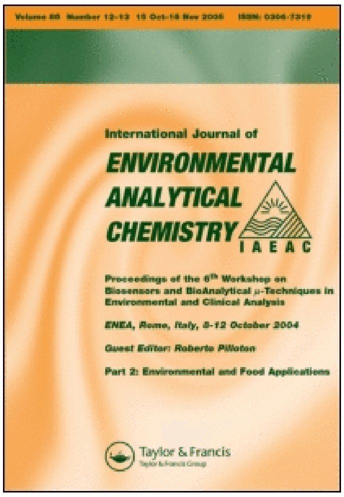

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The Analysis of Mixtures of Hypobromite and Hypochlorite in Dilute Solutions with Thiosulfate

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The analysis of bromine and chlorine in dilute aqueous mixtures is described for the first time. The data show that hypochlorite did not react with thiosulfate in dilute alkaline solutions so that the OBr^- determination proceeded rapidly and quantitatively by potentiometric titration with thiosulfate as titrant. Chlorine was determined by difference following titration of both hypochlorite and hypobromite by the conventional iodometric method with potentiometric detection of the end point. This new method was successfully applied to a study of halogen consumption in swimming pool water that initially contained active chlorine and bromide ion where the concentration of each active halogen was found during exposure to sunlight.

INTRODUCTION

There are many water systems where mixtures of chlorine and bromine might be added for disinfection purposes because in some cases data indicate that the presence of both halogens would be more effective than either one alone. Current interest in their bactericidal applications exists in the area of food processing equipment and together with their algicidal properties, in swimming pools and cooling towers.[1] Field experiments with an open water carrier system involving nightly injection of chlorine and bromine have been reported where the mixed halogen system performed better bactericidally and algaecidally than did either halogen by itself.[2] One problem in studying the chemistry of disinfection in mixed chlorine-bromine systems is that no analytical method exists for chlorine as well as bromine in low concentrations.

Halogen concentrations in disinfection systems are typically in the range of $10^{-6}-10^{-5}$ M.

This report describes a simple and direct technique for the determination of bromine when chlorine is also present in solution and both are in the concentration range described above.

In dilute aqueous solution, the predominent forms of chlorine are hypochlorous acid (HOCl) and hypochlorite ion (OCl^-).

$$HOCl \rightleftarrows OCl^- + H^+ \qquad pK = 7.54 \text{ at } 25°^{3}$$

Bromine exists as hypobromous acid (HOBr) and hypobromite ion (OBr^-).

$$HOBr \rightleftarrows OBr^- + H^+ \ pK = 8.70 \text{ at } 25°C^{1}.$$

With dilute mixtures in alkaline solution (above pH10), thiosulfate reacted quantitatively with OBr^- and not at all with OCl^-. The total active halogen concentration, defined as chlorine plus bromine, was determined by the conventional iodometric method.[4] Both titrations were followed potentiometrically and gave sharp changes in voltage at the equivalence point. Chlorine was found by difference.

The analysis of chlorine and bromine at higher concentrations ($>10^{-3}$M) was reported earlier by Farkas and Lewin.[5] They used the known reaction between phenol and OBr^-[6] to isolate the OCl^- which was subsequently reacted with excess thiosulfate. The solution of unreacted thiosulfate was adjusted to a pH near 4 and then back titrated with iodine to a starch-iodide end point.

Our attempts to extend their method to dilute solutions were unsuccessful due to the prohibitively slow OCl^--thiosulfate reaction. The reaction between OBr^- and thiosulfate, however, was sufficiently rapid for the titration described here. We subsequently found that Evens and Marshall[7] had confirmed the stoichiometry of the bromine-thiosulfate reaction at low concentrations shown in Reaction 1.

$$S_2O_3^{-2} + 4Br_2 + 2H_2O \rightarrow 2SO_4^{-2} + 10H^+ + 8Br^- \qquad (1)$$

which was expected from the standard redox potentials[8] as well as the work of Farkas and Lewin.[5] The corresponding reaction in alkaline solution, given as Reaction 2, has the same 4:1 molar ratio

$$2OH^- + 4OBr^- + S_2O_3^{-2} \rightarrow 2SO_4^{-2} + 4Br^- + H_2O \qquad (2)$$

between bromine and thiosulfate, and was also verified in our laboratory.

The method was applied to a study of consumption of sanitizer (chlorine and bromine) in swimming pool water.

EXPERIMENTAL

Instrumentation:

Potentiometric titrations were carried out with a platinum redox electrode (Orion), a double-junction reference electrode (Orion) to minimize liquid junction potentials, and a digital pH meter (Orion, Model 701) operating in the millivolt mode. It was often possible to expand the scale to give readings with 0.1 mV precision.

Reagents:

All solutions were prepared with chlorine-demand-free water. Distilled and deionized water was chlorinated (ca. 100 ppm OCl^-) and completely photolyzed with 254 nanometer ultraviolet light from an immersible low pressure mercury lamp.

