



## Synthesis, Characterization and Analytical Applications of Novel Potentiometric Sensor Based on Chromium(III)Boratotungstophosphate

PERNITA DOGRA<sup>1,\*</sup>, HARISH K. SHARMA<sup>2</sup> and ANJU PARMAR<sup>1</sup>

<sup>1</sup>Department of Chemistry, M.M. University, Mullana, Ambala-133207, India

<sup>2</sup>Department of Chemistry, M.M. University, Sadhopur, Ambala-134007, India

\*Corresponding author: E-mail: [pernita.dogra@mmumullana.org](mailto:pernita.dogra@mmumullana.org)

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Ion selective electrode based on chromium(III) boratotungstophosphate was successfully fabricated for the detection of Hg(II) ions. The characterization of electroactive material has been done with FTIR, SEM, EDS and X-Ray diffraction studies. Polymeric membranes containing different composition of electroactive material and epoxy resin as binder were prepared. The best performance was shown by the electrode with composition having 40 % electroactive material and 60 % epoxy resin. A reasonably short response time of 6 s was shown together with a life of six months without any divergence in potential. The sensor possessed a near Nernstian slope of  $25 \pm 0.8$  mV decade<sup>-1</sup> over a wide linear range of  $1.0 \times 10^{-1}$  M –  $1.0 \times 10^{-6}$  M Hg(II) ions. The electrode worked satisfactorily in the partially non-aqueous medium also. The working pH range of the sensor was found to be 2.43-8.0. Analytical applicability of membrane sensor was evaluated by using it as an indicator electrode for analysis of Hg(II) ions in different water samples procured from sea and canal waters. The proposed electrode displayed good selectivity for Hg(II) in the presence of some transition metal(II) ions and lanthanide(III) ions.

**Keywords:** Chromium(III) boratotungstophosphate, Mercury(II), Selectivity coefficient, Potentiometric sensor.

### INTRODUCTION

Burning of coal and mining of gold releases a large amount of mercury in the environment [1]. Bio-magnifications caused by consuming mercury containing organisms are also one of the major causes of exposure to mercury [2]. The importance of mercury to the environment cannot be over emphasized. From an environmental point of view, it is highly toxic, causing severe damage to the human central nervous system. Mercury concentrations in drinking, river or sea water are typically below  $5 \mu\text{g L}^{-1}$ , making it extremely difficult to measure using any particular technique. So, it becomes an utmost requirement to detect the presence of mercury in different matrices.

A number of methods, such as atomic absorption spectrometry (AAS) [3,4], X-ray fluorescence spectrometry [5] and potentiometry [6] have been used for determination of mercury in the analytical samples. Very few sensors for potentiometric determination of mercury(II) based on carbon paste electrode (CPE) [7,8] and coated wire electrodes [9,10] have been reported. However, these electrodes are not very fruitful as they

have the problem of low detection limits, a long response time and they suffer from serious interferences by various cations.

Potentiometric sensors based on ion-selective electrodes are suitable for analyzing different chemical species because they offer many advantages such as precision, simplicity, sensitivity, low cost and better selectivity. They are easily reproducible and highly stable with short response time. In this work, the potentiometric sensor based on chromium(III) based ion exchanger has been successfully prepared and used for the detection of  $\text{Hg}^{2+}$  in seawater (Arabian sea) and local canal water (Jan Sui Head, Ambala). No chromium(III) based sensor has been reported in the literature for the determination of mercury(II) ions.

### EXPERIMENTAL

A digital pH-meter 101 (Sr. No.-1402046) was used to measure pH and temperature was measured with a Temperature Meter-18. An electric thermostat oven (Universal) was used for heating the sample at variable temperatures. Digital potentiometer-118 (Sr. No.-1312575) was used for EMF measure-

ments. Effect of heat on the synthesized material (TGA analysis) was observed with Mettler Toledo Star System. Advanced micro-analysis solution AMETAK electron microscope was used to obtain SEM/EDS images. Diffractometer (XPERT-PRO-Sr. No.-11023505) was used for X-ray diffraction studies. IR spectrum was obtained by KBr pellet medium.

To synthesize electroactive material, chromium sulphate, boric acid, orthophosphoric acid and sodium tungstate were used. pH control was done by using NaOH (0.1 M) and HCl (0.1 M). All chemicals were procured from C.D.H. (INDIA), Qualikems and S.D. Fine Chemicals Pvt. Ltd. The reagents used were of analytical grade and of highest purity. Double distilled water (DDW) was used throughout the process.

**Synthesis of electroactive material:** The sensor was synthesized by sol-gel method. Four samples of chromium(III) boratotungstophosphate were prepared by using chromium sulphate, sodium tungstate, orthophosphoric acid and boric acid in different volume ratios (Table-1). The mixture of sodium tungstate, orthophosphoric acid and boric acid was stirred continuously at 60 °C. Chromium sulphate solution was added to this mixture with intermittent shaking. The pH of the mixture was maintained by adding conc. HCl/NaOH. The resultant green coloured gel was kept for 24 h at room temperature and then filtered. The precipitates were washed with double distilled water to remove traces of any sulphates or chlorides. The dried precipitates were kept in distilled water to break into small granules. The granular mixture was then dried at 40 °C. The dried granules were kept overnight in 0.1 M HCl to convert them into H<sup>+</sup> ion form. Intermittent shaking was done and the supernatant liquid was replaced with fresh acid so as to ensure complete conversion of the granules into H<sup>+</sup> ion form. The material thus produced was then washed with demineralized water to remove excess acid before drying finally at 50 °C.

**Ion-exchange capacity (IEC):** Column operation method [11] was used to measure ion-exchange capacity and it was found to be maximum for sample-1 (Table-1).

**Regeneration of electroactive material:** Exchanger was regenerated by keeping it in 0.1M HCl for overnight. It was washed with demineralized water to make it free from all impu-

rities. To check reproducibility of exchanger, ion exchange capacity was determined three times. It was found that there was a decrease of only 7.21 % in exchange capacity after repeated use. NaCl and NaNO<sub>3</sub> were used as eluants and ion exchange capacity was found to be almost similar with both the eluants [12] (Table-1).

