Zirconium(IV) phosphosulphosalicylate-based ion selective membrane electrode for potentiometric determination of Pb(II) ions

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Abstract Zirconium(IV) phosphosulphosalicylate, a cation exchanger was synthesized by mixing zirconium oxychloride to a mixture of 5-sulphosalicylic acid and phosphoric acid. The material showed good efficiency for the preparation of an ion-selective membrane electrode. The membrane was characterized affinity for Pb(II) ions. Due to its Pb(II) selective nature, the ion-exchanger was used as an electroactive by XRD and SEM analysis. The electrode responds to Pb(II) ions in a linear range from 1 \times 10^{-5} \text{ to } 1 \times 10^{-1} \text{ M with a slope of 43.8 mV per decade change in concentration with detection limit of 4.78 \times 10^{-6} \text{ M. The life span of electrode was found to be 90 days. The proposed electrode showed satisfactory performance over a pH range of 4.0–6.5, with a fast response time of 15 s. The sensor has been applied to the determination of Pb(II) ions in water samples of different origins. It has also been used as indicator electrode in potentiometric titration of Pb(II) ion with EDTA.}

1. Introduction

The development and application of ion-selective electrodes (ISEs) for sensitive and selective determination of polluting substances in different ecosystems have been subject of growing interest in recent years (Chandra et al., 2000; Wilson et al., 2010; Parra et al., 2011; Arida et al., 2010). The advantages of ISEs over many other methods are associated with easy handling, low cost, non-destructive analysis and ability to monitor concentration of ions without extensive sample preparation. The need for the determination of toxic heavy metal ions in natural portable and soils waterways has been increased (Ganjali et al., 2002; Amman et al., 1983; Janata et al., 1994). Although a lot of work has been done on ISEs for the determination of anion i.e. Br^- (Singh et al., 2006); SCN^- (Chai et al., 2005); F^- (Gorski et al., 2010), cation i.e. Fe(III) (Ekmecki et al., 2007); Cd(II) (Wardak, 2012; Khan and Alam, 2003); Cr(III) (Sharma and Goel, 2005); Pb(II)
(Jeong et al., 2005; Lee et al., 2004); Cu(II) (Gholivand et al., 2007); Cs(I) (Peper et al., 2005) and drug molecules such as Prenalterol (Khailil and El-Reis, 2003); Hydralazine (Badawy et al., 1988); Biperiden (Khaled et al., 2011); Pethidine (Liu et al., 2002); Phenylephrine hydrochloride (Giahi et al., 2011); Desipramine (Ensafi and Allafchian, 2011); and Atenolol (Nassory et al., 2007) yet there is still a need to carry out research to improve the ion-selective electrode’s parameters such as detection limit, concentration range, pH range and life span to increase the usefulness of the electrode. Extensive efforts have been made to develop good sensitive ISEs for the determination of heavy metal ions. For this purpose many organic and inorganic compounds have been employed as electroactive materials in the fabrication of ISEs i.e. Zirconium(IV)iodosulphosalicylate (Lutfullah et al., 2012a); N,N’ Butylen Bis (Salicylidene Iminato) Copper(II) (Ardakani et al., 2008); Poly-o-toulidine Zr(IV) phosphate (Khan et al., 2008); polypropylene Sn(IV) phosphate (Khan et al., 2011); polypropylene-zirconium titanium phosphate (Khan et al., 2010). Precipitation-based ion-selective membrane electrodes have been successfully employed for quantification of several anions and cations. Among the heavy metals, lead is one of the most commonly encountered toxic metal ions in the environment, which results from manufacturing of automotive batteries, automobile exhaust fumes and metal finishing industries. Lead(II) can damage all tissues particularly the kidneys, liver, brain, nervous and reproductive system; among other adverse effects to human. High lead(II) exposure causes lung cancer and encephalopathy with the following symptoms: irritability, vertigo, insomnia, migraine and even convulsions, seizure and coma (Rashid et al., 2014). To monitor the concentration of lead(II) ions in large number of environmental samples, ISEs can be effectively employed owing to high selectivity, sensitivity, fast response and good precision (Huang et al., 2014, 2013). The ion exchange membranes obtained by embedding inorganic, organic and hybrid ion exchangers as electroactive materials in PVC, a neutral binder, have been studied as potentiometric sensors (Zamani and Ganjali, 2010; Badri and Pouladsaz, 2011; Sharma and Sharma, 2009; Singh et al., 2004). Enormous efforts have been made for to design and synthesize suitable material that are highly selective to Pb(II) ions such as calixarene (Chen et al., 2006), Schiff base (Ardakani et al., 2005), Anthraquinone (Barzegar et al., 2005), N,N’N”-tris(2-pyridylxomethyl) ethane (Kumar et al., 2014), Polysulfoanionanthraquinone (Huang et al., 2014); sulfonic phenylelenediamine (Huang et al., 2013); capric acid (Mousavi et al., 2001) and Tetraphenyl pyrophosphate (Xu and Katsu, 2000). The requirement for the preparation of ISEs is that the electroactive material should exhibit strong affinity for a particular ionic species to be determined and poor affinity to others. Recently zirconium(IV) phosphosulphosalicylate cation exchanger can be synthesized in the laboratory, which exhibited strong affinity for Pb(II) ions (Lutfullah et al., 2012b). In view of this property, we have a report on electroanalytical applications of zirconium(IV) phosphosulphosalicylate as Pb(II) ion selective membrane electrode.

