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Use of Cobalt(II) and Chromium(III) Metal based Schiff-Base Complexes for the Preparation of Potentiometric Sensors to Determine Bromide at Ultra-Low Concentrations

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Abstract

Co(II) and Cr(III) salicylidenic Schiff-base based complexes as novel ionophores were evaluated for the fabrication of bromide-selective electrodes. By incorporating a cation excluder along with various plasticizers (dibutyl phthalate, dioctyl phthalate, 1-chloronapthalene), optimized sensors (CoC7 and CrC7) exhibiting near-Nernstian slopes being 59.4±0.07 and 59.2±0.04 mV decade^{-1}, with a broad linear range (1×10^{-2} to 6.0×10^{-7} and 1×10^{-2} to 8.7×10^{-7} mol·L^{-1}), with low detection limits ($5.5\pm0.13\times10^{-7}$ and $6.5\pm0.07 \times10^{-7}$ mol·L^{-1}) respectively. Selectivity coefficient values of order 10^{-1} or less indicate that the proposed electrodes have superior selectivity for bromide ion over various interfering anions. The developed bromide electrodes demonstrated robust performance within a pH range of 4.0 to 9.0, as well as showed sufficient shelf life (4 and 5 weeks) with up to 20 % (v/v) non-aqueous tolerance and quick response times (12 and 16 s). These electrodes also served as indicator electrodes in the potentiometric titration of bromide ions against $AgNO_3$ and were used in the determination of bromide ion concentration in water samples.

Keywords: Cobalt(II), Chromium(III) Salicylidene Schiff-base complexes, Ionophore, Potentiometric sensor, Bromide ion sensor.

1. Introduction

Bromide (Br^-) is commonly found in both treated and untreated water sources across the world, especially in groundwater. Chlorination or ozonation disinfection methods are extensively employed in drinking water source treatment to eliminate pathogens. However, at low concentrations, these disinfection processes can lead to the formation of various chlorinated and brominated disinfection byproducts (DBPs) which cause significant risks to human health. Among these, bromate (BrO_3^-) stands out as particularly concerning. It is generated from bromide as a precursor and has been recognized by the “International Agency for Research on Cancer (IARC)” as a probable human carcinogen [1-6]. Since bromide is a precursor to bromate, its abundance in water sources has a considerable impact on the quality of drinking water. The low amount of bromide in the water supply and drinking water, however, makes it difficult and necessitates the use of sensitive, rapid, and effective instrumental analysis. Many techniques are available for determining the concentration of bromide ions in various substances such as milk, food items, water, wine, and urine. Over the years, numerous analytical techniques have been developed for this purpose, each with its advantages and limitations. These techniques include ion chromatography (IC),[7] ion-pair reversed phase liquid chromatography,[8] and high-performance liquid chromatography (HPLC),[9] gas chromatography-mass spectrometry (GCMS),[6] inductively coupled plasma mass spectrometry (ICP-MS),[10] capillary zone electrophoresis,[11] cyclic voltammetry,[12] and chemiluminescence.[13] However, these established techniques often require cumbersome infrastructure, entail high maintenance costs, and can be time-consuming. Moreover, they may not be suitable for high-throughput analysis of large sample sets. As a result, the focus of researchers has grown in recent times is developing alternative analytical methods that are reliable, cost-effective, rapid, and convenient for in-situ sample evaluations, such as the potentiometric method.

Ion-selective electrodes (ISEs) have emerged as promising tools for ion determination due to their simplicity, portability, and low cost. These electrodes exploit the selective interaction between the target ion and a specific sensing element, allowing for direct measurement without extensive sample preparation or sophisticated instrumentation. [14] **Figure 1** illustrates the components and the selective mechanism for bromide ion detection using the potentiometric method. In this context, attempts were made to develop new bromide (Br^-) ion-selective PVC membranes with the combination of transition metal complexes. The framework of the ligand and the characteristics of the metal ions in the coordination complex play an important role in affecting the Br^- ion selectivity of these electrodes. Given the significance of the determination of Br^- ion, many bromide ion-selective polymeric membrane electrodes have been studied, using different ionophores such as metal complexes HgS/Hg_2Br_2,[15] chalcogenide glassy-crystalline $AgBr$-Ag_2S-As_2S_3[16] 14-phenyldibenzo[a,j] xantheniu,[17] *bis*(4-hydroxyphenyl)-1,4-diaza-1,3-butadienemercury(II) complex,[18] iron(III)-salen,[19] mesotetraphenylporphyrin manganese(III)-chloride complex and 4,5-dimethyl-3,6-dioctyloxy-o-phenylene-bis(mercurytrifluoroacetate),[20] mercury(II) complex of a pyridine,[21] graphene oxide-aluminium fumarate metal-organic framework (BGO/AlFu MOF),[22] Pt(II) 5,10,15,20-tetra(4-methoxy-phenyl)-porphyrin(PtTMeOPP),[23] 1,3-dihexadecylimidazolium bromide,[24] and azapyrilium ion derivative.[25] Isildak et al. have used cobyrinic acid derivative

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macrocyclic molecule as an ionophore for selective detection of Br^- ion with a concentration range of 1×10^{-2} – 6.0×10^{-7} and 1.0×10^{-1} – 1.0×10^{-4} mol·L^{-1} and with detection limit of 5.5×10^{-7} and 2.2×10^{-5} mol·L^{-1}. [26] While the Br^- ion sensors that were previously reported had strong sensitivity and selectivity towards bromide, many of them were limited by non-Nernstian slope, poor detection limit, and short working concentration range. In context to the above, it is an ugrent need to develop a robust bromide selective sensor with enhanced potentiometric characteristics for low-concentrated bromide detections. In this work, Co(II) and Cr(III) Salicylidene Schiff-bases complexes were investigated as ionophores for Br^- ion detection in aqueous medium based on a potentiometric method. Interestingly, due to the high stability of the Co(II) and Cr(III) complexes and specific interactions among metal center and different anions, an improved potentiometric performance for bromide ion detection in terms of high sensitivity, wide linear range, lower detection limit, and high stability in a wide pH range was recorded. Meanwhile, cobalt and chromium both complexes often have flexible coordination numbers and geometries, which can be customized to fit the size and charge of Br^- ions. This flexibility can improve the binding efficiency and stability of halides. Additionally, the facile synthesis methodology and low cost of all precursors make these complexes an excellent alternative to the expensive commercial bromide exchangers. The advancement made here will benefit future sensor development to detect other anions, such as environmentally important nutrients including NO_3^- and HPO_4^{2-}. The components and the selective mechanism for bromide ion detection using the potentiometric method have been illustrated in Figure 1. In this context, attempts were made to develop new bromide (Br^-) ion-selective PVC membranes with different combination of these transition metal complexes. The framework of the ligand and the characteristics of the metal ions in the coordination complex play an important role in affecting the Br^- ion selectivity of these electrodes.

