Chapter 2 *Spectrophotometric methods of Estimations of Bromide and Bromate ions in Acidic Chloride and Chloride-free Media*

2.1. Introduction

During our efforts to prepare the solid brominating reagents[1] from the intermediates of bromine recovery process, in the present study, it was strongly felt essential to have easy, quick, reliable and precise analytical procedures for the accurate determination of bromide and bromate ions. In fact, the bromide (Br^-) ion estimation is of utmost importance but a difficult problem. Several reports appeared in literature are based on the oxidation of bromide ion to elementary bromine, hypobromite or bromate. In the methods of first kind, the bromide selectively is oxidized employing a variety of oxidizing agents,[2] like $KMnO_4$ in $CuSO_4$, HCl or dilute H_3PO_4 solutions and chromic acid in H_2SO_4 or HNO_3 keeping the other ions unaffected in the residue to elemental bromine which is distilled and estimated by volumetry, gravimetry or colorimetry. On the second kind, bromide is quantitatively oxidized to bromates either by using Cl_2-water[2] or the addition of hypochlorite[3-7] or to hypobromites.[7,9] After the reduction or expulsion of the excess chlorine or hypochlorite, the bromate is estimated iodometrically in acid solution or the hypobromite is reacted with active substrates enabling it to determine by volumetry or photometry. However, these methods are cumbersome and not precise as the hypochlorite reaction with bromide ion is highly pH sensitive while the hypobromite stability is uncertain as it decomposes irreversibly. The decomposition of hypohalites/hypobromite to halates/bromates through the corresponding halites and bromites in weakly acid and weakly alkaline solutions, as well as the effect of pH on the reaction velocity has already been well established.[10,11] Moreover, the presence of ClO_3^- ion, as being an integral part of hypochlorite solution[11b]

may affect bromide estimation because of its strong oxidizing properties in strong acids. The exact analytical errors or detection limits in these methods are not (reported in the literature)yet known except in[12a] one wherein the analytical error is (reported) to be ≤ 0.2%.[13]

Spectrophotometric methods of estimation of bromide ion involve the conversion of bromide to tribromide *via* bromate[9] formation by employing hypoclorite solution or the oxidation of bromide with chloramines-T and the subsequent bromination of phenol red.[14] Chiu and Eubanks[9] have determined the bromide ion photometrically by following the strong absorption band at 267 nm corresponding to tribromide. The detection limit in this method is 0.01 μg/ml or 0.4 μg/ml in excess chloride or sulfate with a coefficient of variation of 4%. However, the observed 15% decrease in the slope of the calibration graph in 3-10% NaCl solutions on account of Br_2Cl^- formation which strongly absorbs at 245 (24,900 $M^{-1}cm^{-1}$) nm[15] is conspicuous. Besides this, there has been serious incongruity on the molar absorptivities of Br_3^- at 267 nm that varies in the range from 25,000 to 39,000 M^{-1} cm^{-1}.[16] On the other hand Hunter and Goldspink[3] have oxidized the bromide to bromate with the help of hypochlorite, reduced to bromine with excess bromide and subsequently reacted with rosaniline to produce red tetrabromorosaniline for measurement. The method is applicable to 0.1 μg of bromide in the presence of high concentrations of chloride, but, rosaniline is identified as cancer suspect(carcinogenic) reagent.[15] On the other hand, the standard method of bromide estimation involving chloramine-T and phenol red[14] has serious short comings like the dependence of accuracy and precession of results[16] on timing of the reaction.

Wang *et al.*[15] have suggested a procedure for trace determination of Br^- ion *via* $BrCl_2^-$ by measuring its characteristic band intensity at 232 (24,900 M^{-1} cm^{-1}) nm. It involves oxidation of Br^- ion by passing Cl_2 (1.07×10^{-4} M) in 0.98 M HCl. In this study, the source of HCl is important when low Br^- content is present. Apparently, the region between 200 – 300 nm is not suitable for the Br^- ion estimation as it is most interference zone wherein intense charge transfer bands, 220 (10,000 M^{-1} cm^{-1}), 230 (350 M^{-1} cm^{-1}) and 233 (18,500 M^{-1} cm^{-1}) nm for Cl_3^- ion,[14,16a,17] and impurities like chromate and ferric ion[16] have been reported in the literature.

Baranowska[18] has reported the halite ion estimation by spectrophotometry using 2-2'-dihydroquinoxalyl by following the band at 685 nm. Hashmi and Ahmad[19] have used ammonium sulfate as reductant in the simultaneous determination of BrO^-, BrO_2^- and BrO_3^- in the presence and absence of Cl^- and Br^-. However, they are cumbersome as well as tedious methods and give inconsistent results on account of absence of dynamic equilibrium between them.

In the present investigation, it is proposed to develop facile, quick, reliable and precise analytical procedures for the estimation of Br^- and BrO_3^- ions both in the presence and absence of excess Cl^- by spectrophotometry. The Br^- ion estimation is based on its reaction with excess BrO_3^- in acid medium and the resultant absorption band i) at 390 nm for aq–Br_2 in the absence and ii) at 335 nm for $BrCl_2^-$ in the presence of excess Cl^- ion. On the contrary, the BrO_3^- ion determination is planned on its rapid reaction in acidic medium with i) excess Cl^- and the resultant absorption band at 335 nm for $BrCl_2^-$ or ii) excess (chloride–free) Br^- ion and the resultant absorption band at 390 nm for Br_3^-. Calibration graphs for Br^- ion estimation in 0.25% $KBrO_3$ – 4% H_2SO_4 and 0.1% $KBrO_3$ – 3 and 5% NaCl – 4% H_2SO_4, media and BrO_3^- ion in 4% KBr – 4% H_2SO_4 and 5% NaCl – 4% H_2SO_4 media were determined. Further, the work is extended to estimate the inorganic Br^- composition in industrial mixtures, sea water samples from different places of varied density, and soil or plant extracts, while, the BrO_3^- concentration in industrial alkaline bromine samples and in de-brominated effluents by the present methods. The redox reaction between BrO_3^- and Cl^- in absence and presence of two equivalents of KBr as an evidence to the formation of BrCl and $BrCl_2^-$ and the reaction stoichiometry in each case is investigated by spectrophotometry. The effects of sulfuric acid as well as Cl^-, Br^- and BrO_3^- ions on the absorption spectra of aq–Br_2 are reinvestigated. Detection limits for Br^- in 0.25% $KBrO_3$ – 4% H_2SO_4 and 0.1% $KBrO_3$ – 3-10% NaCl – 4% H_2SO_4 media, and BrO_3^- in 4% NaBr – 4% H_2SO_4 and 5% NaCl – 4% H_2SO_4 media are established.

2.2. Experimental Section

2.2.1. Materials. The glassware was soaked in chromic acid, washed with detergent and then rinsed with double distilled water. Analytical grade chemicals such as KBr, $KBrO_3$, KI, NaCl, NaBr, $NaBrO_3$ (SD′s chemicals, India), $Na_2S_2O_3.5H_2O$ (Loba Chemie, India), H_2SO_4 (Ranbaxy Fine Chemicals, India) and extra pure Br_2 liquid (Merck Ltd. India) were purchased and used in these investigations. Doubly distilled water was used to prepare all the solutions. About 1 g of dry KBr was dissolved in 100 or 250 ml of double distilled water and it was used as primary standard to prepare all experimental solutions. Similarly, 0.7-1.0 g of dried $KBrO_3$ was dissolved in 100 or 250 ml, further standardized by titrating against standard sodium thiosulfate solution in acidic medium in the presence of KI using starch as an indicator[19] and used to prepare experimental solutions. A solution of 50% (v/v) H_2SO_4 was used to adjust its composition 1-4% in all experimental solutions. The % of $KBrO_3$, NaBr and NaCl are referred to weight/volume while that of H_2SO_4 to volume/volume throughout this chapter. Alkaline bromine mixtures-lime were collected from M/s Saurashtra Chemicals Limited, Porbander and soda ash from M/s Agrocel Industries Limited, Dhordo, Greater Rann of Kutch, Bhuj, both situated in Gujarat, India, while the debrominated effluent samples were obtained from M/s Balarpur Industries Limited, Khawada and M/s Agrocel Industries Limited, Dhordo, Greater Rann of Kutch, Bhuj, both situated in Gujarat, India.

A solution of 0.1 M aqueous Br_2 (aq-Br_2) was prepared by suspending 5 ml of Br_2 under 100 ml water for overnight for equilibration and used to prepare a stock of 5 mM aq-Br_2. The quantity of Br_2 in these solutions was estimated volumetrically by titrating it in the presence of excess KI against 0.1 N standardized sodium thiosulfate solution.[19]

One ml of alkaline bromine mixture (37.2 °Be′) in lime (pH 10.25) and in soda ash (pH 8.73) were collected from the nearest local bromine recovery plants. One ml of each of these equilibrated solutions were diluted to 100 ml and used as stock in the estimation of Br^- and BrO_3^- contents in the original alkaline bromine mixtures.

Seawater samples from different coastal regions of Gujarat, India and bittern at different densities from the experimental salt farm of present Institute were collected and

filtered before Br^- estimation in them. The debrominated effluents were obtained from the nearest local bromine recovery plants.

Salicornia brachiata, Suaeda nudiflora or Salvadora persica seeds were collected from the nearest Bhavnagar coast (21° 75′ N 72° 14′ E) and sown in plastic pots (d, 20 cm; depth 18 cm) filled with horticulture grade (2.5 kg) soil having 0.3% Cl^- and watered initially with distilled water. After 15 days of germination, the pots were irrigated with half-strength nutrient solution (Glenn E. P.; O′Leary J. W. *Plant Cell Environ.* **1984**, *7*, 253-261.) for another 15 days. The plants were then fed with 1000 ml of 0.2 M NaBr solution twice on alternate days and latter with 5000 ml of 0.6 M NaBr solution for five alternate days so as to rise the total NaBr added to the soil amounts to 256 g for increasing the salinity. Simultaneously, plants were also irrigated with nutrient solution prepared without NaBr. The well (50 days) grown *Salicornia brachiata, Suaeda nudiflora* and *Salvadora persica* plants were carefully uprooted and washed thoroughly with tap water followed by distilled water to remove the adhering particles and then air dried. The materials were dehydrated by heating to 70°C in an oven till a constant weight (60-100g depending on the plant species) was obtained, and powdered to 200 (BSS) mesh sieve size. Plant (root, stem and leaves independently) and soil extracts were prepared by different procedures given below and used for bromide estimation.