**Distribution coefficient studies:** The preferential selectivity of electroactive material for a particular metal ion was evaluated by distribution coefficient values (K<sub>d</sub> values). The K<sub>d</sub> values for different metal ions like Sm(III), Mn(II), Ni(II), Co(II), Pb(II), La(III), Cu(II), Cd(II), Hg(II), As(III) were evaluated using the following formula [13]:

$$K_d = \frac{(I-F)}{F} \times \frac{V}{W} \quad (1)$$

where K<sub>d</sub> is the distribution coefficient value, I is the initial volume of EDTA (0.1 M) consumed by cations before equilibrium, F is the final volume of EDTA (0.1 M) consumed by cations after equilibrium, V is the initial volume of the metal ion solution taken for analysis and W is the initial dry mass of ion-exchanger. The values of distribution coefficient (K<sub>d</sub>) are given in Table-2.

TABLE-2  
DISTRIBUTION COEFFICIENT VALUES FOR Hg(II)  
SELECTIVE ELECTRO-ACTIVE SENSOR BASED ON  
CHROMIUM(III) BORATOTUNGSTPHOSPHATE

Metal ions	K <sub>d</sub> values	Metal ions	K <sub>d</sub> values
Sm(III)	62.5	La(III)	25.0
Mn(II)	66.6	Cu(II)	50.0
Ni(II)	57.1	Cd(II)	80.0
Co(II)	66.6	Hg(II)	150.0
Pb(II)	100.0	As(III)	70.0

**Composition of membrane:** The selectivity and sensitivity of ion selective sensors is significantly influenced by the ratio of amount of electroactive material and binder (Table-3). The prepared membranes were diced into circular shape of diameter 2 cm. The membrane which gave reproducible results, best response in terms of concentration range, response time and slope was selected for further potentiometric studies [14].

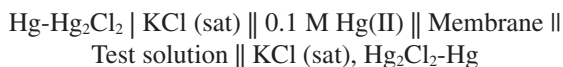
TABLE-1  
CONDITIONS OF SYNTHESIS AND PROPERTIES OF CHROMIUM(III)BORATOTUNGSTO PHOSPHATE

Sample No.	Name of the constituent	Mixing volume ratio	Molar conc. (M)	pH	Temp. (°C)	Colour in H <sup>+</sup> ion form	Morph Ology	IEC (meq g <sup>-1</sup> ) with NaCl	IEC (meq g <sup>-1</sup> ) with NaNO <sub>3</sub>
1	Chromium sulphate	1	1.0	1.0	60	Green	Amorphous	0.704	0.704
	Orthophosphoric acid	1	1.0						
	Boric acid	1	1.0						
	Sodium tungstate	1	1.0						
2	Chromium sulphate	1	0.5	0.0	60	Green	Amorphous	0.563	0.562
	Orthophosphoric acid	1	0.5						
	Boric acid	1	0.5						
	Sodium tungstate	1	0.5						
3	Chromium sulphate	3	1.0	1.0	60	Green	Amorphous	0.347	0.345
	Orthophosphoric acid	1	1.0						
	Boric acid	1	1.0						
	Sodium tungstate	1	1.0						
4	Chromium sulphate	2	1.0	1.0	40	Green	Amorphous	0.300	0.301
	Orthophosphoric acid	1	1.0						
	Boric acid	1	1.0						
	Sodium tungstate	1	1.0						

TABLE-3  
COMPOSITION OF MEMBRANES

Ion selective membrane (%)	Quantity of epoxy resin (g)	Quantity of electro-active material (g)
40	0.60	0.40
50	0.50	0.50
60	0.40	0.60

**EMF measurements:** To measure EMF, the selected membrane was attached to one end of the glass tube having 1.8 cm internal diameter [15,16]. The time needed to equilibrate the membrane was optimized by keeping all the membranes in 0.1 M – 0.001 M solution of  $\text{Hg}(\text{NO}_3)_2$  for variable time period. The membrane which was equilibrated for two days in  $1.0 \times 10^{-1}$  M  $\text{Hg}(\text{NO}_3)_2$  solution gave the best results. All the EMF measurements were conducted using the following cell assembly.



Constant potential values were recorded. The performance of the electrode was further investigated by recording authentic potential values with  $\text{Hg}(\text{II})$  solutions with a concentration range of  $1.0 \times 10^{-8}$  M to  $1.0 \times 10^{-1}$  M.

## RESULTS AND DISCUSSION

**Structural studies of electroactive material:** The presence of external water molecules along with -OH groups and other metal oxides were identified using IR spectrum (Fig. 1). The stretching vibrations due to B-O-B bonding were confirmed [17] by the presence of a strong band at  $740 \text{ cm}^{-1}$ . The presence of  $\text{BO}_3^-$  group was affirmed by the presence of a sharp band at  $1411.2 \text{ cm}^{-1}$  [18].

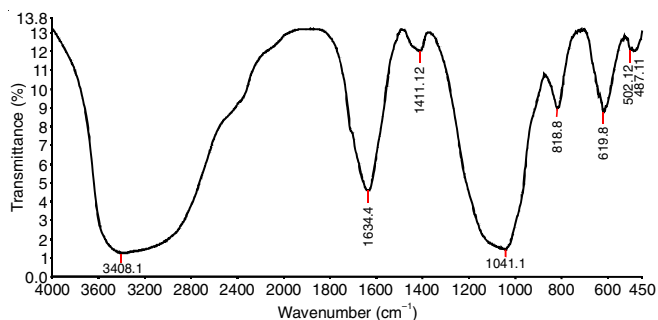


Fig. 1. FTIR of chromium(III) boratungstophosphate

A strong band at  $1634 \text{ cm}^{-1}$  was attributed to H-O-H bending, being representative of strongly bonded -OH group in the matrix [19]. While a band at  $893.11 \text{ cm}^{-1}$  was due to the presence of 12 W-O<sub>b</sub>-W oxygen bridges and corner sharing oxygen bridges which is characteristic of Keggin structure of heteropoly acid salt [20]. The weak bands at 619.8 and  $487.11 \text{ cm}^{-1}$  confirmed the presence of Cr-O deformation vibrations [21]. The presence of stretching vibrations due to Cr-O-Cr was confirmed [22] by a band at  $1052.3 \text{ cm}^{-1}$ . A band at  $502.12 \text{ cm}^{-1}$  affirmed the presence of stretching vibrations characteristic of symmetric and asymmetric bending [23] due to Oa-P-Oa bond in  $\text{PO}_4^{3-}$ . The broadening /shifting of bands from their normal modes were due to coupling of valence shell electrons with vibrational

states of different molecules. So, it was concluded that incorporated water molecules largely affect the properties of heteropolyacid salts [24].