2. Experimental details

2.1. Reagents

Zirconium(IV) oxychloride (CDH(P) Ltd., New Delhi, India), orthophosphoric acid and 5-sulphosalicylic acid (Loba Chemie Pvt. Ltd., Mumbai, India) were used for the synthesis of ion exchange material. Poly (vinyl chloride) (PVC) and dioctylphthalate (DOP) were purchased from Otto Chemie Pvt. Ltd., Mumbai, India. Tetrahydrafuran (THF) was obtained from Merck, India. The nitrate and chloride salts of metal ions were used of analytical grade. The solutions of metal salts were prepared in doubly distilled water and standardized according to appropriate methods.

2.2. Instrumentation

An Eutech Digital pH meter (Cyberscan pH 2100) and digital potentiometer (Systronic Digital Potentiometer 318, India) were used to measure pH and potential, respectively. Powder X ray diffraction (XRD) patterns were recorded on using a diffractometer PW 22XX (Rigaku Miniflex II, Japan) with Cu Kα (λ = 1.54 Å) radiation in the range between 15° and 80°. Atomic absorption spectrometer with an air–acetylene burner was used to determine the concentration of Pb(II) (Model 932 Plus, GBC, Victoria, Australia). The Scanning electron microscope (JSM-6510LV, JEOL, Japan) was used to study the surface of material.

2.3. Synthesis of zirconium(IV) phosphosulphosalicylate ion-exchanger

Zirconium(IV) phosphosulphosalicylate was prepared by mixing of 0.1 mol L⁻¹ zirconium(IV) oxy chloride to a mixture of 0.1 mol L⁻¹ orthophosphoric acid and 0.1 mol L⁻¹ 5-sulphosalicylic acid (Volume ratio 1:2:1) at pH 1. The resulting gel was stirred vigorously on a magnetic stirrer for 8 h. At the final stage, the cation exchanger gel was filtered off and washed with distilled water to remove excess acid. The washed gel was dried at 40 °C in an oven. The dried product was cracked into small granules and converted to H⁺ form by treating with 1 mol L⁻¹ HNO₃ for 24 h with stirring. The excess acid was removed after several washings with distilled water and finally dried at 40 °C (see Scheme 1).

n ZrOCl₂ + n H₃PO₄ + n C₆H₅COOH·OH·SO₂H
At pH = 1

n Zr₂(HPO₄)(C₆H₅COOH·OH·SO₂H)(OH)₃·H₂O
n mole of 1 M Pb(NO₃)₂

n Zr₂(HPO₄)₂(C₆H₅COOH·OH·SO₂H)(OH)₃·H₂O

Scheme 1 Shows synthesis of zirconium(IV) phosphosulphosalicylate (ion-exchanger).

