



Lead(II) ion selective electrodes with PVC membranes based on two bis-thioureas as ionophores: 1,3-bis(*N'*-benzoylthioureido)benzene and 1,3-bis(*N'*-furoylthioureido)benzene

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ABSTRACT

Two PVC membrane ion selective electrodes for Pb(II) ion based on two bis-thioureas: 1,3-bis(*N'*-benzoylthioureido)benzene and 1,3-bis(*N'*-furoylthioureido)benzene as ionophores, are reported. A first membrane formulated using 1,3-bis(*N'*-benzoylthioureido)benzene as carrier exhibited a Nernstian response to Pb(II) over a wide concentration range (4.0×10^{-6} to 1.0×10^{-2} M) with a slope of 31.5 ± 1.6 mV/dec. It showed a fast response time ($t_{90\%} = 14$ s) and could be used for 10 weeks without any divergence in potentials. The membrane formulated using 1,3-bis(*N'*-furoylthioureido)benzene as carrier exhibited a Nernstian response in the concentration range (5.0×10^{-6} to 1.0×10^{-2} M), with a slope of 30.0 ± 1.3 mV/dec. Its response time was $t_{90\%} = 14$ s, and it could be used for 14 weeks without any divergence in potentials. The two proposed potentiometric sensors revealed acceptable selectivities for Pb(II) over a wide variety of other metal ions and could be used in a pH range of 2.2–6.0. Both electrodes were assayed in direct potentiometric determination of lead in soils (10–30 mg/kg range) with very good performance (0.99935 correlation coefficient in the comparison against ICP-MS method).

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1. Introduction

Nowadays, there is a growing interest on research directed to the automation of environmental control, industrial processes and clinical analysis in the medicine field. This progress has encouraged the development of materials for the recognition and sensing of highly pollutant chemical species, such as the heavy metals, which may harm different ecosystems and, in general, the human health.

In this sense, thiourea derivatives are a versatile family of ligands able to form complexes with transition metals and post-transition metals, such as: Ni(II), Cu(II/I), Co(III), Zn(II), Ag(I), Cd(II), Pt(II), Pd(II), Au(III), Rh(III), Re(III), Tc(III), Pb(II), Sb(III), and Bi(III) [1–3]. Coordination chemistry of thiourea derivatives is diverse; they contain S and N atoms which are donor sites available to coordinate with metal ions, but also present specific effects caused by the conformational isomerism, steric hindrance, presence of donor sites in the substituent groups or existence of intra-molecular interactions. This versatility as ligands has fostered the use of thiourea derivatives towards new applications in the field of chemical sensors.

When examining the scientific literature, a number of contributions appear about this topic. Otazo et al. described 46 thiourea derivatives as potential ionophores for ion selective electrodes (ISEs). Some of these were used in potentiometric sensors for heavy metals Pb(II), Cd(II) and Hg(II) [4]. The use of thiourea derivatives was also proposed in the voltammetric determination of Pd(II) and Cd(II) [5,6]. A very recent contribution of Singh et al. described a polymeric membrane electrode with a thiourea derivative as ionophore in the determination of ytterbium with a very low detection limit (5.5×10^{-8} M) [7].

Thiourea derivatives have been generally used in cation selective electrodes by their well known property of forming complex with metal ions. Opposite to this, there are some reports where the thiourea derivatives are used as neutral carriers in selective electrodes for anions [8,9]. Besides, compounds with bis-thiourea functional groups called podands (two arms) have been described in anion selective electrodes [8,9]; podands fundament their interaction on the complex formation with anions through hydrogen bonds [10].

In our case, the possibility that bis-thioureas may be forming complexes with heavy metals is an alternative which has not been sufficiently explored but constitutes an interesting option to obtain ISEs for heavy metals with good performance. Some reports show that molecules with bis-amide and bis-thioamide functional groups

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[11–15] may be employed as ionophores in the determination of Cd(II) and Pb(II).

In this work, it is presented the synthesis and characterization of two new bis-thioureas 1,3-bis(*N'*-benzoylthioureido)benzene (BTB) and 1,3-bis(*N'*-furoylthioureido)benzene (FTB), and their performance results as ionophores in polymeric membrane electrode for heavy metals, specifically Pb(II), Cu(II), Cd(II) and Zn(II). Besides, the detailed application of the proposed sensors in the determination of Pb(II) in a polluted soil sample is described and validated.

