

length containing a drop of mercury in one atmosphere of nitrogen. Finally it was passed through a sharp resonance lamp before it entered the absorption cell into which the sample had been introduced. A photomultiplier (RCA 1P28) was faced directly at the end of the absorption cell. Figure 4 shows the schematic representation of this arrangement.

The signal from each source is allowed to pass through the absorption cell individually by means of a shutter placed between the exciting source and the resonance lamp. The broadened resonance line measures only nonatomic absorption while the sharp resonance line measures both nonatomic and atomic absorption.

The correction for nonatomic absorption in this system is achieved simply by increasing the EHT to the photomultiplier until the signal from the broadened resonance lamp only reads 100%. The subsequent signal from the sharp resonance lamp will then read atomic absorption in % only.

An improved method which is being investigated uses the null method of measurement. It requires a twin-cell arrange-

ment. Each cell is irradiated by the individual sources, and a photomultiplier at the other end of each cell detects the output of the signal. The outputs from the two photomultipliers are then nulled. Because the magnitude of the nonatomic absorption is the same from each source, the differential output is due directly to atomic absorption. The two resonance lamps are excited by a common exciting source and noise due to this is thus canceled. With such an arrangement, an improvement in sensitivity by an order of magnitude can be expected.

A patent has been applied for on this instrument.

#### ACKNOWLEDGMENT

I acknowledge the encouragement given by N. B. Lewis, N. Ducksbury, and O. Goble. I also thank G. Crickmore, E. Futschik, D. San Miguel and H. Wayne for their cooperation in the construction of the instrument.

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## Spectrophotometric Determination of Microquantities of Chlorate, Chlorite, Hypochlorite, and Chloride in Perchlorate

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**The reactions of chlorate, chlorite, and hypochlorite with ferrous and iodide ions, and the applicability of chloranilate procedure for chloride determination in the presence of chlorite and hypochlorite have been investigated spectrophotometrically in the micromolar concentration region. The reduction of chlorate by ferrous ion was found to follow third-order kinetics, and the mechanism consistent with this result is presented. The spectrophotometric procedure based on these studies enables the determination of minute quantities of chlorate, chlorite, hypochlorite, and chloride in perchlorate. The interference of chlorine dioxide and the analysis of the mixtures containing this species are discussed. With this procedure, the time required for the chlorate reduction by ferrous ion to go to completion has been reduced from hours to a few minutes.**

DURING KINETIC STUDIES of the radiolysis of potassium perchlorate, a sensitive, accurate method for determining the radiolytic products in perchlorate was needed. However, at the time this work was initiated, the available analytical methods for the analyses of these products in complex mixtures (1-8) were not entirely satisfactory in the micromolar

concentration range, mainly because of the limited sensitivity of the procedures employed.

Consequently, a sensitive spectrophotometric method was developed for the determination of chlorate, chlorite, hypochlorite, and chloride in the presence of a large quantity of perchlorate. In the present work,  $\text{Fe}^{+2}$  and  $\text{I}^-$  were chosen as the reducing agents for  $\text{ClO}_2^-$ ,  $\text{ClO}_2^-$ , and  $\text{ClO}_3^-$ , and mercuric chloranilate (the mercuric salt of 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone) (9) was used for chloride determination, for these systems offer not only adequate sensitivity but also use of relatively simple procedures.

These three systems were studied in detail to establish the optimum conditions for the rapid determination of the oxychlorine species mentioned above. The interference of chlorine dioxide and the analysis of mixtures containing this species have been discussed.

Recently, Prince (10) reported a satisfactory spectrophotometric procedure (except for  $\text{Cl}^-$ ) for the determinations of oxychlorine compounds based also on the ferrous and iodide systems. His procedure for  $\text{ClO}_3^-$ , however, requires at least a 4-hour reaction period.

In the present work, this reaction period has been reduced to a few minutes with added advantages of more than 30% increase in sensitivity ( $\epsilon_{\text{Fe}^{+2}}^{301 \text{ m}\mu} = 2900$  vs.  $\epsilon_{\text{Fe}^{+2}}^{305 \text{ m}\mu}$ ,  $0.8N$   $\text{H}_2\text{SO}_4$ ,  $28.5^\circ\text{C}$  =  $2200$  liters mole $^{-1}$  cm $^{-1}$ ) and temperature measurement of the sample solution is unnecessary [ $(d\epsilon/\epsilon)/dT = 0$ ]. The sensitivity of the iodide system was also increased by about 50% by measuring  $\text{I}_3^-$  at  $287 \text{ m}\mu$  ( $\epsilon_{\text{I}_3^-}^{287 \text{ m}\mu} = 4.02 \times 10^4$  vs.  $\epsilon_{\text{I}_3^-}^{351 \text{ m}\mu} = 2.65 \times 10^4$  liters mole $^{-1}$  cm $^{-1}$ ).

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(4) M. W. Lister, *Can. J. Chem.*, **30**, 879 (1952).

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(7) J. I. Aznárez and J. V. Vinadé, *Anales Real Soc. Españ. Fis. y Quím. (Madrid)*, **45B**, 1227 (1949); *C.A.*, **46**, 2961d (1952).

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(10) L. A. Prince, *Ibid.*, **36**, 613 (1964).

