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Electrochemical sensors for the determination of Ba(II) ions

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Abstract: Two solid-state membrane and coated wire electrochemical sensors have been developed based on barium sulphate nanoparticles. BaSO$_4$ nanoparticles are synthesized by the chemical co-precipitation technique. BaSO$_4$ nanoparticles disc used to design the solid- state membrane sensor and the BaSO$_4$ nanoparticles utilized to fabricate the coated wire sensor. The two sensors display linear responses over the concentration ranges of 1.0×10^{-5}-1.0×10^{-1} mol L^{-1} Ba^{2+} ions with cationic slopes of 25.7 ± 0.1732 and 29.8 ± 1.29615 mV decade^{-1} for the solid-state membrane and coated wire sensors, respectively. The lower limits of detection are 2.7×10^{-6} and 2.5×10^{-6} mol L^{-1} Ba^{2+} ions for the solid-state membrane and coated wire sensors, respectively. The response time for the two sensors is instantaneous (1 s), the useful life span for the solid-state membrane and coated wire sensors are 2 and 8 months, respectively.

I.   INTRODUCTION

Barium is an alkaline earth metal of the second main group of the sixth period of the periodic table, with an atomic number of 56 and a relative atomic mass of 137.32. Because of its high chemical reactivity, elemental barium does not exist in nature (peana *et al.*, 2021). Barium compounds are widely used in a variety of industrial processes, including electroplating, the glass industry, the petroleum industry, alloying, fixing pigments, in corrosion protection films, drilling muds, paints, bricks, ceramics, glass, and rubber (Martin and Griswold, 2009; García Grajeda *et al.*, 2017; Bouslimi *et al.*, 2021). Barium is a heavy metal that is a contaminant and toxic to the ecological system, and its pollution is a major issue because it is not destroyed by chemical or biological processes, making its removal from the environment difficult (Bouslimi *et al.*, 2021). The toxicity of barium compounds has been well documented for both acute and chronic exposure and is dependent on their solubility (Bhoelan *et al.*, 2014). Although there is no known biological function for barium (II) in humans, it appears to be required for the proper growth of some species, such as desmid green algae.

The Ba^{2+} ion and its soluble compounds poison both animals and humans (particularly chloride, sulphide, nitrate, and hydroxide). In animals, despite the fact that only about 2% of barium (II)consumed in the diet is absorbed, barium (II) tends to concentrate in the bones, where it may compete with calcium (II) (Armelina *et al.*, 2019). Furthermore, higher levels of Ba(II) consumption results in the death of mice due to kidney damage(Wang and Wang, 2008). High barium(II) levels can cause a variety of medical problems in humans, including acute Weakness, hypokalemia, gastrointestinal, cardiac and skeletomuscular stimulation followed by paralysis in severe cases (Krishna *et al.*, 2020; Oskarsson, 2022).

As a result of the foregoing, measuring Ba^{2+} ions in the environment, medicine, and other fields has become critical. Many methods for determining barium (II) ions have been described, such as atomic absorption

spectrophotometry (Jaiswal *et al.*, 2006) , fluorescent chemosensors (Basa *et al.*, 2011), Multi collector inductively coupled Plasma-mass spectrometry (ICP-MS) (Matecha *et al.*, 2021), voltammetry (Ridgway and Wajrak, 2019), X-ray Fluorescence Spectrometry (Savichev and Vodyanitskii, 2009), and flame photomerty (Yofll, Avni and Stiller, 1963). Most of these approaches necessitate expensive tools, time-consuming, sample preparation, and are not suited for on-site testing. As a result, a simple and rapid sensor method with a low cost and quick measurements that can be used in metal ion tests in environmental samples is required. Several PVC-based membrane sensors with various ionophores for determining Ba^{2+} ions have been reported (Saleh, 2000; Hassan, 2003; Singh *et al.*, 2005; Othman, El-Shahawi and Abdel-Azeem, 2006; Zamani, Abedini-Torghabeh and Ganjali, 2006; Abedi and Zamani, 2008; Ma *et al.*, 2009; Zamani *et al.*, 2010; Sahari *et al.*, 2011; Mizani, Saffari and Paiehghadr, 2023). Graphite coated ion selective electrode (Negi and Goswami-Giri, 2017) and modified carbon paste electrode (Kaur, Kaushal and Singh, 2021; Ebrahimi *et al.*, 2022) have also been described. In the present work, a development of highly selective and sensitive Ba^{2+} solid-state membrane and coated wire sensors based on nanoparticles, for the determination of Ba^{2+} ions, are introduced for the first time.

