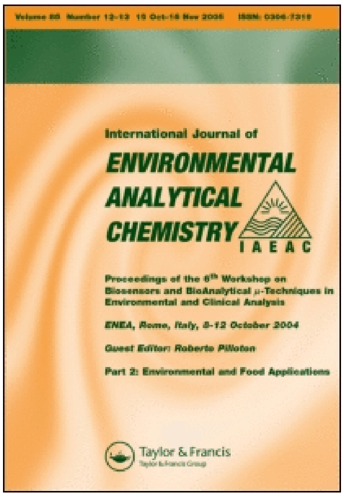

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The Determination of Low Levels of Chlorine in Aqueous Chlorine Dioxide Solutions†

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Palin's titrimetric method for the analysis of chlorine in aqueous chlorine dioxide solutions was found to give low chlorine dioxide and high and variable chlorine estimations. It was determined that glycine, used in the titration for chlorine removal, was reacting with the chlorine dioxide during the titration. Replacement of glycine by oxalic acid gave reproducible and accurate chlorine and chlorine dioxide values. In solutions containing 3.5 to 15 mg of chlorine dioxide, chlorine (0.1 to 0.3 mg) could be determined with a standard deviation of 0.01 mg.

KEY WORDS: Analytical Method, chlorine dioxide, chlorine, water.

INTRODUCTION

Chlorine dioxide has been suggested as an alternative to chlorine for the disinfection of drinking water since it does not produce haloforms.[1] All methods of synthesis of chlorine dioxide produce chlorine as a by-product[2] and to obtain pure chlorine dioxide it is necessary to remove the chlorine by passage through appropriate wash solutions. To facilitate our studies on the reactions of chlorine dioxide under conditions used in potable water treatment a method of analysis was required to monitor low levels of chlorine‡ in aqueous chlorine dioxide.

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‡Chlorine in aqueous solution will exist in equilibrium as hypochlorous acid and hypochlorite ion.

There are no methods available for the direct determination of chlorine in chlorine dioxide and the variety of titrimetric,[3-6] colorimetric[5,7] and amperometric[8] indirect methods are based on differential determination of chlorine. For our purposes the titrimetric methods of Palin[6] and Husband *et al.*[3] appeared to be the most suitable. Our analyses using these methods, however, indicated that they were not satisfactory for the determination of low levels of chlorine in chlorine dioxide solutions. We have, therefore, developed a modified version of Palin's method for the analysis of low levels of chlorine in aqueous chlorine dioxide solutions.

EXPERIMENTAL

Generation of chlorine dioxide

Chlorine dioxide was prepared in 35–40% yield as described by Husband *et al.*[3] and chlorine was removed by passage of the gaseous mixture through a wash bottle containing aqueous sodium chlorite[3] or sodium hydroxide. The chlorine dioxide was collected by dissolving it in cold water and the aqueous solution usually contained ca. 4g chlorine dioxide per liter.

Spectrophotometric quantitation of chlorine dioxide

Chlorine dioxide concentrations in aqueous solution were determined spectrophotometrically by the method of Masschelein.[10]

Titrimetric quantitation of chlorine dioxide-chlorine mixtures

Ferrous Ammonium Sulfate Titrations:[6] Aliquots of chlorine dioxide solution were diluted with water (100 ml) and phosphate buffer (pH 7, 5 ml) and diethyl-p-phenylenediamine solution (5 ml) was added. The solution was then immediately titrated against ferrous ammonium sulfate (0.003 N).

A second aliquot of the chlorine dioxide solution was prepared as above, but before titration with ferrous ammonium sulfate, either glycine (0.20 g) or oxalic acid (0.20 g) was added.

Iodometric Titration:[3] The method of Husband *et al.*[3] was used except that the sodium thiosulfate solution used was 0.0038 N instead of 0.05 N.

Reaction of glycine with chlorine dioxide

Glycine (0.20 g) was dissolved in water (100 ml) and 10 ml of chlorine dioxide (4.00 g/l) solution, together with 5 ml of 0.1 M phosphate buffer (pH 7), were added. The solution was stirred at room temperature and 1 ml aliquots were removed at timed intervals and titrated with ferrous ammonium sulfate.