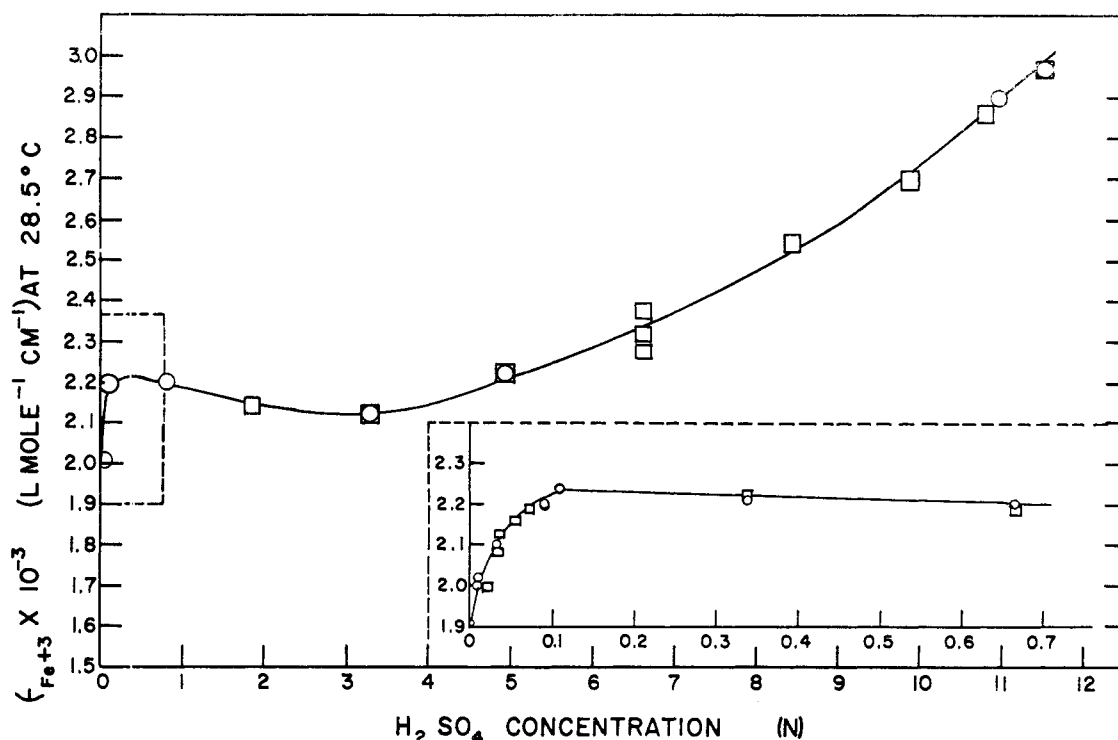


Figure 1. Effect of acidity on  $\epsilon_{\text{Fe}^{+3}}$

○ In absence of other substances    □ In presence of  $1.2 \times 10^{-3} M \text{Cl}^-$

#### EXPERIMENTAL

**Reagents.** C. p. grade chemicals were used without further purification.

Aqueous solutions of  $\text{ClO}_2$  were prepared in a darkened hood essentially according to the methods described by Schmeisser (11). For safety, the scale was reduced to  $1/200$ , and fluorosilicone grease (Dow Corning) was used as a lubricant for ground-glass joints.

**Apparatus.** Except for some experiments where a Beckman DU spectrophotometer was used, a Perkin-Elmer 202 ultraviolet-visible spectrophotometer was employed for absorbance measurements and the recording of all the absorption spectra. For pH measurements, a Beckman Model G pH meter was used.

#### RESULTS AND DISCUSSION

**Procedure III A. Ferrous System.** DETERMINATION OF  $\epsilon_{\text{Fe}^{+3}}$  AS A FUNCTION OF  $\text{H}_2\text{SO}_4$  CONCENTRATION AND TEMPERATURE. To follow the reactions of ferrous ion with chlorate, chlorite, and hypochlorite ions, only  $\epsilon_{\text{Fe}^{+3}}$  has to be known. However, since  $\epsilon_{\text{Fe}^{+3}}$  is known only in  $0.8N \text{H}_2\text{SO}_4$  (10, 12-14),  $\epsilon_{\text{Fe}^{+3}}$  as well as its temperature coefficient was determined as a function of  $\text{H}_2\text{SO}_4$  concentration. The procedure adopted for  $\epsilon_{\text{Fe}^{+3}}$  determination consists of determining  $\epsilon_{\text{Fe}^{+3}}$  very carefully in  $0.8N \text{H}_2\text{SO}_4$  and subsequently in other acid concentrations by comparing the absorbances of  $\text{Fe}^{+3}$  solutions at different acid concentrations. The value obtained for  $\epsilon_{\text{Fe}^{+3}}$  in  $0.8N \text{H}_2\text{SO}_4$  at  $305 \text{ m}\mu$  at  $28.5^\circ \text{C}$  ( $2.20 \pm 0.01$ )  $\times 10^3 \text{ liters mole}^{-1} \text{cm}^{-1}$  agrees well

with the previous results normalized to  $28.5^\circ \text{C}$  using  $[(d\epsilon/\epsilon)/dT] \times 100 = 0.6\%$  [ $2.20 \times 10^3$ ,  $2.21 \times 10^3$  in  $0.75N \text{H}_2\text{SO}_4$ , and  $(2.25 \pm 0.04) \times 10^3 \text{ liters mole}^{-1} \text{cm}^{-1}$ ] (10, 12-14). This value was determined employing iron wire (Schaar & Co.), ferrous ammonium sulfate hexahydrate,  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (Baker & Adamson and Baker analyzed), and ferric ammonium sulfate dodecahydrate,  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (Matheson Coleman & Bell), as the standard substances. Ferrous ion was converted to ferric ion by heating ferrous solutions in the presence of excess hydrogen peroxide in  $0.8N \text{H}_2\text{SO}_4$  and subsequently removing the excess  $\text{H}_2\text{O}_2$  by prolonged heating.

