; therefore, in this case the inclusion of the PenDTF ionophore to the electrode composition may block or at least minimize this undesirable anionic response.

3.5.1. *Redox sensitivity*

In order to verify if the electrode Hg(II)-ISE-PenDTF 1 displays any redox sensitivity, it was immersed in an aqueous solution containing 2.0×10^{-3} mol L^{-1} Hg(II), at open circuit condition, during 48 h. No changes were observed in the solution or at the electrode surface. Moreover, two cyclic voltammetry experiments, not shown, were also performed in the systems: Hg(II)-ISE-PenDTF 1/2 mM Hg(II), 1 M $HClO_4$ and carbon-epoxy matrix/2 mM Hg(II), 1 M $HClO_4$. From these electrochemical experiments it was found that the presence of the ionophore in the ISE avoids the electrochemical reduction and oxidation of mercury in solution. From these experiments it is possible to conclude that the electrode Hg (II)-ISE-PenDTF 1 does not display any redox sensitivity.

3.6. *Analytic application*

3.6.1. *Potentiometric titration*

The Hg(II)-ISE-PenDTF was used as an indicating electrode during the potentiometric titration of 10 ml of an aqueous solution containing 1.0×10^{-3} mol L^{-1} $Hg(NO_3)_2$ using 1.0×10^{-2} mol L^{-1} EDTA (Y) as titrating solution, both at pH 0 and 4 with $HClO_4$. The resulting plots are presented in Fig. 6, where a protracted inflection point can be observed, which strongly suggests that the generalized titration reaction $Hg(II)' + Y' \Rightarrow Hg(II)Y'$, where the terms Hg(II)′, Y′ and Hg(II)Y′, that represent generalized species [33,34], are not quite quantitative.

Fig. 7 shows the predominance zone diagrams (PZD) of the generalized first order species Y′, see Fig. 7a, and Hg(II)′, Hg(II)Y′, see Fig. 7b, for the system $Hg(II)/H_2O/H^+$ and the existence predominance diagram (EPD) of the species of Hg(II), see Fig. 7c; these diagrams were constructed using the methodology described by Rojas-Hernández et al. [33,34], which allowed observing the species participating in the titration reaction, at pH = 0; therefore, it can be concluded that for pH = 0 the representative titration reaction is

$$Hg^{2+} + H_4Y \Rightarrow HgYH^- + 3H^+$$

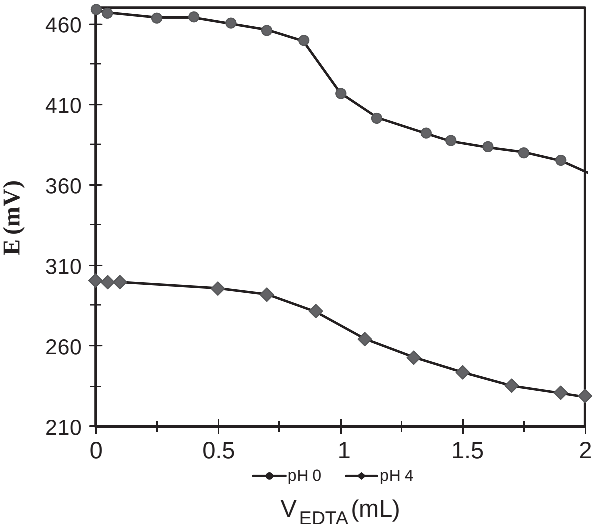

Fig. 6. Potentiometric titration plots of 10 mL of Hg^{2+} 1.0×10^{-3} mol L^{-1} solution with 1.0×10^{-2} mol L^{-1} of EDTA.