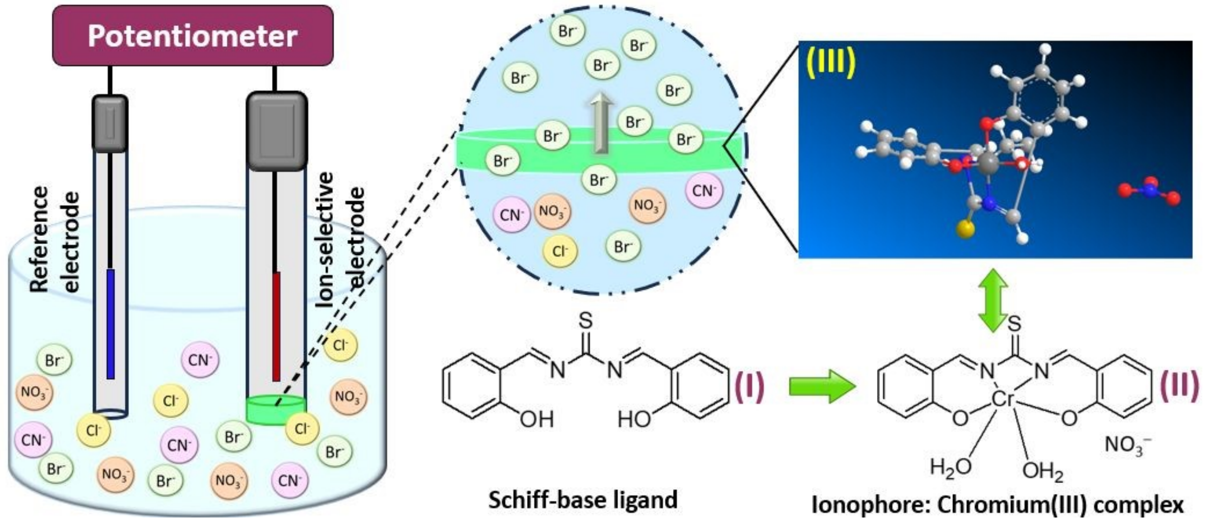

Figure 1. The components and selective mechanism for bromide ion by using a potentiometric method, with Cr(III) complex of salicylidene Schiff-base as an ionophore. Inset: CrC and salicylidene Schiff-base prepared in one-pot preparation (I),

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coordination environment of Cr(III) in the complex CrC, and simulated configuration of the CrC coordination complex.

2. Experimental Section

2.1. Materials

All analytical grade reagents, including cetyltrimethylammonium bromide (CTAB), dioctylphathalate (DOP), dibutyl phthalate (DBP), chloronapthalene (CN), *o*-nitrophenyl octyl ether (NPOE) and tri-*n*-butyl phosphate (TBP), tetrahydrofuran (THF), hydrochloric acid, and sodium hydroxide, salicylaldehyde, thiourea, cobaltous nitrate, chromium nitrate, polyvinyl chloride (PVC) and sodium bromide were purchased from Hi Media (Mumbai MH, India). Stock solutions (0.1M) of metal salts were prepared in double distilled water and used to make dilute solutions of required concentrations.

2.2. Synthesis of Ionophores

The ionophores Co(II) and Cr(III) salicylidene Schiff-base complexes (CoC) and (CrC) were synthesized and characterized by the reported procedure with a slight modification [27]. Salicylaldehyde (10 mmol, 1.22 g) was added to a 20 mL homogeneous ethanolic solution of Cobalt(II) and Chromium(III) nitrate (5 mmol), taken in a 100 mL round bottom flask and the pH of the solution was maintained between 6 and 8 using a liquid ammonia solution. Then a 10 mL ethanolic solution of thiourea (5 mmol, 0.38 g) was mixed with the above solution and this mixture was continuously refluxed for 8 hours. Upon cooling the reaction mixtures to room temperature, Co(II) and Cr(III) Schiff-base complexes were separated as dark brown and dark green precipitates. These precipitates were filtered and washed with cold ethanol and dried in a vacuum desiccator. Co(II) and Cr(III) Schiff-base complexes showed the following characteristics: $[C_{15}H_{12}N_2O_3SCo](NO_3)_2$ yield: 75.5%; m.p. 143°C; and $[C_{15}H_{10}N_2O_2SCr](NO_3)^{\cdot}(H_2O)_{6.7}$ Yield: 79.5%; m.p. ~173 °C.

2.3. Preparation of Electrodes

PVC membrane electrodes based on CoC and CrC were prepared according to the method described by Craggs [30]. To prepare a uniform mixture, membrane components including ionophores (CoC) and (CrC), cationic additive (CTAB), plasticizers (DBP, CN, DOP, o-NPOE, and TBP), and PVC were dissolved in about 5 mL of THF. This concentrated mixture was evenly filled into polyacrylate rings with an internal diameter of 2 cm affixed on a flat glass plate. It was then allowed to evaporate at room temperature (25 ± 2°C) for 24 hrs under ambient humidity (40-50%**)** and the membrane rings were covered, and kept it for a whole day at room temperature to evaporate the solvent. After careful removal of the ring from the platez a transparent membrane with a thickness of 0.5 mm was obtained. Subsequently, the membrane was affixed to one end of a glass tube using Araldite and sealed with epoxy resin to avoid leakage of the internal solution.

The membranes were allowed to acclimate in a 1.0×10^{-1} mol L^{-1} NaBr solution for four days. Potentials were recorded by varying the concentration of the NaBr test solution

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within the range of $1.0\times10^{-8} - 1.0\times10^{-1}$ mol L^{-1}. Each solution was agitated and the potential was recorded once it reached a stable point. The logarithmic function of the Br^- ion activity was then plotted. A saturated calomel electrode (SCE) was used as the reference electrode for the potential measurements, which were performed at 25±0.1°C using an Orion 4-star pH metre with the following cell assembly:

Hg/Hg_2Cl_2 |KCl(satd) | 0.1 M NaBr || PVC membrane || test solution | Hg/Hg_2Cl_2 | KCl(satd).

The activities of Br^- ions were calculated according to the following modified Debye-Huckel approximation equation (1):

$$\log Y = -0.511Z^2\left(\frac{\mu^{1/2}}{1+1.5\mu^{\frac{1}{2}}} - 0.2\mu\right) \quad (1)$$

Where Y is the activity coefficient, Z represents the charge on the ion and μ shows ionic strength.

2.4. Apparatus

Potentiometric experiments were carried out using an ESICO INTERNATIONAL Digital potentiometer Model-118 and the proposed electrode in combination with a double junction Ag/AgCl reference electrode. The pH was calculated using a digital pH meter [ESICO INTERNATIONAL digital pH meter Model-101].