Electron diffraction spectra of chromium(III) boratungstophosphate confirmed the presence of Cr, B, W, P, O characterized by their respective peaks in the spectrum. Atomic ratio of these elements was Cr:B:W:P:O::5.65:1.13:2.10: 3.90: 64.34, respectively. Oxygen content shown in the formula was due to the molecular water, hydroxyl group and oxides. Based on data obtained from EDS analysis, an empirical formula of the synthesized exchanger was deduced as:  $[\text{Cr}_2\text{O}_3]_{5.13}(\text{H}_3\text{BO}_3)_{3.51}(\text{H}_3\text{WO}_4)_{1.90} \cdot n\text{H}_2\text{O}$ .

The external water molecules were consistent only up to  $200^\circ\text{C}$  as shown by thermogravimetric studies (Fig. 2). The sensor experienced a weight loss of 20.5 % upto  $200^\circ\text{C}$ . When the sensor was heated above the recommended temperature, the sensor lost external water molecules. To calculate the number of external water molecules ('n') present in the exchanger, Alberti 'n' formula [25] was used as follows:

$$18n = \frac{X(M+18n)}{100} \quad (2)$$

where X = weight loss (%) at  $200^\circ\text{C}$ , (M+18n) is the molecular weight of the material and 'n' represents the number of water molecules. This gives the value of 'n' as 23.8 24. So the formula of sensor deduced as  $[\text{Cr}_2\text{O}_3]_{5.13}(\text{H}_3\text{BO}_3)(\text{H}_3\text{PO}_4)_{3.51}(\text{H}_3\text{WO}_4)_{1.90} \cdot 24\text{H}_2\text{O}$  with molecular weight 2093.02 a.m.u. The weight loss of 10 % was further observed up to  $500^\circ\text{C}$ . This loss in weight was due to the rearrangement of coordinated water, hydroxyl molecules and other functional groups. There was a regular decline in the weight of exchanger. The weight loss was continued even up to  $800^\circ\text{C}$  i.e. 7.6 % due to loss of coordinated water and hydroxyl groups [26].

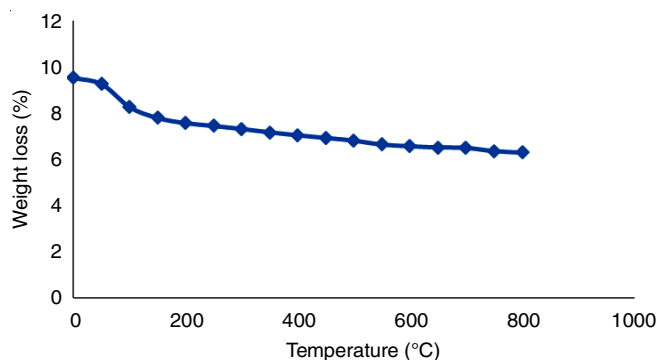


Fig. 2. TGA analysis of chromium(III) boratungstophosphate (CrBWP)

X-ray diffraction (Fig. 3) studies ensured lack of particular angle of diffraction line which affirmed the amorphous nature of heteropoly acid. Scanning electron microscope (Fig. 4) studies revealed that the particles of heteropolyacid salt i.e. chromium(III) boratungstophosphate are broad and irregular in shape.

**Calibration curve and statistical data:** The selectivity of ion selective electrode depends on the mobility of metal ion sensor complex in the membrane and distribution of the metal ions in aqueous phase and membrane. The electrode was characterized on the basis of different parameters like response time, measuring range and slope of calibration curve. The effect of

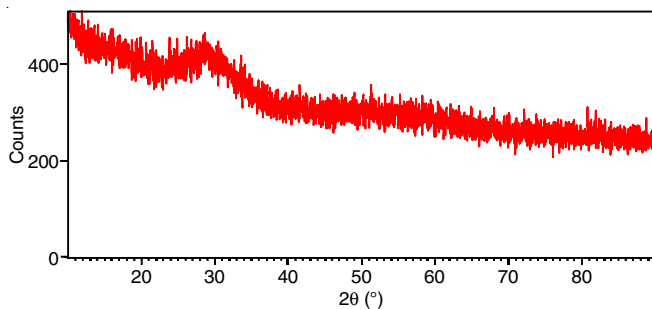


Fig. 3. XRD of chromium(III) boratotungstophosphate

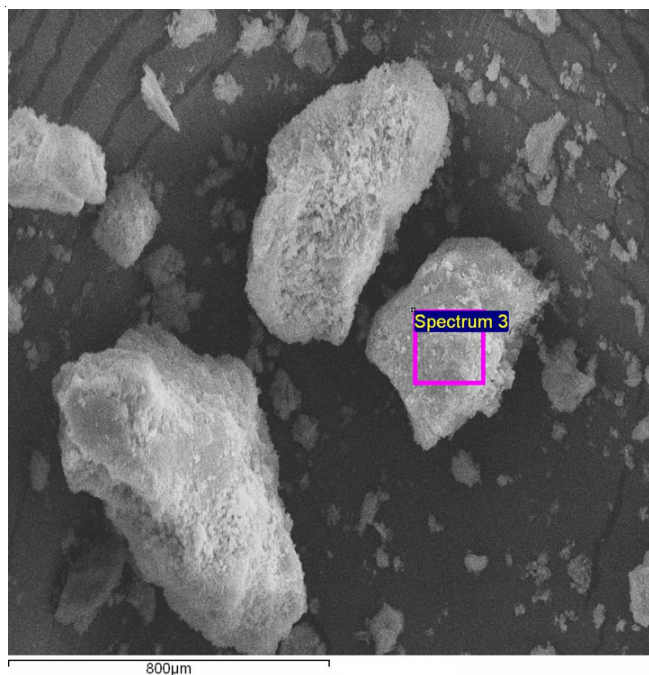


Fig. 4. SEM image of chromium(III) boratotungstophosphate

membrane composition on the potential response of sensor is summed up in Table-4. The electrode with optimum composition *i.e.* chromium(III) boratotungstophosphate:epoxy ratio (w/w) (40:60) showed the best response and gave a near Nernstian slope of  $25.0 \pm 0.8$  mV decade<sup>-1</sup> with very short response time *i.e.* 6 s over the measuring range of  $1.0 \times 10^{-6}$  M to  $1.0 \times 10^{-1}$  M whereas the electrode with composition 60 and 50 % displayed a slope of 18-19 mV decade<sup>-1</sup> in the concentration range of  $1.0 \times 10^{-6}$  M to  $1.0 \times 10^{-1}$  M. A standard deviation of  $\pm 1.0$  mV decade<sup>-1</sup> was observed. EMF values were plotted against log of activities of Hg(II) ions. A representative response curve is shown in Fig. 5.

