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Spectrophotometric estimation of bromide ion in excess chloride media

S. Adimurthy, V.R.K.S. Susarla, M.P. Reddy, G. Ramachandraiah*

Reactive Polymers, Central Salt and Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002, Gujarat, India

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Abstract

The redox reaction between bromate and chloride ions in the presence and the absence of two or less equivalents of bromide ion ascertaining the formation of bromine chloride species of type BrCl and $BrCl_2^-$ in subsequent reactions in 4% H_2SO_4, has been studied by spectrophotometry. Calibration graphs for the bromide ion estimation in 0.1% $KBrO_3$–4% H_2SO_4 medium are determined separately in the presence of known amounts of NaCl. The effect of Cl^- ion percentage on the determination of Br^- ion is studied and reported herewith a suitable equation for a precise, reliable and quick spectrophotometric estimation.

Keywords: Bromide; Chloride; Estimation; Spectrophotometry

1. Introduction

In bromine recovery processes, the bromide ion is oxidized quantitatively by controlled addition of chlorine gas to the acidified seawater samples or bittern [1]. This requires the precise determination of bromide ion in the source as the excess chlorination leads to the loss of bromine in the form of water soluble bromine chlorides of type $BrCl_n^{(n-1)-}$ (where $n = 1–6$) [1]. Most of the reported methods of Br^- ion estimation are based on the oxidation of it to Br_2 or BrO_3^-/BrO^- with suitable oxidizing agents [2–11] which subsequently enable it to measure suitably. However, these methods suffer due to several intricacies [12–14] like pH sensitivity of hypochlorite reaction with Br^- ion; the uncertainty of BrO^- ion stability in basic solutions, and the possible interference of other (ClO_2^- and/or ClO_3^-) integral components of hypochlorite solution.

Besides, a few spectrophotometric methods consisting of the transformation of Br^- to Br_3^- via BrO_3^- [8] by employing hypochlorite solution or the oxidation of Br^- with chloramines-T and the subsequent bromination of phenol red [15] are known. Chiu and Eubanks [8] have determined the bromide ion as Br_3^- adopting the strong absorption band at 266 nm (35,000 M^{-1} cm^{-1}) [16] resultant of three intense bands at 261 nm (15,500 M^{-1} cm^{-1}) 273 nm (16,000 M^{-1} cm^{-1}) and 282 nm (16,200 M^{-1} cm^{-1}) [17]. They have observed 15% decrease in the slope of the calibration graph in 3–10% NaCl solutions which was not explained clearly. Moreover, there was serious incongruity observed on the molar absorptivities of Br_3^- at 267 nm [18,19]. Hunter and Goldspink [3] have oxidized the Br^- to BrO_3^- with the help of hypochlorite, reduced to Br_2 with excess Br^- and subsequently reacted with a carcinogenic material rosaniline [20] and measured. The standard chloramines-T/phenol red [15] method is less sensitive because the accuracy and precision of results depends on timing of the reaction [21].

Wang et al. have suggested a procedure for the trace determination of Br^- ion via $BrCl_2^-$ by measuring its characteristic band intensity at 232 nm (24,900 M^{-1} cm^{-1}) [17] involving oxidation of Br^- ion in 0.98 M HCl with (1.07×10^{-4} M) Cl_2 which was reported to exhibit three strong closely separated absorption bands between 200 and 300 nm [15,18,22].

The present paper reports a rapid, simple, accurate and precise spectrophotometric method for the determination of Br^- in excess BrO_3^-–Cl^- medium. Calibration graphs of

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* Corresponding author. Tel.: +91 278 2568694/2568114/2567760; fax: +91 278 2567562.

E-mail addresses: grama@csmcri.org, gramachandra@rediffmail.com (G. Ramachandraiah).