2. Experimental

2.1. Reagents

The reagents employed in the bis-thiourea synthesis were ammonium thiocyanate (Sigma–Aldrich), *m*-phenylenediamine (Aldrich), furoyl chloride (Fluka), benzoyl chloride (Sigma–Aldrich). The solvents acetone (Panreac), tetrahydrofuran (THF, Fluka), methanol (Panreac), benzene and chloroform (J.T. Baker). The ion selective poly(vinyl chloride) (PVC) membranes were prepared from high-molecular weight PVC (Fluka), using dioctyl sebacate (DOS) and *o*-nitrophenyloctyl ether (*o*-NPOE) (both from Fluka) as plasticizers. The additive used was potassium tetrakis(4-chlorophenyl)borate (KpClPB) (Fluka). The materials used to prepare the solid electrical contact were the epoxy resin components: Araldite M, Araldite M hardener, Araldite M accelerator, dibutyl phthalate (all from Fluka), and graphite powder (BDH, UK) as conductive filler. Other reagents used were of analytical grade; solutions were prepared in doubly distilled water.

2.2. Apparatus

Infrared (IR) spectra were recorded on a spectrophotometer (Tensor 27, Bruker, Germany) in the range of 4000–400 cm^{-1} with Golden Gate attenuated total reflectance (ATR). Mass spectrometry (MS) was performed using ion trap mass spectrometry with electrospray ionization (Esquire 3000, Bruker, Germany). The elemental analysis (EA) was performed using Elemental Analyzer CHNS (3011, EuroVector, Italy). The reference method for lead soil determination were made employing ICP-MS equipment (Agilent 7500ce, Santa Clara, CA).

The emf measurements were performed with a laboratory-made data acquisition system consisting of 32 input channels made with differential instrumentation amplifiers (INA116, Burr-Brown, USA) that adapted the impedance for each sensor. Emf measurements were performed against a double junction Ag/AgCl reference electrode (Thermo Orion 90-02-00). Each channel was noise-shielded with its signal guard. The output of each amplified channel was filtered with a second order low pass active filter centred at a 2 Hz frequency and connected to an Advantech PC-Lab 813 A/D conversion card installed in a PC. Readings were acquired by using custom software developed by our group in Microsoft QuickBasic Version 4.5.

2.3. Synthesis of ionophores

To a mixture of 25 mmol (1.903 g) of ammonium thiocyanate and 25 mL of acetone, a solution formed by 25 mmol (2.897 g) of benzoyl chloride or 2.460 g of furoyl chloride) in 13 mL of acetone was added dropwise. The resulting mixture was stirred under reflux for 1 h and cooled to room temperature. A solution of 12.5 mmol (2.460 g) of 1,3-diaminobenzene in 5 mL of acetone was then added. The solution obtained was stirred at room temperature during 2 h. After cooling, the reaction mixture was poured slowly into 600 mL

of iced water with strong stirring. The bis-thiourea precipitated was filtered and washed with 3×50 mL of water and vacuum dried. For the recrystallization, a mixture of methanol:chloroform (1:1) was employed for (FTB) and THF for (BTB) [4,16]. The purity was tested by TLC using benzene–chloroform (90:10) as solvent.

2.4. Characterization of bis-thioureas

The structures of bis-thioureas were established through Spectroscopic techniques (IR, ^1H NMR), mass spectrometry (MS) and elemental analysis (EA). The molecular weight values and qualitative analysis data correspond favourably with those expected. In the IR a large number of signals are observed with pronounced overlapping resulting in relatively complex spectra. In the study of thiourea derivatives using IR spectroscopy, usually a set of fundamentals involving the N–C and C=S bonds are identified and can be used as indicators of the electronic structure around these bonds. In compounds containing the thioamide group (HNCS) these fundamentals are known as “thioamide” bands: I, II, III and IV [17,18]. These bands have a large contribution from $\nu(\text{C–N}) + \delta(\text{NH})$ (I), $\nu(\text{C–N}) + \nu(\text{C=S})$ (II and III) and $\nu(\text{C=S})$ (IV) motions and are usually reported around 1470, 1250, 1080 and 750 cm^{-1} , respectively [18].

2.5. PVC membranes and sensors

Potentiometric sensors used were all-solid-state ion selective electrodes (ISEs) with a solid electrical contact made from a conductive composite. They were constructed by following a standard procedure developed in our laboratory [19]. Polymeric PVC membranes were formed by solvent casting of a membrane cocktail further diluted with THF (1 mL per 20 mg PVC) on a previously formed 1:1 epoxy–graphite composite solid contact. Membranes were dried and conditioned in a 0.1 M solution of their primary ion for 24 h before use.