II.   MATERIALS AND METHODS

Reagents and materials

All the used chemicals are of high purity, and bi-distilled water is utilized. Sodium sulphate (Na2SO4), barium chloride (BaCl2.2H2O). Sodium hydroxide is obtained from Alpha Chemika. BaSO4 nanoparticles are prepared as described below.

Apparatus

Potentiometric measurements are conducted at room temperature with a PTI-15 digital pH meter using the proposed sensors. The used reference electrode is an EIL-type RJ 23 calomel electrode. A glass Ag-AgCl combination electrode (Consort, 5210 B BB5) is utilized for measuring the pH.

Preparation of barium sulphate nanoparticles

$BaSO_4$ NPs are prepared by the chemical co-precipitation method, by dissolving 24.43 g $BaCl_2.2H_2O$ and 14.205 g Na_2SO_4 in 500 ml of bi-distilled water separately. Excess aqueous NaOH solution (1.0 mol/L) is gradually added to the mixture of $BaCl_2.2H_2O$ and Na_2SO_4, which is kept stirring throughout the reaction to precipitate $BaSO_4$. The pH of the solution is 12.35. After washing the precipitate with bi-distilled water and drying it in the oven, a white powder of $BaSO_4$ nanoparticles is produced

Preparation of the sensors

A solid-state membrane is prepared by pressing 1.0 g of finely powdered $BaSO_4$ nanoparticles under 10 tons of pressure to form a disc with a diameter of 1.3 cm and a thickness of 2.5 mm. The resulted disk is sealed with PVC glue to the end of a pure plastic tube of the same diameter as a first adhesive, and then pure epoxy adhesive is applied to achieve flawless sealing and avoid any possible leak. The internal reference electrode is an Ag-AgCl wire immersed in a $BaCl_2$ internal filling solution of 1.0×10^{-1} mol L^{-1}. The sensor is conditioned by soaking for 48 hours in a 1.0×10^{-1} mol L^{-1} barium chloride solution before use, and it remains in the same solution when not in use.

A coated wire sensor is done by mixing finely powdered $BaSO_4$ nanoparticles with clear silicone rubber in a 50/50 (mass/mass) ratio to achieve a homogeneous mixture. A clean, slightly polished copper wire tip of 8.0 mm in length and 1.0 mm in diameter is dipped several times in the mixture to coat the tip and form a bead, then dried in the air for two days before use. The sensor is kept in a solution of 1.0×10^{-1} mol L^{-1} $BaCl_2$.

Sensor Calibration

The sensors are calibrated by dipping the solid-state membrane or coated wire sensor and the calomel reference electrode in 50-mL beakers containing 25 mL of standard 1.0×10^{-6} - 1.0×10^{-1} mol L^{-1} Ba^{2+} ion solutions. When the potential became constant, the readings are recorded and plotted as a function of the logarithm of the Ba^{2+} ion concentrations. On the other hand, we measured the pH of the standard solutions concurrently with the potential

readings and noticed that the pH values were within the sensors working pH range. Furthermore, because $BaCl_2$ is a strong electrolyte, the ionic strength has no effect on the sensors response. The calibration curve is conducted for determining the Ba^{2+} ion concentrations of the analyte solutions.

Sensor Selectivity

The potentiometric selectivity coefficients $\left(k_{Ba,B}^{pot}\right)$ are measured using the separate solution method(Umezawa *et al.*, 2000; Elmosallamy, Hashem and Abdalmoez, 2022). Calibration of a solid-state membrane sensor or a coated wire sensor is performed with 25 mL of 1.0×10^{-6} - 1.0×10^{-1} mol L^{-1} Ba^{2+} ions, and the potential value corresponding to the concentration of 1.0×10^{-2} mol L^{-1} is determined E_{Ba}. The potential value E_B corresponding to a concentration of 1.0×10^{-2} mol L^{-1} is determined for each interferent. The values of ($k_{Ba,B}^{pot}$) are obtained from equation(Umezawa *et al.*, 2000) :

$$\log(k_{Ba,B}^{pot}) = \frac{E_B - E_{Ba}}{S} + \left(1 - \frac{Z_{Ba}}{Z_B}\right)\log(a_{Ba})$$

Where, E_{Ba} and E_B are the potential values of the Ba (II) and interferent, respectively. S is the slope of the calibration curve, a_{Ba} is the activity of the Ba (II), and Z_{Ba} and Z_B are the charges of the Ba^{2+} ion and interferent, respectively.