Stock bromine solutions were prepared each day by adding 50 μl of liquid bromine by pipet (Eppendorf) to 100 ml of chilled 0.1 M NaOH solution. The reaction

$$Br_2 + 2OH^- \rightarrow OBr^- + Br^- + H_2O$$

also gave equimolar quantities of Br^- ion. Maintaining the solutions at or below 5°C minimized the disproportionation of OBr^- to bromate (BrO_3^-) ion which is thermodynamically favorable but slow at high pH[8].

Stock chlorine solutions were prepared by vacuum distillation of HOCl from chlorine bleach solutions buffered with boric acid.[9] This procedure minimized the concentration of chloride, chlorite, and chlorate ions which are normally found in commercial NaOCl. The stock solutions were standardized daily by the iodometric procedure.

Sodium thiosulfate (0.1 N) was standardized with potassium iodate and diluted to 0.001 N for use with the dilute chlorine-bromine solutions.

For the iodometric analysis, 0.1 g of potassium iodide was added to the alkaline solution followed by adjustment to pH4 with acetic acid.

Synthetic mixtures of chlorine and bromine were prepared by diluting the stock bromine solution in 100 mls of diluted chlorine solution (in 0.1 M NaOH). The solutions were kept cold during storage and titration.

One half of the solution was titrated with thiosulfate to determine OBr^-. The other half was titrated by the iodometric method to find the sum of chlorine and bromine.

For each titration, the voltage was recorded after each addition of titrant. The equivalence point was found by the derivative method (Δmv/Δml).[10]

SAMPLING AND ANALYSIS OF SWIMMING POOL WATER

The water in a 5000 gallon above ground pool at the FMC R & D laboratory at Princeton, NJ was adjusted for hardness, alkalinity (ca. 80 ppm based on $CaCO_3$) and pH. A $\frac{1}{2}$ hp pump was operated continuously. A diatomaceous earth filter was used. Sodium bromide was added until the Br^- ion concentration was 2 or 24 ppm as determined by a bromide ion electrode. The water was chlorinated by a single 30 g addition of $Ca(OCl)_2$ giving a nominal concentration of 1 ppm available chlorine (1.41×10^{-5} M $HOCl + OCl^-$).

Water samples were obtained from four equidistant points 18 inches below the surface and combined to give a single sample from which aliquots for titration were drawn. Titrations were performed immediately at pool-side using the above procedures and apparatus. The solutions for the OBr^- determination were made alkaline by adding 50 mls of 1 M NaOH to approximately 500 mls of water sample.

RESULTS AND DISCUSSION

The values obtained for OBr^- and OCl^- by titrating the synthetic mixtures generally gave good agreement with those expected based on the prior standardization of the dilute bromine solution and concentrated OCl^- solution. Some results for various solution compositions are given in Table 1. Each value is the average of two or three separate determinations. The first three solutions show more variation in the bromine values than in the chlorine values. On closer inspection, solutions two, three and four show strong

TABLE 1

Analysis of Synthetic Mixtures of OCl^- and OBr^-

Moles OBr^- $\times 10^6$ nominal[a]	Moles OBr^- $\times 10^6$ found[b]	Moles OCl^- $\times 10^6$ nominal[c]	Moles OCl^- $\times 10^6$ found[d]
1. 0.46	0.39	2.14	2.14
2. 2.32	2.48	1.01	0.95
3. 2.50	2.52	2.35	2.25
4. 5.00	6.40	2.35	1.65

[a] Based on separate iodometric titrations of 50.00 ml samples of diluted stock solution.
[b] Based on alkaline thiosulfate titration of 50.00 ml sample.
[c] Based on titration of stock solution prior to dilution.
[d] Difference between results in iodometric and alkaline thiosulfate titrations.

evidence of reaction between OCl^- and Br^- which was sometimes unavoidable no matter how consistent the sample handling was. In a sense, these four determinations do represent typical results. The high values for OBr^- along with the corresponding low values for OCl^- can be explained by the participation of Reaction 3.

$$OCl^- + Br^- \rightarrow Cl^- + OBr^- \tag{3}$$

Therefore our analysis is entirely consistent with the expected chemistry of chlorine-bromine mixtures and was capable of following small changes in composition in dilute solutions.

The OBr^- molarity (M) was calculated using the equation:

$$(OBr^-) = \frac{4\,(\text{thiosulfate volume})(\text{thiosulfate conc.})}{(\text{sample volume})}$$

which implies that Reaction 2 was complete under the conditions of the experiments.