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bromide ion estimation in 0.1% $KBrO_3$–4% H_2SO_4 media in the presence of 3, 5 and 10% NaCl are determined separately. The effect Cl^- ion percentage on the determination of Br^- ion is studied and an empirical equation in the presence of $Cl^- > 1.82\%$ is suggested. The reaction between $BrO_3{}^-$ and Cl^- in absence and presence of Br^- ion giving rise to the formation of $BrCl_n{}^{(n-1)-}$ is also investigated.

2. Experimental

2.1. Reagents

All chemicals used were of AR grade and used as received. Stock solution of 0.02–0.10 M KBr and $KBrO_3$ were prepared in double distilled water and diluted as and when required. A solution of 50% (v/v) H_2SO_4 was used to get the desired (4%, v/v) composition. Seawater samples from different coastal regions of Gujarat, India and the bittern samples at different densities from the experimental salt farm belonging to this Institute were collected, filtered and analyzed for total chloride ion content. For the experimental convenience, all the bittern samples were diluted five times with distilled water and used for bromide analysis.

2.2. Procedures

2.2.1. Reactions of chloride ion with bromate ion in the presence and absence of bromide ion

The reaction between Cl^- and $BrO_3{}^-$ was monitored spectrophotometrically with varying concentrations of Cl^- in acidic conditions. This study was carried out with $KBrO_3$ (6 or 3 mM) while varying the Cl^- composition between 0.3 and 7.3% with NaCl in 4% H_2SO_4. Similar experiments were conducted with $KBrO_3$ (6 mM) in the presence of two or less equivalent of KBr by varying Cl^- composition in the range of 1.82–6.10% in 4% H_2SO_4 medium. Spectrophotometric titration was conducted on $BrO_3{}^-$ in the presence of two equivalents of Br^- with varying the concentration of Cl^- ion between 0 and 10 mM with 0.1 M NaCl in 4% H_2SO_4. The concentrations of $BrO_3{}^-$ as $KBrO_3$ at 1 mM and that of Br^- (KBr) at 2 mM were maintained during this study. The spectra in all these cases were recorded after 15 min of equilibration.

2.2.2. Calibration plots of bromide ion estimation

Working standards for bromide ion estimation in Cl^- medium were prepared in the range between 0.01 and 4.2 mM from KBr stock solution while maintaining the percentage of Cl^- to 1.82, 3.03 and 6.07 with NaCl in the experimental solution. To an aliquot (0.3–1.3 ml) of (0.08 M) KBr stock in a standard flask containing 0.75, 1.25 or 2.5 g of NaCl, 3.8 ml for 0.10% or 1.9 ml for 0.05%, of 0.04 M $KBrO_3$, 2 ml of 50% H_2SO_4 was added under cooling, diluted to 25 ml with distilled water and allowed 10–15 min for equilibration. The influence of Cl^- on the bromide ion estimation was followed by keeping the $[Br^-]$ constant at 8 mM in 0.1% $BrO_3{}^-$–4% H_2SO_4 while varying its concentration between 1.8 and 6.1%.

2.2.3. Estimation of chloride ion in seawater and bittern samples

The chloride ion composition in seawater and bittern samples was determined to a precession of ±0.05% by the well known volumetric (Mohr's) method [23]. The samples were diluted appropriately (10–100 times) and used in the chloride ion estimation.

2.2.4. Estimation of bromide ion in seawater and bittern samples

The bromide ion estimation in a given seawater or diluted bittern samples was carried out in 4% H_2SO_4 medium maintaining the percentage of Cl^- between 3 and 6 by adding NaCl externally. To 20 ml of the seawater or (diluted) bittern sample, 0.025 g of $KBrO_3$, 1.25 g of NaCl (3.033% Cl^-) and 2 ml of 50% H_2SO_4 were added. The resulting solution was diluted to 25 ml with distilled water and allowed to stand for 10–15 min for equilibration. The absorbance at 335 nm of the equilibrated solution was noted and the Br^- concentration in it was determined. The above experiment in each case was repeated at least five times and the standard deviation was calculated.