According to IUPAC recommendations, the detection limit is defined by the cross section of two extrapolated linear calibration curves [27,28] and was found to be  $1.0 \times 10^{-6.5}$  M. The potential response of the sensing behaviour of the electrode

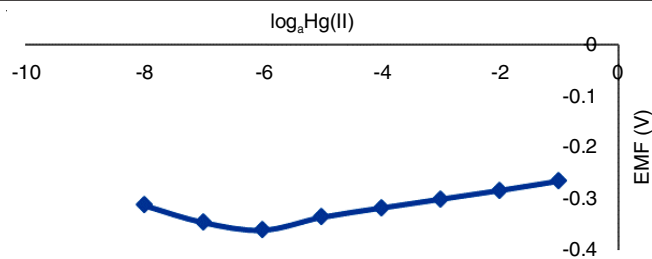


Fig. 5. Calibration curve for mercury selective electrode based on CrBWP (40 %)

remained same whether the EMF was measured from higher to lower or lower to higher concentration [29]. Potential response of the sensor was tested for other cations like Pb(II), La(III), Cd(II), Co(II), Hg(II), As(III), Cu(II), Ni(II), Mn(II), Sm(III) *etc.* Among the different cations tested, Hg (II) showed best linear range of  $1.0 \times 10^{-1}$  M to  $1.0 \times 10^{-6}$  M with Nernstian slope of  $25.0 \pm 0.8$  mV decade<sup>-1</sup>, whereas all other cations showed a sub-Nernstian slope as shown in Fig. 6 (Table-5). It was due to fast ion-exchange kinetics of the complex formed between sensor membrane/sample interface and the highest selectivity of sensor for Hg<sup>2+</sup>. Selectivity is also governed by its partition coefficient between the membrane and sample solution.

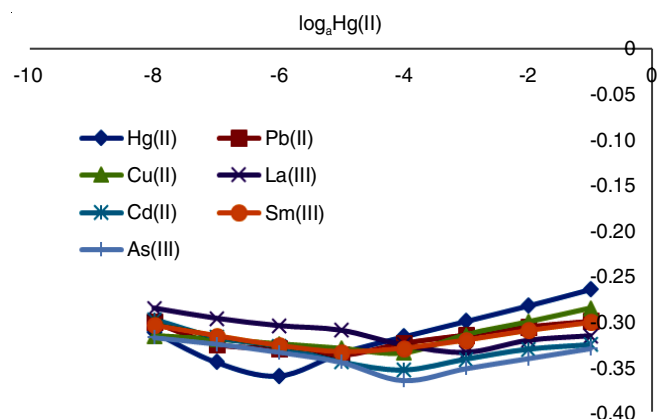


Fig. 6. Potentiometric response of the developed sensor based on CrBWP to different cations (40 %)

TABLE-5  
POTENTIOMETRIC RESPONSE OF THE DEVELOPED  
SENSOR BASED ON CrBWP TO DIFFERENT CATIONS (40 %)

Cation	Linear range (M)	Response time (s)	Slope (mV decade <sup>-1</sup> )
Cd(II)	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$	16.0	13.5
As(III)	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$	20.0	10.5
Sm(III)	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$	17.0	9.25
Cu(II)	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$	23.0	11.0
La(III)	$1.0 \times 10^{-3}$ to $1.0 \times 10^{-1}$	18.0	8.0
Pb(II)	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$	23.0	11.5
Hg(II)	$1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$	6.0	25.0

TABLE-4  
OPTIMIZATION OF MEMBRANE

Electro-active material	Electrode No.	Electro-active material (%)	Binder	Slope (mV decade <sup>-1</sup> )	Detection limit (M)	Response time (s)
CrBWP	E-1	40	Epoxy	$25.0 \pm 0.8$	$1.0 \times 10^{-6.5}$	6.0
CrBWP	E-2	50	Epoxy	$19.0 \pm 0.7$	$1.0 \times 10^{-6.0}$	13.0
CrBWP	E-3	60	Epoxy	$18.0 \pm 0.5$	$1.0 \times 10^{-6.0}$	17.0



**Response time:** The appraisal of analytical applicability of ion selective electrode was done by measuring static and dynamic response time [30]. The response time of ion-selective electrode is the average time required to obtain a potential within  $\pm 0.1$  V of the final steady-state potential after a ten-fold increase or decrease in the concentration of analyte upon successive immersion in a series of interested ions. The change in the EMF was plotted from the moment solution of concentration  $1.0 \times 10^{-6}$  M Hg (II) ions was added with respect to time for the sensor to show the response. The response time was obtained from the plot and found to be 6 s. The Hg(II) solution with a 10 times difference in the concentration was added in the sequence of high to low concentration to check the practical reversibility of sensor and the EMF was measured for each such addition of Hg(II) solution [31]. The graph of EMF vs. time for sensor is shown in Figs. 7 and 8. The sensor response time remained unchanged whether the potential was recorded from higher to lower concentrations or *vice-versa*.

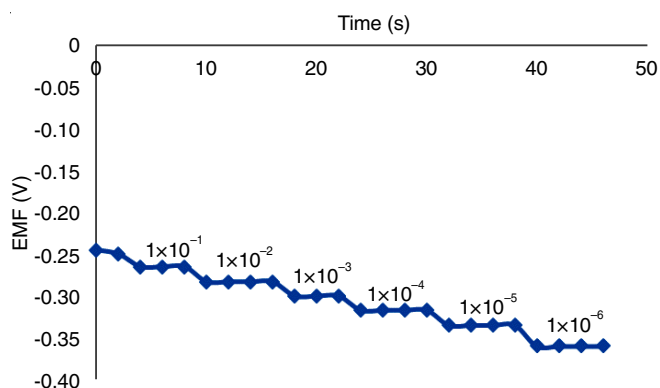


Fig. 7. Dynamic response time of the sensor based on CrBWP for stepwise change in the concentration of Hg(II) ions ( $1.0 \times 10^{-1}$  M to  $1.0 \times 10^{-6}$  M Hg(II) ions)