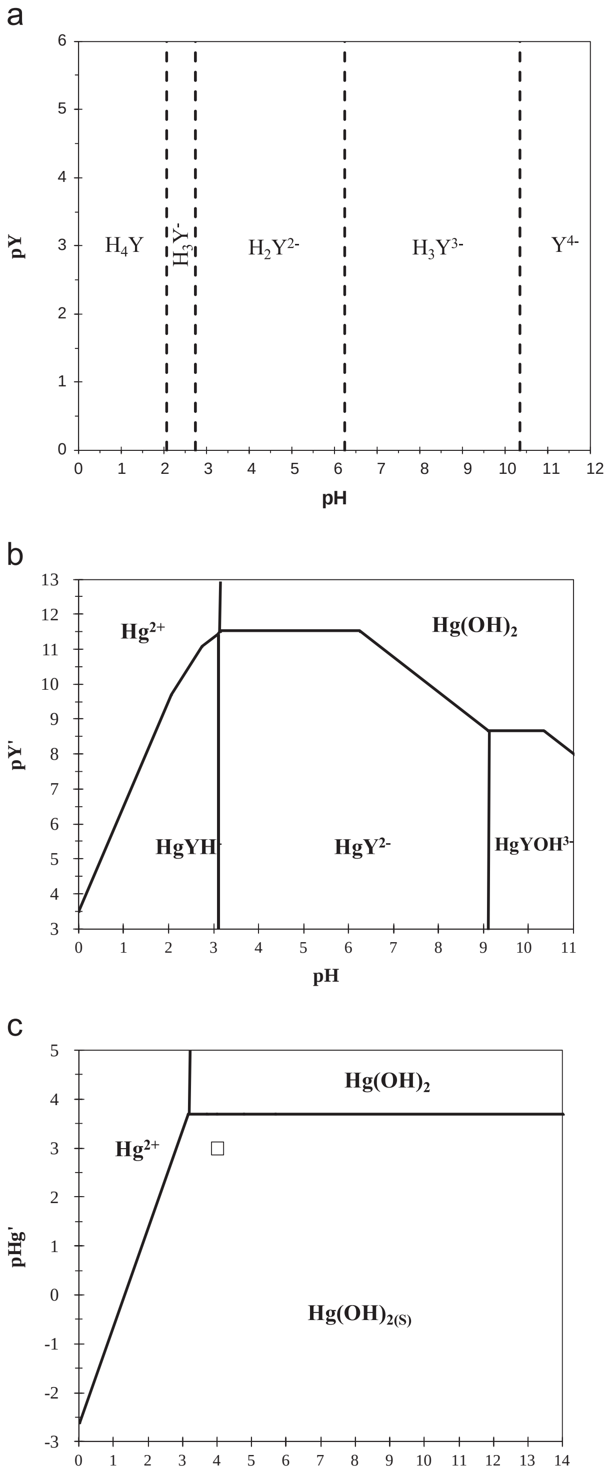

Fig. 7. Predominance zone diagrams (PZD) for the system $Hg(II)/H_2O$. (a) PZD for Y′, (b) PZD for Hg(II)′ and (c) existence predominance diagram (EPD), for Hg(II); the symbol □ represents the point (pH, pHg′) = (4, 3).

with $\log K_r' = 3.5$. Thus, in agreement with Ringbom [35], a reaction of this type is quantitative if $K_r'C_o \geq 10^5$ where C_o is the initial Hg(II) concentration. As in this case the $K_r'C_o = 10^{0.5}$, the reaction is not quantitative.