2.6. Evaluation of potentiometric response

Sensor calibration consisted on the recording of potential after accumulated microadditions of concentrated primary ion solution over a fixed initial volume. The detection limit (LD) was taken as the intersection of the two asymptotic behaviours of the calibration curve, as recommended by IUPAC [20]. Reproducibility was examined by repeated monitoring of the slope and the LD of calibration curve. The activity coefficients of ions in solution were calculated according to the Debye–Hückel formalism [21]. Selectivity characteristics were determined according to the IUPAC recommended fixed interference method [22] (FIM). pH influence, determined as the Reilley diagram [23] was recorded in a NaOH solution at two concentration of $\text{Pb}(\text{NO}_3)_2$ solution (of 1.0×10^{-3} and 1.0×10^{-4} M) varying the pH from 10 to 2 with HNO_3 . The response time ($t_{90\%}$) of tested sensors was determined as the time required to achieve 90% of steady potential [24] corresponding to four additions of primary ion, when the concentrations were rapidly increased by 1 dec.

2.7. Lead soil determination

For lead soil determination, 4 g of soil were placed in a 100 mL round bottom flask with 31 mL concentrated nitric acid (65%). After fitting a water condenser, the mixture was heated to boiling until the volume was reduced to 10 mL. 25 mL of water were next added down the condenser before filtration of the mixture. The filtered residue was rinsed twice with 5 mL of water, reunited with the extract, and then diluted with deionized water to mark of volumetric flask. The lead content was measured using the proposed

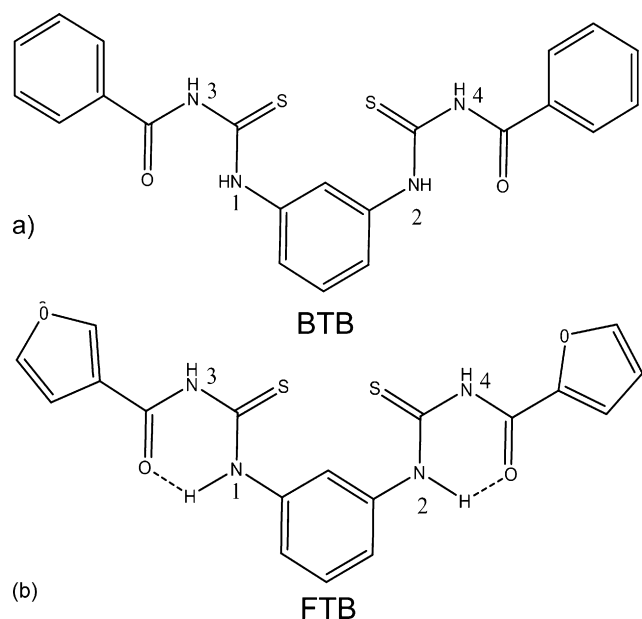


Fig. 1. Structure of bis-thioureas used as ionophores. (a) 1,3-bis(*N*-benzoylthioureido)benzene (BTB) and (b) 1,3-bis(*N*-furoylthioureido)benzene (FTB).

Pb(II)-sensors and also by inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and discussion

3.1. Synthesis and characterization of bis-thioureas

The bis-thioureas suggested as ionophores (Fig. 1) have as clear advantage a quick and easy synthesis and purification. They contain furoyl, or benzoyl groups to increase their lipophilicity, a desired feature to promote their solubility in the polymeric membrane and to prevent leaching to the aqueous solutions tested. Besides, the different coordination sites (N, O and S) in specific geometry and with different chemical hardness can influence selectivity towards different metals. Table 1 shows the main data of the synthesis and characterization of both compounds. Good yields were obtained of 79.2 and 84.9% for FTB and BTB, respectively.

The main IR bands have been identified and Table 1 shows their frequency values. The stretches of N–H groups vibrations at 3322 and 3271 cm^{-1} for BTB and FTB, respectively. Carbonyl vibration $\nu(\text{C}=\text{O})$ detected to 1666 cm^{-1} for BTB and 1667 cm^{-1} for FTB. There is a shift of these bands to shorter wavelengths than expected; this is attributed by several authors [4,16,25] to the formation of intramolecular hydrogen bonds (Fig. 1b). In this configuration the S atom is arranged outside the molecule preventing the formation of very stable chelates.

Table 1
Characterization of the bis-thioureas synthesized.