3. Results and Discussion

The ionophores of Co(II) and Cr(III) salicylidene Schiff-base complexes (CoC) and (CrC) as were synthesized using a facile one-pot method by refluxing the metal nitrate, thiourea, and salicylaldehyde in ethanol according to the reported procedure [27]. **Figure 1** presents the Schiff-base ligand (inset I) and one of its corresponding chromium complexes as a representative example (insets II and III). The structure and chemical functionality of the complexes were characterized by the ATR-FTIR spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and CHN analysis**.** The FTIR analysis revealed a characteristic band at 1599 cm^{-1} in the Schiff-base ligand, attributed to the stretching vibration of the C=N bond. This indicates successful condensation between the amine group of thiourea and the aldehyde group of salicylaldehyde, resulting in the formation of the Schiff-base ligand. In the Co(II) complex, the band apeared slightly shifted to higher wavenumber at 1625 cm^{-1} and for Cr(III) complex, this band appeared slightly shifted to a lower wavenumber at 1591 cm^{-1}, suggesting the coordination of azomethine nitrogen with Co and Cr atoms (**Figure S1**). Both the ligand and metal complexes Co(II) and Cr(III) display sharp crystalline peaks in their XRD spectra (**Figure S2**), indicating their crystalline nature. Furthermore, XPS analysis was performed to study the oxidation state of the Co and Cr after complexation. The survey scan spectra (**Figure S3 A**) demonstrated the presence of C, N, O, S and Cr and Co in the CoC and CrC complexes. The high resolution spectra of Co 2p displayed a displayed a single doublet feature characteristics of Co $2p_{3/2}$ at 781.2 eV and Co $2p_{1/2}$ at 787.1 eV and for Cr 2p displayed a single doublet feature characteristics of Cr $2p_{3/2}$ at 577.2 eV and Cr $2p_{1/2}$ at 587.1

eV, confirming a homogenous Co(II) and Cr(III) oxidation state in the complex.[28] CHN elemental analysis of the Co(II) and Cr(III) complexes compared to theoretical calculations suggested the $[C_{15}H_{10}N_2O_2SCo](NO_3)^{\cdot}(H_2O)_{6.}$ and $[C_{15}H_{10}N_2O_2SCr](NO_3)^{\cdot}(H_2O)_{6.7}$ structure for the CoC; Cr(II) and CrC; Cr(III) complexes of salicylidenic Schiff-base (SI; CHN analysis results). Based on the above characterization data, the CoC and CrC were confirmed as a mononuclear complexes with Co(II) and Cr(III) to ligand ratio of 1:1 (**Figure 1, inset II**).

Further, UV-visible (UV-Vis) spectroscopy is employed to analyze the interaction between CoC and CrC ionophores and bromide ions due to its capability to detect molecular interactions based on changes in absorbance. UV-Vis absorption spectra of CoC and CrC were recorded, using an equimolar quantity of NaBr solution each having a 1.0 × 10^{-3} mol·L^{-1} concentration in methanol. UV–Vis spectra, as shown in **Figures 2 (A & B)** can discern the interlinkage between the metal chelates and bromide ions. The considerable changes in the absorbance of CoC at 245 and CrC (246 and 255 nm) were noted in the absorption spectra with an equimolar amount of bromide ion solution.[29] Here, the results strongly imply that ionophores form 1:1 complexes with the bromide ion. On the other hand, there were negligible changes in the UV-Vis spectra of CoC and CrC ionophores when recorded in the presence of other anions. The perceived spectral shifts, coupled with the significant increase in absorbance peaks in CoC and CrC spectra following contact with the bromide ion-containing solution, indicate the favorable coordination of the bromide ion by the ionophore. The change in UV-Vis indicates the interaction between the ionophores and bromide ion.

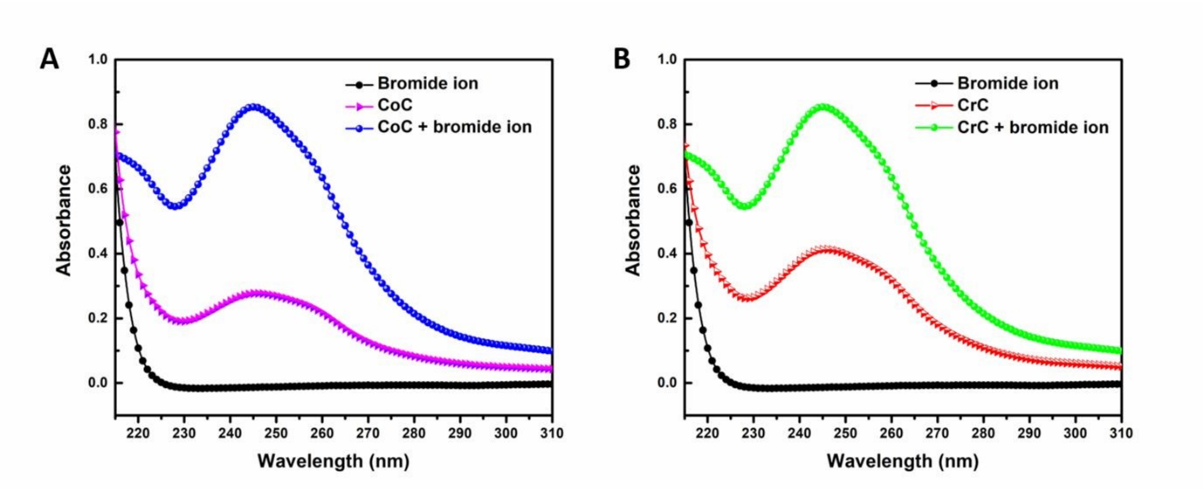

Figure 2. The absorption spectra of (A) CoC and (B) CrC with bromide ion (NaBr 1.0 × 10^{-3} mol·L^{-1}) solution in MeOH.

To understand the coordination behavior of both CoC and CrC with different anions, a conductometric titration method was carried out. Conductometric study was performed by titrating 20 mL 1.0 × 10^{-4} mol·L^{-1} of anion solution against 1.0 × 10^{-2} mol·L^{-1} solution of

CoC and CrC. The conductance (S·cm^{-1}) of the solution was precisely noted for each addition of ionophores. The results showed that among several anions studied, the conductance of Br$^-$ ion solution was greatly affected with the addition of CoC and CrC. The observed variation in conductance of Br$^-$ ion solution with the metal complexes is plotted in Figure 3 which explains that the conductance of bromide ion solution starts decreasing quickly with the addition of the metal complexes. Once all bromide ions are consumed, no further change in conductance occurs, resulting in the conductometric titration curve reaching a nearly straight line at the end point. An exact stoichiometry ratio of 1:1 is indicated for the end of the final product of the reaction at the end of the conductometric titration curve.