Plant (root, stem and leaves independently) extracts were prepared by (i) suspending 0.2 g of powder in 70 ml distilled water or 0.1 N HNO_3 solution followed by digesting on a hot water bath for 2 h, (ii) digesting 0.2 g of powder in 10 ml of conc. HNO_3 or (iii) direct ashing 0.2 g of powder or fusing it with NaOH-Na_2CO_3 mixture at 550 °C. The residue left in each case was treated with 20 ml of water, filtered and washed with hot water. The filtrate was collected, diluted to 100 ml with distilled water and used for bromide estimation. About 200 g of soil sample fed with sodium bromide-nutrient solution, was treated with 50 ml of 30% H_2O_2 for 24 h, soaked in 200 ml distilled water for another 24 h to extract inorganic bromide which was filtered, diluted to one liter and used for bromide analysis.

2.2.2. Equipment. Absorption spectra were recorded on Shimadzu UV-160 spectrophotometer with a built-in thermo stated (± 0.1 °C) cell compartment coupled to a

temperature controlling unit. An Adair Dutt digital *p*H meter sensitive to 0.01 *p*H was used to measure *p*H of all experimental solutions.

2.2.3. Sample preparation. Working standards for Br^- estimation in the range between 0.01 and 28 mM (0.8 to 224 μg/ml) in Cl^-–free medium, were prepared from KBr stock. To an aliquot (1-10 ml) of KBr stock in a standard flask containing 1 ml of 1% $KBrO_3$, 2 ml of 50% H_2SO_4 was added under cooling to give 0.25% and 4%, respectively after dilution to 25 ml with distilled water and allowed 10-15 min for equilibration. Working standards for Br^- ion estimation in Cl^- medium were prepared in the range between 0.01 and 4.2 mM (0.8 to 336 μg/ml) from KBr stock while maintaining % of NaCl to 3, 5 or 10 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 of 0.04 M $KBrO_3$ for 0.10% or 1.9 ml of 0.04 M $KBrO_3$ for 0.05%, 2 ml of 50% H_2SO_4 for 4% was added under cooling, diluted to 25 ml with distilled water and allowed 10-15 min for equilibration.

Working standards for BrO_3^- estimation (as $BrCl_2^-$ or Br_3^- ion) in the range between 0.01-1.5 mM, were prepared by proper dilution of its stock solution. To an aliquot (1-10 ml) of $KBrO_3$ stock in a standard flask containing 1.25 g for 5% of NaCl, or 1 g of NaBr and 2 ml of 50% H_2SO_4 for 4% was added under cooling, diluted to 25 ml with distilled water, and allowed 10-15 min for equilibration.

To 1-4 ml of alkaline bromine stock in 25 ml standard flask, 2 ml of 50% H_2SO_4 was added and made upto the mark under cooling and allowed 10-15 min for equilibration. 1 g of NaBr in the case of BrO_3^- estimation was also added to it. The absorbance at 390 nm was measured.

To 23 ml of sea water/bittern after five fold dilution, 0.025 g of (0.1%) of $KBrO_3$ and 2 ml of 50% H_2SO_4 were added and the Br^- content in it was estimated from the absorbance data at 335 nm.

To 2-5 ml of the soil extract or 10 ml of the plant extract, 2.5 ml of 0.042 M (0.07%) of $KBrO_3$ and 2 ml of 50% H_2SO_4 were added and the Br^- content in it was estimated from the absorbance data at 390 nm.

The BrO_3^- composition in the debrominated industrial effluents was determined from the absorbance of its 10 ml solution diluted to 25 ml in the presence of 1 g NaBr at 390 nm or 1.25 g NaCl and 2 ml of 50% H_2SO_4.

2.2.4. Spectrophotometric measurements. Absorption spectra of the equilibrated samples under investigation were recorded between 200-600 nm in a 10 mm quartz cuvette at 25 °C. Double distilled water was used in all the cases as the reference unless otherwise mentioned.

2.3. Results

The spectrophotometric methods developed in the present investigations for Br^- and BrO_3^- estimations are based on the facts that (i) the oxy acids of bromide like bromous and hypobromous acids are unstable and decompose (Eqs 2.1-2.4) in strongly acidic or basic solutions and produce Br^- and BrO_3^- as ultimate end-products[10,11,18,21] and (ii) Br^- and BrO_3^- ions rapidly react in acidic solutions in 5:1 mole ratio liberating reddish-yellow Br_2 (Eq 2.5) in absence or $BrCl_2^-$ in excess Cl^- medium,[15] which show characteristic absorption bands in the visible or near visible region. The redox reactions of Cl^- with BrO_3^- in the absence and in the presence of two equiv of Br^- giving BrCl which subsequently gives $BrCl_2^-$ ion in the following steps and confirmation of their stoichiometry are investigated in the present study by spectrophotometry and the results are presented.

$$3BrO^- \longrightarrow 2Br^- + BrO_3^- \quad (2.1)$$

$$2BrO^- \longrightarrow BrO_2^- + Br^- \quad (2.2)$$

$$2BrO_2^- \longrightarrow BrO^- + BrO_3^- \quad (2.3)$$

$$BrO_2^- + BrO^- \longrightarrow Br^- + BrO_3^- \quad (2.4)$$

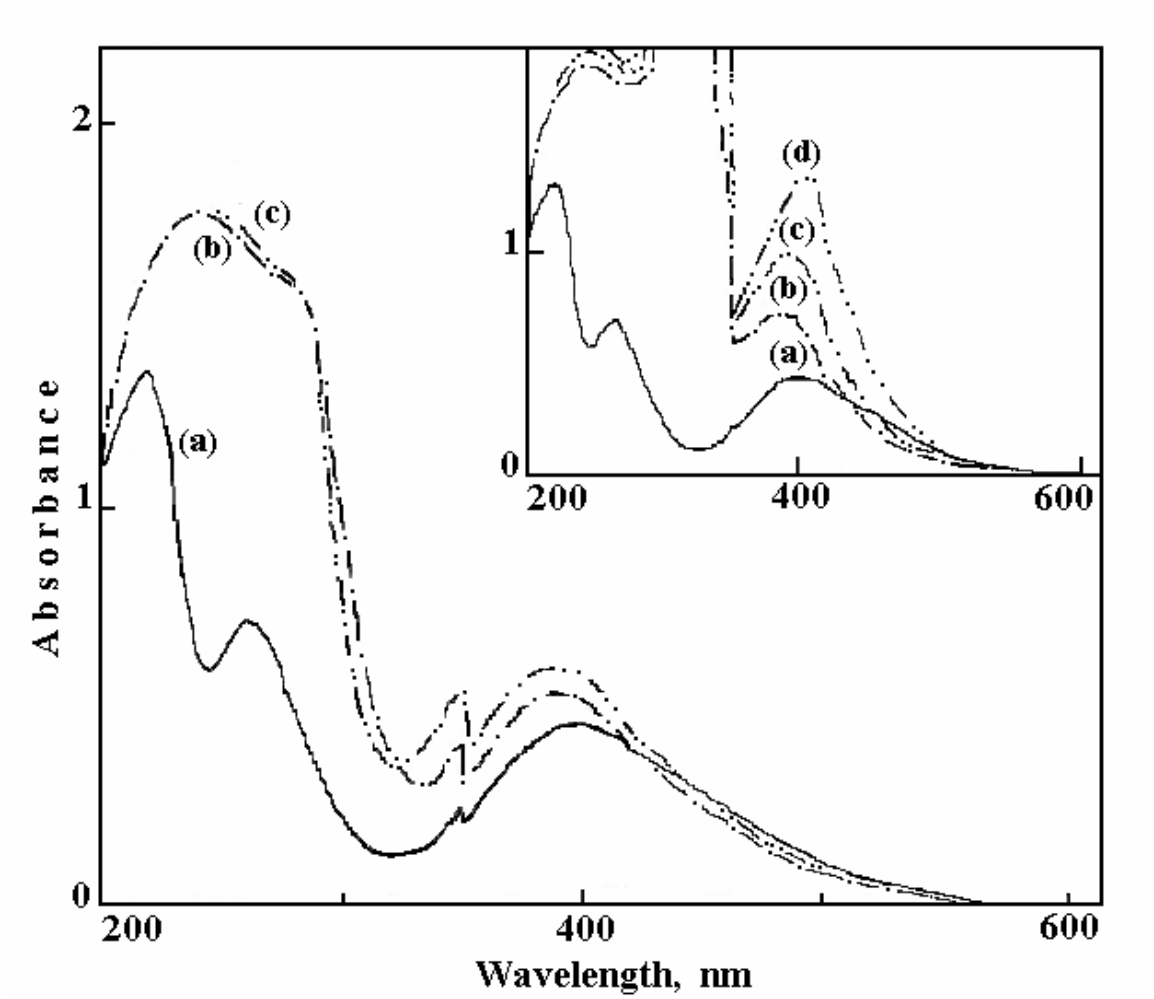
$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O \quad (2.5)$$

The literature search[3,9,16,22] revealed that the electronic spectra of aq–Br_2 and its different forms are indecisive. Thus, the spectrophotometric behavior of aq–Br_2 has first been reinvestigated in order to ascertain the results obtained here and to throw more light

on the spectral effects of different components which normally escort in the evaluation of Br^- and BrO_3^- ions.