Ionophore	Yield (%)	m.p. ($^{\circ}\text{C}$)	Chemical formula	Mass spectrum m/z (M^+)	Elemental analysis	IR	^1H NMR (DMSO- d_6)
BTB	84.9	218 \pm 2	$\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2$ (434.5)	434.1	Calculated: C, 60.81; H, 4.18; N, 12.89; S, 14.76. Found: C, 59.07; H, 4.05; N, 12.05; S, 14.32.	ν 3322 (NH), 1666 (C=O), 1523 (I), 1260 (II), 1142 (III), 738 (IV)	6.48–8.22 (m, 14H, arom. H), 11.32 (s, 2H, 2NH), 12.20 (s, 2H, 2NH)
FTB	79.2	226 \pm 2	$\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}_4\text{S}_2$ (414.5)	413.1	Calculated: C, 52.16; H, 3.40; N, 13.52; S, 15.47. Found: C, 51.97; H, 3.35; N, 13.55; S, 15.32.	ν 3271 (NH), 1667 (C=O), 1518 (I), 1237 (II), 1073 (III), 752 (IV)	6.45–8.13 (m, 10H, arom. H), 11.21 (s, 2H, 2NH), 12.11 (s, 2H, 2NH)

In 1523 cm^{-1} (BTB) and 1518 cm^{-1} (FTB) a medium intensity band appears thioureido band I, thioureido band II observed at 1260 and 1237 cm^{-1} for BTB and FTB, respectively, thioureido band III at 1142 cm^{-1} for BTB and 1073 cm^{-1} for FTB, and thioureido band IV at 738 and 752 cm^{-1} for BTB and FTB, respectively.

In the ^1H NMR spectra of both compounds, 3 main groups of signals are observed: two D_2O exchangeable singlets were assigned to NH protons and a multiplet corresponding to aromatic protons. The most deshielded signal ($\delta = 12.20$ and 12.11 ppm for BTB and FTB, respectively) was assigned to N (3)H and N (4)H. This chemical shift is that high because these protons form hydrogen bonds [4,16,25]. This was demonstrated by a correlation analysis of δ NH in DMSO- d_6 vs. σ Hammett and by addition of europium (III) in CDCl_3 [26]. The signal assigned to protons N (1)H and N (2)H was found at $\delta = 11.32$ ppm and at 11.21 ppm for BTB and FTB, respectively. The presence of 2 NH residues confirms the formation of bis-thiourea derivatives. Between $\delta = 6$ ppm and 8.3 ppm multiplets were found and were assigned to aromatic protons in both compounds.

3.2. Optimization of the membrane composition

ISEs employing PVC membranes based on BTB and FTB as neutral ionophore were found to be highly responsive to Pb(II) in respect to several other cations. Therefore, the performance of the electrodes for lead ions was firstly studied in detail. In order to test the ISE performance, several characteristics were investigated, including: selectivity, response time, sensitivity, lifetime, working pH range of the electrode at different concentrations of the metal ion, and the effect of the membrane composition.

It is well known that the sensitivity and selectivity obtained for a given ionophore depend significantly on the membrane composition and the nature of plasticizer and additives used [27,28]. Several membrane compositions were investigated by varying the ratio of plasticizers and ionophores (BTB and FTB). The potentiometric response of the membrane was greatly improved with minute amounts of lipophilic anionic additive, KpClPB.

Among the different compositions studied (Table 2), the membrane incorporating 33.0% PVC, 61.5% DOS, 0.5% KpClPB and 5.0% BTB exhibited the better Nernstian response. Also, the sensor 4 employing 8% BTB (Table 2) showed good response, but presenting strong potassium interference due to high concentration of the additive KpClPB. For FTB ionophore the best result was obtained with 33.0% PVC, 64.7% DOS, 0.3% KpClPB and 2.0% FTB. Both membranes had a preferential Pb(II) response, as demonstrated when performing different single ion calibration towards different heavy metals. Fig. 2 shows the calibration curve against Cu(II), Cd(II), Zn(II) and Pb(II). All measurements were made under the same conditions and after conditioning in the corresponding ions. Two are the electrodes that can be identified in the figure with responses close to the Nernstian behaviour, these are: the electrode containing BTB (31.5 ± 1.6 mV/dec) from 4.0×10^{-6} to 1.0×10^{-2} M Pb^{2+} , and

Table 2

Optimization of the selective membrane formulation.