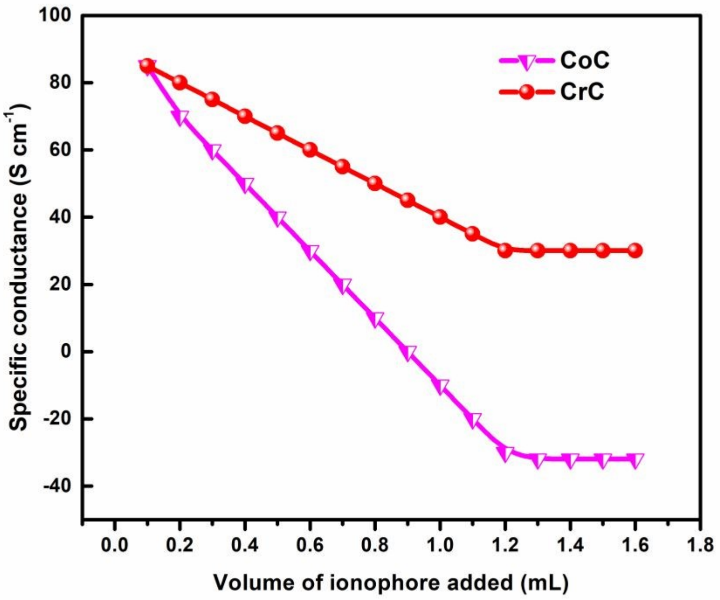

Figure 3. Variation in conductance (S·cm^{-1}) of bromide ion solution with CoC and CrC ionophore.

One of the most critical parameters that sheds light on an ion electrode's functional selectivity is the ion-ionophore complexation occurring within the membrane. The sandwich membrane method was employed to calculate the formation constants for the 1:1 ion-ionophore complex. A concentration-polarized sandwich membrane was formed by fusing together two membrane segments, of which only one contained the ionophore. The formation constants were then calculated by the following equation (**2**). [30]

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{Z_I} \right)^{-n} \exp\left(\frac{E_M z_I F}{RT} \right) \qquad \textbf{(2)}$$

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Where *n* represents ion-ionophore complex stoichiometry, L_T is total concentration of ionophore in membrane segment, R_T is the concentration of lipophilic additives, E_M is membrane potential and *R*, *T* and *F* are constant having their usual meaning. z_I is the charge on the ion. The formation constants for different ion-ionophore complexes are given in **Table 1**. These values revealed that CoC (7.09 ± 0.16) and CrC (6.90 ± 0.06) complexes forms the most stable complex with Br^- ion compared to the other anions. The higher formation constant values with Br^- ions support the notion that CoC and CrC complexes can be looked at as potential ionophores for bromide ions detection and its membrane may serve as a bromide selective electrode.

Table 1: Stability constant values of ionophores (CoC) and (CrC) with different anions by sandwich membrane method (*n* = 3)

Anion (X^{n-})	(Log β_{CoCX}) ± σ	(Log β_{CrCX}) ± σ
Br^-	7.09 ± 0.16	6.90 ± 0.06
I^-	5.02 ± 0.02	4.91 ± 0.22
Cl^-	4.95 ± 0.35	4.80 ± 0.25
CO_3^{2-}	4.91 ± 0.07	4.75 ± 0.08
SO_4^{2-}	4.83 ± 0.66	4.70 ± 0.55
CN^-	4.57 ± 0.36	4.45 ± 0.32
F^-	4.43 ± 0.26	4.31 ± 0.12
SCN^-	3.72 ± 0.27	3.66 ± 0.10
NO_2^-	3.71 ± 0.16	3.55 ± 0.61
NO_3^-	3.02 ± 0.72	3.04 ± 0.07
Sal^-	2.92 ± 0.26	2.75 ± 0.14

The compositions of potentiometric membrane electrodes fabricated by incorporating CoC and CrC were optimized by adjusting the amounts of other membrane ingredients.[31] All the electrodes were calibrated In 10^{-1} M NaBr solution before potentiometric studies. The results show the potentiometric characteristics of bromide selective electrodes based on ionophores CoC (CoC**1** to CoC**10**) and **CrC** (CrC**1** to CrC**10**) which were evaluated as a function of bromide ion concentration in the range of 10^{-8} to 10^{-1} mol·L^{-1} (**Table 2**). The electrodes with 6 mg of CoC and 94 mg PVC (CoC**1**) and 5 mg of CrC and 95 mg of PVC (CrC**1**) exhibited potentiometric characteristics demonstrating sub-Nernstian slopes (36.2 mV·$decade^{-1}$ for CoC and 38.1 mV·$decade^{-1}$ for CrC of Br^-), high detection limit (2.5×10^{-4} mol·L^{-1}) for CoC and (2.0×10^{-4} mol·L^{-1}) for CrC with narrow working concentration ranges ($5.0 \times 10^{-4} - 1.0 \times10^{-3}$ mol·L^{-1}) and ($5.5 \times 10^{-4} - 1.0 \times10^{-2}$ mol·L^{-1}). The sensitivity, linearity, and selectivity of a given ionophores are significantly influenced by the membrane composition, particularly the type of plasticizer used.[32] Therefore, numerous combinations of membrane constituents (as listed in **Table 2 and 3**) were tested to identify the membrane that provides high performance and reproducible results. Subsequently, the membrane electrode with the highest performance was chosen for thorough potentiometric analyses. According to previously published works, a cation excluder enhances the potentiometric properties of an anion-selective electrode and increases its selectivity [33]. To improve electrode performance, a cation exchanger (CTAB) was mixed with membrane composition.

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Potential studies given in **Table 2 and 3** revealed that the electrodes (CoC**2**) and (CrC**2**) having 3 mg CTAB exhibited some improvement in slope, detection limit and working concentration range.

Table 2. Optimized PVC membrane compositions based on CoC and their potentiometric response as bromide ion selective electrodes.

Electrode no.	Membrane ingredients (mg)				Slope (mV·decade⁻¹ of [Br⁻])	Linear range (mol·L⁻¹)	Detection limit (mol·L⁻¹)
	Ionophore (CoC)	CTAB	Plasticizer	PVC			
CoC1	6	0	0	94	36.2	5.0×10^{-4} - 1.0×10^{-3}	2.5×10^{-4}
CoC2	6	3	0	91	45.4	6.9×10^{-5} - 1.0×10^{-2}	3.0×10^{-5}
CoC3	6	3	55, DOP	36	51.7	7.1×10^{-6} - 1.0×10^{-2}	3.4×10^{-6}
CoC4	6	3	55, NPOE	36	62.4	7.3×10^{-6} - 1.0×10^{-2}	3.7×10^{-6}
CoC5	6	3	55, CN	36	63.0	5.3×10^{-6} - 1.0×10^{-2}	2.5×10^{-6}
CoC6	6	3	55, TBP	36	56.8	1.5×10^{-6} - 1.0×10^{-2}	9.2×10^{-6}
CoC7	6	3	55, DBP	36	59.4	6.0×10^{-7} - 1.0×10^{-2}	5.5×10^{-7}
CoC8	5	3	55, DBP	37	57.9	5.7×10^{-6} - 1.0×10^{-2}	3.6×10^{-6}
CoC9	7	3	55, DBP	35	59.1	6.2×10^{-6} - 1.0×10^{-2}	5.6×10^{-6}
CoC10	6	2	55, DBP	37	57.6	3.7×10^{-6} - 1.0×10^{-2}	1.8×10^{-6}

Table 3. Optimized PVC membrane compositions based on CrC and their potentiometric response as bromide ion selective electrodes.