2.3.1. Absorption Spectra of aq–Br_2 and influence of other ions. Absorption spectra of 1-15 mM aq–Br_2 in pure water were studied between 200 – 600 nm. The spectrum of the solution containing 2.63 mM aq–Br_2, depicted in Figure 2.1A (a), shows two well defined peaks at 219 (507 M^{-1} cm^{-1}) and 260 (270 M^{-1} cm^{-1}) nm and a broad band at 390 (172 M^{-1} cm^{-1}) nm. Interestingly, the latter one (170 M^{-1} cm^{-1}) was only reported in literature.[15] The absorbance at 219 (slope, 147; intercept, 0.918), 260 (slope, 286; intercept, 0.057) and 390 (slope, 286; intercept, 0.057) nm increased linearly with the increase in concentration of aq–Br_2. However, in 1-4% H_2SO_4, the aq–Br_2 exhibited the two bands at 219 and 390 nm as before, while the peak at 260 nm appeared as a shoulder with 38-46% reduced intensity. Paradoxically, the 219 and 260 nm bands were dramatically increased in their intensities in the presence of NaCl–, NaBr– and $NaBrO_3$–H_2SO_4 mixtures with an attenuate shift to higher wave numbers. Interestingly, the band at 390 nm was partially affected.

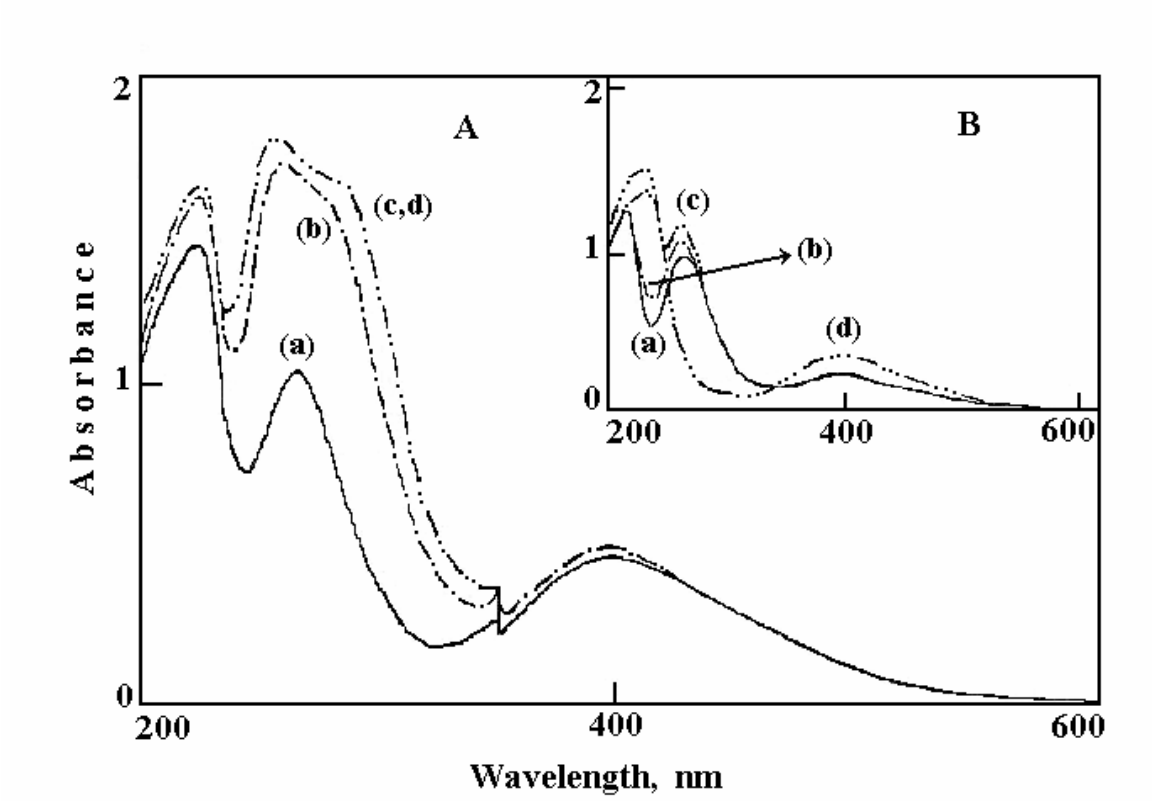
The effect of Cl^- ion was studied with 1-5% NaCl. In 1% NaCl, the bands at 219 and 260 nm were appeared as broad bands, due to a closely separated group of bands, centered at 244 and 281 nm as shown in Figure 2.1A(b), while 390 nm band being unaltered and their intensities increased by about 1.27, 2.07 and 1.21 times in 1% and 1.31, 2.17 and 1.39 times in 5% NaCl, respectively. An increase (1.24-1.36 times) in the band intensity at 390 nm was only observed (Figure 2.1A(c)) when H_2SO_4 was also added.



Figures 2.1. Absorption spectra of (**A**) 2.63 mM Br_2-water in (a) 0% NaCl; (b) 4% NaCl; (c) a mixture of 4% NaCl - 4% H_2SO_4 at 25 °C. (**B**) 2.63 mM Br_2-water in (a) 0% NaBr; (b) 1.2% NaBr; (c) a mixture of 1.2% NaBr - 4% H_2SO_4; (d) a mixture of 2% NaBr - 4% H_2SO_4 at 25 °C.

The spectra of aq-Br_2 were studied in 1–5% NaBr and in a mixture of 0.4–4.0% NaBr-4% H_2SO_4. Representative data are furnished in Figure 2.1 B(a-d). As evident in Figure 2.1 B(b), an intense broad band at 244 nm followed by another intense band between 260-350 nm replacing the bands at 219 and 260 nm in Figure 2.1A(a) were observed. The intensities of these strong charge transfer bands increased with the increase in concentration of NaBr. They were further enhanced in H_2SO_4. Subsequently, the band at 390 nm was intensified at initial (<0.8%) additions of NaBr and decreased thereafter. Measurements showed that the intensity of the 390 nm band was enhanced to about 79% in 0.4%, 85% in 0.8%, 72% in 1.2%, 53% in 1.6% and 32% in 2% NaBr solutions due to intricate nature of Br^- ion with aq-Br_2 molecules which is well known to give rise to tri-

bromide (Br_3^-) ion. However, at a given NaBr composition, the band intensity at 390 nm augmented with the increase in the composition of H_2SO_4 as shown in Figure 2.1B(b-d).



Figures 2.2. Absorption spectra of (**A**) 2.63 mM Br_2-water in (a) 0.2 mM NaBr; (b) 1.6 mM NaBr; (c) 2.4 mM NaBr at 25 °C. (**B**) Absorption spectra of 1.26 mM Br_2-water in (a) pure water; (b) 4% H_2SO_4; (c) 2% $NaBrO_3$; (d) a mixture of 2% $NaBrO_3$ and 4% H_2SO_4 at 25 °C.

The effect of low (0.1 - 2.5 mM) concentrations of NaBr on the spectra of aq-Br_2 was also considered. Some of the important observations are presented in Figure 2.2 A. Figure 2.2A(b,c) confirms the presence of 1-4% NaBr wherein the bands at 219 and 260 nm grew in intensity and appeared as a broad band at 244 nm. Concurrently, a new broad band was observed at 282 nm which intensified further as the concentration of NaBr increased in the solution. Apart from this, there was not much conspicuous change in the band at 390 nm.

Spectral effects of 4% H_2SO_4, 2% $NaBrO_3$ and their mixture on aq-Br_2 were studied independently and the results are furnished in Figure 2.2 B. The band positions and their intensities at 219 and 390 nm remained steady while that at 260 nm increased by about 6.6% in H_2SO_4, (Figure 2.2 B(b)). In contrast, the band at 219 nm shifted to 244 nm with

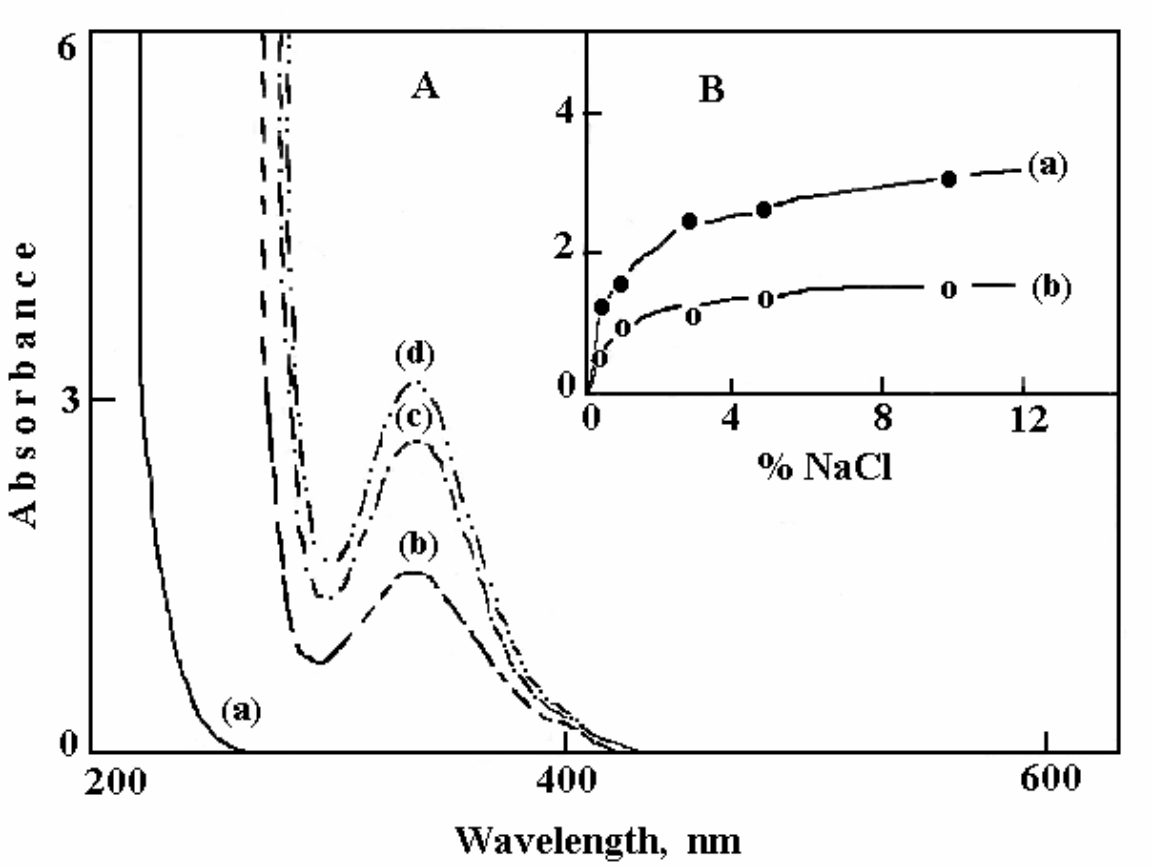
a corresponding (10%) increase in the height maintaining the 390 nm band more or less same while that of 260 nm increased by about 15% in $NaBrO_3$ (Figure 2.2 B(c)). The band at 219 nm which shifted to 244 nm in $NaBrO_3$ was observed again in $NaBrO_3$-H_2SO_4 mixture (Figure 2.2 B(d)) with the subsequent disappearance of the band at 260 nm and 67% enhancement of the band height at 390 nm.