Preparation of standard chlorine dioxide-chlorine mixtures

Pure chlorine dioxide solution was diluted with water to give an approximate concentration of 0.7 mg ml. The concentration of the solution was then determined spectrophotometrically.[10]

The chlorine solution was prepared by adding chlorine gas to water and its concentration was determined by titration with ferrous ammonium sulfate.[6]

The chlorine dioxide-chlorine solutions were prepared by adding aliquots of the chlorine solution, equivalent to 0.1, 0.2 and 0.3 mg, to 5, 10 and 20 ml portions of the chlorine dioxide solution. The concentrations of chlorine and chlorine dioxide were then determined by differential titration with ferrous ammonium sulfate using either glycine or oxalic acid.

RESULTS AND DISCUSSION

A direct spectrophotometric determination of chlorine dioxide in the presence of chlorine, using acid chrome violet K (ACVK) has been reported[10] and the accuracy of the technique has been verified using electron spin resonance spectrometry.[11] There is no method, however, for direct quantitation of chlorine in the presence of chlorine dioxide. Instead the amount of chlorine is determined by differential titration. Husband *et al.*[3] used differential iodometric titration (Eqs. 1–3).

$$Cl_2 + 2I^- \rightarrow 2\,Cl^- + I_2 \qquad (1)$$

$$2\,ClO_2 + 2I^- \rightarrow 2\,ClO_2^- + I_2 \qquad (2)$$

$$ClO_2^- + 4I^- + 4H^+ \rightarrow Cl^- + 2I_2 + 2\,H_2O \qquad (3)$$

Titration at neutral pH with thiosulfate gives a titre (titre A) representing chlorine and one-fifth of the chlorine dioxide value (Eqs. 1–2). The solution is then acidified and the titration continued to give a second titre (titre B, Eq. 3). If titre B is equal to four times titre A, then there is no chlorine present in the solution. Husband *et al.* reported that ca. 1% chlorine relative to chlorine dioxide could be detected by this method. However, in our hands the method was not found to be satisfactory. Although the acid titre was found to be equal to four times the neutral titre, indicating the absence of chlorine, the absolute value obtained for the chlorine dioxide concentration was considerably lower than that obtained spectrophotometrically. Bray[12] has reported that iodometric titrations of chlorine dioxide solutions gave low and variable values for chlorine dioxide concentrations.

In the method of Palin[6] two titrations are made, one in the presence of glycine, the second in the absence of glycine. The glycine reacts with any chlorine present and the difference between the two titrations gives the amount of chlorine present (Eqs. 4–6).

$$H_2N-CH_2-COOH+2Cl_2 \rightarrow Cl_2N-CH_2-COOH+2HCl. \qquad (4)$$

$$3\,Fe^{2+}+2\,ClO_2 \rightarrow 2\,Fe^{3+}+Fe\,(ClO_2)_2 \qquad (5)$$

$$2\,Fe^{2+}+Cl_2 \rightarrow 2\,Fe^{3+}+2\,Cl^- \qquad (6)$$

The chlorine formed during the synthesis of chlorine dioxide was removed by passage through sodium chlorite.[3] Analysis of the resultant chlorine dioxide solution using Palin's method indicated the presence of 10% chlorine with respect to chlorine dioxide (Table I, Column 2, 3). Bugaenko and Roshchektaev have purified chlorine dioxide from the accompanying chlorine by scrubbing with alkali.[9] When this modification was used analysis of the chlorine dioxide solutions, by Palin's method, still indicated that up to 3% chlorine was present (Table I, Column 2, 3). However, comparison of the chlorine dioxide concentration as determined spectrophotometrically (Table I, Column 1) with that obtained titrimetrically (Table I, Column 3) showed a discrepancy between the two values. This difference was essentially equivalent to the estimated chlorine concentration which led us to believe that this was not a true chlorine concentration but represented some reaction of chlorine dioxide with glycine.

A separate experiment was, therefore, carried out, in which glycine was dissolved in chlorine dioxide solution under the same conditions as for the titration, and aliquots were removed at time intervals and analyzed for chlorine dioxide (Table II). It is evident that glycine does react with chlorine dioxide and is not a suitable reagent in these titrations. Malonic acid had been used previously for chlorine removal in differential titrations[5] but was replaced with glycine by Palin[6] who claimed improved results. In colorimetric determinations of chlorine dioxide oxalic acid has also been used for removal of chlorine.[13] It was, therefore, decided to modify Palin's method[6] and replace the glycine with oxalic acid for removal of chlorine in the titration procedure. The results showed that the spectrophotometric (Table I) and titrimetric determinations (Table I, Column 5) of chlorine dioxide then agreed more closely and also that