Electrode no.	Membrane ingredients (mg)				Slope (mV·decade⁻¹ of [Br⁻])	Linear range (mol·L⁻¹)	Detection limit (mol·L⁻¹)
	Ionophore (CrC)	CTAB	Plasticizer	PVC			
CrC1	5	0	0	95	38.1	5.5×10^{-4} -1.0×10^{-2}	2.0×10^{-4}
CrC2	5	3	0	92	47.2	5.0×10^{-5} - 1.0×10^{-2}	2.5×10^{-5}
CrC3	5	3	55, CN	37	66.5	7.5×10^{-6} - 1.0×10^{-2}	3.9×10^{-6}
CrC4	5	3	55, NPOE	37	61.1	4.3×10^{-6} - 1.0×10^{-2}	2.6×10^{-6}
CrC5	5	3	55, TBP	37	53.3	1.5×10^{-6} - 1.0×10^{-2}	1.1×10^{-6}
CrC6	5	3	55, DOP	37	58.0	5.9×10^{-6} - 1.0×10^{-2}	2.1×10^{-6}
CrC7	5	3	55, DBP	37	59.2	8.7×10^{-7}- 1.0×10^{-2}	6.5×10^{-7}
CrC8	4	3	55, DBP	38	51.4	4.3×10^{-6} - 1.0×10^{-2}	3.6×10^{-6}
CrC9	3	3	55, DBP	39	56.8	9.0×10^{-5} - 1.0×10^{-2}	7.0×10^{-5}
CrC10	5	4	55, DBP	36	55.4	4.1×10^{-6} -1.0×10^{-2}	2.2×10^{-6}

It was further seen from **Table 2** that the membranes of CoC with different types of plasticizers *viz.,* CN, NPOE, TBP, DOP, and DBP (electrode nos. CoC3–CoC7) performed better than the membrane without plasticizer showcasing wider working concentration ranges and improved slopes. DBP plasticized membrane electrode CoC7 showed the best performance among all the plasticized membranes, exhibited the widest working concentration range of 6.0×10^{-7} – 1.0×10^{-2} mol·L^{-1} with a Nernstian slope of 59.4 mV·decade^{-1} of [Br$^-$] and low detection limit 5.5×10^{-7} mol·L^{-1}. Similar results were also obtained with the membranes of CrC in **Table 3** with different types of plasticizers *viz.,* CN, NPOE, TBP, DOP, and DBP (electrode nos. CrC3–CrC7) performed better than the membrane without plasticizer showcasing wider working concentration ranges and improved slopes. DBP plasticized membrane electrode CrC7 showed the best performance among all the plasticized membranes, exhibited the widest working concentration range of 8.7×10^{-7} – 1.0×10^{-2} mol·L^{-1} with a Nernstian slope of 59.2 mV·decade^{-1} of [Br$^-$] and low detection limit

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6.5×10^{-7} mol·L^{-1}. Due to the very low polarity and great mobility of DBP compared to other plasticizers explored, DBP is supposed to provide sufficient conditions for the integration of Br^{-} ions into the membrane before coordinating with the metal in complexes.[33]

The effect of varying amounts of ionophores (CoC7, CoC8, CoC9) and (CrC7, CrC8, CrC9) was also studied, and it was observed that reducing the ionophore concentration in the membrane phase significantly changed the potentiometric characteristics of the electrode (CoC8, CoC9) and (CrC8),(CrC9) did not show improved performance. The potentiometric responses were similarly decreased for the CoC10 and CrC10 which had ~~a~~ an increased concentration of CTAB, leading to increased interference from foreign cations in the solution. This is evident from the performance comparison of all these electrodes shown in **Table 2 and 3** indicating that the electrode CoC7 and CrC7 is the best-performing electrodes and the optimum composition of the CoC7 is determined to be CoC: DBP:CTAB:PVC in a ratio of 6:55:3:36 (mg) and in CrC7 is determined to be **CrC**: DBP: CTAB: PVC in a ratio of 5:55:3:37 (mg). The potential responses of the CoC and CrC7 electrodes were evaluated by contentiously changing the internal solution from 1.0×10^{-1} to 1.0×10^{-8} mol·L^{-1} and its potentiometric data were observed from their calibration curve. The study found minor differences in the Nernstian slope of electrodes in dilute solutions (1.0×10^{-3} and 1.0×10^{-4} mol·L^{-1}), affecting their operating range and detection limitations. Therefore, the suitable concentration of internal Br^{-} solution was determined to be 1.0×10^{-2} mol·L^{-1} for further studies of CoC7 and CrC7.

The equilibration time of ISEs is an important parameter affecting their performance. For the activation of electrodes, the potential response of the electrodes were measured after soaking them in a 1.0×10^{-2} mol·L^{-1} bromide solution for distinct time periods. Stable and reproducible results were obtained after conditioning the electrodes for a period of 12 hours. However, extending the equilibration time beyond 12 hours showed no improvement in the performance of the CoC7 and CrC7. The best performing electrodes, CoC7 and CrC7, were used under the above-explained state. The calibration plots of these electrodes shown in **Figure 4** disclose that they can operate over a broad working concentration range (6.0×10^{-7}-1.0×10^{-2} mol L^{-1} and 8.7×10^{-7} – 1.0×10^{-2} mol·L^{-1}) showing Nernstian responses (59.4 and 59.2 mV·decade^{-1} of [Br^{-}]) with lower detection limits as 5.5×10^{-7} and 6.5×10^{-6} mol·L^{-1}, respectively.

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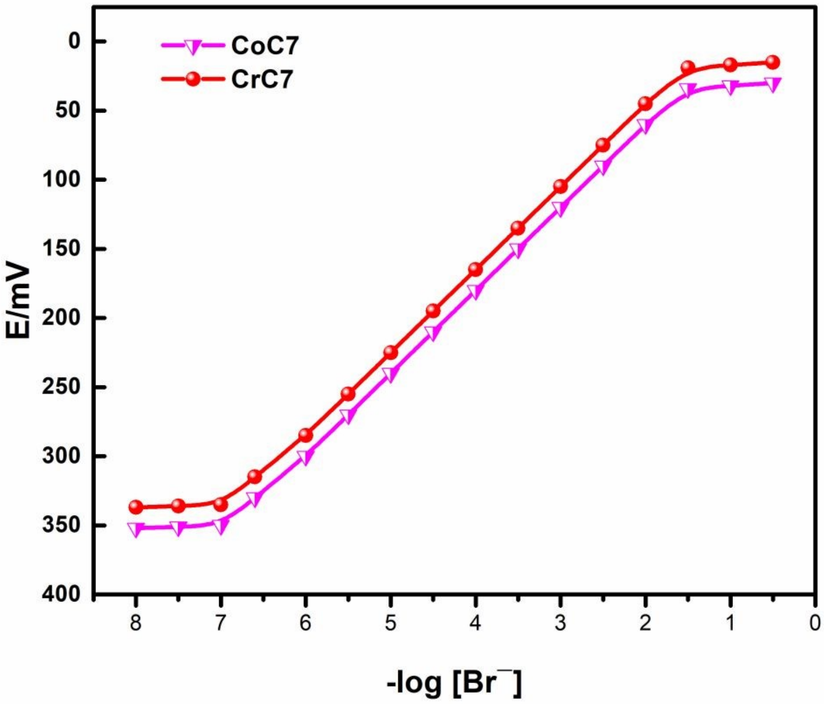

Figure 4. Calibration curve for the best performing electrode CoC7 and CrC7.