As can be seen from Figure 1,  $\epsilon_{\text{Fe}^{+3}}$  varies in a complicated manner, while its temperature coefficient, expressed as  $[(d\epsilon/\epsilon)/dT] \times 100$ , decreases linearly from  $0.7\%$  near neutral solution to  $0\%$  at  $10.9N$ . The absence of a temperature effect at  $10.9N$  was thoroughly checked by numerous  $\epsilon_{\text{Fe}^{+3}}$  determinations which yielded a constant value of  $2.90$  ( $0.014$  standard deviation)  $\times 10^3 \text{ liters mole}^{-1} \text{cm}^{-1}$  in the  $26^\circ$  to  $36^\circ \text{C}$  temperature range.

The analytical significance of these findings is obvious. Thus, in chlorate analysis where  $10.9N \text{H}_2\text{SO}_4$  was used, the temperature measurement or control can be eliminated and the sensitivity is increased by  $32\%$  over that in  $0.8N \text{H}_2\text{SO}_4$ . In addition, the entire absorption curve in the  $190$ - to  $390\text{-m}\mu$  range was found to shift slightly to the lower wavelength. Thus, the absorption maximum near  $300 \text{ m}\mu$  shifts from  $306 \text{ m}\mu$  in  $0.11N$  to  $301 \text{ m}\mu$  in  $10.9N$ . These changes arise probably from the increasing degree of sulfate ion participation in the formation of complex ion with  $\text{Fe}^{+3}$  as shown below (15a, 16).

- (11) M. Schmeisser, in "Handbook of Preparative Inorganic Chemistry," 2nd ed., G. Brauer, ed., Part II, Section 5, Methods II and IV, pp. 301-2, Academic Press, New York, 1963.
- (12) A. O. Allen, "Radiation Chemistry of Water and Aqueous Solution," p. 21, Van Nostrand, New York, 1961.
- (13) T. H. Chen, unpublished result used in earlier work [see ref. 14].
- (14) T. H. Chen and E. R. Johnson, *J. Phys. Chem.*, **66**, 2249, 2068 (1962).

- (15) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed., p. 636 (a), p. 585 (b), p. 560 (c), p. 559 (d), Macmillan, New York, 1958.
- (16) Fred Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 61, 63 (1961).

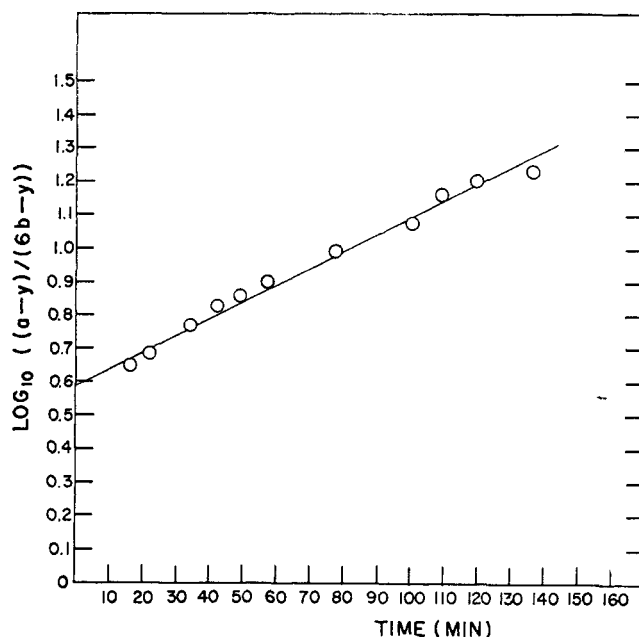
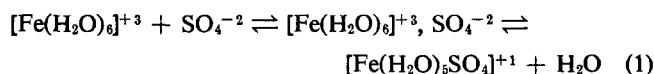


Figure 2.  $\text{ClO}_3^- + \text{Fe}^{+2}$  at constant excess  $\text{H}_2\text{SO}_4$  concentration (3.64N)

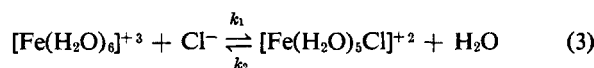


at high  $\text{H}_2\text{SO}_4$  concentration, and



at low acidity medium (cf. insert, Figure 1).