The membrane was prepared by the method of Coetzee and Basson (1971). Zirconium(IV) phosphosulphosalicylate was
ground to a fine powder and mixed thoroughly with PVC dissolved in THF and finally mixed with 10 drops of DOP, used as plasticizer. The mixing ratio of zirconium(IV) phosphosulphosalicylate was varied with a fixed content of PVC and DOP in order to obtain a membrane with best performance. The resulting solutions were carefully poured into a glass-casting ring placed on a smooth glass plate and allowed to evaporate at room temperature. The resulting membrane was cut to size and mounted at the lower end of Pyrex glass tube (i.d. 2.8 cm) with the help of araldite. Thus, several membranes of varying composition were prepared and investigated. The membrane (M-2) with best performance characteristics and reproducible results has been chosen for detailed studies. Then the assembly was dried in air for 24 h. The tube was filled with 0.1 mol L\(^{-1}\) lead nitrate solution. The electrode was finally conditioned for 24 h by soaking in 0.1 mol L\(^{-1}\) lead nitrate solution with pH 4.5. A saturated calomel electrode (SCE) was immersed in the tube for electrical contact and another SCE was used as external reference electrode (see Scheme 2).

2.5. Characterization of the membrane

The parameters, which affect the performance of membrane were investigated. These parameters such as membrane water content, thickness, swelling and porosity have been determined after conditioning the membrane.

2.5.1. Conditioning of the membrane

For the purpose of conditioning, the membranes were equilibrated with 1 mol L\(^{-1}\) sodium chloride solution containing about 1 mL of sodium acetate solution to neutralize the acid present in the membrane and obtain a pH the range of 5–6.5.

2.5.2. Water content

The conditioned membranes were immersed in distilled water and equilibrated for 24 h to elute the diffusible salt. The weight of wet membrane was determined after removing surface water. Then the wet membrane was dried under vacuum at a temperature of 60 °C until a constant dry weight was obtained. The percentage water content was calculated using the following relation:

\[
\text{Water content (\%)} = \frac{m_w - m_d}{m_w} \times 100
\]

where \(m_w\) is the mass (g) of wet membrane and \(m_d\) is the mass (g) of dry membrane.

2.5.3. Thickness and swelling

The thickness of membrane was measured by screw gauge. The difference between average thickness of membrane equilibrated with 1 mol L\(^{-1}\) NaCl for 24 h and the dry membrane is the measure of swelling.

2.5.4. Porosity

Porosity (\(\varepsilon\)) is regarded as the volume of water incorporated in the cavities per unit membrane volume and is calculated from the following relation:

\[
\varepsilon = \frac{m_w - m_d}{A L \rho_w}
\]

where \(m_w\) and \(m_d\) are the mass (g) of wet and dry membrane, respectively. \(L\) is the thickness of the membrane, \(A\) is the area of the membrane and \(\rho_w\) is the density of water.

2.6. Potential measurements

All measurements were taken at 25 ± 1 °C with the following assembly:

![Scheme 2](image)

Scheme 2  Shows performance of zirconium(IV) phosphosulphosalicylate ion-exchanger membrane (ZPS) electrically interact to Pb(II) ions.
The potentials were measured at pH 4.5 with a digital potentiometer (Systronics Digital Potentiometer 318, India). The performance of electrodes was examined by measuring potentials of solutions containing lead ion in 10⁻⁷ to 10⁻¹ mol L⁻¹ concentration range. After performing the experiment, membrane electrode was removed from the test solution and kept in a 0.1 mol L⁻¹ lead nitrate solution.