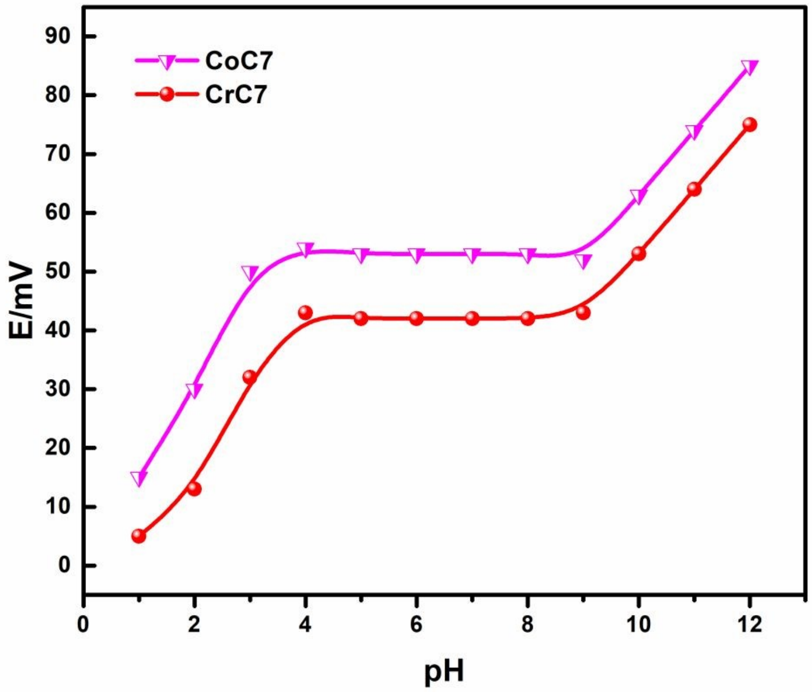

Figure 5. Effect of pH on performance of proposed electrodes solution with bromide at a concentration of 1.0 × 10^{-2} mol·L^{-1}.

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For the determination of a suitable pH range for the considered electrode, the effect of pH on the performance of the CoC7 and CrC7 was assessed in 1.0×10^{-2} M mol·L^{-1} bromide ion solution. The pH range between 1.0 to 12.0 was adjusted by addition of desired amount of dilute HCl and NaOH solutions. The potential response for this study is shown in **Figure 5** showed that the potentials remained unchanged within the pH range of 4.0 to 9.0, making this working pH range suitable for further studies. The deviations in potentials beyond this pH range may be attributed to the oxidation of bromide in the acidic solution (below pH 4.0) and as a result of hydrolysis (above pH 9.0) of metal complexes. To determine the response time of the suggested electrodes, the concentration of the Br^- solution was sequentially changed from 1.0×10^{-2} mol·L^{-1} to 1.0×10^{-6} mol·L^{-1}. The potential responses were depicted in **Figures 6(A & B)** and the results suggested that the time required for getting the stable potential value after immersing the electrodes successively in a series of bromide ion solutions is 12 and 16 seconds for CoC7 and CrC7 respectively. This study indicates rapid exchange kinetics between bromide ions and ionophores at solution-membrane interface. To examine the reversibility of these electrodes, the process was reversed by measuring the potential from high to low concentrations and the response time of these electrodes remained unchanged. Furthermore, the reproducibility of the electrodes were also checked with a set of three duplicate electrodes of CoC7 and CrC7, and their potentiometric investigations were performed under identical conditions. The results were found to be in well agreement (± 0.06 mV), indicating their reliable and reproducible performance.

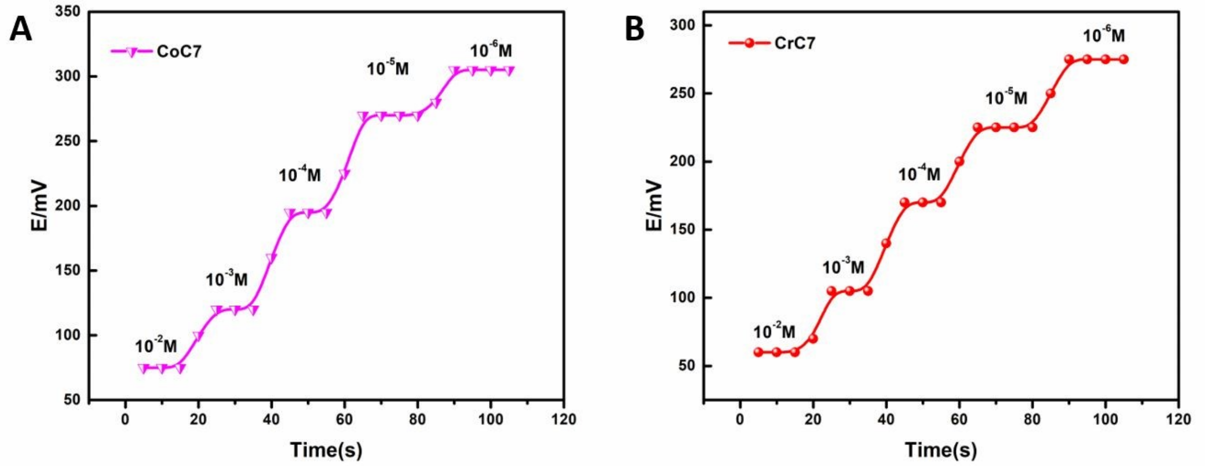

Figure 6. (A & B) Dynamic response time of CoC7 and CrC7 electrode.

The lifetime of an ISE is an important feature that describes its active lifespan for accurately estimating primary ions in the test solution. To evaluate the lifetime of the proposed bromide selective electrodes, ee, the proposed electrodes were used daily over a period of 1 hour each day for 2 months (8 weeks). The slopes and detection limits were measured from the derived calibration plots are given in **Table 4**. The experimental results

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showed that there was no significant change in the potentiometric characteristics of electrodes CoC7 and CrC7 up to 5 weeks. However, over time the potential responses of this electrodes gradually deteriorated showing sub-Nernstian slopes and elevated detection limits. It is noteworthy that the electrode was stored in 0.1 M NaBr solution when not in use.

Table 4: Life time study of the proposed electrodes CoC7 and CrC7.