III.   RESULTS AND DISCUSSION

Performance characteristics of the sensors

The two sensors are designed as shown in an experimental section, and their electrochemical performance is evaluated in accordance with IUPAC recommendations (Buck and Lindner, 1994). They demonstrate linear response over the concentration ranges of 1.0×10^{-5} - 1.0×10^{-1} mol L^{-1} Ba^{2+} ions, with cationic slopes of 25.7 ± 0.1732 and 29.8 ± 1.29615 mV decade^{-1}, for the solid-state membrane and coated wire sensors, respectively (Fig.1) and (Table 1). The Nernstian slope is displayed by the coated wire sensor, whereas the sub-Nernstian slope is shown by the solid-state membrane sensor. The lower limits of detection for the solid-state membrane and coated wire sensors are 2.7×10^{-6} and 2.5×10^{-6} mol L^{-1} Ba^{2+} ions, respectively (the concentration of Ba (II) ions at the point of intersection of the extrapolated midrange and final low concentration level segments of the calibration plot can be used as the lower limit of detection). The response times for the two sensors are instantaneous (1 s), the useful lifetime for the solid-state membrane is 2 months, and was quite long (8 months) for coated wire sensor. Following that, the calibration slope gradually decreased.
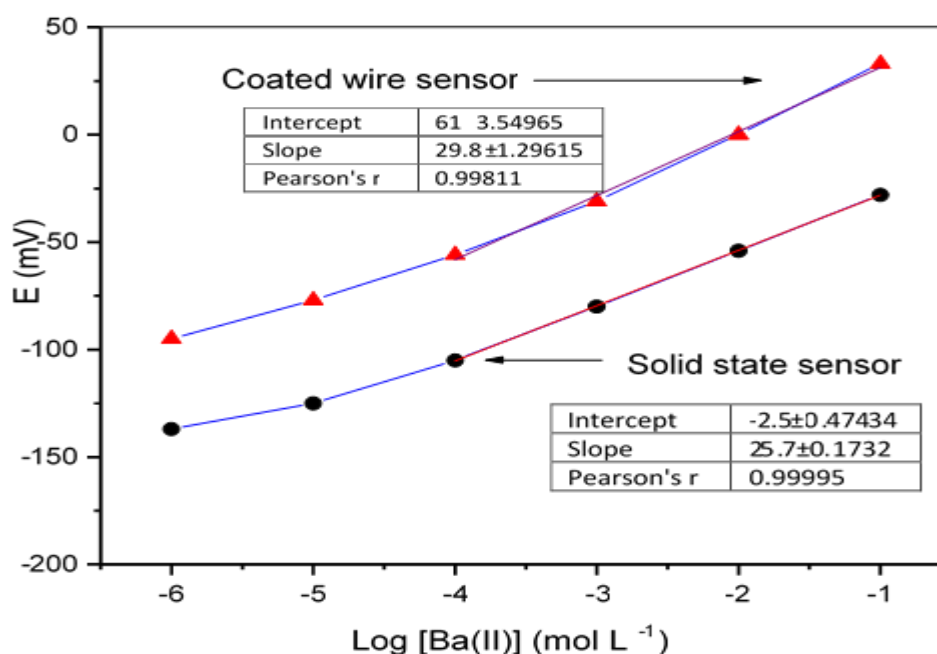

Coated wire sensor	
Intercept	61 3.54965
Slope	29.8±1.29615
Pearson's r	0.99811

Solid state sensor	
Intercept	-2.5±0.47434
Slope	25.7±0.1732
Pearson's r	0.99995

Fig. 1 Potentiometric responses of the solid-state membrane and coated wire sensors.