3. Results and discussion

Zirconium(IV) phosphosulphosalicylate behaves as a cation exchanger. The ion exchange capacity of the material was found to be 2.20 meq/g for K⁺ ions. Moreover, the distribution studies (Kd) of some metal ions were performed in distilled water and different concentrations of HNO₃. The Kd value for Pb(II) was 1088.88 whereas for other metals Mg (II), Ca (II), Sr (II), Cd (II), Mn (II), Ba (II), Zn (II), Cu (II), Fe (II), Th (IV) were less than 200. The Kd value for Co (II), Cr (III) and Al (III) was 300, 500 and 516.66, respectively. It was observed that the material has maximum selectivity toward Pb(II), while other metal ions are poorly adsorbed (Lutfullah et al., 2012b). Therefore, zirconium(IV) phosphosulphosalicylate was used as an electroactive component for the fabrication of a heterogeneous ion-selective membrane electrode sensitive to Pb(II) ions. The XRD pattern of membrane indicates the semicrystalline nature of electroactive material (Fig. 1).

Fig. 2 shows the SEM images of (A) PVC membrane (B) PVC based zirconium(IV) phosphosulphosalicylate membrane and (C) electroactive material only. It can be seen that the surface of the membrane is smooth but not homogeneous.

Various samples of zirconium(IV) phosphosulphosalicylate membranes were prepared keeping the amount of PVC (200 mg) and DOP (10 Drops) constant, while varying the amount of electroactive material (particle size varies from 8 nm to 48 nm) to change the thickness of membrane coating. The membrane thickness, porosity, swelling and water content were determined and reported in Table 1. As can be seen from Table 1, the thickness, porosity, and water content of prepared membrane increased with increasing amount of electroactive material. Generally it is required that the ideal membrane should have less thickness, moderate swelling, porosity and water content capacity. Membrane M-2 is selected owing to its better mechanical strength with moderate thickness, swelling, porosity and water content. The membrane ion-selective electrode fabricated from this membrane (M-2) was characterized by studying the response time, pH range, working concentration range, slope, selectivity and life span (see Table 2).

3.1. Effect of pH

The effect of pH on the potential was studied in the range of 1–6.5. For this, a series of solutions of variable pH were prepared, keeping the concentration of Pb(II) constant (1 × 10⁻² mol L⁻¹ and 1 × 10⁻³ mol L⁻¹). The pH value of the solution

![Figure 1](image1.png)  
**Figure 1** XRD image of zirconium(IV) phosphosulphosalicylate membrane.

![Figure 2](image2.png)  
**Figure 2** SEM image of (A) PVC membrane (B) PVC based zirconium(IV) phosphosulphosalicylate membrane and (C) electroactive material only.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Membrane composition</th>
<th>Thickness (mm)</th>
<th>Water content (%)</th>
<th>Porosity</th>
<th>Swelling (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZPS (mg)</td>
<td>PVC (mg)</td>
<td>DOP drops</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-1</td>
<td>100</td>
<td>200</td>
<td>10</td>
<td>0.33 ± 0.031</td>
<td>2.54</td>
</tr>
<tr>
<td>M-2</td>
<td>150</td>
<td>200</td>
<td>10</td>
<td>0.36 ± 0.05</td>
<td>2.78</td>
</tr>
<tr>
<td>M-3</td>
<td>200</td>
<td>200</td>
<td>10</td>
<td>0.43 ± 0.07</td>
<td>7.14</td>
</tr>
</tbody>
</table>

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was adjusted with the addition of HNO₃. The results are presented in Fig. 3.

Fig. 3 indicates that the potential remains constant in the pH range of 4–6.5. Above pH 6.5, precipitation occurs due to the formation of lead hydroxide. At lower pH, electrode has a greater response to the hydrogen ions than the Pb(II) in solution (Lutfullah et al., 2012a, 2014).

3.2. Working concentration range of electrode

The potential response of the membrane electrode sample M-2 at variable concentration of Pb(II) ions at pH 4.5 indicates a rectilinear range from 1·10⁻⁵ to 1·10⁻¹ mol L⁻¹ (Fig. 4).

