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ORIGINAL PAPER

Analysis of halogens in wastewater with a new prepared ion selective electrode

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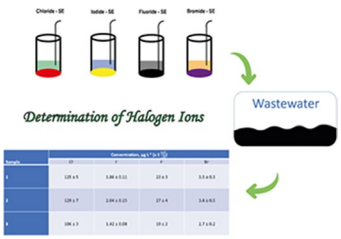
Abstract

Ion selective electrode can rapidly, sensitively detect their corresponding ions and are suitable for field testing. Chloride, fluoride, iodide and bromide ions were analyzed using the ion selective electrodes in previous studies and a new membrane electrode for bromide ion. The bromide selective electrode has a composition of 25% tridodecylmethylammonium bromide, 55% polyvinyl chloride, and 20% dibutyl phthalate and has a slope of 57.4 ± 0.3 mV against $1 \times 10^{-6} - 0.1$ mol dm^{-3} bromide ion. It works in a wide pH range. Response time is 20 s, lifetime is 5 months. It is not sensitive to any other ion. The analytical performances of the electrodes were investigated. Cl^-, F^-, I^-, Br^- ions in the samples taken from Ankara tea were measured and their selectivity was found to be good compared to the selective electrodes in the literature.

Graphical abstract



Keywords Chloride · Fluoride · Iodide · Bromide · Selective electrode · Wastewater

Introduction

Water is a nutrient and an important solvent used in the vital functions of living things. When water is affected by environmental influences, it contains many anions and cations. These anion and cation analyze are becoming important. While there are many methods for the determination of cations, there are certain methods for anion analysis. All halogens are nonmetals. Since these elements have a high tendency to give chemical reactions, they are found in nature as salts. The usage areas of halogens in industry are wide. Therefore, it is extremely important to develop acquisition and analysis methods. Among anions, halogens are elements with a high tendency to chemical reaction. Chloride forms compounds with many metals [1], fluorine is important for dental health [2], goiter disease occurs in iodine deficiency [3], bromide was used in the treatment of epilepsy in the past [4].

Many analysis methods have been used in halogen analysis. Halogen determinations were made in coal [5, 6], pet food [7], and honey [8]. In the indirect analysis of halogens, ICP was used. Another method, ICP, was used in the analysis of halogens [9–11].

These methods are both expensive and pre-concentration processes. Here, the importance of ion selective electrodes has emerged. Chloride determinations were carried out with a chloride selective electrode, either membrane or solid state [12–15]. The slope of these electrodes was found to be sensitive to the Nernst equation. The factors affecting

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Table 1 The optimization of the electrode ingredients ($1.0\times10^{-1}-1.0\times10^{-6}$ M, $N=5$)

Electrode number	TMABr/wt%	PVC/wt%	DBF/wt%	Slope/mV/decade	R^2
1	10	60	30	22.3 ± 0.5	0.8573
2	20	50	30	37.2 ± 0.4	0.9259
3	**25**	**55**	**20**	**57.4 ± 0.3**	**0.9992**
4	30	50	20	47.4 ± 0.6	0.9789
5	35	45	20	41.8 ± 0.7	0.9681
6	40	40	20	33.6 ± 0.9	0.9028

the sensitivity were examined and chloride analyzes were performed on various samples. There are studies on other halogen ions such as iodide [16–20], fluoride [21–26], and bromide [27–29] electrodes.

In this study, analyzes of halogens in wastewater were made with ion selective electrodes that we prepared. Chloride, iodide, and fluoride are the electrodes that were included in our work first. Bromide is the electrode we have just developed. The optimum conditions of this electrode were examined and validation procedures such as determination limits were carried out. The halogen ions in the waste waters were made with both electrode and ion chromatography method and the results were compared.

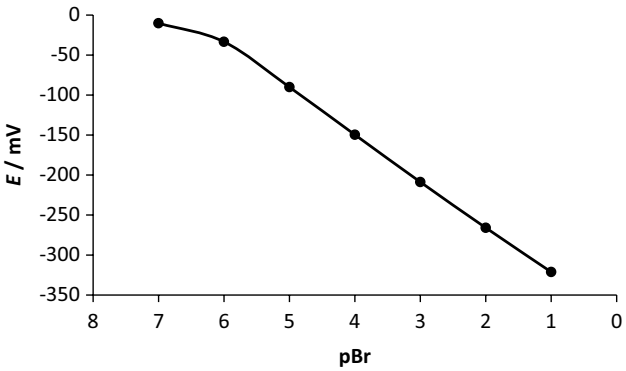

Fig. 1 Calibration curves for the new bromide electrode (25% TMABr, 55% PVC, 20% DBF)

Results and discussion

Properties of electrodes sensitive to Cl, I, F ions

Cl-SE prepared using tridodecylmethylammonium chloride ion exchanger and I-SE prepared using tridodecylmethylammonium iodide ion exchanger are membrane electrodes. Their slopes in the concentration range of $10^{-5}-10^{-1}$ M are 55 ± 2 mV for Cl-SE and 54 ± 1 mV for I-SE. With these two electrodes, measurements can be made in the pH 2–8 range. Response times are 40–60 s, and their lifespan is about 5 months when used 4 times a day. It has no sensitivity to other ions.