At pH 4, the representative titration reaction is

$$Hg(OH)_2 + H_2Y^{2-} \Rightarrow HgY^{2-} + 2H_2O$$

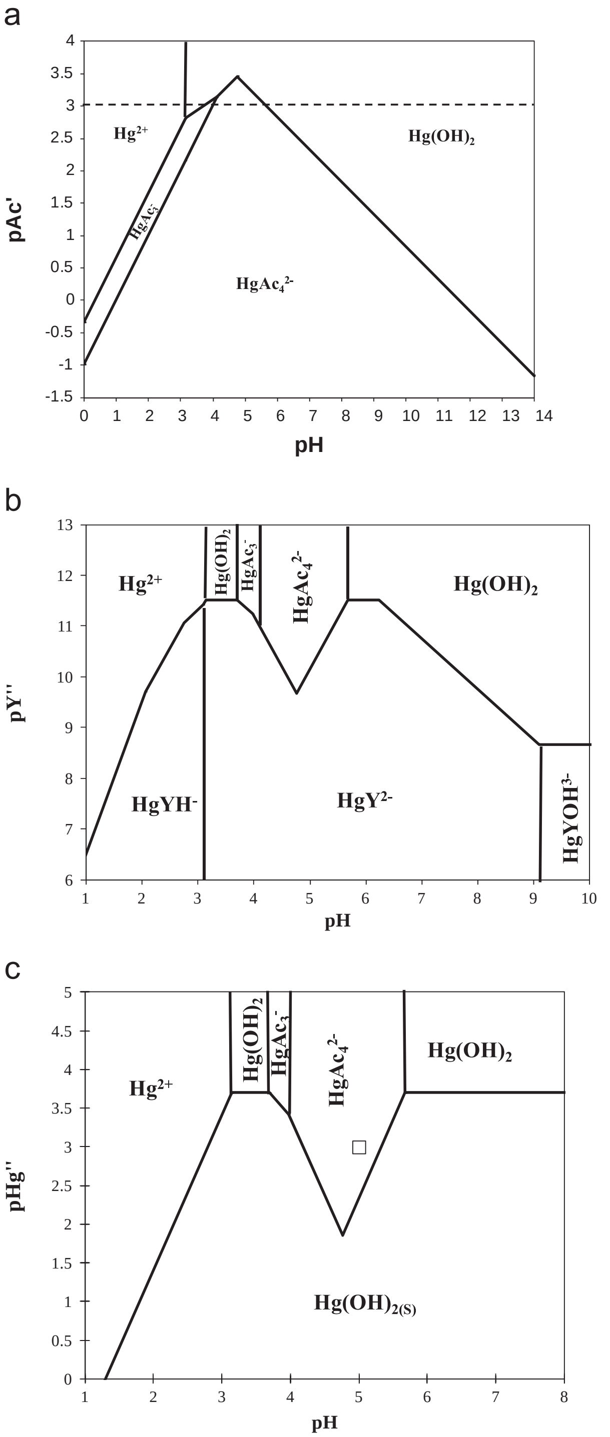

Fig. 8. Predominance zone diagrams (PZD) for the system Hg(II)/Ac/H_2O: (a) PZD for Hg″, the dotted line represents the cut pAc′=3, (b) PZD for HgY″ at pAc′=3.0 and (c) existence predominance diagram (EPD) for Hg(II) at pAc′=3, the symbol □ represents the point (pH, pHg″)=(5, 3).

which has a log $K'_r = 11.52$, when dealing with species in solution, however Fig. 7c shows the presence of the insoluble mercury hydroxide species, which disfavors the titration reaction and abates the reaction quantitativity.

Since the formation of Hg(II) insoluble species decreases the quantitativity of the reaction with EDTA titration, it becomes necessary to explore the possibility of increasing the mercury solubility, then the system Hg(II)/Ac/H_2O/H^+ was analyzed in order to establish the optimal conditions that guarantee the quantitativity of the mercury titration reaction with EDTA. Fig. 8 presents the PZDs of the generalized species at second order Hg(II)″, see Fig. 8a, and Hg(II)Y″, see Fig. 8b, for the system Hg(II)/Ac/H_2O/H^+; the horizontal dashed line in Fig. 8a indicates the first order buffering effect at pAc′=3.0.

Fig. 8c presents the EPD diagram of the Hg(II)″ species; this diagram was also built using the methodology described by Rojas-Hernández et al. [33,34]. From this diagram it can be preliminary concluded that the mercury hydroxide does not precipitate at pHg(II)″=3 after imposing a pH at 5.0 in the system with 1.0×10^{-3} mol L^{-1} HAc/Ac^- buffer.

From Figs. 7a and 8a and b it can be also concluded that the Y″=H_2Y^{2-}, Hg(II)″=$HgAc_4{}^{2-}$ and Hg(II)Y″=HgY^{2-}. This way, the Hg (II) representative titration reaction using EDTA at pH 5.0 imposed with 1.0×10^{-3} mol L^{-1} HAc/Ac^- buffer is

$$HgAc_4^{2-} + H_2Y^{2-} \Rightarrow HgY^{2-} + 4Ac^- + 2H^+$$

where the reaction constant is given by

$$K_r = \frac{[HgY^{2-}][AC^-]^4[H^+]^2}{[HgAc_4^{2-}][H_2Y^{2-}]}$$

If the concentration of acetate ions and protons is imposed, then K_r can be expressed as the biconditional constant K_r'' where $logK_r'' = -11.84 + 4pAc' + 2pH = 10.16$ and because in this case K_r'' $C_o = 10^{7.16}$, the reaction is quantitative.