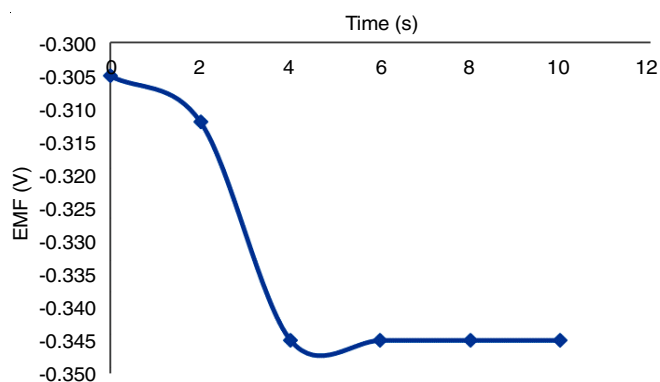


Fig. 8. Static response time obtained practically for the developed potentiometric sensor based on CrBWP by the addition of Hg(II) ( $1.0 \times 10^{-2}$  M Hg(II) ions)

**Sensor selectivity:** The sensor selectivity was predicted in terms of selectivity coefficient values. It was expressed as a response shown by ISE to the primary ion in the presence of other ions present in analyte solution. The interference by different ions was found by fixed interference method (FIM) [32]. Interfering ion solutions with concentration  $2.0 \times 10^{-3}$  and  $2.0 \times 10^{-4}$  M were mixed with  $2.0 \times 10^{-1}$  –  $2.0 \times 10^{-8}$  M of Hg(II) ions. The selectivity coefficient  $K_{A,B}^{pot}$  was calculated using Nicolsky-Eisenman equation:

$$K_{A,B}^{pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \quad (3)$$

where  $K_{A,B}^{pot}$  is the potentiometric selectivity coefficient;  $Z_A$  and  $Z_B$  are the charges of primary and interfering ions;  $a_A$  and  $a_B$  are the activities of primary ion A and the interfering ion B, respectively. According to Nicolsky-Eisenman equation, if the value of  $K_{A,B}^{pot} < 1$ , then ISE responds to primary ions more selectively than the corresponding interfering ions and if value of  $K_{A,B}^{pot} > 1$ , then ISE responds towards interfering ions preferably than primary ions [33].

The selectivity coefficient values of the reported electrode are shown in Table-6. The values indicated that developed sensor exhibited highest selectivity for Hg(II) ions over a number of other cations. The typical selectivity pattern for other hazardous metal ions predicted by the reported electrode is given as below: Hg(II) > La(III) > Sm(III) > Co(II) > Pb(II) > Ni(II) > Cd(II) > Mn(II) > Cu(II) > As(III) (with  $2.0 \times 10^{-3}$  M concentration of interfering ion solution); while Hg(II) > La(III) > Sm(III) > Ni(II) > Mn(II) > Co(II) > As(III) > Pb(II) > Cu(II) > Cd(II) (with  $2.0 \times 10^{-4}$  M concentration of interfering ion solution).

Interfering ion (B)	Selectivity coefficient values ( $K_{A,B}^{pot}$ )	
	$2.0 \times 10^{-3}$ M	$2.0 \times 10^{-4}$ M
Cd(II)	$2.60 \times 10^{-4}$	$1.9 \times 10^{-4}$
Ni(II)	$2.80 \times 10^{-4}$	$1.7 \times 10^{-3}$
Cu(II)	$1.80 \times 10^{-4}$	$2.6 \times 10^{-4}$
Sm(III)	$3.50 \times 10^{-2}$	$1.6 \times 10^{-3}$
La(III)	$3.70 \times 10^{-2}$	$1.8 \times 10^{-3}$
Co(II)	$3.04 \times 10^{-3}$	$2.8 \times 10^{-4}$
Mn(II)	$2.00 \times 10^{-3}$	$3.0 \times 10^{-4}$
Pb(II)	$2.80 \times 10^{-4}$	$1.9 \times 10^{-4}$
As(III)	$3.50 \times 10^{-4}$	$2.5 \times 10^{-4}$

**Effect of internal solution concentration:** For quantitative measurements with ISE, studies were carried out to reach the optimum experimental conditions. From Fig. 9, it was clearly visible that the behaviour of electrode was unaffected by change in the concentration (Table-7). There was an expected change in the intercept of calibration curve, which was same as observed by Sharma *et al.* [34].

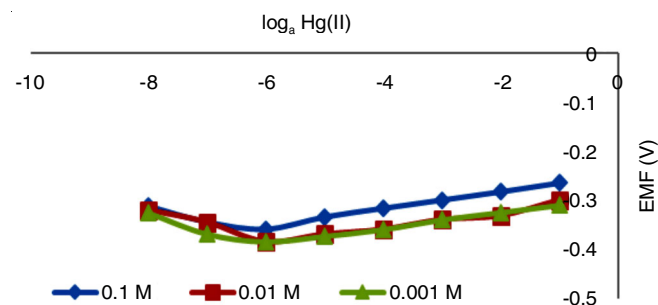


Fig. 9. Calibration curve showing effect of internal solution on 40 % electrode based on CrBWP

TABLE-7  
EFFECT OF INTERNAL SOLUTION ON THE RESPONSE OF Hg(II) SELECTIVE ELECTRODE BASED ON CHROMIUM(III)BORATOTUNGSTOPHOSPHATE

Solution No.	Concentration of internal solution (M)	Membrane composition (%)	Slope (mV decade <sup>-1</sup> )	Response time (s)	Linear concentration range (M)
1	1.0 × 10 <sup>-1</sup>	60	18.0	17.0	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>
	1.0 × 10 <sup>-1</sup>	50	19.0	13.0	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>
	1.0 × 10 <sup>-1</sup>	40	25.0	6.0	1.0 × 10 <sup>-6.5</sup> to 1.0 × 10 <sup>-1</sup>
2	1.0 × 10 <sup>-2</sup>	60	21.5	15.0	1.0 × 10 <sup>-6.2</sup> to 1.0 × 10 <sup>-1</sup>
	1.0 × 10 <sup>-2</sup>	50	18.0	14.0	1.0 × 10 <sup>-5.8</sup> to 1.0 × 10 <sup>-1</sup>
	1.0 × 10 <sup>-2</sup>	40	23.0	15.0	1.0 × 10 <sup>-6.0</sup> to 1.0 × 10 <sup>-1</sup>
3	1.0 × 10 <sup>-3</sup>	60	20.0	14.0	1.0 × 10 <sup>-6.2</sup> to 1.0 × 10 <sup>-1</sup>
	1.0 × 10 <sup>-3</sup>	50	19.5	13.0	1.0 × 10 <sup>-5.1</sup> to 1.0 × 10 <sup>-1</sup>
	1.0 × 10 <sup>-3</sup>	40	24.0	15.0	1.0 × 10 <sup>-6.4</sup> to 1.0 × 10 <sup>-1</sup>

**Effect of pH and non-aqueous solution:** The influence of pH on the performance of electrode was studied over a pH range of 2.0-12.0. It was clear from the curve (Fig. 10) that the potential remained constant in the pH range of 2.43-8.0. Therefore, this range was assumed to be the working pH range for the electrode assembly. The change in the EMF value with increase or decrease in pH was due to hydrolysis of Hg(II) ions, contribution of H<sup>+</sup> ions from the solution and by charge transport process of the electrode, thereby causing interference.