3.3. Response time and life span of the membrane electrode

For analytical applications, the response time and the lifetime of a sensor are of critical importance. According to IUPAC recommendations, the response time may be defined as the time between the addition of analyte to the sample solution and the time when a limiting potential has been reached. The response time of the electrode was tested by measuring the time required to achieve a steady state potential for 0.01 mol L⁻¹ Pb(NO₃)₂ solution at pH-4.5. It was observed that the response time of zirconium(IV) phosphosulphosalicylate membrane was 15 s (Fig. 5). This parameter must be checked every time before using it for analytical measurement. The membrane ion selective electrode prepared could be used satisfactorily for three months (Table 3).

3.4. Slope and detection limit

The slope of the calibration curve was 43.8 mV/decade change in Pb(II) ion concentration. The detection limit of Pb(II) was determined from the intersection of two extrapolated segments of calibration curve and found to be 4.78·10⁻⁶ mol L⁻¹ Pb(II) ion concentration (Fig. 6).

3.5. Potentiometric selectivity

The potentiometric selectivity coefficient, $K_{ij}$, of ion-selective electrode was evaluated using two solution method (Umezawa et al., 2000). For an electrode responding to the primary ion $i$ of activity $a_i$ and charge $z$, in the presence of an

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Slope (mV/decade of activity)</th>
<th>Linear range (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>10</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>20</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>30</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>40</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>50</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>60</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>70</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>80</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>90</td>
<td>43.8 ± 0.5</td>
<td>1.0 x 10⁻⁵–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>100</td>
<td>40.8 ± 0.5</td>
<td>1.0 x 10⁻⁴–1.0 x 10⁻¹</td>
</tr>
<tr>
<td>110</td>
<td>38.0 ± 0.5</td>
<td>5.5 x 10⁻⁴–1.0 x 10⁻¹</td>
</tr>
</tbody>
</table>

Figure 3 Effect of pH on the electrode response.

Figure 4 Calibration curve for determination of Pb(II) ions.

Figure 5 Response of Pb(II) selective-ZPS membrane electrode for 0.01 mol L⁻¹ Pb(NO₃)₂ at different time intervals.
interfering ion \( j \) of activity \( a_j \) and charge \( z_j \), the potential \( E \) is obtained by the equation (Umewara et al., 2000):

\[
E = \text{constant} + \left( \frac{2.303RT}{F} \right) \log(a_i + K_{ij}a_j^{z_j/z_i}) \tag{1}
\]

The potential in the presence of the primary ion \( i \) of activity \( a_i \) is obtained by the equation:

\[
E' = \text{constant} + \left( \frac{2.303RT}{zF} \right) \log a_i \tag{2}
\]

From Eqs. (1) and (2), the selectivity coefficient is expressed as:

\[
K_{ij} = \left( 10^{(E'/E - 1)z_i/z_j} - 1 \right) a_j^{z_j/z_i} / a_i
\]

The selectivity coefficients, \( K_{ij} \), have been determined from the cell potentials with \( 1 \times 10^{-2} \) mol L\(^{-1}\) Pb(II) ions and with \( 1 \times 10^{-2} \) mol L\(^{-1}\) Pb(II) + \( 1 \times 10^{-2} \) mol L\(^{-1}\) interfering ion. Table 3 lists the potentiometric selectivity data of PVC based zirconium(IV) phosphosulphosalicylate membrane electrode for the interfering ion relative to Pb(II). The electrode preferentially responds to the primary ion if \( K_{ij} < 1 \) (Gupta et al., 2002). The selectivity coefficient values of various alkali metals are quite low indicating that ions do not interfere, whereas alkaline and transition metal ions are highly interfering metals (Lutfullah et al., 2014).