No.	Ionophore (%)		Plasticizer (%)		KpCIPB (%)	PVC (%)	Slope (mV/dec)	Linear range (M)
	BTB	FTB	DOS	<i>o</i> -NPOE				
1	2.0	–	65.0	–	0.0	33.0	20.2 ± 3.2	2.0 × 10 ⁻⁵ to 1.0 × 10 ⁻²
2	2.0	–	64.7	–	0.3	33.0	24.2 ± 3.2	4.0 × 10 ⁻⁶ to 1.0 × 10 ⁻²
3	5.0	–	61.5	–	0.5	33.0	31.5 ± 1.6	4.0 × 10 ⁻⁶ to 1.0 × 10 ⁻²
4	8.0	–	58.0	–	2.0	33.0	30.6 ± 2.3	1.0 × 10 ⁻⁶ to 1.0 × 10 ⁻²
5	2.0	–	–	65.0	0.0	33.0	16.2 ± 3.2	8.0 × 10 ⁻⁵ to 1.0 × 10 ⁻²
6	2.0	–	–	64.7	0.3	33.0	19.9 ± 2.2	2.0 × 10 ⁻⁵ to 1.0 × 10 ⁻²
7	5.0	–	–	61.5	0.5	33.0	22.3 ± 1.5	6.0 × 10 ⁻⁶ to 1.0 × 10 ⁻³
8	8.0	–	–	58.0	2.0	33.0	24.5 ± 3.0	9.0 × 10 ⁻⁶ to 1.0 × 10 ⁻³
9	–	2.0	65.0	–	0.0	33.0	14.5 ± 3.1	1.0 × 10 ⁻⁵ to 1.0 × 10 ⁻²
10	–	2.0	64.7	–	0.3	33.0	30.0 ± 1.3	5.0 × 10 ⁻⁶ to 1.0 × 10 ⁻²
11	–	5.0	61.5	–	0.5	33.0	26.3 ± 1.4	9.0 × 10 ⁻⁶ to 1.0 × 10 ⁻²
12	–	8.0	58.0	–	2.0	33.0	24.5 ± 2.5	3.0 × 10 ⁻⁶ to 1.0 × 10 ⁻²
13	–	2.0	–	65	0.0	33.0	15.9 ± 3.1	8.0 × 10 ⁻⁵ to 1.0 × 10 ⁻³
14	–	2.0	–	64.7	0.3	33.0	19.9 ± 3.1	8.0 × 10 ⁻⁵ to 1.0 × 10 ⁻³
15	–	5.0	–	61.5	0.5	33.0	21.4 ± 2.3	9.0 × 10 ⁻⁵ to 1.0 × 10 ⁻³
16	–	8.0	–	58.0	2.0	33.0	20.5 ± 3.3	8.0 × 10 ⁻⁵ to 1.0 × 10 ⁻³

the electrode containing FTB (30.0 ± 1.3 mV/dec) from 5.0 × 10⁻⁶ to 1.0 × 10⁻² M Pb²⁺.

3.3. Performance of sensors

For analytical applications, specially if in automated operation, the response time of a sensor is an important feature. Fig. 3 shows the measured potentials of the proposed sensors corresponding to four decade additions of Pb(NO₃)₂ solution, from the background till 10⁻³ M. The transient response observed for the one-decade step concentration changes had the typical exponential profile in all the cases. The response time (*t*_{90%}) for the two proposed electrodes were 14 s for the wide concentration range (10⁻⁵ to 10⁻² M Pb²⁺) and 22 s for 10⁻⁶ M Pb²⁺.

The effect of pH of the test solution on the response of the two best electrodes was examined at two Pb(II) concentrations (1.0 × 10⁻³ and 1.0 × 10⁻⁴ M). This study showed the range of pH 2.6–6.8 for BTB membrane, and 2.4–6.0 for FTB membrane, where sensitivities maintained a constant value close to 30 mV/dec. At higher pH's, sensitivity decreased down to 23 mV/dec for both membranes. As illustrated in Fig. 4, for 1.0 × 10⁻³ M Pb²⁺, responses