TABLE I

Comparison of analytical methods for chlorine dioxide-chlorine determinations

Purification method	Spectrophotometric determination[a]	Titrimetric determination[a] ferrous ammonium sulfate			
		Glycine		Oxalic acid	
	ClO_2	Cl_2	ClO_2	Cl_2	ClO_2
$NaClO_2$	—	0.32 ± 0.05	3.75 ± 0.02	0.12 ± 0.01	3.94 ± 0.01
NaOH	4.06	0.11 ± 0.02	3.82 ± 0.03	N.D.[b]	3.98 ± 0.01

[a] All values in g/l.

[b] Not detectable (less than 0.01 mg).

sodium hydroxide was more effective than sodium chlorite for preparing chlorine dioxide free from chlorine (Table I, Column 4).

In order to compare Palin's method and our modification for detecting low levels of chlorine in aqueous chlorine dioxide, separate stock solutions of chlorine and chlorine dioxide were prepared. The concentration of the chlorine dioxide solution was determined spectrophotometrically and that of the chlorine solution by titration with ferrous ammonium sulfate. A series of solutions was then prepared by mixing aliquots of the two stock solutions and the amounts of chlorine and chlorine dioxide were determined by Palin's method and by our modified method. It can be seen from the results in Table III that the use of glycine to remove chlorine in the titration procedure leads to high and variable chlorine estimates and to low chlorine dioxide estimates. In addition it would appear that an increase in chlorine concentration increases the rate of reaction of chlorine dioxide with glycine and gives progressively lower values for chlorine dioxide. When oxalic acid is used instead of glycine both the estimations of chlorine dioxide and chlorine are in good agreement with the correct values. The minimum detectable amount of chlorine under these conditions was 0.1 mg which represents less than 1% relative to the 14.6 mg chlorine dioxide aliquot.

TABLE II

Decrease in chlorine dioxide concentration in the presence of glycine

Time (minutes)	Amount of ClO_2 remaining[a] (g/l)
0	0.032
3	0.024
7	0.023
10	0.021
20	0.019
30	0.017
60	0.015

[a] Decrease in chlorine dioxide concentration in a water blank was negligible during one hour.

Palin's method when modified by using oxalic acid instead of glycine gives accurate estimates for chlorine dioxide and hence permits the determination of low levels of chlorine in aqueous chlorine dioxide solutions.

TABLE III

Analysis of low levels of chlorine in aqueous chlorine dioxide solution

Amount added (mg)		Amount found (mg)[a] using glycine		Amount found (mg)[b] using oxalic acid	
ClO_2	Cl_2	ClO_2	Cl_2	ClO_2	Cl_2
3.6	0	3.36 ± 0.07	0.18 ± 0.08	3.77 ± 0.07	0 ± 0.009
3.6	0.1	3.20 ± 0.09	0.38 ± 0.03	3.83 ± 0.01	0.09 ± 0.01
3.6	0.2	3.21 ± 0.14	0.42 ± 0.09	3.78 ± 0.06	0.19 ± 0.01
3.6	0.3	2.92 ± 0.15	0.65 ± 0.07	3.79 ± 0.03	0.30 ± 0.01
7.1	0	7.01 ± 0.12	0.16 ± 0.07	7.22 ± 0.06	0 ± 0.008
7.1	0.1	6.86 ± 0.22	0.41 ± 0.05	7.21 ± 0.01	0.10 ± 0.01
7.1	0.2	6.76 ± 0.08	0.39 ± 0.02	7.22 ± 0.01	0.20 ± 0.01
7.1	0.3	6.57 ± 0.05	0.68 ± 0.05	7.20 ± 0.01	0.29 ± 0.01
14.3	0	13.71 ± 0.25	0.55 ± 0.05	14.59 ± 0.01	0 ± 0.009
14.3	0.1	13.27 ± 0.28	0.24 ± 0.06	14.61 ± 0.02	0.09 ± 0.01
14.3	0.2	13.20 ± 0.40	0.33 ± 0.06	14.67 ± 0.12	0.20 ± 0.01
14.3	0.3	13.06 ± 0.11	0.50 ± 0.11	14.63 ± 0.03	0.30 ± 0.01

[a] Average and estimate of standard deviation for triplicate determinations.

[b] Average and estimate of standard deviation for duplicate determinations.

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