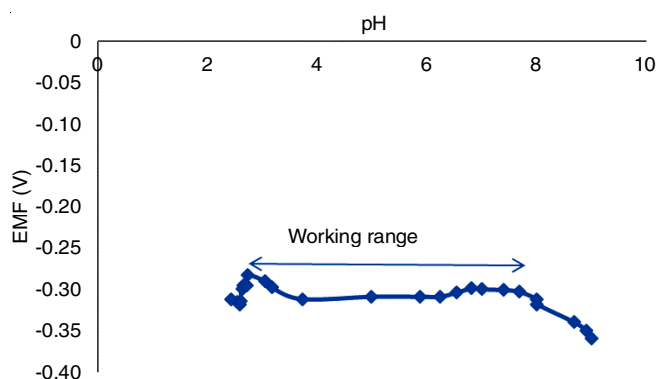


Fig. 10. Effect of pH on mercury selective electrode based on CrBWP

The effect of partially non-aqueous solution on the performance of electrode was also investigated by using ethanol-water, methanol-water and acetone-water mixtures [35]. The electrode worked well in mixture having 10, 20 and 30 % (v/v) partially non-aqueous solution (Fig. 11) and the resulting values are summarized in Table-8. It was elucidated from the data that the expected change in the intercept of the calibration curve was same as observed by Dogra *et al.* [36].

TABLE-8  
EFFECT OF PARTIALLY NON AQUEOUS MEDIUM ON THE WORKING OF Hg(II) IONS SELECTIVE ELECTRODE BASED ON CrBWP

Solvent	Percentage (v/v)	Slope (mV decade <sup>-1</sup> )	Detection limit (M)
Acetone	10 %	24.5	1.0 × 10 <sup>-6.7</sup>
	20 %	24.0	1.0 × 10 <sup>-6.2</sup>
	30 %	24.0	1.0 × 10 <sup>-6.0</sup>
Ethanol	10 %	24.0	1.0 × 10 <sup>-6.0</sup>
	20 %	24.5	1.0 × 10 <sup>-6.4</sup>
	30 %	24.5	1.0 × 10 <sup>-6.2</sup>
Methanol	10 %	24.0	1.0 × 10 <sup>-6.0</sup>
	20 %	24.0	1.0 × 10 <sup>-6.3</sup>
	30 %	24.0	1.0 × 10 <sup>-6.4</sup>

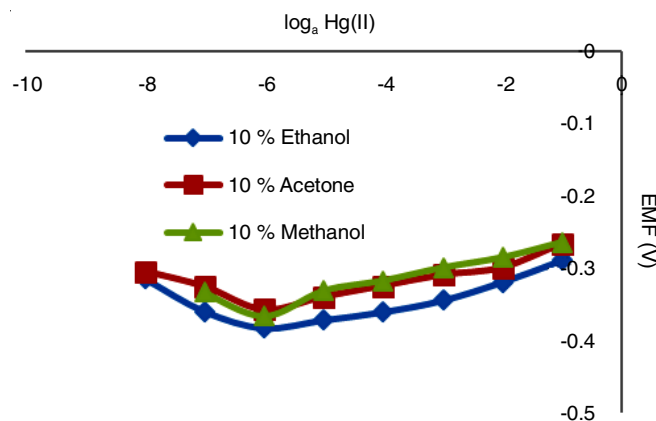


Fig. 11. Effect of partial non aqueous solutions on the working of Hg(II) ions selective electrode based on CrBWP

### Analytical applications

**Indicator electrode:** The sensor was also used as an indicator electrode in the potentiometric titrations with EDTA and oxalic acid solutions [37]. A 10 mL of 0.01 M Hg(II) ion solution was titrated with 5 × 10<sup>-3</sup> M EDTA and oxalic acid solution separately. A sharp inflection point at the titrant volume (corresponding to end point) confirms the formation of 1:1 complex between EDTA/oxalic acid solution and Hg(II) ions (Fig. 12) [38]. The results revealed that the electrode can be successfully used as indicator electrode.

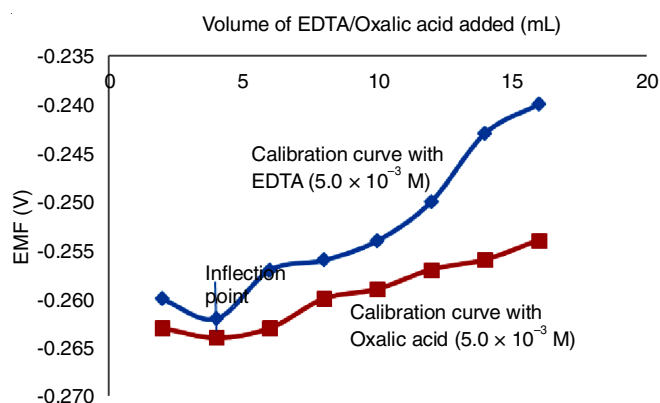


Fig. 12. Potentiometric titration curve using proposed sensor as an indicator electrode (5.0 × 10<sup>-3</sup> M oxalic acid/EDTA)

**In real samples:** The proposed electrode was successfully used for determination of Hg(II) in sea water and river water. The results were compared with the data obtained by AAS

TABLE-9  
POTENTIOMETRIC DETERMINATION OF Hg(II) IONS IN DIFFERENT WATER  
SAMPLES USING MERCURY SELECTIVE ELECTRODE BASED ON CrBWP

Sample name	Amount of Hg found by using proposed electrode in (mg L <sup>-1</sup> )	Amount of Hg found by AAS (mg L <sup>-1</sup> )	RSD (%)	Recovery (%)	WHO limit (PTWI)
Canal water (Jan Sui Head, Ambala)	0.660	0.700	0.0640	94.20	1.6 µg/kg
Sea water (Goa Sea Beach)	0.069	0.073	0.0141	94.52	0.5-3 ng L <sup>-1</sup>
Lab sample	1.500	1.580	0.0200	94.93	–

(Table-9). The water samples were collected from different sea beaches of Goa (India) and from the local canal at Jansui Head (Ambala city). The results indicated that the concentration of Hg(II) in different samples obtained potentiometrically was in good agreement with that obtained from AAS. Thus, the proposed electrode was highly accurate, precise and reproducible and can be easily applied for quantification of Hg(II) in real samples.