2.3. Apparatus

Electronic absorption spectra were recorded employing a quartz cell of 1 cm path length on Shimadzu UV-160 spectrophotometer with a built-in thermo stated cell-compartment coupled with a temperature-controlling (±0.1 °C) unit [24].

3. Results and discussion

A fast and precise spectrophotometric method has been developed in the present study to determine the bromide ion concentration using 0.1% $BrO_3{}^-$–4% H_2SO_4 mixture as a reaction medium having $Cl^- > 1.82\%$. It is based on the facts that (i) Br^- and $BrO_3{}^-$ ions rapidly react in acidic solutions in 5:1 mole ratio liberating Br_2 (Eq. (1)) in the absence or $BrCl_n{}^{(n-1)-}$ in the presence of excess Cl^-, which show characteristic absorption bands in the visible or near visible region [21] (ii) the oxy acids of bromide like bromous and hypobromous acids are unstable and decompose to Br_2 and $BrO_3{}^-$ (Eqs. (2–5)) in chloride-free acidic/basic solutions [12–14,25–27].

$$5Br^- + BrO_3{}^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \tag{1}$$

$$3BrO^- \rightarrow 2Br^- + BrO_3{}^- \tag{2}$$

$$2BrO^- \rightarrow BrO_2{}^- + Br^- \tag{3}$$

$$2BrO_2{}^- \rightarrow BrO^- + BrO_3{}^- \tag{4}$$

$$BrO_2{}^- + BrO^- \rightarrow Br^- + BrO_3{}^- \tag{5}$$

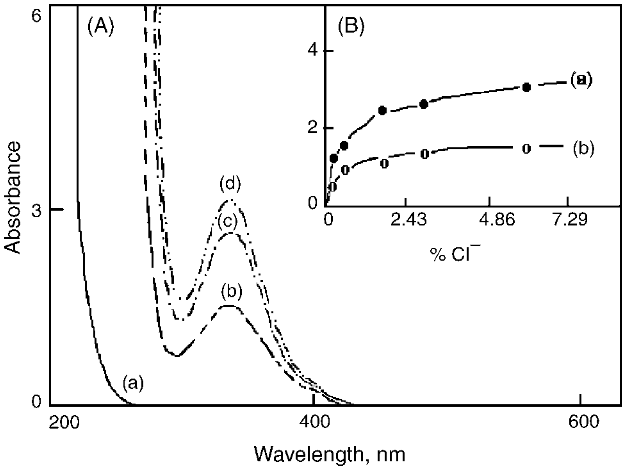

Fig. 1. (A) Absorption spectra of 6 mM BrO_3^- in 4% H_2SO_4 containing (a) 0%; (b) 0.61%; (c) 3.03%; (d) 6.07% Cl^- at 25 °C. (B) Plot of absorbance of (a) 6 mM; (b) 3 mM BrO_3^- at 335 nm in 4% H_2SO_4 vs. percentage of Cl^- added at 25 °C.

3.1. Reactions of chloride ion with bromate ion

The reaction between Cl^- and BrO_3^- was studied in 4% H_2SO_4 solution by recording the absorption spectra of BrO_3^- ion with varying concentrations of Cl^- ion. It was carried out with $KBrO_3$ at two different concentrations (6 and 3 mM) while varying the Cl^- concentration between 0.3 and 6.5% with (0.5–10%) NaCl. An intense absorption band at 230 nm and another broadband at 335 nm were developed and intensified with the increase in percentage of Cl^- (Fig. 1A). In both the cases, the absorbance at 335 nm enhanced linearly with the increase in percentage of Cl^- between 0.30 and 1.21% (85–170 mM) and almost levelled-off at 1.82% and above (Fig. 1B), indicating complete conversion of BrO_3^- ion to BrCl. The small increase in the absorbance on and after 1.82% Cl^- is accounted for the further reaction of BrCl with Cl^- ion. Interestingly, the plot, absorbance versus mole equivalents Cl^- added per mole of $KBrO_3$ (Fig. 2 (a)) showed two absorbance regions separated by an inflection at five which signifies the involvement of five Cl^- ions in the reaction (Eq. (6)) to produce BrCl and $BrCl_2^-/BrCl_n^{(n-1)-}$ in subsequent reactions (Eq. (7)).