The results of the Hg(II) titration are shown in Fig. 9. The titrant added caused a potential diminution as a result the Hg(II) ion concentration decreases due to formation of an EDTA complex. The Hg(II) ions quantity in solution can be determined precisely from the resulting titration plots, where from the volume obtained at the equivalence point was $0.97 \pm 6.0 \times 10^{-3}$ mL, this gives then a Hg(II) concentration of $(9.7 \pm 0.7) \times 10^{-5}$ mol L^{-1}.

Additionally, Fig. 9 shows the titration curve of the same concentration of Hg (II) and in the same conditions using a commercial mercury cup electrode: overlapping the curves shows the similarity of the equivalence points, indicating that the sensor proposed here can be used adequately for titration of Hg (II) ions.

3.7. Comparison with the literature

Table 4 shows some Hg(II) selective electrodes reported in the literature, where the type of compound used as recognition element can be found, the electrode configuration and some analytic parameters such as: their Nernstian response as well as the working interval, so that a good comparison can be established with the one

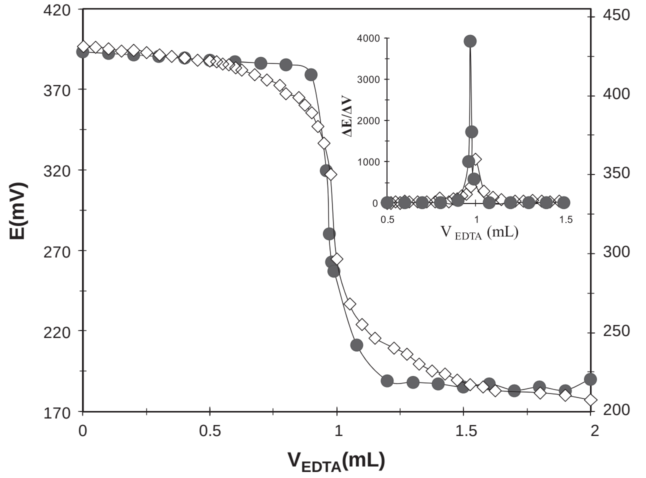

Fig. 9. Potentiometric titration curve of Hg^{2+} 1.0×10^{-3} mol L^{-1} 10 ml solution with 1.0×10^{-2} mol L^{-1} of EDTA. (●) Using the sensor Hg(II)-ISE-PenDTF 1 and (□) using a mercury cup electrode (secondary axis).

Table 4
Recent Hg(II)-selective electrodes proposed in the literature.