As the OCl^- concentration increases, it is expected that the thiosulfate-OCl^- reaction will become significant so that dilute bromine and moderate to high concentrations (10^{-4} M) of chlorine will be difficult to analyze quantitatively by this method but might be suitable for the method of Farkas and Lewin.[5]

The results of the pool water analysis are given in Table 2. They represent two sunny days in late summer. The Cl + Br concentrations found by the iodometric method show a rapid decrease in the oxidizing power of the water, which is related to its disinfectant potential, following both afternoon and morning chlorinations. The disappearance of the halogens was caused by photodecomposition initiated by the ultraviolet fraction of sunlight absorbed by OCl^-[11], OBr^-[12,13] and HOBr[13]. HOCl has a much smaller extinction coefficient than these species above 290 nm making its photochemistry negligible. The OBr^- concentration also decreased from an initial value rapidly established by Reaction 3. The concentration of OBr^- at any time depended on its rate of formation and destruction and was therefore influenced by the OCl^- (HOCl) and Br^- ion concentrations as well as the absorbance of each species and the light intensity of the actinic wavelengths reaching the pool water. It was thus possible, as shown for day 1 in Table 2, for the total halogen values as determined by iodometry to approach the value obtained by the thiosulfate titration indicating that only bromine remained as the active species at the end of the day.

In summary, a new quantitative method has been developed for bromine when chlorine is also present and both are in the $10^{-6} - 10^{-5}$ M concentration range. The method was demonstrated by analyzing chlorinated pool water that contained Br^- ion and was found capable of determining the distribution of chlorine and bromine in the pool water throughout a sunny day. This provided a rigorous test of the method since the pool water analysis gave

TABLE II

Halogen consumption test pool parameters

Chlorination with $Ca(OCl)_2$

Water temperature, °C	22	18.5–20
Bromide ion, ppm	2	24
pH	7.7	7.8
	Day 1	Day 2

Time \ ppm available	Cl + Br	Br	Cl + Br	Br
8:45 AM				
9:00				
9:30			1.02	
10:00				0.57
10:30			0.77	
11:00				
11:15				0.23
11:30				
1:15 PM				0.02
1:30			0.24	
2:15	0.87			
2:30		0.37		
3:00	0.46			
3:15		0.44	0.03	
3:30				
3:45	0.29			
4:00				
4:20		0.35		

reasonable values for each species and the potentiometric titration curves resembled the more carefully controlled laboratory experiments.

The titration for OBr^- was limited at very low concentrations by a small change in voltage at the equivalence point and the OBr^--thiosulfate stoichiometry which accounts for its factor of eight times lower sensitivity than the iodometric titration. It should be possible to evaluate titration curves from even more dilute solutions by utilizing the Gran–Sorenson[14] or Ingelman and Still[15] methods which are particularly sensitive for finding equivalence points when no apparent inflection occurs. At OCl^- concentrations greater than 10^{-4} M, where the OCl^--thiosulfate reaction rate becomes significant, OCl^- would not interfere with the OBr^- determination if the OBr^- and OCl^- concentrations are comparable.

References

1. G. C. White, *Handbook of Chlorination*, Van Nostrand Reinhold Company, New York, 1972.
2. Y. Kott, *Water Res.* **3**, 265 (1969); Y. Kott and J. Edlis, ibid, 251. The algae *chlorella sorokiniana* and *cladophora sp.* as well as planktonic algae *cosmarium* and *chroococcus* were very sensitive to bromine and mixed halogen action. *Anabena Oocystes* and other planktonic algae were not effected by the treatments.
3. J. C. Morris, *J. Phys. Chem.* **70**, 3798 (1966).
4. *Chemical Analysis*, H. A. Laitenen, McGraw-Hill Book Co., New York, 1960.
5. L. Farkas and M. Lewin, *Anal. Chem.* **19**, 665 (1947).
6. A. W. Francis, *J. Amer. Chem. Soc.* **48**, 1635 (1926); M. M. Spring, *Ind. Eng. Chem. Anal. Ed.* **13**, 357 (1941).
7. R. E. Evans and D. R. Marshall, *Anal. Chim. Acta.* **56**, 117 (1971).
8. W. M. Latimer, *Oxidation Potentials*, Prentice Hall, Inc. Englewood Cliffs, NJ 1952.
9. R. L. Taylor and C. Bostock, *J. Chem. Soc.* 444 (1912).
10. *Treatise on Analytical Chemistry*, Part 1. Volume 11. Theory and Practice, I. M. Kolthoff and P. J. Elving. Wiley-Interscience, John Wiley and Sons, New York, 1975.
11. G. V. Buxton and M. S. Subhani, *J.C.S. Faraday I*, **68**, 958 (1972).
12. A. Treinen, *Israel J. Chem.* **8**, 103 (1970).
13. Unpublished quantum yields obtained in the FMC Princeton Research Laboratories for HOBr and OBr^- (10^{-3} M), $(HOBr)=0.71$. ϕ $(OBr^-)=0.17$. The results are based on potassium ferrioxalate actinometry at 365 nm and are similar to the values found for OCl^- (Reference 11).
14. G. Gran, *Acta Chem. Scand.* **4**, 559 (1950); *Analyst*, II, 66 (1952).
15. F. Ingleman and E. Still, *Talanta*, **13**, 1431 (1966).