### 3.6. Analytical application

The electrode was successfully applied to the determination of Pb(II) in water samples obtained from different origins. 50 mL of each sample was taken and diluted to 100 mL with distilled water and appropriate volume of HNO\(_3\) for adjusting pH 4.5. Then the potential of diluted solution was measured and concentration of Pb(II) was calculated from the calibration curve. The concentration of Pb(II) samples was also determined by flame atomic absorption spectrometry (FAAS) and results are reported in Table 4. The sensor was found to be in satisfactory agreement with that obtained from FAAS. Student \( t \) test value was also calculated and found that experimental \( t \) value is less than tabulated \( t \) value at 95% confidence level, means the null hypothesis that there is no significant difference between the two experimental means. The performance of ZPS membrane electrode has been compared with other lead (II) selective membrane electrode (Table 5). As can be seen from the table that the present electrode showed better performance in terms of response time and slope per decade change in concentration.

The analytical utility of this membrane electrode has also been established by employing it as an indicator electrode in the potentiometric titration of Pb(NO\(_3\))\(_2\) with an EDTA solution as titrant. For this, a 2.0 mL of 0.01 mol L\(^{-1}\) of Pb(NO\(_3\))\(_2\) solution was pipetted out in 50.0 mL volumetric flask and adjusting pH 4.5. This solution is poured in a beaker and titrated with an EDTA solution; the electrode potential was measured after each addition of 0.5 mL of EDTA. The addition of EDTA causes a decrease in potential as a result of the formation of Pb(II)-EDTA complex. The results are shown in Fig. 7. The amount of Pb(II) ions in solution can be accurately determined from the titration curve.

### Table 3 Selectivity coefficient \( K_{ij} \) for various interfering ions (M\(^{z_j+}\)).

<table>
<thead>
<tr>
<th>Interfering ions ( M^{z_j+} )</th>
<th>Selectivity coefficient value ( K_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>3.74 \times 10^{-6}</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>3.74 \times 10^{-6}</td>
</tr>
<tr>
<td>K(^+)</td>
<td>3.74 \times 10^{-6}</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>1.17 \times 10^{-2}</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>1.17 \times 10^{-2}</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>1.17 \times 10^{-2}</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>1.17 \times 10^{-2}</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>2.75 \times 10^{-2}</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>1.35 \times 10^{-2}</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>1.97 \times 10^{-2}</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>1.54 \times 10^{-2}</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>1.02 \times 10^{-2}</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>1.02 \times 10^{-2}</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>2.22 \times 10^{-2}</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>3.74 \times 10^{-2}</td>
</tr>
</tbody>
</table>

### Table 4 Pb(II) determination in water samples using potentiometry with ZPS-based sensor and FAAS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb(II) added (mg L(^{-1}))</th>
<th>Pb(II) found (mg L(^{-1}))</th>
<th>Recovery (%)</th>
<th>Pb(II) found (mg L(^{-1}))</th>
<th>Recovery (%)</th>
<th>Student ( 'r' ) test</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>8.39</td>
<td>8.40 \pm 0.37</td>
<td>100.11</td>
<td>8.28 \pm 0.51</td>
<td>98.68</td>
<td>1.128</td>
</tr>
<tr>
<td>Waste water from electroplating industry</td>
<td>59.70</td>
<td>59.74 \pm 0.54</td>
<td>100.06</td>
<td>59.90 \pm 0.51</td>
<td>100.33</td>
<td>1.499</td>
</tr>
<tr>
<td>Ground water</td>
<td>5.30</td>
<td>5.32 \pm 0.38</td>
<td>100.37</td>
<td>5.33 \pm 0.38</td>
<td>100.56</td>
<td>1.618</td>
</tr>
</tbody>
</table>

\( ^* \) Standard deviation based on five replicate measurements.
solution. The potentiometric titration of Pb(II) ions with EDTA ion concentration. It could be used as indicator electrode in Potentiometric titration of Pb(II) against EDTA Figure 7

ZPS based electrode for potentiometric determination of Pb(II) ions 7

0 to Aligarh Muslim University for financial assistance (Non-


Wilson, D., Maria, de los Angeles Arada, Alegret, S., Del Valle, M., 2010. 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. J. Hazard. Mater. 181, 140–146.