Ref.	Ionophore	Type of electrode	Slope (mV decade^{-1})	Linear interval (mol L^{-1})	pH range	Selectivity ($K^{Pot}_{\mathrm{Hg(II)},j}$)
[36]	Dithiophosphorus macrocyclic compound	Membrane	30.2	1.0×10^{-6}–1.0×10^{-1}	3.0–6.0	Pb^{2+}; 6.4×10^{-2}, Cd^{2+}; 6.2×10^{-3}, Ni^{2+}; 4.2×10^{-3}, Co^{2+}; 6.9×10^{-3}, Mg^{2+}; 7.3×10^{-4}, Fe^{2+}; 8.2×10^{-4}
[37]	Dibenzyl calix[4]arene-dithiacrown	Membrane	29.5	3.0×10^{-7}–3.0×10^{-2}	—	Cd^{2+}; 5.5×10^{-3}, Co^{2+}; 5.2×10^{-4}, Cu^{2+}; 4.1×10^{-4}, Ni^{2+}; 2.8×10^{-4}, Pb^{2+}; 7.4×10^{-3}, Zn^{2+}; 7.4×10^{-4}
[38]	8,17-bis(pyren-1-ylmethyl)-6,7,8,9,15,16,17,18-octahydrodibenzo[*f,m*][1,8,4,11] dithiodiazacyclotetradecine	Membrane	27.6	1.0×10^{-6}–1.0×10^{-2}	4.0–4.5	–
[39]	Benzothiazole azocalix[4]arene (BTC4)	Carbon paste	—	1.0×10^{-4}–1.0×10^{-2}	–	–
[40]	26,27,28-tris-benzyloxy-25-hydroxy-5,11,17,23-tetra-tert-butyl-calix[4]arene	Membrane	29.4	1.0×10^{-6}–1.0×10^{-1}	1.5–4.0	Ca^{2+}; 5.3×10^{-3}, Sr^{2+}; 3.8×10^{-4}, Ba^{2+}; 1.9×10^{-3}, Co^{2+}; 3.5×10^{-3}, Zn^{2+}; 1.3×10^{-3}, Pb^{2+}; 5.1×10^{-3}, Cd^{2+}; 4.7×10^{-3}, Ni^{2+}; 7.4×10^{-2}, Cu^{2+}; 5.9×10^{-3}, Sn^{2+}; 1.2×10^{-3}
[41]	N,N′-bis(pyridin-2-ylmethyl)-p-tert-butylcalix[4]arene-diaza-crown	Membrane	−27.8, −52.7	1.0×10^{-6}–1.0×10^{-2}	–	–
[42]	N,N′-bis(salicylaldehyde)-phenylendiamine	Membrane	58.8	3.2×10^{-7}–3.2×10^{-4}	3.8–7.8	Cd^{2+}; 2.3×10^{-3}, Mg^{2+}; 1.9×10^{-4}, Ca^{2+}; 6.1×10^{-4}, Ba^{2+}; 3.9×10^{-4}, Zn^{2+}; 2.2×10^{-3}, Ni^{2+}; 5.3×10^{-4}, Li^{2+}; 2.3×10^{-4}, Co^{2+}; 4.1×10^{-3}, Cu^{2+}; 1.4×10^{-1}, Pb^{2+}; 1.1×10^{-2}
[43]	1-furan-2-yl-4-(4-nitrophenyl)-2-phenyl-5H-imidazole-3-oxide	Membrane	29.3	1.0×10^{-5}–1.0×10^{-1}	1.0–4.0	–
[44]	1,3,bis(2-methoxybenzene) triazene (MBT)	Membrane	30.2	1.0×10^{-7}–1.0×10^{-2}	2.6–4.2	Zn^{2+}; 1.8×10^{-3}, Pb^{2+}; 3.8×10^{-3}, Ni^{2+}; 2.3×10^{-3}, Cd^{2+}; 5.8×10^{-3}, Mg^{2+}; 2.2×10^{-5}
[45]	Oxadiazaphosphepina derivatives	Membrane	29.4	1.0×10^{-6}–1.0×10^{-1}	0.9–4.5	–
This work	O,O′-(2,2′-bifenylen) dithiophosphate pentyl	Composite	33.7	5.3×10^{-7}–1.0×10^{-2}	0.0–5.0	Table 3

reported herein. The sensor proposed in this work presents useful advantages, not just in construction but also in actual working, as well as in synthesis of the recognition element. Because this is an inner solid contact electrode, hence an internal reference electrode is eliminated, just as the reference solution, thus facilitating construction, maintenance and ease of handling.

The sensor exhibits another relevant advantage with respect to those based on polymeric membranes found in the literature, regarding such components as the plasticizer and the ion exchanger that are essential to prepare the polymeric blend. Other comparative advantage of this electrode as referred to those based on polymeric membranes, is that if the latter were to suffer some damage or were contaminated, they would not be regenerated easily, whereas that reported here enables proper regeneration of the sensor's active sites on the surface, that may have gotten inactive or blocked, merely by lightly grinding away the surface in order to obtain a new set of fully available active sites. The ionophore used in this work is approximately 60 times less expensive to that of obtained as compared to the polymeric membranes of some of the sensors referred here [36,38–40], which have the added disadvantage of not showing better analytic parameters.