Time (weeks)	Electrode CoC		Electrode CrC	
	Slope (mV)	Detectionlimit (mol L^{-1})	Slope (mV)	Detection limit (mol·L^{-1})
1	59.4±0.2	5.5×10^{-7}	59.2±0.2	6.5×10^{-7}
2	59.4±0.04	5.5×10^{-7}	59.2±0.3	6.5×10^{-7}
3	59.4±0.5	5.8×10^{-7}	59.1±0.4	6.8×10^{-7}
4	59.2±0.3	6.5×10^{-7}	59.1±0.4	6.8×10^{-7}
5	59.1±0.4	4.1×10^{-6}	59.0±0.6	7.5×10^{-7}
6	58.2±0.7	5.5×10^{-6}	58.8±0.7	3.5×10^{-6}
7	57.6±0.8	9.4×10^{-5}	58.2±0.9	4.5×10^{-6}
8	56.9±0.5	1.5×10^{-5}	57.1 ±0.5	1.7×10^{-5}

The functioning of CoC7 and CrC7 both electrodes were also evaluated in partially non-aqueous solutions as shown in **Table 5** with methanol-water, ethanol-water and acetonitrile-water solutions of different concentrations, and calibration curves were recorded. It was observed that that electrode could tolerate up to 20 % (v/v) non-aqueous content as there was negligible change in their slope and linear working range at this concentration. However, above 20 % non-aqueous content, the slope and working range are considerably reduced which could be due to membrane degradation from leaching of ionophores or other ingredients from PVC matrix.

Table 5: Performance of proposed electrodes in partially non-aqueous media.

Non-aqueous content (%, v/v)	Electrode CoC7		Electrode CrC7	
	Working concentration range (mol L^{-1})	Slope (mV decade^{-1} [Br])	Working concentration range (mol L^{-1})	Slope (mV decade^{-1} [Br])
Nil	6.0×10^{-7}-1.0×10^{-2}	59.4	8.7×10^{-7}- 1.0×10^{-2}	59.2
Methanol				
10	6.0×10^{-7}-1.0×10^{-2}	59.4	8.7×10^{-7}- 1.0×10^{-2}	59.2
20	6.0×10^{-7}-1.0×10^{-2}	59.4	8.7×10^{-7}- 1.0×10^{-2}	59.2
30	2.6×10^{-6}-1.0×10^{-2}	58.5	3.7×10^{-6}- 1.0×10^{-2}	58.0
35	5.0×10^{-6}-1.0×10^{-2}	57.9	8.2×10^{-6}- 1.0×10^{-2}	57.5
Ethanol				
10	6.0×10^{-7}-1.0×10^{-2}	59.4	8.7×10^{-7}- 1.0×10^{-2}	59.2
20	6.0×10^{-7}-1.0×10^{-2}	59.4	8.9×10^{-7}- 1.0×10^{-2}	59.1
30	8.5×10^{-6}-1.0×10^{-2}	58.9	2.7×10^{-6}- 1.0×10^{-2}	58.4
35	9.2×10^{-6}-1.0×10^{-2}	57.9	7.5×10^{-6}- 1.0×10^{-2}	57.6
Acetonitrile				
10	6.0×10^{-7}-1.0×10^{-2}	59.4	8.7×10^{-7}- 1.0×10^{-2}	59.2
20	6.1×10^{-7}-1.0×10^{-2}	59.3	8.9×10^{-7}- 1.0×10^{-2}	59.1
30	4.5×10^{-6}-1.0×10^{-2}	58.5	4.7×10^{-6}- 1.0×10^{-2}	58.3
35	3.1×10^{-6}-1.0×10^{-2}	57.9	5.5×10^{-6}- 1.0×10^{-2}	58.0

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Selectivity is a crucial response characteristic of an ion selective electrode, it permits the prediction of how an ISE will perform in the analysis of real-life samples. The IUPAC recommended fixed interference method (FIM) was used to determine the potentiometric selectivity coefficient (SC) for the assumed electrode in presence of various foreign anions (A^{n-}). The SC in this method was determined using potential measurements of Br^- ion solutions of different concentrations ranging from 10^{-2} to 10^{-8} M and containing a fixed concentration of interfering ion (1.0×10^{-2} M). The SC values for several anions are given in **Table 6**. Moreover, the SC values for all the interfering ions are much less than 1.0, it can be concluded that the proposed Co(II) and Cr(III) complexes based electrodes is highly selective to Br^- ions over interfering ions studied.[34,35]

Table 6: Selectivity coefficients of proposed electrodes for various interferring anions

Interfering anions (B)	Selectivity coefficient ($-\mathrm{Log}K_{\mathrm{Br}^-,\,\mathrm{B}}$) Electrode CoC7	Electrode CrC7
CN^-	1.38	1.27
SCN^-	1.50	1.31
Sal-	1.84	1.62
F^-	1.43	1.22
NO_2^-	1.62	1.39
Cl^-	1.38	1.18
I^-	1.43	1.17
NO_3^-	1.56	1.26
SO_4^{2-}	2.20	2.30
CO_3^{2-}	1.03	1.05

The proposed electrodes CoC7 and CrC7 exhibited good performance as indicator electrode in the potentiometric titration of Br^- ions with $AgNO_3$ and proved their analytical applicability. For this purpose, a 20 mL solution of 1.0×10^{-2} mol·L^{-1} NaBr was titrated against 1.0×10^{-1} mol·L^{-1} $AgNO_3$ solution at pH 6.0 and the potential response observed using CoC7 and CrC7 were presented in **Figure 7**. The resultant titration plot has a conventional sigmoid shape, with a sharp endpoint that matches the 1:1 stoichiometry of the precipitated silver bromide. As a result, potentiometric titration may be used to approximate Br^- ions using the recommended electrodes.

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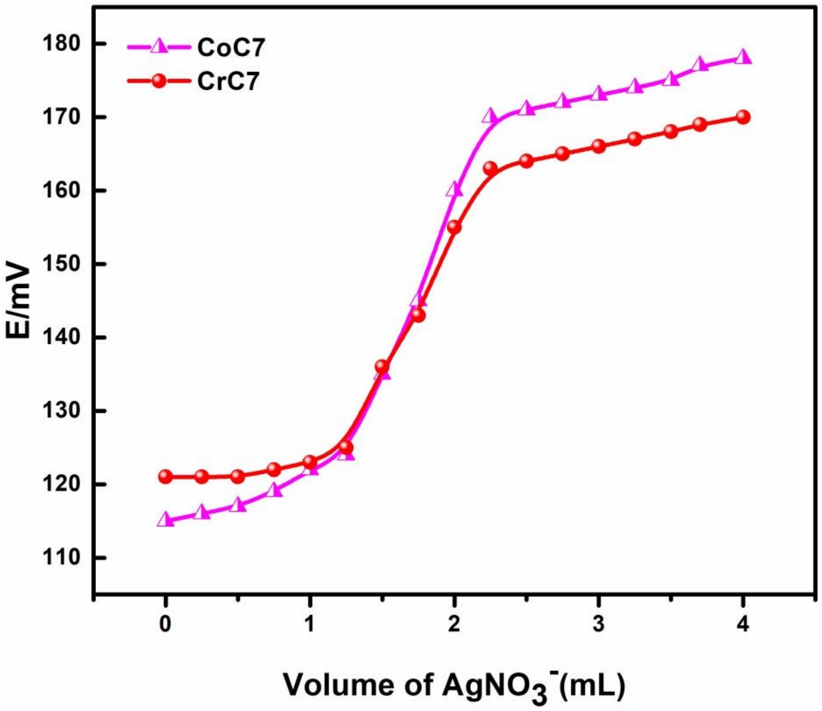

Figure 7. Potentiometric titration of 20 mL solution of 1.0 × 10^{-2} mol·L^{-1} NaBr against 1.0 × 10^{-1} mol·L^{-1} $AgNO_3$ solution.