**Statistical verification of analytical data:** The analytical data obtained for the real samples by AAS as well as by the proposed electrode was further verified with statistical methods [39]. It was done by performing F-Test and t-Test at 95 % confidence level. The calculated F-values were less than the critical F-value at 95 % confidence level (Table-10). It was observed that critical t-value was greater than calculated t-value so null hypothesis (significant difference between the results obtained by official method and that obtained by using proposed sensor) was rejected. It was also observed that probability value ('p' value) was greater than alpha (> 0.05) which provided the evidence that the proposed electrode can be suitably used to check the presence of Hg<sup>2+</sup> in the real samples.

TABLE-10  
STATISTICAL VERIFICATION OF THE DATA  
OBTAINED FOR THE DETERMINATION OF Hg(II)  
IONS IN REAL-LIFE SAMPLES USING MERCURY  
SELECTIVE ELECTRODE BASED ON CrBWP

Sample name	Recovery by Hg(II) selective electrode (%)	F-Test	T-Test
Canal water	94.81	2.14	0.2
Sea water	94.52	1.20	0.4
Lab sample	94.93	2.15	0.2

**Comparability of proposed electrode with reported sensors selective for mercury ions:** The working of proposed electrode was compared with the reported sensors selective for mercury [40-44] and found that electrode based on chromium(III) boratungstophosphate was superior with respect to its properties (Table-11).

**Shelf-life of electrode:** The EMF measurements were carried out over a considerable period of time to determine life time of the electrode. The electrode displayed constant potential reading within ± 1 V for day to day measurements and the calibration curve did not change by more than ± 1 V over a period of six months. After six months, the linear range becomes limited.

## Conclusion

Chromium(III) boratungstophosphate can be easily prepared for making sensor for the detection of Hg(II) ions. The electrode has a long life, wide detection limit and excellent pH range. The electrode exhibited good tolerance to partially non-aqueous solvents and can also be used as indicator electrode with potential stability. Presence of other metals did not have any influence on the selectivity of electrode. The electrode was also used successfully for the direct determination of mercury ions in canal water and sea water.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

TABLE-11  
COMPARISON OF NEW ELECTRODES WITH ALREADY REPORTED SENSORS SELECTIVE FOR MERCURY IONS (Hg<sup>2+</sup>)

Name of the sensor	Slope (mV decade <sup>-1</sup> )	Linear range (M)	pH range	Response time (s)	Detection limit (M)	Interference by other cations	Ref.
4-(4-N,N-dimethylphenyl)-2,6-diphenylpyrillium tetrafluoroborate	34.0	1 × 10 <sup>-8</sup> to 1 × 10 <sup>-6</sup>	2.5-7.0	180 s	1 × 10 <sup>-8</sup>	Alkaline earth metals and alkali metal ions	[40]
Diphenylthiocarbazon	29.7	5.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-2</sup>	3.5-8.0	60-120 s	3.0 × 10 <sup>-7</sup>	Na <sup>+</sup> , K <sup>+</sup> , Zn <sup>2+</sup> , Cu <sup>2+</sup> , Cr <sup>3+</sup> , Fe <sup>2+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	[41]
Substituted thiourea	28.4 ± 1.0	1 × 10 <sup>-7</sup> to 1 × 10 <sup>-1</sup>	–	30 s	7.0 × 10 <sup>-8</sup>	–	[42]
Triocetyl methyl ammonium thiosalicylate	44.08 ± 1.0	1.0 × 10 <sup>-9</sup> to 1.0 × 10 <sup>-2</sup>	3.0-9.0	5 s	1.0 × 10 <sup>-10</sup>	–	[43]
Tetrazolium-triiodomercurate	55.4 ± 0.4	1.0 × 10 <sup>-6</sup> to 6.0 × 10 <sup>-1</sup>	4.0-9.0	30-50 s	4.0 × 10 <sup>-6</sup>	Ca <sup>2+</sup> , Mg <sup>2+</sup> , Cu <sup>2+</sup> , Cr <sup>3+</sup> , Na <sup>+</sup> , Zn <sup>2+</sup>	[44]
Chromium(III)boratungstophosphate	25.0	1 × 10 <sup>-6</sup> to 1 × 10 <sup>-1</sup>	2.43-8.0	6 s	1.0 × 10 <sup>-6.4</sup>	–	Present work