Table 1 Potentiometric response characteristics of the solid-state membrane and coated wire sensors.

Parameter	Solid-state membrane sensor	Coated wire sensor
Slope (mV) decade^{-1}	25.7±0.1732	29.8±1.29615
Intercept (mV)	-2.5±0.47434	61±3.54965
Correlation coefficient (r)	0.99986	0.99435
Lower limit of linear range (mol L^{-1})	1.0×10^{-5}	1.0×10^{-5}
Lower limit of detection (mol L^{-1})	2.7×10^{-6}	2.5×10^{-6}
Working pH range for 1.0×10^{-2} (mol L^{-1})	2.1 – 10.7	1.9– 8.8
Response time (s) for 1.0×10^{-3} (mol L^{-1})	1	1
Life span (month)	2	8

Effect of the pH

The influence of pH change on the potential is conducted using 10^{-2} mol L^{-1} of Ba^{2+} ion solution over the pH range of 2-11 to obtain the useful pH range for the two potentiometric sensors (Fig. 2), (Table 1). Dilute HCl acid and/or sodium hydroxide solutions are used to test the pH. The pH-potential relationship shows that the pH values for solid-state membrane and coated wire sensors are constant over the pH ranges of 2.1 – 10.7 and 1.9– 8.8, respectively for 10^{-2} mol/L BaCl$_2$.

At pH values greater than 8.8, for coated wire sensor the potential is slightly decreased, most likely due to OH$^-$ ion interference.
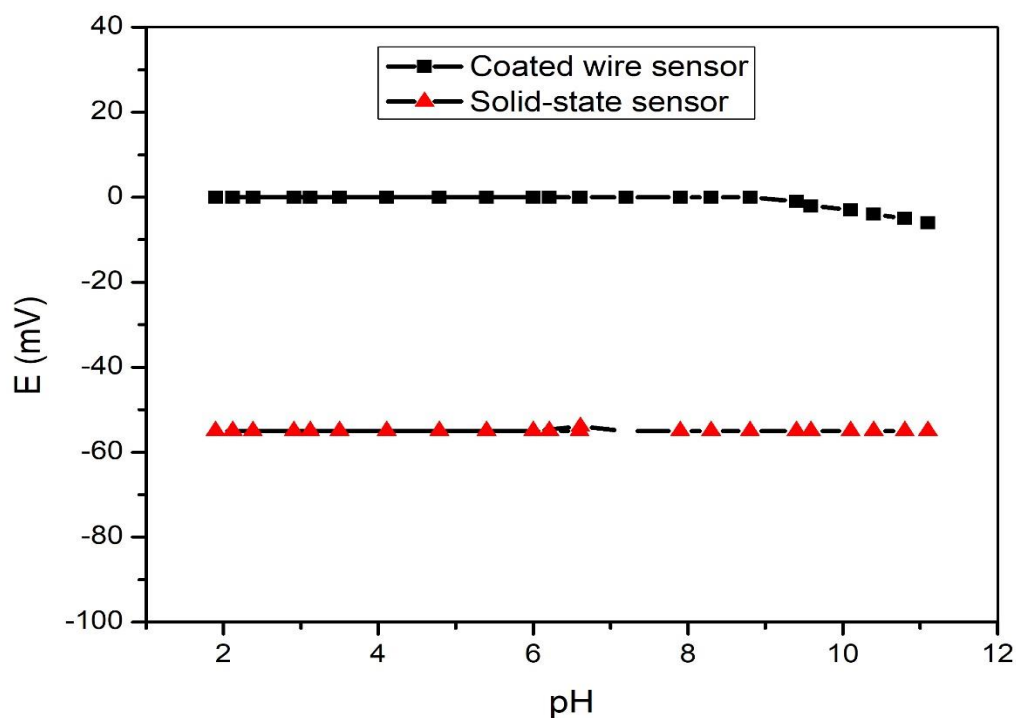

Fig. 2 pH profile of solid-state membrane and coated wire sensors for 10^{-2} mol/L BaCl$_2$

Effect of the foreign ions

The potentiometric responses of the two sensors are examined in the presence of some interferents, such as NH_4^+ ion, 6 non-transition, and 7 transition metals, to demonstrate their selectivity. Using the separate solution method (Umezawa *et al.*, 2000), the potentiometric selectivity coefficients $\left(k_{Ba,B}^{pot}\right)$ were calculated. Table2 shows the results revealing that the two sensors have significantly selectivity for Ba (II) ions over 13 common transition and non-transition metal ions. In other words, the data revealed that the two sensors have high selectivity for Ba^{2+} ion over the listed bi and trivalent metal ions. In general the solid-state membrane sensor is more selective than the coated wire sensor.