Naturally occurring bromide ions can contaminate drinking water due excess use of fertilizers and percolation of industrial wastewater in the groundwater. We used the proposed Co(II) complex based CoC7 and Cr(III) complex based CrC7 electrodes to assess Br^- ion concentration in tap water samples. In this study, tap water samples were initially spiked with Br^- ions of concentration 25 mg·L^{-1}, 50 mg·L^{-1} and 100 mg·L^{-1}. Subsequently, 100 mL of every spiked water sample was collected in distinct beakers, and 2 mL of $NaNO_3$ (0.1 M) solution was added as an ionic strength adjuster (ISA). The solution was stirred vigorously before the potentiometric analysis. The results for estimating Br^- ion concentration in tap water samples are given in **Table 7**. The concentration determined by this electrodes are slightly higher than the amount of Br^- ion added to the test samples, indicating that the bromide ions were already present in tap water samples before the addition. The results of the atomic absorption spectrometer (AAS) and the potentiometric analysis of the bromide ion in the tap water sample by the proposed electrodes were compared. The results presented in Table 7 demonstrate a significant level of agreement between the two methods, thereby confirming the suggested electrodes' ability for rapid measurement.

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Table 7: Potentiometric determination of Br$^-$ ion in tap water sample using the proposed electrodes.

Sample no.	Added bromide concentration (mg L^{-1})	Found bromide concentration (mg L^{-1})		
		Sensor CoC7	Sensor CrC7	AAS
1.	25	25.3±0.15	25.3±0.12	25.7±0.06
2.	50	50.5±0.05	50.4±0.06	50.7±0.12
3.	100	101.3±0.05	101.1±.0.1	101.5±0.06

*Standard deviation of three measurement

The potentiometric characteristics of the developed bromide ion electrodes CoC7 and CrC7 based Co(II) and Cr(III) complexes of salicylidenic Schiff-base were compared with the previously reported Br$^-$ ion electrode (**Table 8**). This comparison revealed that the CoC7 and CrC7 electrodes operates in a wide linear working concentration range compared to other electrodes with low detection limits and has a faster response time, possibly caused by the both complexes tend to be strong and durable, which is important for the longevity and reliability of ion selective electrodes. In addition, this electrodes exhibited an ideal Nernstian behavior with a very low detection limit, further enhancing their utility and reliability in Br$^-$ ion determination under different environmental conditions.

Table 8: Comparison of the performance of the proposed bromide selective electrodes with the previously reported electrode.

Ref. no	Slope (mV·decade^{-1})	Linear range (mol·L^{-1})	Detection limit (mol·L^{-1})	pH range
[15]	58.0	10^{-1}–10^{-6}	5.0×10^{-7}	3.5–9.0
[16]	59.2–60.4	1×10^{-1}–2×10^{-6}	3×10^{-7}	2.0–10.0
[17]	61±1	1.0×10^{-1} – 3.2×10^{-5}	2.0×10^{-5}	4.5 – 8.5
[18]	59.1±0.5	10^{-5}–10^{-1}	5.0×10^{-6}	4.0–9.5
[19]	59.0	7.0×10^{-6}–1.0×10^{-1}	6.0×10^{-6}	3.0–9.0
[20]	–	1.0×10^{-8} – 1.0×10^{-6}	2.0×10^{-9}	–
[21]	61.0 ± 0.9	3.0×10^{-2} – 1.0×10^{-5}	4.0×10^{-6}	4.5 – 7.5
[22]	54.53 ± 0.15	1.0×10^{-7}– 1.0×10^{-1}	7.1×10^{-8}	–
[23]	64.4± 0.4	1.0×10^{-1} – 1.0×10^{-5}	8.0×10^{-6}	6.0 – 12.0
[26]	-	1.0×10^{-1} – 1.0×10^{-4}	2.2×10^{-5}	4.0 – 10
[24]	63±1	1.0×10^{-1}– 1.0×10^{-6}	1.6×10^{-5}	2.0–11.0
CoC7	**59.4**	$\mathbf{6.0\times10^{-7} – 1.0\times10^{-2}}$	$\mathbf{5.5\times10^{-7}}$	**4.0 –9.0**
CrC7	**59.2**	$\mathbf{8.7\times10^{-7} – 1.0\times10^{-2}}$	$\mathbf{6.5\times10^{-7}}$	**4.0 –9.0**

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4. Conclusion

In conclusion, as a new category of bromide ionophore, a mononuclear Co(II) and Cr(III) coordination complexes of salicylidene Schiff-base were synthesized and their potentiometric responses were studied. Both the electrodes demonstrated very high sensitivity with a Nernstian slope of 59.4±0.07 and 59.2±0.04 mV·decade^{-1} of [Br$^-$], a wide working concentration ranges (6.0×10^{-7} - 1.0×10^{-2} mol·L^{-1}) and ($8.7 \times 10^{-7} - 1.0 \times 10^{-2}$ mol·L^{-1}) and extremely low detection limits as $5.5\pm0.13\times10^{-7}$ mol·L^{-1} and $6.5\pm0.07\times10^{-7}$ mol·L^{-1}. Operating effectively in the pH range of 4.0 to 9.0, the electrodes exhibited short response times of 12 and 16 seconds and shelf lives of 4 and 5 weeks. A comparative analysis with previously reported sensors setups for bromide detection highlights its superiority over many sensors in terms of detection limit, working concentration range, high selectivity and quick response time. Especially, cobalt and chromium both can subsites in multiple oxidation states (e.g., Co(II) and Co(III) and Cr(III) and Cr(IV), allowing for redox-based sensing mechanisms, that maybe another reason for these excellent performances. This mechanism is undergoing further investigation, which can be advantageous in designing sensors by switching states upon interconnection with bromide ions to increase the detection capabilities. This work indicates the transition metal complexes can be considered as a valuable addition to the family of bromide ionophores, promising enhanced accuracy and efficiency in bromide ion detection applications in the areas of food production, pharmaceuticals, and water quality management.

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Conflict of Interest

The authors declare no conflict of interest.

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