## REFERENCES

1. R.A. Bernhoft, *J. Environ. Public Health*, **2012**, Article ID 460508 (2012); <https://doi.org/10.1155/2012/460508>.
2. S. Bose-O'Reilly, K.M. McCarty, N. Steckling and B. Lettmeier, *Curr. Probl. Pediatr. Adolesc. Health Care*, **40**, 186 (2010); <https://doi.org/10.1016/j.cppeds.2010.07.002>.
3. M.W. Hinds, *Spectrochim. Acta B Spectrosc.*, **53**, 1063 (1998); [https://doi.org/10.1016/S0584-8547\(98\)00171-2](https://doi.org/10.1016/S0584-8547(98)00171-2).
4. P. Bermejo-Barrera, E.M. Verdura-Constenla, A. Moreda-Piñeiro and A. Bermejo-Barrera, *Anal. Chim. Acta*, **398**, 263 (1999); [https://doi.org/10.1016/S0003-2670\(99\)00453-5](https://doi.org/10.1016/S0003-2670(99)00453-5).
5. L. Bennun and J. Gomez, *Spectrochim. Acta B Spectrosc.*, **52**, 1195 (1997); [https://doi.org/10.1016/S0584-8547\(97\)00003-7](https://doi.org/10.1016/S0584-8547(97)00003-7).
6. B. Rezaei, S. Meghdadi and S. Bagherpour, *Sensors*, **8**, 1469 (2008); <https://doi.org/10.1109/JSEN.2008.920719>.
7. A.A. Ismaiel, M.M. Aroua and R. Yusoff, *Am. J. Anal. Chem.*, **3**, 859 (2012); <https://doi.org/10.4236/ajac.2012.312113>.
8. M. Javanbakht, F. Divsar, A. Badieli, M.R. Ganjali, P. Norouzi, G.M. Ziarani, M. Chalooosi and A. Abdi Jahangir, *Anal. Sci.*, **25**, 789 (2009); <https://doi.org/10.2116/analsci.25.789>.
9. R.W. Cattrall and C.-P. Pui, *Anal. Chem.*, **48**, 552 (1976); <https://doi.org/10.1021/ac60367a033>.
10. K.R. Mahajan, R.K. Puri, A. Marwaha, I. Kaur and M.P. Mahajan, *J. Hazard. Mater.*, **167**, 237 (2009); <https://doi.org/10.1016/j.jhazmat.2008.12.107>.
11. P. Dogra, H.K. Sharma and N. Sharma, *Res. J. Chem. Environ.*, **15**, 897 (2011).
12. P. Dogra, H.K. Sharma and A. Parmar, *Res. J. Chem. Environ.*, **21**, 21 (2017).
13. H.K. Sharma and N. Sharma, *E-J. Chem.*, **6**, 1139 (2009); <https://doi.org/10.1155/2009/301016>.
14. F. Ahmadi and N. Asaadi, *Iran. J. Pharm. Res.*, **12**, 645 (2013).
15. K.S. Harish, V. Neha and J.K. Kapoor, *E-J. Chem.*, **8**, 155 (2011); <https://doi.org/10.1155/2011/358039>.
16. S.K. Mittal, R. Kumar, P. Dogra and H.K. Sharma, *Res. J. Chem. Environ.*, **11**, 47 (2007).
17. J.R.S. Brownson, M.I. Tejedor-Tejedor and M.A. Anderson, *Chem. Mater.*, **17**, 6304 (2005); <https://doi.org/10.1021/cm051568f>.
18. S.A. Nabi, S. Usmani and N. Rehman, *Ann. Chim. Fr.*, **21**, 521 (1996).
19. G.P. Singh, P. Kaur, S. Kaur, D. Arora, P. Singh and P.D. Singh, *Mater. Phys. Mech.*, **14**, 31 (2012).
20. A.I. Tropecelo, M.H. Casimiro, I.M. Fonseca, A.M. Ramos, J. Vital and J.E. Castanheiro, *Appl. Catal. A Gen.*, **390**, 183 (2010); <https://doi.org/10.1016/j.apcata.2010.10.007>.
21. S. Borghese, A. Blanc, P. Pale and B. Louis, *Dalton Trans.*, **40**, 1220 (2011); <https://doi.org/10.1039/c0dt01329c>.
22. C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, **22**, 207 (1983); <https://doi.org/10.1021/ic00144a006>.
23. Rakesh, S. Ananda and N.M.M. Gowda, *Modern Res. Catal.*, **2**, 127 (2013); <https://doi.org/10.4236/mrc.2013.24018>.
24. R. Kumar, H.K. Sharma and P. Dogra, *Int. J. Environ. Anal. Chem.*, **91**, 280 (2011); <https://doi.org/10.1080/03067310903278528>.
25. G. Alberti, P. Cardini-Galli, U. Costantino and E. Torracca, *J. Inorg. Nucl. Chem.*, **29**, 571 (1967); [https://doi.org/10.1016/0022-1902\(67\)80063-0](https://doi.org/10.1016/0022-1902(67)80063-0).
26. P. Dogra and J. Sharma, *Res. J. Chem. Environ.*, **12**, 35 (2017).
27. H.K. Sharma, P. Dogra and R. Kumar, *Int. J. Pure Appl. Chem.*, **4**, 287 (2009).
28. H.K. Sharma, P. Dogra, A.K. Gupta and F. Koohyar, *Quim. Nova*, **37**, 1324 (2014); <http://dx.doi.org/10.5935/0100-4042.20140198>.
29. H.K. Sharma and P. Dogra, *Am. Chem. Sci. J.*, **4**, 457 (2014); <https://doi.org/10.9734/ACSJ/2014/5527>.
30. M. Tutulea-Anastasiu, D. Wilson, M. del Valle, C. Schreiner and I. Cretescu, *Sensors*, **13**, 4367 (2013); <https://doi.org/10.3390/s130404367>.
31. E. Mahmoud, A. Abdollahain and S. Sahabnasagh, *Eur. J. Anal. Chem.*, **12**, 107 (2017).
32. Y. Umezawa, K. Umezawa and H. Sato, *Pure Appl. Chem.*, **67**, 507 (1995); <https://doi.org/10.1351/pac199567030507>.
33. Y. Umezawa, P. Bühlmann, K. Umezawa, K. Tohda and S. Amemiya, *Pure Appl. Chem.*, **72**, 1851 (2000); <https://doi.org/10.1351/pac200072101851>.
34. S.K. Mittal, R. Kumar, P. Dogra and H.K. Sharma, *J. Anal. Chem.*, **65**, 1045 (2010); <https://doi.org/10.1134/S1061934810100102>.
35. C. Mohan, K. Sharma and S. Chandra, *Anal. Bioanal. Electrochem.*, **9**, 35 (2017).
36. P. Dogra, R. Kumar and H.K. Sharma, Proceedings of International Congress of Chemistry and Environment, Kuwait, p. 500 (2007).
37. S.K. Mittal and H.K. Sharma, *J. Anal. Chem.*, **60**, 1069 (2005); <https://doi.org/10.1007/s10809-005-0240-5>.
38. A.M. Radalla, *Beni-Suef Univ. J. Basic Appl. Sci.*, **4**, 174 (2015); <https://doi.org/10.1016/j.bjbas.2015.05.012>.
39. M.I. Yousry, H. Ibrahim and O.R. Shehab, *J. Electroanal. Chem.*, **666**, 11 (2011); <https://doi.org/10.1016/j.jelechem.2011.11.024>.
40. X. Yu, Z. Zhou, Y. Wang, Y. Liu, Q. Xie and D. Xiao, *Sens. Actuators B: Chemical*, **123**, 352 (2007); <https://doi.org/10.1016/j.snb.2006.08.041>.
41. A.K. Hassan, *Mod. Chem. Appl.*, **1**, 111 (2013); <https://doi.org/10.4172/2329-6798.1000111>.
42. M. Javanbakht, F. Divsar, A. Badieli, M.R. Ganjali, P. Norouzi, G.M. Ziarani, M. Chalooosi and A.A. Jahangir, *J. Anal. Sci.*, **25**, 789 (2009); <https://doi.org/10.2116/analsci.25.789>.
43. A.A. Ismaiel, M.M. Aroua and R. Yusoff, *Sensors*, **14**, 13102 (2014); <https://doi.org/10.3390/s140713102>.
44. M.N. Abbas and G.A.E. Mostafa, *Anal. Chim. Acta*, **478**, 329 (2003); [https://doi.org/10.1016/S0003-2670\(02\)01520-9](https://doi.org/10.1016/S0003-2670(02)01520-9).