The apparent lack of a  $\text{Cl}^-$  effect on  $\epsilon\text{Fe}^{+3}$  (Figure 1) indicates that  $\text{Cl}^-$ , at about  $1.2 \times 10^{-3}M$ , does not participate significantly in the complex ion formation (Equation 3) (16). This finding is to be expected, because the equilibrium concentration of  $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{+2}$  calculated from the rate constants of Equation 3 under the experimental conditions  $[(\text{Fe}^{+3}) = 2.5 \times 10^{-4}M, (\text{Cl}^-) = 1.2 \times 10^{-3}M \text{ in } \text{H}_2\text{SO}_4 \text{ medium}]$  amounts to only about  $10^{-6}M$ .



$$k_1 = 9.4 \text{ mole}^{-1} \text{ sec}^{-1}, \quad k_2 = 2.3 \text{ sec}^{-1} \text{ at } 25^\circ \text{C}$$

Thus, in the mixture analysis,  $\text{Cl}^-$ , arising from the original sample as well as the reduction of  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$ , and  $\text{ClO}^-$  by  $\text{Fe}^{+2}$ , will not interfere with the absorbance measurements.

**REACTION OF  $\text{ClO}_3^-$  WITH  $\text{Fe}^{+2}$ .** *Reaction Kinetics and Mechanism.* Although the standard potentials of the electrochemical reactions associated with the over-all reductions of  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ ,  $\text{HClO}_2$ ,  $\text{HClO}$ , and  $\text{Cl}_2$  to  $\text{Cl}^-$ , respectively, are essentially the same (about 1.5 volts) (17a, 18a, b), chlorate and perchlorate are much poorer oxidizing agents than others mentioned (19). No doubt, the oxidizing action of chlorate

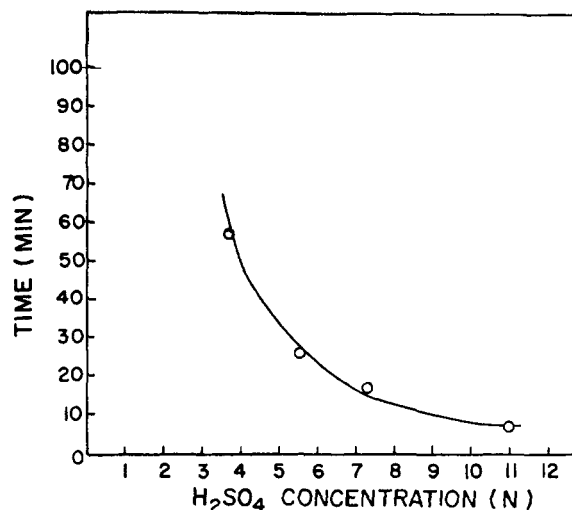


Figure 3. Approximate reaction period required for complete reduction of  $\text{ClO}_3^-$  by  $\text{Fe}^{+2}$  in  $\text{H}_2\text{SO}_4$

$$(\text{Fe}^{+2})_0 = 0.38 \times 10^{-3}M \text{ (in } 7.28N \text{ H}_2\text{SO}_4)$$

$$0.51 \times 10^{-2}M$$

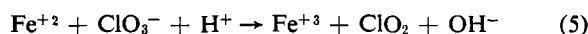
$$(\text{ClO}_3^-)_0 = 0.4751 \times 10^{-4}M \text{ (in } 5.46N \text{ H}_2\text{SO}_4)$$

$$0.9502 \times 10^{-4}M$$

$$\text{Temp. ca. } 31^\circ \text{C}$$

and perchlorate is governed by the slow rate-determining steps. These steps are likely to be, as Latimer has pointed out, the first stages of  $\text{ClO}_4^-$  and  $\text{ClO}_3^-$  reductions (18c), as the lower potentials associated with these stages (18d) would effectively retard the reactions. This interpretation is supported, at least in the case of chlorate reduction by  $\text{Fe}^{+2}$ , by the experimental evidences (20-24). Thus, the reaction was found to be kinetically of the third order (Equation 4) and this can then be attributed to the initial rate-determining stage of chlorate reduction (Equation 5). The acidity dependence is still somewhat uncertain, however (23, 24).

$$-d(\text{Fe}^{+2})/dt = k(\text{Fe}^{+2})(\text{ClO}_3^-)(\text{H}^+) \quad (4)$$



In the present work, the kinetics of  $\text{ClO}_3^-$  reduction by  $\text{Fe}^{+2}$  in  $\text{H}_2\text{SO}_4$  medium was also examined. The emphasis was, however, on the analytical application—viz., the establishment of the optimum conditions for rapid  $\text{ClO}_3^-$  reduction.

In one of the kinetic studies, the reaction was investigated at constant excess  $\text{H}_2\text{SO}_4$  concentration. A typical second-order straight-line plot was obtained (see Figure 2 and Equations 6, 7, 7-1, and 7-2) under the experimental conditions employed  $[(\text{H}^+) = 3.64N, (\text{Fe}^{+2})_0 = 2.04 \times 10^{-3}M, (\text{ClO}_3^-)_0 = 0.9502 \times 10^{-4}M, \text{ at about } 28^\circ \text{C}]$ .

$$-d(\text{ClO}_3^-)/dt = k(\text{H}^+)(\text{Fe}^{+2})(\text{ClO}_3^-) \quad (6)$$

or

$$d(\text{Fe}^{+3})/dt = 6k(\text{H}^+)(\text{Fe}^{+2})(\text{ClO}_3^-) \quad (7)$$

$$dy/dt = K(a-y)(6b-y) \quad (7-1)$$

(17) C. D. Hodgman *et al.*, eds., "Handbook of Physics and Chemistry," 44th ed., p. 1743 (a), p. 1757 (b), Chemical Rubber Co., Cleveland, Ohio, 1962.