$$BrO_3^- + 5Cl^- + 6H^+ \rightarrow BrCl + 3H_2O + 2Cl_2(\uparrow) \qquad (6)$$

$$BrCl + Cl^- \overset{K}{\rightleftharpoons} BrCl_2^- \qquad (7)$$

Contrastingly, Hunter and Goldspink [3] in a similar reaction, have suggested a 1:6 (BrO_3^-:Cl^-) stoichiometry and proposed the Br^- ion formation instead of BrCl, with the liberation of three equivalent of Cl_2. The formation of $BrCl_2^-$ (477 M^{-1} cm^{-1}) from BrCl (Eq. (7)) was presumed between 5 and 6 equivalents of Cl^- added per mole of $KBrO_3$ in Fig. 2(a) and the equilibrium constant, K was calculated as 3.3 M^{-1} which is closely comparable with the reported data, 6.0 M^{-1} in 1N $HClO_4$ at 25 °C [17].

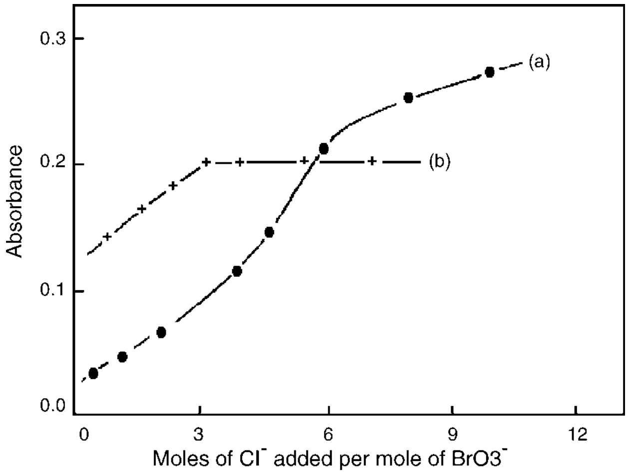

Fig. 2. Moles of Cl^- added per mole of BrO_3^- vs. absorbance at (a) 335 nm, $[BrO_3^-]$ = 6 mM; (b) 390 nm, $[BrO_3^-]$ = 1 mM, $[Br^-]$ = 2 mM at 25 °C.

3.2. Reaction of chloride ion with bromate ion in the presence of bromide

The absorption spectra of 6 mM (0.1%) $KBrO_3$ with varying concentrations of (0.004–6.5%) Cl^- and (0–12 mM) KBr in (4%) H_2SO_4 were studied. At all concentrations of $Cl^- > 0.3\%$, the spectra showed the band at 335 nm which was found to decrease with the decrease in the Br^- concentration confirming its participation in the overall reaction (Eq. (8)) giving rise to stable $BrCl/BrCl_2^-$ species [17,28–31]. On the other hand, the spectral data at $Cl^- < 0.3\%$, showed a broad absorption band at 390 nm instead of 335 nm showing that the $BrCl/BrCl_2^-$ are less stable, and hence hydrolyses to BrOH (Eq. (9)) which concomitantly decomposes to Br_2 and BrO_3^- (Eq. (10)) under the present experimental conditions [17]. The stoichiometry of Cl^- ion in Eq. (8) was established separately by spectrophotometric titration. In these experiments, the concentration of $KBrO_3$ was kept at 1 mM and that of KBr at 2 mM while Cl^- concentration varied between 0 and 10 mM in 4% H_2SO_4. The plot, absorbance at 390 nm against moles of Cl^- (Fig. 2(b)) added per mole of BrO_3^- is linear up to 3 and leveled there after, indicating the participation of 3 Cl^- ions instead of 5 as in the case of BrO_3^- alone (Eq. (6)).