2.3.2. Reaction of Cl^- ion in the absence and the presence of two equiv of Br^- with BrO_3^- in 4% H_2SO_4. Before describing the spectrophotometric method for the estimation of Br^- and BrO_3^- ions, an intrinsic study revealing the spectral behavior of BrO_3^- ion reaction with Cl^- ion in the absence and in the presence of two equiv of Br^- ion, the stoichiometry, and the products identification was carried out.

*Reaction of Cl^- ion in the absence of two equiv Br^- ion***.** The absorption spectral changes of $KBrO_3$ at two different concentrations in aqueous acidic solutions, in acidic-Cl^- medium alone were studied between 200 and 600 nm. The concentration of $KBrO_3$ in these studies, was kept at 6 mM (0.1%) or 3 mM (0.05%) while effecting the Cl^- concentration between 0.3% and 6.1% with 0.5 - 10% NaCl in 4% H_2SO_4. The spectra in each case, was recorded after 15 min equilibration. Some of the important observations and the spectra obtained in the absence of NaCl are presented in Figure 2.3A. An intense absorption band at 230 nm and another broad band at 335 nm were observed in all. The intensity of these bands was enhanced with the increase in % of NaCl. The absorbance at 335 nm was ploted *vs* %NaCl at 0.1% and 0.05% of $KBrO_3$ and are in Figure 2.3B. The data in Figure 2.3 B(a,b) revealed that the absorbance increases linearly in both the cases, initially with the increase %NaCl between 0 and 2% and leveled off at 3% and above on account of completion of the redox reaction between BrO_3^- and Cl^-, initiated by acid protons.

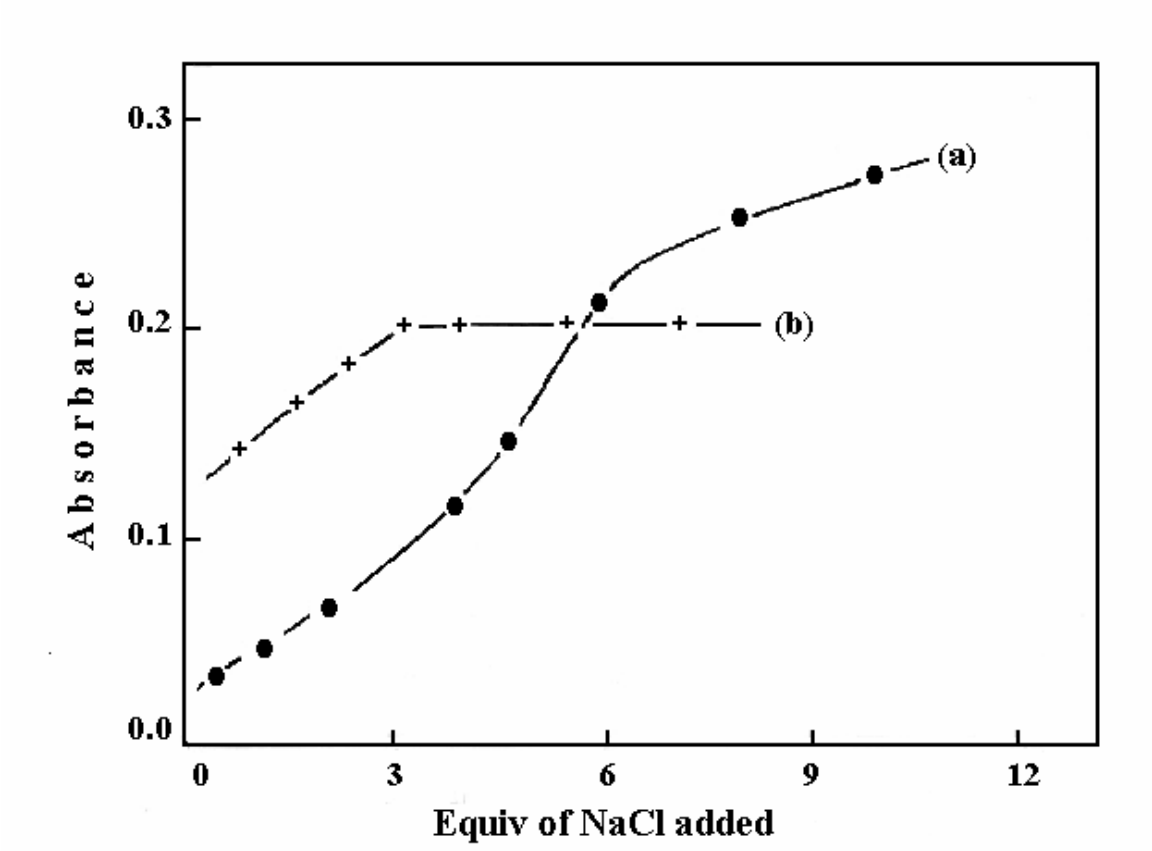
To reinforce further, the reaction stoichiometry between BrO_3^- and Cl^-, independent experiments identical to the above, were conducted, wherein the $KBrO_3$ concentration was kept constant at 6 mM (0.1%) in 4% H_2SO_4, while varying the NaCl concentration between 0 and 80 mM. In all these experiments, a weak absorption band as seen in Figure 2.3 A(b-d) was observed at 335 nm. The plot of absorbance at 335 nm *vs* moles of NaCl added per mole of $KBrO_3$ taken (Figure 2.4 (a)), showed an S-type profile having two

NaCl dependent absorbance regions separated by a poor inflection starting at around 5. This signified that five Cl^- ions are directly participating in its redox reaction with BrO_3^- ion in acidic medium which gives rise to BrCl or $BrCl_2^-$ that absorbs at 335 nm.



Figures 2.3. (**A**) Absorption spectra of 0.10% (6 mM) $KBrO_3$ in 4% H_2SO_4 containing (a) 0% NaCl; (b) 1% NaCl; (c) 5% NaCl; (d) 10% NaCl at 25 °C. (**B**) Plot of Absorbance of (a) 0.10 % $KBrO_3$; (b) 0.05 % $KBrO_3$ at 335 nm in 4% H_2SO_4 *vs* %NaCl added at 25 °C.

Reaction of Cl^- in the presence of two equiv Br^- ion. A solution of 0.1% (6 mM) $KBrO_3$ in 4% H_2SO_4-3-10% NaCl mixture in the absence and presence of two equiv KBr showed identical spectra similar to that shown in Figure 2.3 A(b-d), except a difference in absorbance between 200-400 nm indicating that identical species were formed in both the cases. The band intensity at 335 nm has enhanced considerably in the presence of two equiv of KBr or less. The enhancement in the band intensity revealed that the concentration of species responsible for it is increased when two equiv of KBr was

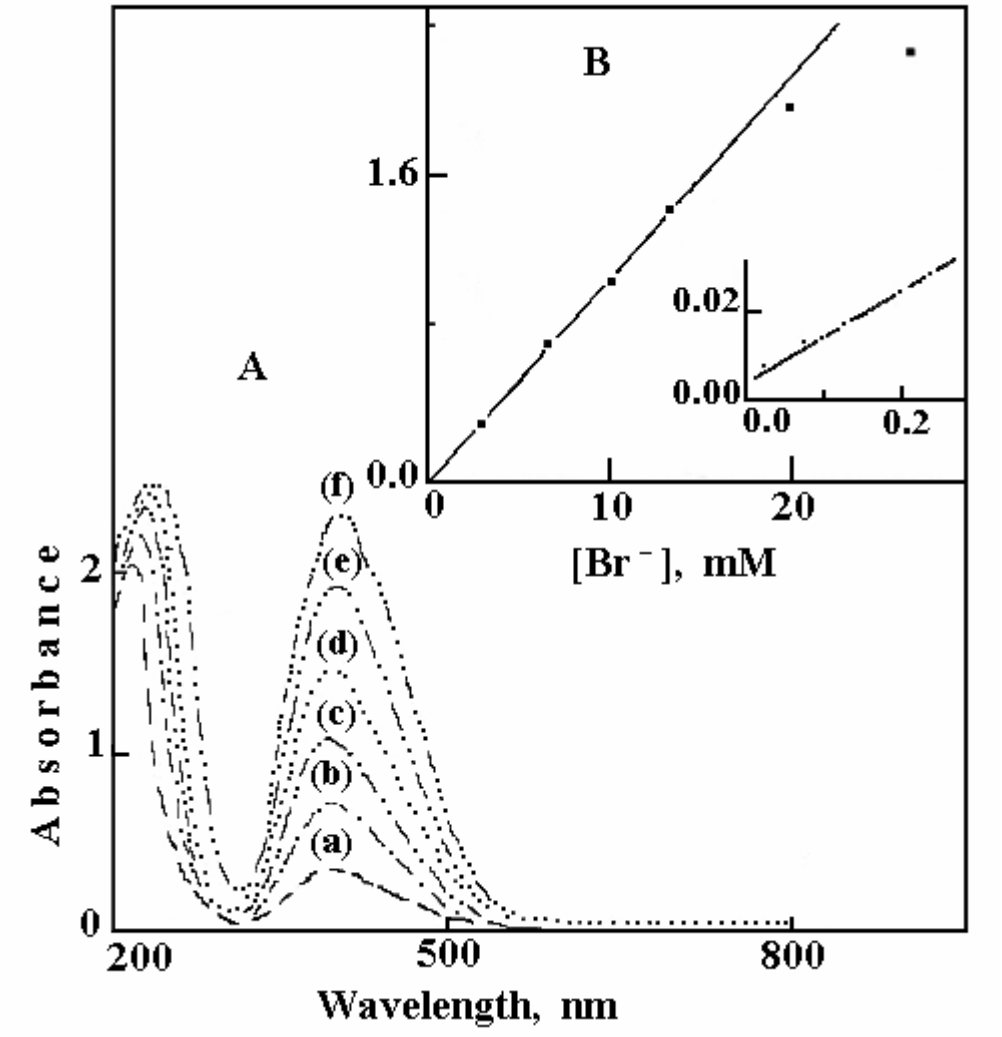


Figures 2.4. Equiv of NaCl added *vs* Absorbance at (a) 335 nm when $KBrO_3$ = 6 mM in 4% H_2SO_4; (b) 390 nm when $KBrO_3$ = 1 mM, KBr = 2 mM in 4% H_2SO_4 at 25 °C.