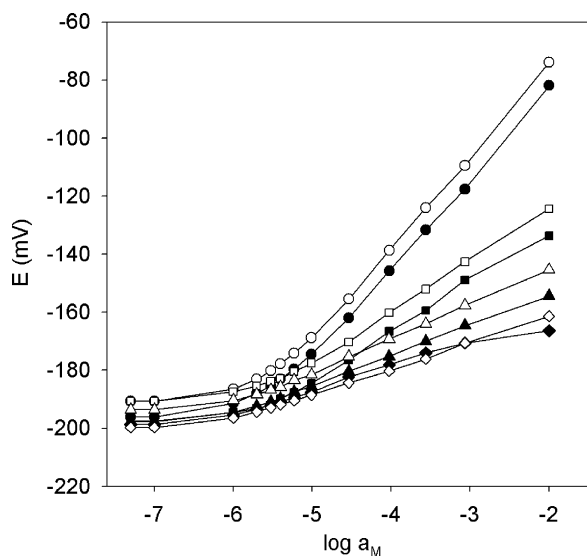


Fig. 2. Emf response of ion-selective electrodes based on BTB and FTB with Pb²⁺, Cu²⁺, Cd²⁺, and Zn²⁺ ions (○, Pb²⁺; □, Cu²⁺; △, Cd²⁺; ◇, Zn²⁺ with BTB membrane; ●, Pb²⁺; ■, Cu²⁺; ▲, Cd²⁺; ◆, Zn²⁺ with FTB membrane).

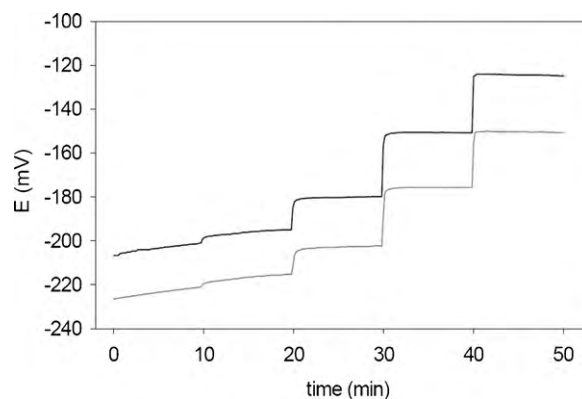


Fig. 3. Dynamic potentiometric responses of the proposed electrodes based in BTB and FTB membranes. Response corresponding to four one-decade concentration step changes from acetate buffer background to 10⁻³ M Pb²⁺ (–, BTB membrane; —, FTB membrane).

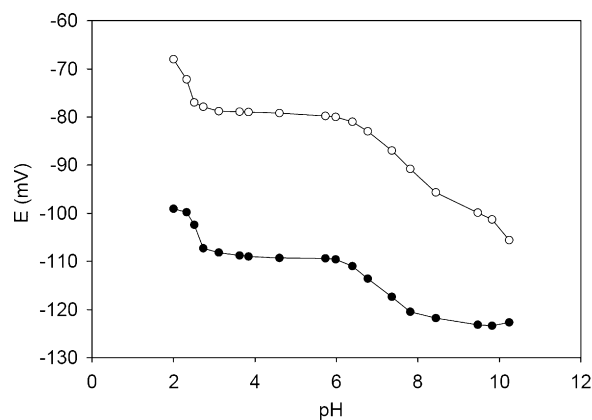


Fig. 4. pH dependence on the response of the Pb(II)-ISEs based on BTB and FTB (○–, BTB membrane; ●–, FTB membrane). Conditions: 1.0 × 10⁻⁴ M Pb²⁺ in a pH 10 NaOH solution successively acidified with HNO₃.

are maintained constant between pH 2.2 and 6.0. Variation of the potential at pH < 2.6 could be related to protonation of the ligands in the membrane phase, which resulted in a loss of its ability to form complexes with the Pb²⁺ ions. At the higher pH's, the potential drop may be due to the hydrolysis of the Pb²⁺ ions. Given the working pH range is slightly reduced at lower Pb(II) concentrations, therefore,

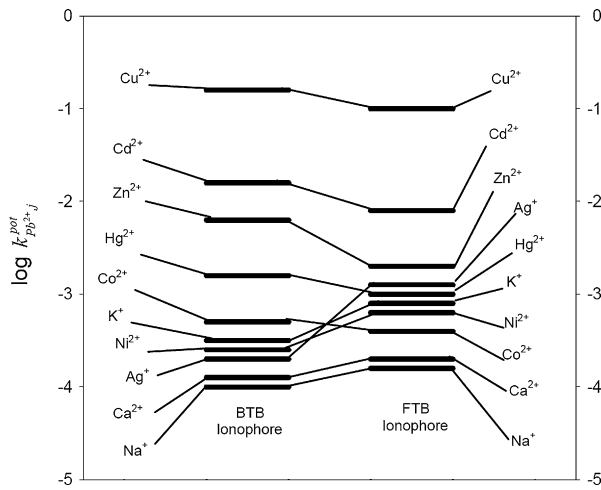


Fig. 5. Selectivity pattern for the Pb(II)-ISEs based on BTB and FTB ionophores.

all of the measurements were performed at pH 4.0 (employing an acetate buffer).