$$BrO_3^- + 2Br^- + 3Cl^- + 6H^+ \rightarrow 3BrCl + 3H_2O \qquad (8)$$

$$BrCl + H_2O \rightleftharpoons BrOH + H^+ + Cl^- \qquad (9)$$

$$5HBrO \rightarrow BrO_3^- + 2Br_2 + 2H_2O + H^+ \qquad (10)$$

3.3. Calibration plots of bromide ion estimation in different chloride concentrations

Absorption spectra of 16 μM–4.16 mM Br^- were recorded separately in 1.82, 3.04 or 6.07% Cl^- with NaCl in 0.1% $KBrO_3$ and 4% H_2SO_4 mixture. All the spectra showed a broad band at 335 nm followed by a group of

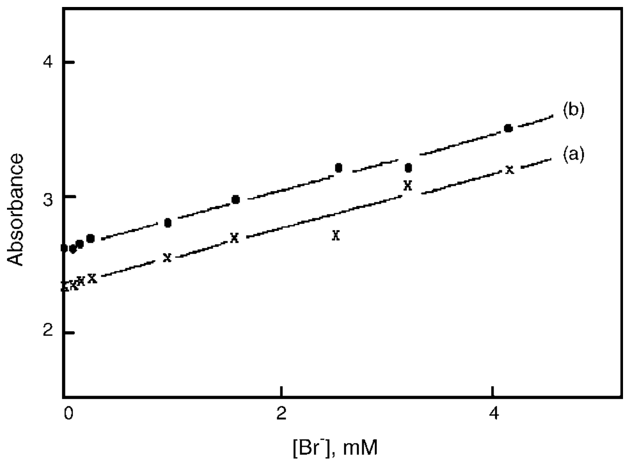

Fig. 3. Plot of [Br$^-$] vs. absorbance at 335 nm in 0.1% $KBrO_3$–4% H_2SO_4 mixture containing (a) 1.82%; (b) 3.03% Cl$^-$ at 25 °C.

closely separated intense bands in the UV-region between 300 and 200 nm. At all percentage of Cl$^-$, the absorbance at 335 nm increased linearly with the increase in the concentration of Br$^-$ investigated. However, the plots of [Br$^-$] versus absorbance (Abs) at 335 nm (Fig. 3(a and b)), depicted for 1.82 and 3.04% Cl$^-$ are parallel having almost same slope with different intercepts. The data was fit to the equations $Abs_{335} = 212.76$ [Br$^-$] + 2.352 in 1.82%; $Abs_{335} = 217.96$ [Br$^-$] + 2.595 in 3.04% and $Abs_{335} = 212.17$ [Br$^-$] + 3.109 in 6.07% Cl$^-$ having almost a common slope with distinct intercepts, which clearly indicates that the absorbance at 335 nm is arbitrarily attributed to the sum of two (chloride-dependent and chloride-independent) functions which were evaluated in the following sections. The lower and higher detection limits as reflected from the experimental data (Fig. 3) under the present set of conditions (1.82–6.07% Cl$^-$) for Br$^-$ estimation are 5 μM (0.4 ppm) and 12 mM (960 ppm), respectively. They remained same when 0.25% $KBrO_3$–4% H_2SO_4–3–10% NaCl medium was used indicating that the background concentrations of chloride and bromate ions have negligible effect in the determination.