present. In order to establish the stoichiometry of Cl^- in this reaction spectrophotmetric titration was conducted. In these studies, the concentration of $KBrO_3$ was kept at 1 mM (0.05%) and that of KBr at 2 mM while varying the Cl^- concentration between 0 and 10 mM with 0.1 M NaCl in 4% H_2SO_4. The spectra in each case, was recorded after 15 min of equilibration. The data, unlike in Figures 2.3 A, showed a broad band at 390 nm. The absorbance at 390 nm was plotted against equiv of NaCl added to the mixture $KBrO_3$ and KBr and is shown in Figure 2.4(b). The data in Figure 2.4(b) reflected that the absorbance enhancement linearly as the Cl^-:BrO_3^- mole ratio tends to 3 and leveled off thereafter indicating that three mole Cl^- ions react with BrO_3^- ion in the presence of two equiv of Br^- in acidic solutions.

2.3.3. Calibration plots for Br^- and BrO_3^- ions estimations in Cl^-–free medium. Br^- ion estimation. Absorption spectra of 0.02-30 mM (1.6-2400 ppm) Br^- were studied in 0.25%

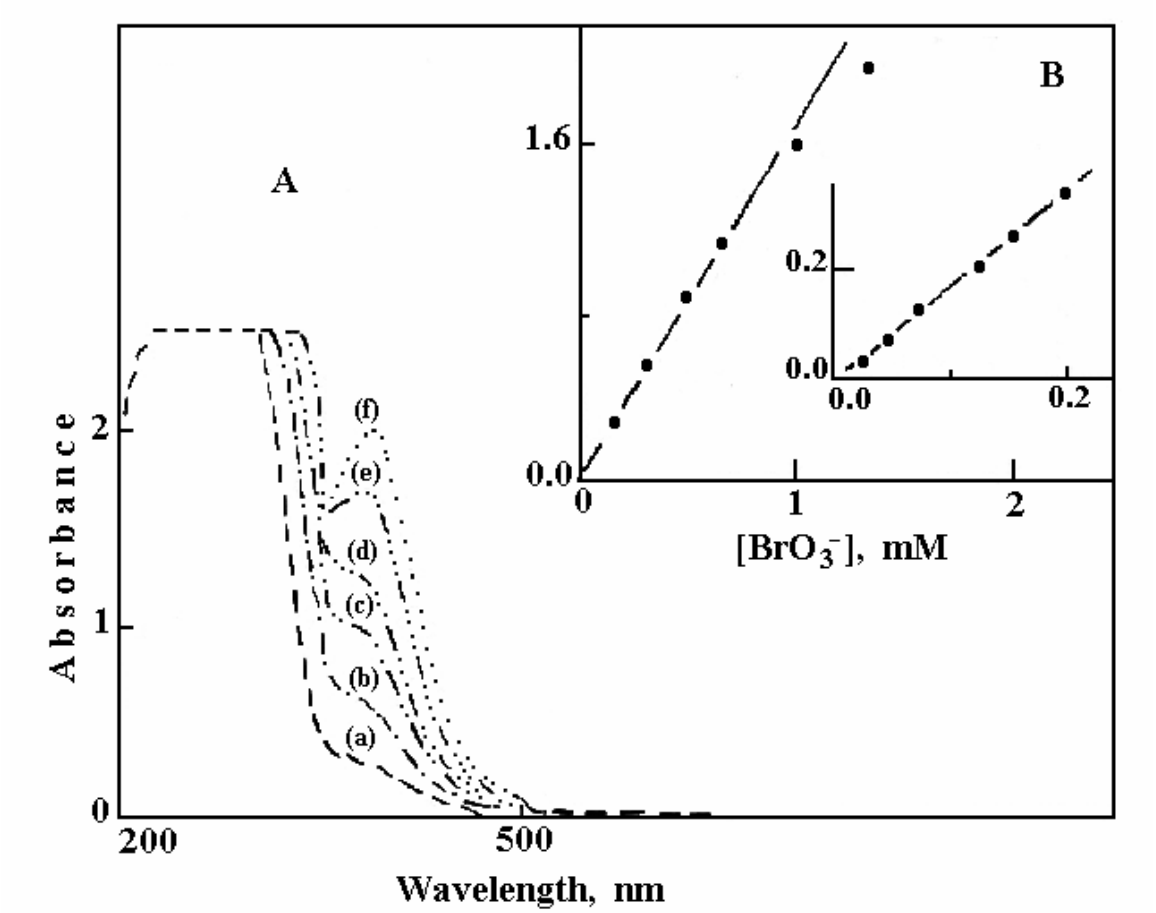
$KBrO_3$ – 4% H_2SO_4 solutions. The spectral results of Br^- in the concentration range of 3-30 mM are explained in Figure 2.5A. In all cases, two charge transfer peaks matching to



Figures 2.5. Absorption spectra of (**A**) 0.25% $KBrO_3$ – 4% H_2SO_4 mixture containing (a) 3.42; (b) 6.83; (c) 10.25; (d) 13.61; (e) 20.49; (f) 27.32 mM KBr at 25 °C. (**B**) Plot of [Br^-] *vs.* Absorbance at 390 nm. The data between 0.02 – 17 mM fits to the linear equation y = 105 x + 0.003 (r = 0.9998).

those observed in the case of aq-Br_2 in 2% $NaBrO_3$–4% H_2SO_4 mixture, Figure 2.5 B(d), were observed. The intensity of the band at 390 nm increased with the increase in the concentration of Br^-. However, the plot of [Br^-] *vs* absorbance at 390 nm (Figure 2.5 B) showed that the increase was linear between 0.02-16 (1.6 or 1280 ppm) mM demonstrating the validity of Beer-Lambert's law. The data, in these concentration limits, fit to the linear equation y = 105 x + 0.003.

BrO_3^- ion estimation. Absorption spectra of 0.02-1.36 mM (3-227 ppm) BrO_3^- were studied in 4% NaBr–4% H_2SO_4 solution. The spectral results of BrO_3^- in the concentration range between 0.15-1.40 mM are explained in Figure 2.6 A. In all cases, a broad shoulder spreading over 380 and 408 nm along with a strong band at 267 nm, is accounted for Br_3^- species.[9] Unlike in the case of Br^- ion, the intensity of this shoulder

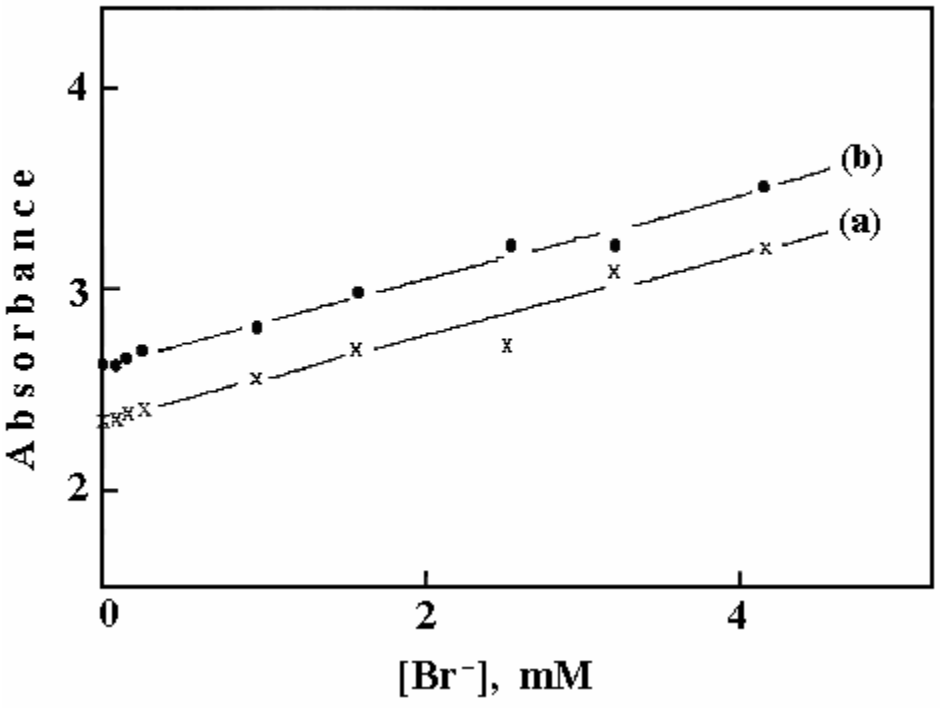


Figures 2.6. Absorption spectra of (**A**) 4% NaBr – 4% H_2SO_4 mixture containing (a) 0.171; (b) 0.314 (c) 0.512; (d) 0.682; (e) 1.023; (f) 1.364 mM $KBrO_3$ at 25 °C. (**B**) Plot of [BrO_3^-] *vs.* Absorbance at 390 nm. Regression line fits to the linear equation: y = 1659 x – 0.0004 (r^2 = 0.9994) for all values of [BrO_3^-] between 0.02 – 1.00 mM.

was scarcely affected by the Cl^- ion. The intensity measured at 390 nm increased with the consequent increase in the concentration of BrO_3^-. However, the plot of [BrO_3^-] *vs.* absorbance (Figure 2.6 B) was linear between 0.02-1.00 mM or 3-130 ppm indicating the validity of Beer-Lambert's law. The data in these concentration limits, fit to the linear equation y = 1659 x – 0.0004. The deviation observed in Figure 2.6 B at high (>1 mM) BrO_3^- concentration is obvious and it may be accounted for the loss of

Br_3^-/Br_2 due to its high volatility. The lower and upper detection limits for BrO_3^- estimation under the present set of (4% NaBr–4% HSO_4) conditions are estimated and works out to be 5 μM and 1 mM, respectively.