(18) W. M. Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solution," 2nd ed., p. 53 (a), p. 55 (b), p. 57 (c), p. 56 (d), p. 224 (e), p. 64 (f), p. 67 (g), p. 54 (h), Prentice-Hall, New York, 1952.

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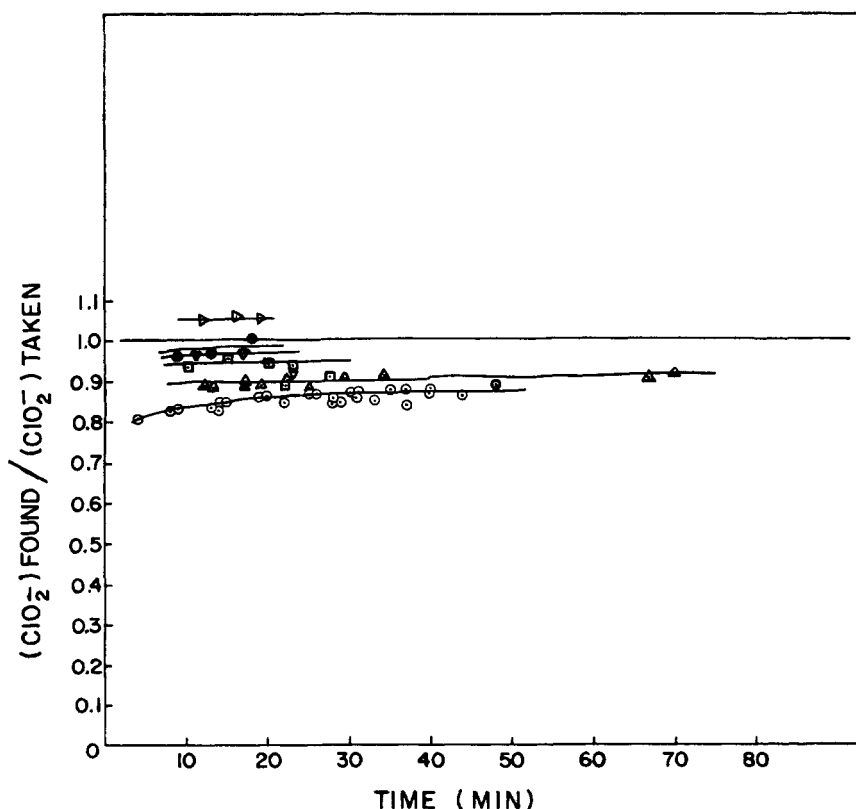
(24) A. M. Azzam and I. A. W. Shimi, *Z. Physik. Chem.*, **33**, 190 (1962).

Figure 4. Acidity dependence of  $\text{ClO}_2^- + \text{Fe}^{+2}$

- 0.66N
- △ 0.32N
- 0.16N
- ▽ 0.082N
- 0.043N
- ▲ 0.021N

$$(\text{Fe}^{+2}) = 0.918 \times 10^{-2} M$$

$$(\text{ClO}_2^-) = 1.58 \times 10^{-4} M$$



$$[(a - 6b)/2.303]Kt =$$

$$\log_{10}[(a - y)/(6b - y)] - \log_{10}(a/6b) \quad (7-2)$$

where

$$y = (\text{Fe}^{+3})$$

$$a = (\text{Fe}^{+2})_0$$

$$b = (\text{ClO}_3^-)_0$$

$$K = k(\text{H}^+)^r$$

Moreover, neither 0.001% KI nor 0.01 % ammonium molybdate was found to catalyze the reaction.

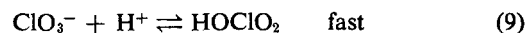
Further evidence for the first-order dependence on  $(\text{Fe}^{+2})$  or  $(\text{ClO}_3^-)$  has been obtained in much lower acidity medium by varying the initial reactant concentration ratios and observing the rate of  $\text{Fe}^{+3}$  formation at the initial stage of the reaction where the maximum change of any reactant concentration is less than 2%. This study yielded the values of  $1.10 \pm 0.08$ ,  $1.02 \pm 0.08$ , and  $0.90 \pm 0.08$  for the orders of reaction with respect to  $\text{Fe}^{+2}$ ,  $\text{ClO}_3^-$ , and  $\text{H}_2\text{SO}_4$  concentrations, and also a value of  $(2.2 \pm 0.2) \times 10^{-2}$  liters<sup>2</sup> mole<sup>-2</sup> sec<sup>-1</sup> for the third-order rate constant,  $k$ , in Equations 6 in the concentration ranges studied [ $(\text{Fe}^{+2})_0 = (1.02 \text{ to } 2.04) \times 10^{-3} M$ ,  $(\text{ClO}_3^-)_0 = (1.90 \text{ to } 3.80) \times 10^{-4} M$ ,  $(\text{H}^+) = 0.11 \text{ to } 0.22 N$ , temperature =  $24.3 \pm 0.4^\circ \text{C}$ ]. In Figure 3, the results of further acidity dependence studies are shown. Only low  $\text{Fe}^{+2}$  concentrations were used, so that a high reagent blank arising from ca. 0.3%  $\text{Fe}^{+3}$  contamination and serious air oxidation can be avoided. The experimental results (circles) fit Equation 8 (solid line) well,