F-SE, on the other hand, is a solid crystal electrode prepared from slightly soluble salts of CaF_2, Ag_2S, Cu_2S. The slope of this electrode in the concentration range of $10^{-5}-10^{-1}$ M is 26 ± 2 mV. Measurements can be made with the F-SE in the pH 2–10 range. Response time is 60 s and lifetime is approximately 2 years when used 4 times a day. It has no sensitivity to other ions.

Sensitivity of bromide selective electrode

Bromide selective electrode (Br-SE) was prepared in 6 different components with a membrane mass of 0.5 g and its sensitivity to Br^- between 1×10^{-6} and − 0.1 mol dm^{-3} was measured and shown in Table 1. According to the values

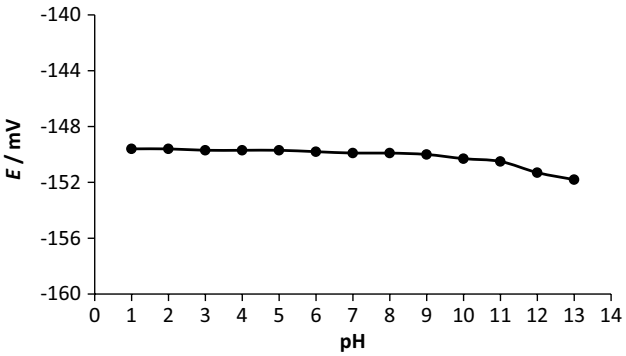

Fig. 2 pH dependence of bromide electrode

obtained, the electrode component with the highest sensitivity was seen as 25% tridodecylmethylammonium bromide (TMABr), 55% polyvinyl chloride (PVC), and 20% dibutyl phthalate (DBF) and given in Fig. 1. Further studies were carried out on this electrode.

To measure the sensitivity of Br-SE to pH, the potential values of 1×10^{-4} mol dm^{-3} Br^- at different pH values were recorded and given in Fig. 2. It was observed that pH had no effect on the sensitivity of our electrode [30]. This was identified as an important advantage. The response time of the electrode was determined as 20 s and its lifetime was

Table 2 The selectivity coefficient, K^{pot}, of the proposed toward interfering ions

Interferences	K^{pot}	Interferences	K^{pot}
Cl^-	1.05×10^{-3}	CN^-	1.06×10^{-3}
F^-	1.48×10^{-3}	SO_3^{2-}	1.84×10^{-4}
I^-	1.36×10^{-3}	SO_4^{2-}	2.17×10^{-4}
NO_3^-	1.52×10^{-3}	CO_3^{2-}	2.38×10^{-4}

Table 3 Analytical parameters of the applied method

Electrode	LOD/μmol dm^{-3}	LOQ/μg dm^{-3}	R^2	Linear range/μg dm^{-3}
Cl	1.02	1.28	0.9985	1–10,000
I	1.33	1.36	0.9986	1–10,000
F	1.56	1.87	0.9962	5–7000
Br	1.21	1.43	0.9992	1–10,000

LOD limit of detection, *LOQ* limit of quantification, R^2 coefficient of determination

determined as 5 months by making 10 measurements every day.

The K^{pot} of the proposed Br-SE is obtained using mixed solution method (Eq. 1) [31]. The potential was measured when there was 1.0×10^{-3} mol dm^{-3} Br^- in the cell. Then, the potential values were recorded by adding 1.0×10^{-5} mol dm^{-3} with 1.0×10^{-1} mol dm^{-3} solutions of the cations that can be found in the real sample. The selectivity coefficients are shown in Table 2.

$$K^{pot} = \left\{a_{BR}\left[\exp^{(\Delta E z BrF/RT)} - 1\right]\right\}/\left(a_M\right)^{zBr/zM} \quad (1)$$

where ΔE is $E_{(Br+M)}$–$E_{(Br)}$, $E_{(Br+M)}$ is the potential of primary and interfering ions, $E_{(Br)}$ is the potential of primary ion, a_{Br} and a_M are the activity for primary and interfering ions, zBr and zM are the charge of primary and interfering ions.