2.3.4. Calibration plots for Br^- and BrO_3^- ions estimations in excess Cl^- medium. Br^- ion estimation. Absorption spectra of 16 μM – 4.16 mM Br^- were studied in 1.82, 3.04 or 6.07 % Cl^- as 3, 5 or 10% NaCl, respectively in 0.1% (6 mM) $KBrO_3$ and 4% H_2SO_4 mixture as suming that the [Br^-] in sea water samples ranges between 0.007-0.02%. All

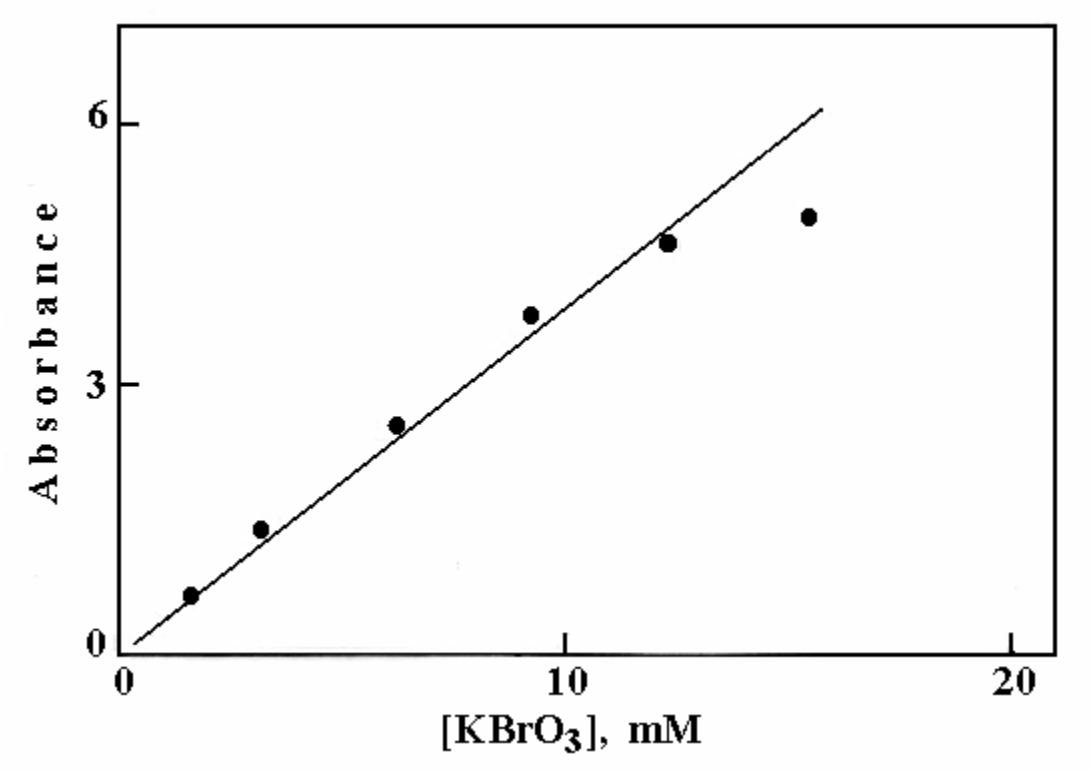


Figures 2.7. Plot of [Br^-] *vs.* Absorbance at 335 nm in 0.1% $KBrO_3$ – 4% H_2SO_4 mixture containing (a) 1.82%; (b) 3.03% Cl^- at 25 °C. Regression line fits to the linear equation (a) Abs_{335} = 212.76 [Br^-] + 2.316 (r^2 = 0.9526); (b) Abs_{335} = 217.96 [Br^-] + 2.595 (r^2 = 0.9928).

the spectra showed a broad band at 335 nm followed by a group of closely separated intense bands in the UV-region between 300-200 nm. At all % of Cl^-, the absorbance at 335 nm increased linearly with the increase in the concentration of Br^- investigated. However, the plots of [Br^-] *vs.* absorbance at 335 nm (Figure 2.7 (a,b)), depicted for 1.82, and 3.04 %Cl^- are parallel having almost same slope with different intercepts. The data

fit to the equation 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^-.

*BrO_3^- ion estimation***.** Absorption spectra of 1.52 – 15.2 mM (195 – 1,950 ppm) BrO_3^- ($KBrO_3$), were studied in 5% NaCl – 4% H_2SO_4 mixture with the assumption that in 5% NaCl medium, all the BrO_3^- ion reacts completely with Cl^- to show maximum absorption at 335 nm. In all cases, the spectra exhibited a broad band at 335 nm similar to



Figures 2.8. Plot of [$KBrO_3$] *vs* Absorbance at 335 nm in 5% NaCl – 4% H_2SO_4solution at 25 °C. Regression line fits to the linear equation: y = 426.2 x (r^2 = 0.9974) for all values of [$KBrO_3$] between 1.52 - 10 mM.

that seen in Figure 2.3 A(b-d). The change in absorbance at 335 nm with the variation in the molar concentration of $KBrO_3$ was plotted and depicted in Figure 2.8. The data in Figures 2. 8 revealed that the plot is linear between 1 and 12 mM of $KBrO_3$ satisfying the Beer-Lambert's law and deviating thereafter at higher concentrations. The data obtained between 1 mM and 10 mM $KBrO_3$, under present set of experimental conditions, fit to the average equation, y = 426.20 x, passing through origin.

2.4. Discussion and Conclusions

2.4.1. Spectral behavior of aq-Br_2 Molecular bromine is reputed to dissociate to Br^+ and Br^- ions in an established equilibrium (Eq 2.6)[3]. In turn, these ions interact in neutral conditions with water molecules leading to the formation of BrOH and HBr (Eqs 7 and 8). Eign and Kustin[23] who reported the equilibrium constant K_h (4.4 x 10^{-9}) for Eq 2.9, have suggested, by analogy with aq-Cl_2, (K_h = 1.0 x 10^{-3})[24] the formation BrOH and HBr by the hydrolysis of aq-Br_2. Pink[25] has determined the equilibrium constant spectrophotometrically for the hydrolysis step (Eq 2.9) of Br_2. In fact, Chapin[11a] who has isolated BrOH from free Br_2 in 0.3 N HNO_3 by precipitating Br^- as AgBr with $AgNO_3$ too supports such a hydrolysis reaction.

$$Br_2 \rightleftharpoons Br^+ + Br^- \qquad (2.6)$$

$$Br^+ + H_2O \rightleftharpoons BrOH + H^+ \qquad (2.7)$$

$$Br^- + H_2O \rightleftharpoons HBr + OH^- \qquad (2.8)$$

$$Br_2 + H_2O \rightleftharpoons BrOH + H^+ + Br^- \qquad (2.9)$$

Thus, the bands at 219, 260 and 390 nm evidenced in Figures 2. 1A(a) are stark responses of aq-Br_2 and its hydrolyzed species. In contrast, Soulard *et al.*[22] have reported a single band at 329 (345 M^{-1} cm^{-1}) for BrO^-, 260 nm (160 M^{-1} cm^{-1}) for BrOH and 390 nm (175 M^{-1} cm^{-1}) for Br_2 which are analogous to those in Figure 2.1A(a). Our independent experiments have disclosed that BrOH exhibits one sharp band at 260 nm and a weak broad at 390 nm.

The dramatic changes observed in Figure 2.1 A(b,c) in acidic and neutral conditions of NaCl, designate that the charge transfer bands, 219, 260 and 390 nm of aq-Br_2 are largely affected even at low concentrations of Cl^-. This accounts for the establishment of reaction equilibrium between aq-Br_2 or its hydrolysed products and added Cl^- ion that drives to the formation of Br_2Cl^- which absorbs at 245 (24,900 M^{-1} cm^{-1}) nm and 380 (560 M^{-1} cm^{-1}) nm from aq-Br_2 (Eq 2.10) or *via* BrCl (Eq 2.11).[15,26] Kanyaev and Shilov[27] have already reported the equilibrium constant (K = 2.95 x 10^{-5}) for reaction established between BrCl, Cl^- and BrOH (Eq 2.11).

$$aq\text{-}Br_2 + Cl^- \rightleftharpoons Br_2Cl^- \quad (2.10)$$

$$BrCl + H_2O \rightleftharpoons BrOH + H^+ + Cl^- \quad (2.11)$$

The bands at 244 nm, 260-350 and 390 nm replacing the bands of aq-Br_2 in Figure 2. 1A(a) and rising as a function of externally added Br^- [Figure 2. 1B(b-d) and Figure 2. 2A(a-c)], in both neutral and acidic media are momentous evidences for the formation of Br_3^- ion. An intense band at 266 nm (35,000 M^{-1} cm^{-1}) has already been reported earlier for Br_3^- ion.[22] Strangely, the band at 390 nm observed in Figure 2. 1 B(b-d) for Br_3^- ion was not reported earlier by other investigators.[15,22]

The marginal increase in peak intensity of the band at 260 nm in 4% H_2SO_4 seen in Figure 2.2B(b), confirms the shift in the equilibrium (Eq 2.12) towards the stabilization of BrOH ($K_a = 2 \times 10^{-9}$)[23] of aq-Br_2 and reinforces its greater stability in the presence of one equiv of Br^- of aq-Br_2 as in Eq 2.9.

$$BrOH \rightleftharpoons H^+ + BrO^- \quad (2.12)$$

The results in Figure 2.2 B(c) reveal that there is no substantial effect of added BrO_3^- on the spectra of aq-Br_2, while those in Figure 2.2B(d) illustrate a different effect of acidic BrO_3^- wherein 260 nm band is suppressed and 390 nm band is intensified concomitantly. This is accounted for the decomposition of BrOH to Br^- and BrO_3^- ions (Eq 2.1) and reaction of Br^- and BrO_3^- in 5:1 mole ratio to give Br_2 in strong acids (Eq 2.5). This, in other words, implies that i) BrOH is not as stable as aq-Br_2 in strongly acidic BrO_3^- ion solutions, as a result the hydrolysis of aq-Br_2 (Eq 2.9) is suppressed. From Figure 2.2 B (a,d), it is also revealed that the absorbance of non-hydrolyzed Br_2 has relatively greater absorbance at 390 nm than the hydrolyzed one. This may be a favorable point to follow this band in the Br^- ion estimation in excess BrO_3^-.