Table 2Potentiometric selectivity coefficients$\left(k_{Ba,B}^{pot}\right)$ of the solid – state membrane and coated wire sensors.

Interferent, B	Solid-state membrane sensor	coated wire sensor
Na^+	1.32×10^{-2}	2.15×10^{-2}
K^+	1.16×10^{-2}	3.26×10^{-2}
NH_4^+	1.24×10^{-2}	2.0×10^{-2}
Ca^{2+}	5.75×10^{-5}	10.60×10^{-2}
Mg^{2+}	3.311×10^{-5}	5.90×10^{-2}
Al^{3+}	1.88×10^{-6}	3.18×10^{-2}
Pb^{2+}	2.75×10^{-5}	1.30×10^{-2}
Mn^{2+}	7.585×10^{-5}	4.50×10^{-3}
Co^{2+}	5.75×10^{-5}	7.60×10^{-2}
Cu^{2+}	4.78×10^{-5}	5.10×10^{-2}
Cd^{2+}	8.317×10^{-5}	15.80×10^{-2}
Ni^{2+}	3.63×10^{-5}	2.50×10^{-3}
Cr^{3+}	1.56×10^{-5}	2.7×10^{-2}
Zn^{2+}	2.3×10^{-5}	4.7×10^{-2}

A comparison between the developed sensors and the reported sensors.

For further study, potentiometric response characteristics of the solid-state membrane and coated wire sensors are compared with different sensors reported in the literature (Table 3). According to the comparison, the developed sensors have a shorter response time than the all-reported sensors. The coated wire sensor also has a longer life span.

Table 3 Comparison of the developed Ba (II) sensors with different reported sensors in the literature

Sensor type	Slope mV/decade	Linear range mol L^{-1}	Detection limit mol L^{-1}	Working pH range	Response time (s)	Life span (month)	Reference
PVC based on the complex ion associate barium(II)	28.5	1.0×10^{-5}-1.0×10^{-1}	2.5×10^{-6}	4.5-10.0	20	*	(Othman, El-Shahawi and Abdel-Azeem, 2006)
PVC based on neutral bidentate organophosphorus compounds	30	1.0×10^{-5}-1.0×10^{-1}	5.0×10^{-6}	3.0-11.0	60	2	(Saleh, 2000)
PVC based on DDB liver drug as a novel ionophore	30.0	1.0×10^{-5}-1.0×10^{-1}	5.0×10^{-6}	4.0 – 9.0	*	2	(Hassan, 2003)
PVC based on 4-4^{-}-Methylenediantipyrine	29.7	1.0×10^{-6}-1.0×10^{-2}	5.6×10^{-7}	3.4 – 10.6	15	2	(Abedi and Zamani, 2008)
PVC based on Calix[4]crown-6	29.10	1.0×10^{-6}-1.0×10^{-3}	7.1×10^{-7}	4.0 - 10.0	10	*	(Sahari *et al.*, 2011)
PVC based on Dimethyl 1-Acetyl-8-oxo-2,8-dihydro-1H -pyra-zolo[5,1-a]isoindole-2,3-dicarboxylate	29.7	1.0×10^{-6}-1.0×10^{-1}	7.6×10^{-7}	3.0 - 11.0	10	2	(Zamani, Abedini-Torghabeh and Ganjali, 2006)
PVC based on 2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene	30. 0	1.41×10^{-6}-1.0×10^{-1}	*	2.5 - 7.0	18	3	(Singh *et al.*, 2005)
PVC based on (DHUT)	29.60	1.0×10^{-6}-1.0×10^{-2}	5.6×10^{-7}	2.6 - 11.0	15	**2**	(Zamani *et al.*, 2010)
Carbon paste based on modified Ag nanoparticles	*	6×10^{-11} - 8.0×10^{-10}	4.5×10^{-11}	*	*	*	(Ebrahimi *et al.*, 2022)
polymeric membrane based on a macrocyclic tetrabasic ligand	29.70	3.6×10^{-6}-1.0×10^{-1}	1.9×10-6	2.5 - 7.5	10	2	(Ma *et al.*, 2009)
Solid-state membrane sensor based on ZnS nanoparticles	25.7	1.0×10^{-5}-1.0×10^{-1}	2.7×10^{-6}	2.1 – 10.7	1	2	This work
Coated wire based on silicone rubber and ZnS nanoparticles	29.8	1.0×10^{-5}-1.0×10^{-1}	2.5×10^{-6}	1.9– 8.8	1	8	This work