$$t = 793/(\text{H}^+)^2 \quad (8)$$

and the catalytic nature of acidity dependence at high concentrations might be inferred. The approximate nature of this experiment does not allow any definite conclusion. It,

nonetheless, offers a ready explanation for the long reaction period required (at least 4 hours in  $1.02 \times 10^{-2} M \text{Fe}^{+2}$  and  $1.87 N \text{H}_2\text{SO}_4$ ) to achieve quantitative reaction in the procedure of Prince (10) and incomplete reaction (92%) in the procedure employed by Heal (1) in  $1.0 \times 10^{-2} M \text{Fe}^{+2}$  and  $0.6 N \text{H}_2\text{SO}_4$  even after 1-hour heating in boiling water in a sealed tube. Evidently too low acidity was the cause of the long reaction period encountered by both workers.

Thus, the present work lends further support to the third-order kinetics found by earlier workers. Furthermore, it indicates the possibility of higher order acidity dependence at high acid concentrations. The following scheme is suggested to explain the third-order kinetics.



rate-determining (10)

The fast protonation process is included in this scheme, as it is generally believed that the proton plays the role of weakening the strong bond between the negative oxygen atom and the positive central chlorine atom (25).

**Analytical Application to Chlorate Determination.** The foregoing kinetic studies have established that chlorate can be reduced to  $\text{Cl}^-$  by  $\text{Fe}^{+2}$  quantitatively within a few minutes. For analytical applications, a series of experiments was run to determine the applicability of the procedure derived from the kinetic studies to the wide range of chlorate concentration ( $0.25 \times 10^{-5}$  to  $4 \times 10^{-5} M$ ) under optimum conditions ( $1.02 \times 10^{-2} M \text{Fe}^{+2}$  in  $10.9 N \text{H}_2\text{SO}_4$ ). The possible effect of perchlorate ion at 1% concentration was also examined. The results obtained were in good agreement (within 2%) with the concentrations of standard solutions, and no inter-

(25) J. O. Edwards, "Inorganic Reaction Mechanisms," p. 138, W. A. Benjamin, New York, 1964; *Chem. Revs.*, **50**, 458 (1952).

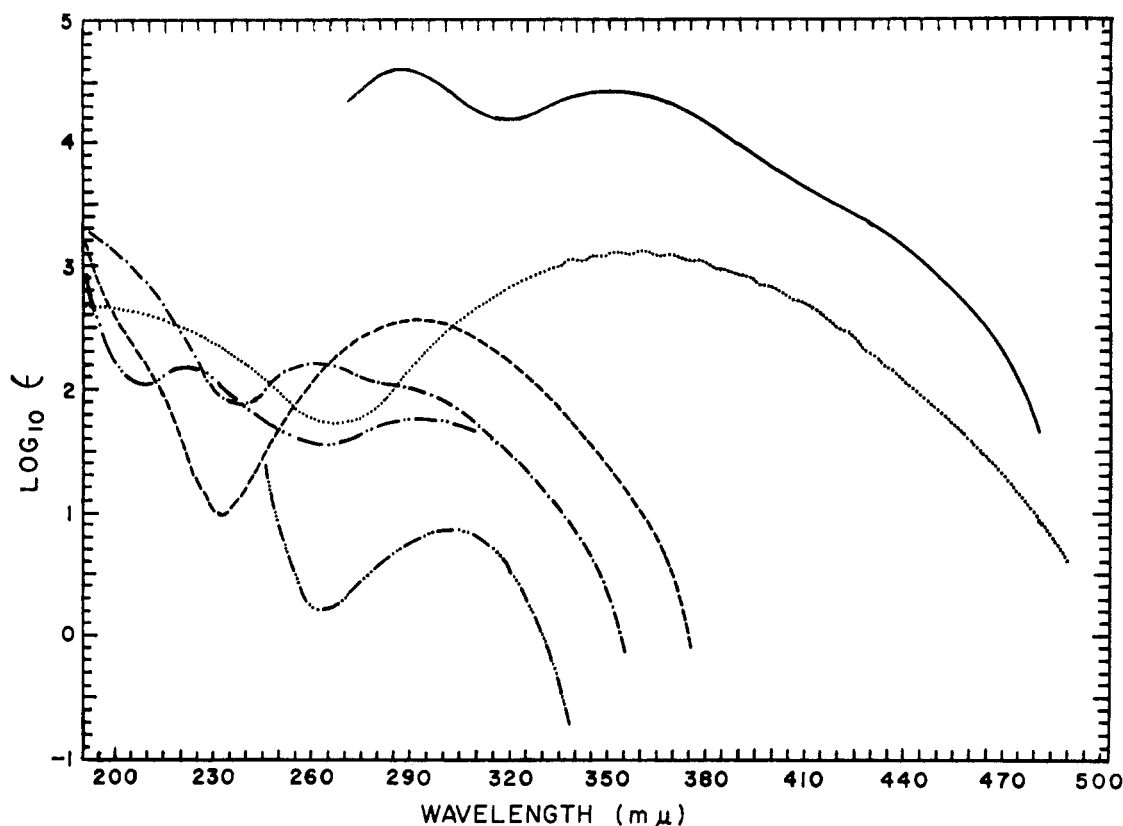


Figure 5. Ultraviolet-visible absorption spectra

—————	$I_3^-$
.....	$ClO_2(aq.)$
-----	$ClO^-$
- · - · -	$ClO_2^-$
-----	$3.7 \times 10^{-5} M NaClO$
-----	$NO_3^-$

ference was encountered in the presence of high concentration of  $ClO_4^-$ .