2.4.2. Reaction of Cl^- with BrO_3^- in the absence and presence of two equiv of Br^-. Schulek, Burger and Pungor[28] have studied the reaction of excess Cl^- ion, under acidic

conditions, with BrO_3^- ion in presence of two equiv Br^- (Eq 2.13) ion and suggested, first time, the formation of BrCl in two stages *via* the formation of Br_2 in aqueous solution.

$$BrO_3^- + 2Br^- + 3Cl^- + 6H^+ \longrightarrow 3BrCl + 3H_2O \qquad (2.13)$$

BrCl which depicts < 240 (>166 M^{-1} cm^{-1}) and 343 (70 M^{-1} cm^{-1}) nm bands, further reacts with Cl^- in aqueous acidic (~ 1 N) solution and produce stable $BrCl_2^-$ ion (Eq 2.14) absorbing at 232 (32,700 M^{-1} cm^{-1}) and 343 (312 M^{-1} cm^{-1}) nm.[15] On the other hand, BrCl in Cl^-–free acid solutions, hydrolyses (Eq 2.10) to give BrOH,[15] which in turn, is reported[15] to give Br_2 along with BrO_3^- ion through disproportionation (Eq 2.15).

$$BrCl + Cl^- \rightleftharpoons BrCl_2^- \qquad (2.14)$$

$$5BrO^- + 4H^+ \longrightarrow BrO_3^- + 2Br_2 + 2H_2O \qquad (2.15)$$

The redox reaction between BrO_3^- and Cl^- in the presence of two equiv of Br^- was also investigated in the present studies. The identical spectral results obtained in the reaction of BrO_3^- with excess Cl^- ion in the absence (Figure 2.3A) and the presence of two equiv of Br^- ion in 4% H_2SO_4 indicate that the reactions in both the cases are identical and similar in nature to those depicted in Eqs 2.13 and 2.14. Thus, the end product in both the cases is concluded confirmed to be BrCl or $BrCl_2^-$ ion. Ipso facto, the small UV shift in the bands position in the present study to 335 and 230 nm from the reported values for BrCl and $BrCl_2^-$ may be accounted for high acidity in the medium. The redox reaction between BrO_3^- (E° for BrO_3^-, H^+/Br(I) as HBrO, +1.45 V)[29] and Cl^- (E° for Cl_2/Cl^-, +1.359 V)[29] giving BrCl is empirically given as in Eq 2.16 which is followed by Eq 2.14 to give $BrCl_2^-$ finally.

$$BrO_3^- + 5Cl^- + 6H^+ \longrightarrow BrCl + 3H_2O + 2Cl_2(\uparrow) \qquad (2.16)$$

The data seen in Figure 2.4 (a) tacitly revealed that the four-electron reduction of BrO_3^- ion, not reported earlier, by Cl^- to Br(I) is probably an inseparable four fast one-electron steps. In contrast, the liberation of two equiv of Cl_2 gas is confirmed by carrying

out independent tests, wherein the evolution of green color gas was observed when 0.1-0.5 ml of 12 N HCl was added to 100-200 mg of $KBrO_3$. 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 equiv of Cl_2. With the help absorbance data between 5 and 6 moles of NaCl added per mole of $KBrO_3$ in Figure 2.4(a) and the empirical Eq 2.17, the equilibrium constant (K) for formation of $BrCl_2^-$ ion (Eq 2.14) is calculated to be 3.3 M^{-1} which closely compares with the value 6.0 M^{-1} at 25 °C, μ=1.0 M in ~1 N $HClO_4$ reported earlier.[15] The hypothesis made here is that BrCl forms completely at 5 equiv of NaCl added to $KBrO_3$ solution and the enhancement in the absorbance between 5 and 6 equiv of NaCl added is for the formation more absorbing $BrCl_2^-$ ion. Further, the molar absorptivity for $BrCl_2^-$ ion considered in these calculations was calculated (477 M^{-1} cm^{-1}) under the present experimental conditions from the maximum absorbance data in Figure 2. 3(b) between 5% and 10% NaCl.

$$K = \frac{[BrCl_2^-]}{[BrCl][Cl^-]} \qquad (2.17)$$

where $[BrCl_2^-]$ = change in absorbance at 335 nm/molar absorptivity of $BrCl_2^-$; [BrCl] = $[BrO_3^-]$–$[BrCl_2^-]$ and $[Cl^-]$ = {6 – (equiv of NaCl added) x $[KBrO_3]$}.

It is axiomatic that BrO_3^- and Br^- ions spontaneously react in 1:5 mole ratio in strong acids and liberate Br_2 even in the presence of Cl^- ions– the experimental data in the present investigations reveal that unlike in Figure 2.3, the reduction of BrO_3^- ion to Br(I) is preferably affected by Br^- (E° for Br_2/Br^-, +1.087 V)[29]ion, to that of Cl^- (E° for Cl_2/Cl^-, +1.359 V)[29], when possessing two equiv of Br^- ion is present in acidic excess Cl^- solution. Further, the data observed in 0.5 – 10% NaCl (Figure 2.3 A) and 3-10% NaCl in the presence of two equiv of Br^- showed neither the formation of the band at 390 nm, similar to that observed for aq-Br_2 in Figure 2.1A(a) nor disappearance of it, so the formation of BrCl in two stages as suggested earlier in the literature,[28] *via* Br_2 (Eq 2.13) is ruled out. This coupled with the data in Figure 2.4(b), it safely concludes that the two Br^- ions, instead of less favorable Cl^- ion, are oxidized sequentially each by two one-

electron steps to give rise to two Br(I) species by BrO_3^- ion which in turn reduced to Br(I)species. Latter, the Br(I) reacts with Cl^- ion from the medium and produces BrCl and $BrCl_2^-$ as shown in Eqs 2.13 and 2.14. Further, the appearance of 390 nm band during the spectrophotometric titration of BrO_3^- ion by varying Cl^- ion concentration in the presence of two equiv of Br^- could be the bottom line of the hydrolysis of BrCl to BrOH (Eq 2.11) and concomitant decomposition of the latter to Br_2 and BrO_3^- ion (Eq 2.15). These could be the probable reasons for the absence of inflection in the plot Figure. 2.4(b), unlike in Figure 2.4(a), and saturation of absorbance at 390 nm beyond 3 equiv of NaCl added to the $KBrO_3$ solution.

*2.4.3. Spectrophotometric Br^- ion estimations in the absence and the presence of Cl^- ion***.** It is interesting to note that the spectral data in Figure 2.5 A is replica of that observed for Br_2 in presence of $KBrO_3$ and H_2SO_4. Therefore it can be concluded that the absorbance at 390 nm used in the Br^- calibration (Figure 2.5B) is totally for non-hydrolyzed aq-Br_2 present in the standards. Moreover, the possibility of interference of gratuitous bands with that of aq-Br_2 in the spectrum was ruled out. On the other hand, the non-linearity of the plot Figure 2. 5B at higher Br^- concentration is attributed for its loss during analysis caused by its high volatility. The lower and higher detection limits as estimated from the data under the present set of conditions for Br^- are 5 μM (0.4 ppm) and 16 mM (1280 ppm).

In the presence of Cl^-, the Br^- ion reacts with BrO_3^- producing stable $BrCl_2^-$ which absorbs at 230 and 335 nm under the present set of experimental conditions. Following the 335 nm band is more idealistic than the other because it is considerably away from noisy (200-300 nm) zoning where most of the likely impurities show strong evidence. The chloride ion dependence of intercept in Figure 2.7 could be explained for the influence of chloride ion on the species BrCl (70 M^{-1} cm^{-1}) and $BrCl_2^-$ (312 M^{-1} cm^{-1}), which absorb at a single wavelength.[15] In fact, the microscopic analysis of the data in Figure 2.3 and 2.4 suggest that the BrO_3^- ion in the presence of 0-2 two equiv of Br^- reacts with Cl^- in the limits $0.30\% < Cl^- < 1.82\%$ giving BrCl. At lower % of Cl^- ion (<0.3), BrCl rapidly hydrolyses to BrOH wherein the 390 nm band appears instead of 335 nm band while at higher ($1.82\% \leq Cl^- \leq 6.06$) BrCl converts to $BrCl_2^-$ with an enhanced

absorbance at the same band position, 335 nm through an equilibrium step (Eq. 2.14). On the basis of experimental data (Figure 2.3, 2.4 and 2.7), the chloride ion dependent absorbance spectra at 335 nm band for Br^- estimation in 0.1% BrO_3^--4% H_2SO_4 media is then explained by Eq. 2.18 which may be rewritten as Eq 2.19 after considering the equilibrium, Eq. 2.14 and assuming that Br^- ion conversion to BrCl is complete at 1.8% Cl^- and the observed influence of Cl^- at higher %Cl^- ion is due to the formation of more absorptive $BrCl_2^-$ ions.

$$Abs_{335} = m_1 [BrCl] + m_2' [BrCl_2^-] + C \quad (2.18)$$

$$Abs_{335} = [m_1 + m_2' K [\{ \%Cl_T^- - 1.82\}] [BrCl] + C \quad (2.19a)$$

$$Abs_{335} = [m_1 + m_2 [\{ \%Cl_T^- - 1.82\}] [BrCl] + C \quad (2.19b)$$

where $[Br^-] = [BrCl]$, $m_2' K = m_2$, $\%Cl_T^-$ = Total % of Cl^- ion present in solution. Eq. 2.19 becomes to Eq 2.20 at $\%Cl_T^- = 1.82$, $[Br^-] = [BrCl]$ and $[BrCl_2^-]$ is negligible. Under these approximations, the values of m_1 and C_1 are taken as the slope and intercept of the plot, Figure 2. 7(a) as 212.76 and 2.32, respectively.