Chiu and Eubanks [8] have reported the lower detection limit as 0.01 ppm in absence and 0.4 ppm in presence of excess Cl$^-$ ion for the estimation of Br$^-$ as Br_3^- ion by following the absorption band at 267 nm. In contrary, Anagnostopoulou and Koupparis [32] have determined spectrophotometrically the Br$^-$ to 0.09 ppm level in Cl$^-$ medium by automated flow injection analysis using chloramine-T and Phenol red. Besides, Hunter and Goldspink [3] have measured the Br$^-$ to 0.1 ppm by oxidizing it to BrO_3^- with hypochlorite, and subsequently reacted with excess Br$^-$ and rosaniline in acidic medium. Although the lower detection limit found in the present study is higher by about one–four times than the above values, the present method is quick, reliable and precise as the problems associated with the oxidant, possible interfering species/ions like Cl_2, Cl_3^-, Br_3^-, etc. and the effect of the reagents are eliminated.

3.4. Evaluation of standard equation for bromide ion estimation

The variation in the intercepts in Fig. 3 could be explained for the influence of chloride ion on the species BrCl (ε, 70 M^{-1} cm^{-1}) and $BrCl_2^-$ (ε, 312 M^{-1} cm^{-1}), which absorb at a single wavelength [17]. In fact, the data in Figs. 1 and 2 suggest that the chloride ion reacts with the BrO_3^- ion of the medium in both the presence and the absence of ($\leq$2 equivalent) Br$^-$ giving rise stable BrCl in the limits of 0.30% < Cl$^-$ < 1.82%, BrOH at all percentage of Cl$^-$ < 0.3 and $BrCl_n^{(n-1)-}$ at percentage of Cl$^-$ ion higher than 1.82, possibly involving BrCl and $BrCl_2^-$ through an equilibrium step (Eq. (7)). Thus, the observed absorbance at 335 nm is then accounted for

$$Abs_{335} = m_1[BrCl] + m'_2[BrCl_2] + C \tag{11}$$

$$Abs_{335} = [m_1 + m_2[\{\%Cl_T^- - 1.82\}][BrCl] + C \tag{12}$$

where [Br$^-$] α [BrCl], m_2 α K, $\%Cl_T^-$ = total percentage of Cl$^-$ ion in the experimental solution. At $\%Cl_T^- = 1.82$, [Br$^-$] + [BrO_3^-] = [BrCl] in which case Eq. (12) reduces to Eq. (13).

$$Abs_{335} = m_1[BrCl] + C_1 \tag{13}$$

Under these approximations, the values of m_1 and C_1 are obtained from the slope and intercept of the plot, Fig. 3(a) as 212.76 and 2.32, respectively. The difference of Eqs. (12) and (13) resulting to Eq. (14) is then considered to explain the effect of Cl$^-$ ion between 1.82 and 6.07%.

$$\Delta(Abs_{335}) = m_2[\{(\%Cl_T^-) - 1.82\}][BrCl] + C_2 \tag{14}$$

where $C = C_1 + C_2$. In order to determine the values of m_2 and C_2, the absorption spectra of 8 mM Br$^-$ ion were recorded with different percentage of Cl$^-$ between 1.82 and 6.1 in 0.1% BrO_3^-–4% H_2SO_4 and $\Delta(Abs_{335})$ was plotted against $\{(\%Cl_T^-)–1.82\}$ (Fig. 4). From the slope and intercept of the Fig. 4, the values of m_2 as 0.269 and C_2 as 0.422 were obtained. Then, Eq. (12) describing the Br$^-$ ion determination under present experimental conditions (%Cl$^-$ > 1.82%) gets simplified to Eq. (15).

$$Abs_{335} = 212.76[Br^-] + 0.27[\{\%Cl_T^- - 1.82\}][Br^-] + 2.74 \tag{15}$$

3.5. Applications

Various seawater and bittern samples of variable density were collected from selected places along the Gujarat coast for determining the bromide ion composition by the present method. The bittern samples were diluted (five times) prior to use to have chloride and bromide concentrations in the desired range and employed. The percentage of Cl$^-$ in all experimental solutions was maintained between 3 and 6 by adding NaCl externally to minimize the errors by the possible variations in