Lastly, comparing with other devices already reported that are not based on potentiometric measurements, the electrode herein proposed is even more advantageous because the synthesis routes of chromosensor compounds elevate the overall costs of sensors. Ref. [39] reports a chromosensor that is approximately 590 times more expensive to obtain, with respect to the recognition element used in the sensor reported here.

4. Conclusions

The electrode based on O,O′-(2,2′-biphenylene)dithiophosphate pentyl (PenDTF) showed a good Nernstian response for Hg(II) (even in the presence of divalent metal ions) within an ample concentration range. The applicable pH interval, lower detection limit, and potentiometric selectivity coefficients of the sensor, strongly suggest that the sensor propounded is comparable with those of other methods used for the determination of this ion, giving additional advantages with respect to other sensors proposed in the literature [35,37–39]. The sensor based on PenDTF exhibits different advantages like in the synthesis cost of the ionophore, in the design of the renewable inner solid contact that can be used for various experiments after light abrading and the elimination of the inner reference solution that turns the sensor maintenance-free, thus favoring safe storage. The sensor examined can be used as an indicator electrode in determining Hg(II) ions, since its response is comparable with commercial electrodes using the same principle.

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References

[1] S. Engst, S.M. Miller, Biochemistry 38 (1999) 3519–3529.
[2] H. Qian, L. Sahlman, P.O. Eriksson, C. Hambraeus, U. Edlund, I. Sethson, Biochemistry 37 (1998) 9316–9322.
[3] R.K. Mahajan, R. Kaur, V. Bhalla, M. Kumar, T. Hattori, S. Miyano, Sens. Actuators B 130 (2008) 290–294.

[4] I. Bontidean, A. Mortari, S. Leth, N.L. Brown, U. Karlson, M.M. Larsen, J. Vangronsveld, P. Corbisier, E. Csoregi, Environ. Pollut. 131 (2004) 255–262.

[5] J.L. Hobman, N.L. Brown, in: A. Sigel, H. Sigel (Eds.), Metal Ions in Biological Systems, Marcel Dekker, New York, 1997.

[6] J.L. Hobman, J.R. Wilson, N.L. Brown, D.R. Lovley, Environmental Microbe Metal Interactions, ASM Press, Herndon, 2000.

[7] R.D. Maeco, G. Clarke, B. Pejctc, Electroanalysis 19 (1987) 1987–2001.

[8] X. Yu, Z. Zhou, Y. Wang, Y. Liu, Q. Xie, D. Xiao, Sens. Actuators B 123 (2007) 352–358.

[9] M.E. Páez-Hernández, K. Aguilar-Arteaga, M. Valiente, M.T. Ramírez-Silva, M. Romero-Romo, M. Palomar-Pardavé, Anal. Bioanal. Chem. 380 (2004) 690–697.

[10] M.E. Páez-Hernández, K. Aguilar-Arteaga, C. Galán-Vidal, M.T. Ramírez-Silva, M. Romero-Romo, M. Palomar-Pardavé, Environ. Sci. Technol. 39 (2005) 7667–7670.

[11] Z.L. Peng, F. Qu, Q. Song, J.M. Lin, Electrophoresis 26 (2005) 3333–3340.

[12] H. Hintelmann, R.D. Evans, J.V. Villeneuve, J. Anal. At. Spectrom. 10 (1995) 619–624.

[13] I. Palchetti, S. Majid, A. Kicela, G. Marrazza, M. Mascini, Int. J. Environ. Anal. Chem. 83 (2003) 701–711.

[14] P. Buhlmann, E. Pretsch, E. Bakker, Chem. Rev. 98 (1998) 1593–1687.

[15] F. Bakhtiarzadeh, S.A. Ghani, J. Electroanal. Chem. 624 (2008) 139–143.

[16] V.K. Gupta, S. Chandra, H. Lang, Talanta 66 (2005) 575–580.

[17] A.K. Singh, R.P. Singh, S. Mehtab, J. Inclusion Phenom. Macrocycl. Chem. 60 (2008) 9–15.

[18] A.A. Khan, T. Akhtar Inamuddin, Anal. Sci. 24 (2008) 881–887.