$$Abs_{335} = m_1 [BrCl] + C_1 \quad (2.20)$$

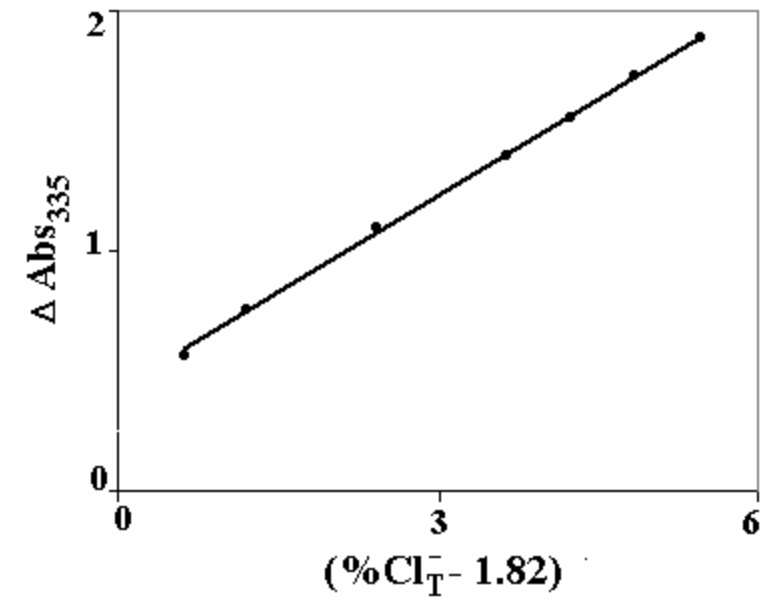
The difference of Eqs. 2.19 and 2.20 is considered as Eq. 2.21 to explain the effect of Cl^- ion between 1.82% and 6.07%.

$$\Delta(Abs_{335}) = m_2 [\{(\%Cl_T^-) - 1.82\}] [BrCl] + C_2 \quad (2.21)$$

where $C = C_1 + C_2$. In order to determine the values of m_2 and C_2, absorption spectra of 8 mM Br^- ion were recorded in 0.1% BrO_3^-–4% H_2SO_4 with variable %Cl^- ion between 1.82 and 6.1. From the slope and intercept of plot $\Delta(Abs_{335})$ *vs* $\{(\%Cl_T^-) - 1.82\}$ (Figure 2.9), the values of m as 0.269 and C_2 as 0.422 were obtained. Thus the final equation for Br^- ion estimation in excess (>1.82%) Cl^- is given as Eq. 2.22.

$$Abs_{335} = [212.76 + 0.27 [\{ \%Cl_T^- - 1.82\}] [Br^-] + 2.74 \quad (2.22)$$

Chiu and Eubanks[9] 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 sharp contravention, Anagnostopoulou and Koupparis[30] 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



Figures 2.9. Plot of $\Delta(Abs_{335})$ *vs* $\{(\%Cl_T^-)-1.82\}$. $[Br^-]$ = 8 mM in 0.1 M $KBrO_3$ – 4% H_2SO_4 medium at 25 °C. Regression line fits to the linear equation $Abs_{335} = 0.269\ [\%Cl_T^- - 1.82] + 0.422$ (r^2 = 0.9991).

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 4-40 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.

Employing the calibration data in Figure 2.5B and Figure 2.7, the composition of Br^- ion present in industrial alkaline bromine mixtures, extracts of soil and plant materials and seawater samples from different places, of variable density has been determined and tabulated in Tables 2.1-2.3. In Cl^- free medium, the spectra obtained in all cases was found to be exactly identical to that in Figure 2.5A. The data in Table 2.1 obtained for alkaline bromine mixtures are less than the value (250 g/l) expected by the industries.

The divergence, 20 g/l in case of lime-Br_2 mixture and 8 g/l in case of soda ash-Br_2 mixture, is palpable when impurities such as Cl_2 and ClO^- oxidize some of the Br^- ion to BrO_3^- causing to exceed its solubility ceilings. The molar solubilities of alkali ($NaBrO_3$, 0.1976 M) and alkaline earth $Ca(BrO_3)_2$ (<0.198 M) metal bromates have reportedly been lower than the corresponding (NaBr, 0.9475 M and $CaBr_2$, 0.725 M) bromides.[31] Interestingly, the data in Table 2.2 reveal that the soil fed with 0.072 g (8%) of Br^- is left with 0.063 g (6.3%) losing the rest (1.7%) to the plant on irrigation. Comparison of Br^- content in the plant material show that the accumulation of Br^- ion in the plant *Salicornia brachiata* is 1.33 times more as compared to that in *Suaeda nudiflora* and it is 2.53 times more as compared to that of *Salvadora persica*. This signifies that the order of their succulent property decreases in the order of *Salicornia brachiata* > *Suaeda nudiflora* > *Salvadora persica*. Further, the data indicate that the accumulation of Br^- in leaf seems to be 1.3 to 1.6 times more as compared to that in stem and 2.8 to 3.3 times larger as compared to that in root. More deposition in leaf is accounted for the maintenance of osmotic potential flow of water along with dissolved salts within the plant against gravity. Among all extraction procedures, the hot water extraction of Br^- ion from plant material is preferred to these as it gives maximum yield. The absence of Br^- ion by using concentrated HNO_3 could be due to possible oxidation of Br^- to elemental Br_2 and its loss to atmosphere due to high volatility. The lower Br^- ion yield by direct ashing and fusing methods at 550 °C might have been caused by the loss of Br^- as HBr.

Table 2.1. Composition of Br^- and BrO_3^- ions in industrial alkaline bromine mixtures and debrominated effluent.

Sample	Br^- (g/l)	BrO_3^- (g/l)
Lime-Br_2	230± 0.3	83 ± 0.3
Soda ash-Br_2	242 ± 0.4	91 ± 0.3
Debrominated effluents		
Agrocel		[a]0.0063 g/l [b]0.0067 g/l
Balarpur		[a]0.0114 g/l [b]0.0109 g/l

[a]4% NaBr-4% H_2SO_4); [b]5% NaCl-4% H_2SO_4)

The Br^- composition in all sea water samples (Table 2.3) having 3.5 to 4.5 °Be′ is in alignment with that of normal seawater[32] except at Gogha (0.477 g/l) and Dwaraka (0.495 g/l) where maximum salt manufacturing industries are located. Obviously, the Br^- ion

concentration in seawaters of this institute enhances as evaporation continues with the concomitant increase in the density.

2.4.4. Spectrophotometric BrO_3^- ion estimations in the absence and the presence of Cl^- ion. The deviation observed in Figure 2.6 B at low (>1 mM) BrO_3^- concentration is obvious as it reacts with 6 equiv Br^- to give Br_3^-. This may be accounted again for the loss of Br_3^-/Br_2 due to its high volatility. The lower and upper detection limits for BrO_3^- estimation under the present set of (4% NaBr – 4% H_2SO_4) conditions were 5 μM (0.6 ppm) and 1 mM (128 ppm).

Table 2.2. Composition of Br^- ion in different parts of plants and irrigated soil.

Plant/material	Plant part	Extraction Method	[a]Br^- g/g of material
Fed Soil (0.3% Cl^-)	---	Water	0.063
Salicornia brachiata	Stem	Hot water	0.443
		0.1 M HNO_3	0.442
		Conc. HNO_3	ND
		Direct ashing at 550 °C	0.387
		Fusing with NaOH-Na_2CO_3 at 550 °C	0.404
	Root	Hot water	0.200
Suaeda nudiflora	Root	Hot water	0.155
	Stem	Hot water	0.332
	Leef	Hot water	0.432
Salvadora persica	Root	Hot water	0.086
	Stem	Hot water	0.175
	Leef	Hot water	0.287

[a]The deviation calculated from the average of at least five experimental readings is ±0.025% (w/w)

In 5% NaCl-4% H_2SO_4 mixture, the BrO_3^- ion rapidly is reduced by 5 equiv of Cl^- ion to give aq-BrCl (Eq 2.15) which in subsequent reaction with excess Cl^- gives a considerably stable $BrCl_2^-$ ions (Eq 2.13). The data in Figure 2.8 confirms that the formation of $BrCl_2^-$ from BrO_3^- can be easily followed by monitoring its absorption band at 335 nm without much interference caused by other suspected impurities. The deviation at high (>12 mM) concentration of BrO_3^- ion is due to the loss of BrCl by evaporation during the study. The lower and upper detection limits for BrO_3^- ion estimation in the

present (5% NaCl – 4% H_2SO_4) medium are 50 μM (6.4 ppm) and 10 mM (800 ppm). Contrastingly, the lower limit is 10 times larger in 5% NaCl – 4% H_2SO_4 than that in 4% NaBr – 4% H_2SO_4 medium. However, the comparison of the data in Figure 2.6B and 2.8, revealed that the estimation of high (>1 mM) concentrations of BrO_3^- ion is possible in 5% NaCl – 4% H_2SO_4 but not in 4% NaBr – 4% H_2SO_4 medium.

Table 2.3. Composition of Br^- ion in seawater samples from different places having variable densities.

Sample Source	Density	Cl^- (g/l)	[a]Br^- (g/l)
Gogha	1.0285	15.0	0.477
Diu	1.0200	18.2	0.177
Alang	1.0275	18.8	0.153
Mahuva	1.0310	22.0	0.152
Dwaraka	1.0310	21.6	0.495
Okha	1.0315	22.0	0.122
Kandla	1.0330	32.2	0.393
Bhavnagar[b]	1.0250	17.7	0.154
	1.0560	36.5	1.972
	1.1970	164.8	2.045
	1.2130	184.8	3.848
	1.2350	189.8	4.713
	1.2740	170.5	5.260
	1.3200	18.5	6.375

[a]The deviation calculated from the average of at least five experimental readings is ±0.028% (w/w); [b]Sea water samples collected from the Institutes experimental salt form.

Using the data in Figures 2.6B and 2.8, the BrO_3^- ion composition in the debrominated effluents from two industries, was quantified and depicted in Table 2.1. The values obtained in both the 4% NaBr – 4% H_2SO_4 and the 5% NaCl – 4% H_2SO_4 media are closely comparable.

2.5. References

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