In order to investigate the selectivity of the two proposed Pb(II) ISEs, perhaps as the most important characteristic of a membrane sensor, its response was examined in the presence of various foreign ions according to fixed interference method. The resulting values are illustrated in Fig. 5. As can be seen, for the BTB membrane and Cu(II) and Cd(II) ions, their selectivity coefficients are higher than 10^{-2} , which reveals some reversible interfering effect in the Pb(II) selective electrode functioning. However, it should be noted that, although the Cd(II) similarity, there is a rather more severe interference of Cu(II) ion. For the other metals considered, the selectivity coefficients range at about 10^{-3} or smaller, indicating they would not significantly disturb the functioning of the Pb(II) selective membrane. Considering the FTB membrane, the potentiometric selectivity coefficients of the most interfering ions (Cu(II) and Cd(II)) are slightly improved with respect to BTB membrane. The other ions do not interfere significantly with the FTB membrane, as before.

The lifetime of the electrodes was determined by recording its potential at an optimum pH value and plotting its calibration curve each day. It was observed that there was no significant change in the slope and detection limit (DL) of the electrodes on the following day. The BTB membrane electrode was tested over a period of 10 weeks to investigate its stability. During this period, the electrode was daily used, the values of slope and DL reproductibility were 31.5 ± 1.6 mV/dec and $(1.6 \pm 0.3) \times 10^{-6}$ M, respectively. Also, the FTB membrane electrode was tested over a period of 14 weeks to investigate its stability, and during this period the analytical parameters were found to be reproducible, the values of slope and

DL reproductibility of 30.0 ± 1.3 mV/dec and $(1.9 \pm 0.9) \times 10^{-6}$ M, respectively.

The stability and reproductibility of the electrodes were also tested. Repeated monitoring of potentials (20 measurements) on the same portion of the sample at 1.0×10^{-3} and 1.0×10^{-4} M Pb^{2+} resulted in standard deviations of -151.8 ± 0.7 and -120.6 ± 0.8 mV for BTB membrane ISE and for FTB membrane ISE -176.3 ± 0.6 and -146.4 ± 0.7 mV, respectively.

Table 3 lists, for comparative purposes, the main performance characteristics (linear range, detection limit, lifetime and slope) of some of the lead-selective electrodes from the literature [29–35], against data of the proposed lead ISEs. As can be seen, the proposed lead-selective electrodes are comparable or improve many of those reported in relevant characteristics of response such as concentration range, selectivity coefficient for potential interfering ions, having similar Nernstian slopes and acceptable DL. If the two proposed sensors are compared one to the other, very similar features are noticed, such as detection limit, sensitivity and linear range of response; also precision and response time values are equivalent for both of them. The only feature to mark is the better selectivity and longer lifetime of the FTB membrane electrode, making it slightly preferable among the options tested.

3.4. Application of the proposed sensors in lead soil determination

The two proposed Pb(II) sensors were found to work well under laboratory conditions. To assess the applicability of the both ISEs to real samples, an attempt was made to determine lead in 6 different samples of soils road, coming from outside of the Barcelona city, and compare results against a reference method.

The amount of lead was obtained by ISE method employing standard addition technique, but first, samples had their pH adjusted to 4.0 (acetate buffer). To cover the different possible lead in soil values, the approximate concentration and volume of added standard were calculated by the methodology proposed by Horvai and Pungor [36], in terms of achieving adequate precision in the analysis. Lead added to the samples was between 0.5 and 1 times of the analyte concentration in the sample, thus yielding the proper emf change for precise calculation.

Calibration data was performed in a blank solution of analyte extraction reagents. To assess the reliability of the results, each sample was analyzed by triplicate using both methods. The results of performed analysis are shown in Table 4; as can be seen, concentration values of the extracts were in the lower linear range of response of the proposed sensors. Precisions obtained were always in the same range for both methods and the two ISEs tested.

When results obtained by reference method and the two ISEs are statistically compared, a satisfactory agreement is

Table 3
Comparison of the response characteristics of different Pb(II) ISEs.