*Not mentioned

IV.   CONCLUSION

The developed sensors are sensitive, quick, and low-cost, and they provide reliable procedures for barium(II) estimation. Because there is no need for long or tedious separation procedures or expensive and sophisticated instruments, the sensors can be used directly. Meanwhile, the proposed sensors are simple to construct and exhibits high sensitivity and selectivity, a wide linear range, a low detection limit, and a fast response time to Ba^{2+} ion.

Furthermore, the coated wire sensor has a long life span (8 months) and was easy to design. These characteristics make the developed sensors appealing and practical tools for the determination of barium(II).

V.   RERERENCES

Abedi, M.R. and Zamani, H.A. (2008) 'Barium(II)-PVC Membrane Sensor Based on 4-4′-Methylenediantipyrine as a Neutral Carrier', *Anal. Lett.*, 41, pp. 2251–2266.

Armelina, M.J.A. *et al.* (2019) 'Concentrations of Se, Ba, Zn and Mn in Brazil nuts', *Braz. J. Rad. Sci*, 7, pp. 1–10.

Basa, P.N. *et al.* (2011) 'Site-Selective Imination of an Anthracenone Sensor: Selective Fluorescence Detection of Barium(II)', *J. Org. Chem.*, 76, pp. 7866–7871.

Bhoelan, B.S. *et al.* (2014) 'Barium toxicity and the role of the potassium inward rectifier current', *Clin. Toxicol.*, 52, pp. 584–593.

Bouslimi, H. *et al.* (2021) 'Effects of Barium Stress in Brassica juncea and Cakile maritima: The IndicatorRole of Some Antioxidant Enzymes and Secondary Metabolites', *Phyton*, 90, pp. 145–158.

Buck, R.P. and Lindner, E. (1994) 'Recommendations for nomenclature of ionselective electrodes (IUPAC Recommendations 1994)', *Pure Appl. Chem.*, 66, pp. 2527–2536.

Ebrahimi, N. *et al.* (2022) 'Designing a novel DNA-based electrochemical biosensor to determine of Ba^{2+} ions both selectively and sensitively', *Anal. Biochem.*, 642, p. 114563.

Elmosallamy, M.A.F., Hashem, H.A. and Abdalmoez, F.F. (2022) 'New solid-state membrane and coated wire potentiometric sensors for the determination of Zn(II) ions based on nanoparticles', *Anal. Bioanal. Chem.*, 414, pp. 8277–8287.

García Grajeda, B.A. *et al.* (2017) 'Selective and colorimetric detection of Ba^{2+} ions in aqueous solutions using 11-mercaptoundecylphosphonic acid functionalized gold nanoparticles', *RSC Advances*, 7, pp. 31611–31618.

Hassan, S.A.M. (2003) 'DDB liver drug as a novel ionophore for potentiometric barium (II) membrane sensor', *Talanta*, 59, pp. 161–166.

Jaiswal, A.K. *et al.* (2006) 'Determination of Barium in forensic samples by atomic absorption spectrophotometer', *J. Forensic Med. Toxicol.*, 23, pp. 6–8.

Kaur, R., Kaushal, S. and Singh, P.P. (2021) 'MWCNTs/SnZrMoP nano-composite as Ba (II)-selective electrode and heterogeneous catalyst for esterification of primary alcohols', *Chem. Pap*, 75, pp. 2379–2393.

Krishna, S. *et al.* (2020) 'Barium Poisoning with Analytical Aspects and its Management', *Int. J. Adv. Res. Med. Chem.*, 2, pp. 20–27.