According to Table 2, the K^{pot} value of the Cl ion is seen as 1.05×10^{-3}. This coefficient shows that when there are 1×10^{-3} M Br^- ions in the solution, and there are Cl^- ions in the solution about 1000 times, our electrode is sensitive to Cl^- ion as well as Br^- ion.

Calibration of all electrodes and analytical applications

By calibrating all electrodes, limit of detection (LOD), amount of detection (LOQ), correlation coefficient, and slope equation of each were measured and given in Table 3.

In addition, the halogen concentrations in the solution were added from standard solutions and the % recovery values were given in Table 4. According to these values, it was determined that the validation values of the method were very good.

Table 4 The recovery values of the method against the added analyte amounts for Ankara river sample

Analyte	Added/μg dm^{-3}	Found/μg dm^{-3}	Recovery/%
Cl	0	BLQ	–
	1.50	1.49 ± 0.12	99
	3.25	3.23 ± 0.27	99
I	0	BLQ	–
	1.00	0.98 ± 0.04	97
	2.00	1.95 ± 0.15	98
F	0	BLQ	–
	2.00	1.87 ± 0.18	94
	3.00	2.93 ± 0.24	97
Br	0	BLQ	–
	1.00	0.97 ± 0.08	97
	2.00	1.95 ± 0.11	98

BLQ below of the limit of quantification

Table 5 The halogen amounts in 3 different wastewater samples (CI 95%, $N=5$)

Sample	Concentration/μg dm^{-3} $\left(x \pm \frac{txS}{\sqrt{N}}\right)$			
	Cl^-	I^-	F^-	Br^-
1	125 ± 5	1.86 ± 0.11	23 ± 3	3.5 ± 0.3
2	129 ± 7	2.04 ± 0.15	27 ± 4	3.8 ± 0.5
3	106 ± 3	1.42 ± 0.08	19 ± 2	2.7 ± 0.2

x average value, s standard devaluation, t student's t test

The halogen ion values of the wastewater samples taken from Ankara tea were measured as the average of 5 measurements according to the 95% confidence level and it is shown in Table 5.

The results were compared with ion chromatography and are shown in Table 6. The t test was applied to the results obtained from both methods and it was seen that they were compatible with each other. According to this comparison, it is understood that the sensitivity of the electrodes we prepared is high.

Conclusion

In this study, it was determined that the sensitivity and selectivity of Cl, I, F, and Br sensitive electrodes were high. It has been seen that low concentration halogen ions can be determined easily and quickly with these electrodes. The absence of interfering ions and their workability in wide pH ranges

Table 6 Comparison of the results of sample (1) with the analysis of ion chromatography

Method	Cl^-/μg dm^{-3}	I^-/μg dm^{-3}	F^-/μg dm^{-3}	Br/μg dm^{-3}
Selective electrode	125 ± 5	1.86 ± 0.11	23 ± 3	3.5 ± 0.3
Ion chromatography	127 ± 6	1.89 ± 0.14	25 ± 4	3.5 ± 0.5
t test ($t_{critical}$ = 3.18)	2.87	1.52	2.16	1.83

are also very important advantages. The halogens in sample 1 were measured by ion chromatography. The results of both methods were found to be compatible with each other. Analysis results in wastewater samples also show that our electrodes are good.

Experimental

Chloride, fluoride, iodide, and bromide solutions were prepared from salts of NaCl, NaF, KI, and NaBr (Merck). Deionized water was used in these solutions. CaF_2, Ag_2S, Cu_2S, tridodecylmethylammonium iodide (TMAI), tridodecylmethylammonium bromide (TMABr), polyvinyl chloride (PVC), dibutyl phthalate (DBF), and tetrahydrofuran (Merck) chemicals were used in the preparation of the electrodes.

Apparatus

Potential measurements and pH measurements were performed with Jenway-3040 ion meter (Dunmow, UK) in 0.1 mol dm^{-3} $NaNO_3$ at room temperature. Orion Ag/AgCl (Boston, USA) was used as reference electrode.

Preparation of the electrodes

The chloride electrode [15], iodide electrode [16], and fluoride electrode [22] used in the measurements here were prepared in the specified processes.

In this study, a new bromide selective electrode was prepared for the first time and used for measurements. A mixture of Br-SE, 25% TMABr, 55% PVC, and 20% DBF was dissolved in THF with a total membrane mass of 0.5 g. It was waited for about 6 h for the solvent to evaporate. The membrane was glued to a PVC tube and the excess was cut off. Internal reference electrode Ag/AgCl and internal reference solution 0.5 mol dm^{-3} NaBr were put into it. They were kept in 1×10^{-4} mol dm^{-3} Br^- solution for a day and the measurements were also used.

Wastewater samples

Wastewater samples for the determination of halogen ions were brought from Ankara Stream. These samples were acidified with HCl and anion analyzes were performed within 3 h.

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