Reference	Slope (mV/dec)	Detection limit (M)	Linear range (M)	Lifetime (weeks)	Interfering ions with $\log k^{\text{pot}}_{Pb^{2+},j} \geq -2$
Proposed electrode (BTB)	31.5 ± 1.6	$(1.6 \pm 0.3) \times 10^{-6}$	4.0×10^{-6} to 1.0×10^{-2}	10	Cu^{2+} , Cd^{2+}
Proposed electrode (FTB)	30.0 ± 1.3	$(1.9 \pm 0.9) \times 10^{-6}$	5.0×10^{-6} to 1.0×10^{-2}	14	Cu^{2+}
[15]	29.7 ± 0.6	2.0×10^{-6}	3.6×10^{-6} to 1.3×10^{-2}	8	Ba^{2+}
[29]	32.5	5.0×10^{-7}	1.0×10^{-6} to 1.0×10^{-1}	>8	Hg^{2+} , Tl^+ , Ag^+
[30]	29.1	3.0×10^{-6}	5.0×10^{-6} to 1.0×10^{-1}	>24	Cu^{2+} , Cd^{2+}
[31]	33.1	1.8×10^{-5}	5.8×10^{-5} to 1.0×10^{-2}	8	Ag^+ , Cd^{2+} , Ca^{2+} , Hg^{2+}
[32]	28.6	2.0×10^{-6}	3.1×10^{-6} to 6.3×10^{-3}	8	Hg^{2+}
[33]	29.5 ± 0.4	3.2×10^{-7}	7.7×10^{-7} to 1.0×10^{-1}	10	Hg^{2+} , Ag^+ , Fe^{2+}
[34]	28.3	2.8×10^{-5}	5.0×10^{-5} to 1.0×10^{-2}	8	Zn^{2+} , Ca^{2+} , Cd^{2+} , Ni^{2+} , K^+ , Ag^+ , Mn^{2+} , Tl^+ , Li^+ , NH_4^+ , Sr^{2+}
[35]	29.2	1.0×10^{-5}	2.0×10^{-5} to 5.0×10^{-2}	8	Zn^{2+} , Ca^{2+} , Cd^{2+} , Ni^{2+} , Na^+ , Ag^+ , Mg^{2+}

Table 4

Determination of lead concentration in soil samples employing the proposed Pb(II) ISEs, and comparison against a reference ICP-MS method.

Sample	ICP-MS (mg/kg)	ISEs-standard addition	
		BTB (mg/kg)	FTB (mg/kg)
1	18.8 ± 0.6	17.9 ± 0.5	18.6 ± 0.6
2	19.7 ± 0.6	19.0 ± 0.7	20.1 ± 0.6
3	20.9 ± 0.6	21.2 ± 0.7	21.1 ± 0.7
4	16.4 ± 0.5	15.9 ± 0.6	16.2 ± 0.5
5	12.8 ± 0.4	12.5 ± 0.6	13.0 ± 0.5
6	36.1 ± 1.0	35.8 ± 0.8	35.4 ± 0.9

obtained. Linear regression of BTB-ISE results vs. ICP-MS yielded a correlation of $R=0.9987$ ($n=6$) with a comparison line $y=(1.008 \pm 0.071)x - (0.57 \pm 1.56)$; linear regression of FTB-ISE yielded a correlation of $R=0.99935$ ($n=6$) with a comparison line $y=(0.965 \pm 0.048)x + (0.69 \pm 1.06)$. As can be seen, both fitted regression lines were indistinguishable from the theoretical $y=x$ comparison line, with slightly better comparison for the FTB-ISE. Analogously, if a paired samples Student's t test is performed, calculated t statistics are: $t=2.36$ for the BTB-ISE vs. ICP-MS and $t=0.31$ for the FTB-ISE vs. ICP-MS. In both cases, t statistics were below the tabulated critical value of $t^*=2.57$ (5 degrees of freedom and 95% confidence level), demonstrating that there are no significant differences between results obtained with the ISE methods and the reference. In short, both sensors showed similar results during their application to the determination of lead in soils.

4. Conclusions

In this work, two new bis-thioureas 1,3-bis(*N'*-benzoylthioureido)benzene, BTB, and 1,3-bis(*N'*-furoylthioureido)benzene, FTB, have been successfully synthesised and characterized. Compounds showed to be very adequate when used as neutral carrier in ISEs with polymeric membrane for determining Pb(II). This is demonstrated by good performance characteristics obtained during application, as sensitivity, stability, response time, detection limit, and precision and linear range. The main structural difference between the two proposed ionophores (furoyl and benzoyl terminals groups) only affected the lifetime and selectivity of the electrodes, in favour of the FTB membrane electrode. On the basis of the results discussed in this paper, the two proposed electrodes can be used for Pb^{2+} ion determination in contaminated soils with good performance.

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