**Reaction Rate in 0.11N  $H_2SO_4$ .** In the determination of chlorate in the presence of chlorite and hypochlorite, the sum of chlorite and hypochlorite is determined in 0.11N  $H_2SO_4$ . This acidity was chosen so that the constant  $\epsilon_{Fe^{+3}}$  region (insert, Figure 1) can be utilized not only to avoid error in  $\epsilon_{Fe^{+3}}$  due to slight variation in the acidity of the reaction medium, but also to minimize the reaction of chlorate with  $Fe^{+2}$ . At this low acidity, the reduction of  $3.8 \times 10^{-3} M ClO_3^-$  proceeded only to about 1% completion in  $1.02 \times 10^{-2} M Fe^{+2}$  after a 10-minute reaction period. The chlorate correction in chlorite and hypochlorite analysis, therefore, will be insignificant on account of the essentially inert nature of  $ClO_3^-$  under these conditions.

**REACTION OF  $ClO_2^-$  WITH  $Fe^{+2}$ .** Because the potentials associated with various stages of the chlorine potential diagram are generally considerably higher in acidic than in alkaline media (17a, 18d), the rate of reduction of  $ClO_2^-$  to  $Cl^-$  by  $Fe^{+2}$  should increase as the acidity of the reaction medium increases. The results of one series of experiments (Figure 4) in the present work, however, were contrary to this expectation. The somewhat high results in 0.02N  $H_2SO_4$  are due undoubtedly to the experimental error involved in  $\epsilon_{Fe^{+3}}$  determination, because  $\epsilon_{Fe^{+3}}$  is strongly dependent on the acidity below 0.1N (insert, Figure 1). Moreover, the results seem to be sensitive to the manner of reagent addition. The procedure used for the preparation of solutions is described below. One-milliliter portions of standard  $ClO_2^-$  solutions

( $1.58 \times 10^{-3} M$ ) were transferred to dry 10-ml volumetric flasks. Then, to the flasks was added the acidic  $Fe^{+2}$  solution ( $1.0 \times 10^{-2} M Fe^{+2}$  in 0.023 to 0.73N  $H_2SO_4$ ) from a 10-ml pipet to make up to the mark, and the solutions were mixed thoroughly. The incomplete reduction of  $ClO_2^-$  in 1 to 2N  $H_2SO_4$  medium was also observed by Minczewski and Glabisz (26).

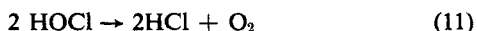
The unexpected acidity dependence could probably be attributed to the partial conversion of  $ClO_2^-$  in acid medium to  $ClO_2$ . This is supported by the spectrophotometric observation of the slow appearance of broad  $ClO_2$  absorption near 360 mμ with the concurrent decrease of  $ClO_2^-$  absorption near 261 mμ in the spectrum of dilute  $ClO_2^-$  solution ( $2.5 \times 10^{-3} N$ ) even in very dilute  $H_2SO_4$  ( $8 \times 10^{-3} N$ ).

Because of the difficulties encountered above, another series of experiments was conducted with the following changes in the experimental procedure. Lower  $ClO_2^-$  concentrations (up to  $8 \times 10^{-5} M$ ) were employed,  $Fe^{+2}$  [as  $FeSO_4(NH_4)_2 \cdot SO_4 \cdot 6H_2O$  crystals] was added to  $ClO_2^-$  prior to acidification to avoid the possible decomposition of  $ClO_2^-$ , and 1.1N  $H_2SO_4$  was used for acidification of solutions to 0.11N. With this modification, quantitative results (within about 2%) were obtained after a few minutes. However, if  $ClO_2^-$  is acidified before  $Fe^{+2}$  addition, lower results for  $ClO_2^-$  may be obtained. Thus, although quantitative results for  $5 \times 10^{-5} M ClO_2^-$  could be obtained if the acidification was immediately followed

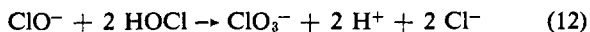
(26) J. Minczewski and U. Glabisz, *Talanta*, **5**, 179 (1960).

by  $\text{Fe}^{+2}$  addition, only 82 and 20% reductions could be achieved if  $\text{Fe}^{+2}$  addition was made 5 and 15 minutes after acidification, respectively. Moreover, once the reaction is retarded, it proceeds very slowly to completion. Again,  $\text{ClO}_2$  formation may have caused this retardation.