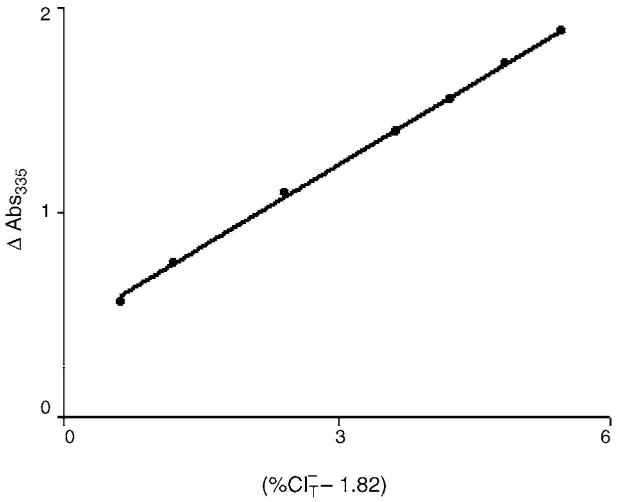

Fig. 4. Plot of $\Delta(\text{Abs}_{335})$ vs. $\{(\%\text{Cl}_T{}^-)–1.82\}$. $[\text{Br}^-] = 8$ mM in 0.1 M $KBrO_3$–4% H_2SO_4 medium at 25 °C.

the chloride ion. The absorbance at 335 nm and the percentage of Cl^- due to seawater/bittern solution in experimental solution were substituted in Eq. (16), and the composition of bromide ion present in the original seawater/bittern samples were then computed. The chloride and bromide ion compositions, thus obtained as the average of five similar experiments, are tabulated in Table 1. The percentage of error in bromide ion concentration (Table 1) caused by the deviation in chloride ion determination was considered negligible, as the changes occur in the denominator of Eq. (16), is ineffective. The standard deviation was calculated and included in the Table 1. The Br^- composition in all seawater samples having 2.8–4.6° Be′ is in alignment with that of normal seawater [1] except at few places like Gogha (0.477 g/l) and Dwaraka (0.495 g/l) where maximum salt manufacturing industries were located. Identical results were obtained when experiments were done in the presence and the absence of both calcium and magnesium.

Table 1
Br^- and Cl^- compositions in seawater and bittern samples from different places along Gujarat coast

Sample source	°Be′	%Cl^- (w/v)	Br^- (g/l)[a]
Gogha	3.95	1.50	0.477
Diu	2.84	1.82	0.177
Alang	3.89	1.88	0.153
Mahuva	4.36	2.20	0.152
Dwaraka	4.36	2.16	0.495
Okha	4.43	2.20	0.122
Kandla	4.63	3.22	0.393
Bhavnagar	3.54	1.77	0.154
	7.69	3.65	1.972
	23.90	16.48	2.045
	25.50	18.48	3.848
	27.60	18.98	4.713
	31.20	17.05	5.260
	35.20	1.85	6.375

[a] Standard deviation was found to vary between 0.0005 and 0.001.

$$[\text{Br}^-] = \frac{\text{Abs}_{335} - 2.74}{211.709 + 0.27(\%\text{Cl}^-)} \qquad (16)$$

4. Conclusion

A quick and reliable spectrophotometric method is developed for the determination of Br^- in excess $BrO_3{}^-$ in the presence of excess Cl^-. The calibration graphs for Br^- ion estimation in 0.1% $KBrO_3$–4% H_2SO_4 medium in the presence of 1.82–6.07% Cl^- are determined. The influence of Cl^- ion on the determination of Br^- ion is studied and an empirical equation (Eq. (16)) for Br^- estimation has been proposed. The reaction between $BrO_3{}^-$ and Cl^- in absence and presence of Br^- ion giving $BrCl_n{}^{(n-1)-}$ is also investigated.

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