Ma, Y.-H. *et al.* (2009) 'A highly selective polymeric membrane barium(II) electrode based on a macrocyclic tetrabasic ligand as neutral carrier', *Anal. Bioanal. Chem.*, 395, pp. 855–862.

Martin, S. and Griswold, W. (2009) 'Human Health Effects of Heavy Metals', *CHSR*, 15, pp. 1–6.

Matecha, R.M. *et al.* (2021) 'A single column separation method for barium isotope analysis of geologic and hydrologic materials with complex matrices', *Geochem. Trans.*, 22, pp. 1–9.

Mizani, F., Saffari, S. and Paiehghadr, M. (2023) 'Trace Amounts Determination of Barium Ions by a New Ion-Selective Electrode based on 4′4″(5″)-Di-Tert-Butyldibenzo-18-Crown-6', *Anal. Bioanal. Electrochem.*, 15.

Negi, G. and Goswami-Giri, A.S. (2017) 'Rapid determination of barium ion in water using ion selective electrode', *AJRC*, 10, pp. 517–519.

Oskarsson, A. (2022) 'Barium', in *Handbook on the Toxicology of Metals*. Elsevier, pp. 91–100.

Othman, A.M., El-Shahawi, M.S. and Abdel-Azeem, M. (2006) 'A novel barium polymeric membrane sensor for selective determination of barium and sulphate ions based on the complex ion associate barium(II)–Rose Bengal as neutral ionophore', *Anal. Chim. Acta*, 555, pp. 322–328.

peana, M. *et al.* (2021) 'Environmental barium: potential exposure and health-hazards', *Arch. Toxicol.*, 95, pp. 2605–2612.

Ridgway, S. and Wajrak, M. (2019) 'Development of an In-Field Method for the Detection of Barium in Various Water Samples Using Differential Pulse Anodic Stripping Voltammetry', *Int. J. Electrochem*, 2019, pp. 1–7.

Sahari, s *et al.* (2011) 'Synthesis, Complexation and Use of Calix[4]crown-6 as a Novel Neutral Ionophore for the Preparation of a Selective and Sensitive PVC-Membrane Potentiometric Sensor for Ba2+ Ion', *J. Iran. Chem. Soc.*, 8, pp. 879–888.

Saleh, M.B. (2000) 'Neutral bidentate organophosphorus compounds as novel ionophores for potentiometric membrane sensors for barium(II)', *Fresenius J Anal Chem*, 367, pp. 530–534.

Savichev, A.T. and Vodyanitskii, Yu.N. (2009) 'Determination of barium, lanthanum, and cerium contents in soils by the X-ray radiometric method', *Eurasian J. Soil Sci.*, 42, pp. 1461–1469.

Singh, A.K. *et al.* (2005) 'Novel potentiometric sensor for monitoring barium(II) based on 2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene', *Sens. Actuators B: Chem.*, 106, pp. 779–783.

Umezawa, Y. *et al.* (2000) 'Potentiometric Selectivity Coefficients of Ion-Selective Electrodes. Part I. Inorganic Cations (Technical Report)', *Pure Appl. Chem.*, 72, pp. 1851–2082.

Wang, D.Y. and Wang, Y. (2008) 'Phenotypic and Behavioral Defects Caused by Barium Exposure in Nematode Caenorhabditis elegans', *Arch. Environ. Contam. Toxicol.*, 54, pp. 447–453.

Yofll, J., Avni, R. and Stiller, M. (1963) 'Elimination of phosphate interference in flame photometric determination of strontium and barium', *Anal. Chim. Acta*, 28, pp. 331–335.

Zamani, H.A. *et al.* (2010) 'Construction of barium (II) PVC membrane electrochemical sensor based on 3-deoxy-d-erythro-hexos-2-ulose bis (thiosemicarbazone) as a novel ionophore', *Desalination*, 250, pp. 56–61.

Zamani, H.A., Abedini-Torghabeh, J. and Ganjali, M.R. (2006) 'A Highly Selective and Sensitive Barium(II)-Selective PVC Membrane Based on Dimethyl 1-Acetyl-8-oxo-2,8-dihydro- 1H-pyra-zolo[5,1-a]isoindole-2,3-dicarboxylate', *Electroanalysis*, 18, pp. 888–893.