[19] N. Fiol, F. de la Torre, P. Demeyere, A. Florido, I. Villaescusa, Sens. Actuators B 122 (2007) 187–194.

[20] M.T. Lai, J.S. Shih, Analyst 111 (1986) 891–895.

[21] V.K. Gupta, A.K. Singh, A. Al Khayat, B. Gupta, Anal. Chim. Acta 590 (2007) 81–90.

[22] R.K. Mahajan, I. Kaur, T.S. Lobana, Talanta 59 (2003) 101–105.

[23] L. Perez-Marin, E. Otazo-Sanchez, G. Macedo-Miranda, P. Avila-Perez, J. A. Chamaro, H.L. Lopez-Valdivia, Analyst 125 (2000) 1787–1790.

[24] R.K. Mahajan, R. Kaur, I. Kaur, V. Sharma, M. Kumar, Anal. Sci. 20 (2004) 811–814.

[25] M. Castro, J. Cruz, E. Otazo, L.P. Marın, J. Phys. Chem. A 107 (2003) 9000–9007.

[26] L.P. Marın, M. Castro, E. Otazo, G.A. Cisneros, Int. J. Quantum Chem. 80 (2000) 609–622.

[27] F. Pérez-García, C.A. Galán-Vidal, J.G. Albarado-Rodríguez, M.E. Páez-Hernández, N. Andrade-López, M.T. Ramírez-Silva, Sep. Sci. Technol. 48 (2013) 736–740.

[28] F. Pérez-García, J.G. Albarado-Rodríguez, C.A. Galán-Vidal, M.E. Páez-Hernández, N. Andrade-López, Struct. Chem. 21 (2010) 191–196.

[29] IUPAC, Pure Appl. Chem. 48 (1976) 127–142.

[30] M.H. Mashhadizadeh, M. Talakesh, M. Peste, A. Momeni, H. Hamidian, M. Mazlumd, Electroanalysis 18 (2006) 2174–2179.

[31] R.K. Mahajan, R.K. Puri, A. Marwaha, I. Kaur, M.P. Mahajan, J. Hazard. Mater. 167 (2009) 237–243.

[32] Y. Umezawa, K. Umezawa, H. Sato, Pure Appl. Chem. 67 (1995) 507–518.

[33] A. Rojas Hernández, M.T. Ramírez Silva, J.G. Ibañez, I. González, J. Electrochem. Soc. 138 (2) (1991) 365–371.

[34] A. Rojas-Hernández, M.T. Ramírez-Silva, I. González, J.G. Ibañez., Anal. Chim. Acta 246 (1991) 435–441.

[35] A. Ringbom, Formación de Complejos en Química Analítica, Alhambra, Madrid, 1979.

[36] B. Patel, A. Kumar, S.K. Menon, J. Inclusion Phenom Macrocyclic Chem. 64 (2009) 101–108.

[37] Y. Yang, X. Cao, M. Surowiec, R.A. Bartsch, Tetrahedron 66 (2010) 447–454.

[38] B. Palkiran, A.D. Ozel, S. Palayan, E. Canel, U. Ocak, E. Kilic, Monatsh. Chem. 141 (2010) 829–839.

[39] H. Bingol, E. Kocabas, E. Zor, A. Coskum, Talanta 82 (2010) 1538–1542.

[40] M. Hosseine, M. Rahimi, H.B. Sodeghi, Int. J. Environ. Anal. Chem. 89 (2009) 407–422.

[41] Y. Kim, J. Kim, K.N. Kim, S. Chang, T.D. Chung, Anal. Sci. 25 (2009) 567–570.

[42] H.M. Abu.Shawish, J. Hazard. Mater. 167 (2009) 602–608.

[43] R.K. Mahan, R.K. Puri, A. Marwaha, I. Kaur, M.P. Mahajan, J. Hazard. Mater. 167 (2009) 237–243.

[44] M.K. Rofouei, M. Mohammadi, M.B. Gholivand, Mater. Sci. Eng. 29 (2009) 2154–2159.

[45] R.K. Puri, V. Kumar, M.P. Mahajan, R.K. Mahajan, J. Inclusion Phenom. Macrocyclic Chem. 69 (2011) 263–271.