**REACTION OF  $\text{ClO}^-$  WITH  $\text{Fe}^{+2}$ .** The reduction of  $\text{ClO}^-$  to  $\text{Cl}^-$  by  $\text{Fe}^{+2}$  was investigated in detail in  $\text{H}_2\text{SO}_4$  medium below 0.22*N* (mainly 0.11*N*). Numerous experiments were performed at room temperature under varied conditions, but in all cases  $\text{Fe}^{+2}$  solutions were added to  $\text{ClO}^-$  solutions prior to acidification. The results, however, were not too reproducible; in the concentration ranges studied ( $1.02 \times 10^{-2}$  to  $2.06 \times 10^{-2}M$   $\text{Fe}^{+2}$ ,  $0.9 \times 10^{-5}$  to  $13.7 \times 10^{-5}M$   $\text{ClO}^-$ , 0.11 to 0.22*N*  $\text{H}_2\text{SO}_4$ ), the degree of  $\text{ClO}^-$  reduction to  $\text{Cl}^-$ , after few minutes' reaction, ranges from 95% at low  $\text{ClO}^-$  concentration to only about 75% completion at high  $\text{ClO}^-$  concentration. Moreover, the results seem to be affected only slightly (a few per cent) by a threefold change in  $\text{Fe}^{+2}$  or a two-fold change in  $\text{H}_2\text{SO}_4$  concentration. The incompleteness of  $\text{ClO}^-$  reduction could not be attributed to the decomposition of  $\text{HClO}$  by Equation 11, since the reaction could be completed within 20 to 80 minutes,



nor does Equation 12 play a significant role,



for the slowness of  $\text{ClO}_2^-$  reduction under these conditions could not account for the experimental observations.

To speed up the reaction, the reaction mixtures, adjusted to pH 2.7 to 3.8 by adding 0.02*N*  $\text{H}_2\text{SO}_4$  or  $3.5 \times 10^{-4}M$   $\text{NaHCO}_3$ , were heated for 5 minutes at 40°C prior to absorbance measurements in the next series of experiments. The absorbance measurements were made in 0.11*N*  $\text{H}_2\text{SO}_4$  at room temperature 10 minutes after acidification. Heating treatment nearly accomplished the quantitative reduction (90% at pH 2.8 and 96% at pH 3.8) of  $1.35 \times 10^{-4}M$   $\text{ClO}^-$ . The improved results at higher pH can be attributed to the increased reducing power of  $\text{Fe}^{+2}$  (18*e*, 27*a*), and it can be readily shown that under the experimental conditions employing  $1.02 \times 10^{-2}M$   $\text{Fe}^{+2}$ , the oxidation potential increases from -0.66 volt at pH 2.8 to -0.57 volt at pH 3.8. In fact, at higher pH (ca.  $5 \times 10^{-3}M$   $\text{NaHCO}_3$ ) the reagent blank begins to reduce  $\text{O}_2$  in air so efficiently as to render the procedure useless. For this reason, in another series of experiments, the temperature of the reaction medium was further increased to 50°C while pH was maintained at 3.8. The results obtained from four sets of experiments agree well with the concentrations of standard  $\text{ClO}^-$  solutions up to about  $13 \times 10^{-5}M$ , but at higher concentration ( $22 \times 10^{-5}M$ ) seem to be somewhat low (3%). However, even at this concentration, quantitative agreements could be obtained if the absorbance is measured 20 minutes after acidification.

**Procedure III. B. Iodide System.** ABSORPTION OF  $\text{I}_3^-$ , CHLORITE, CHLORINE DIOXIDE, AND HYPOCHLORITE IN THE ULTRAVIOLET VISIBLE REGION.

**Absorption of  $\text{I}_2$  in Aqueous KI Solution.** In aqueous KI solution,  $\text{I}_2$  exhibits two intense absorption peaks centering at 287 and 351  $m\mu$ , the former being about 50% more intense than the latter (Figure 5). The absorbances at these wavelengths were examined in  $2.41 \times 10^{-2}M$  KI solutions at

pH 8.3 and 3.1. These solutions closely approximate the optimum reaction media employed in the analytical procedure. Low KI concentration was used to render air oxidation of reagent blank insignificant even in dilute acid solutions. Beer's law was obeyed in both acidic and alkaline media in the concentration range studied (up to  $4 \times 10^{-6}M$ ). The molar absorptivities,  $\epsilon [\text{I}_3^- + \text{I}_2(\text{aq.})]$ , which were employed to follow the reactions of oxidizing species with  $\text{I}^-$ , are: at pH 8.3,  $(3.83 \pm 0.02) \times 10^4$  at 287  $m\mu$  and  $(2.51 \pm 0.02) \times 10^4$  at 351  $m\mu$ ; at pH = 3.1  $(3.86 \pm 0.02) \times 10^4$  at 287  $m\mu$  and  $(2.54 \pm 0.02) \times 10^4$  liters mole $^{-1}$  cm $^{-1}$  at 351  $m\mu$ . These values correspond essentially to

$$\{[\text{I}_3^-]/[\text{I}_3^-] + (\text{aq. } \text{I}_2)\} \epsilon \text{I}_3^- \text{ or } \{K(\text{I}^-)/[1 + K(\text{I}^-)]\} \epsilon \text{I}_3^-$$

where  $K$  is the equilibrium constant in Equation 13, as  $\epsilon \text{I}_2(\text{aq.})$  is only about 1% (28) or less (29) of  $\epsilon \text{I}_3^-$ .



The equilibrium constant,  $K$ , was calculated from the result of a study to determine the effect of KI concentration on  $\epsilon [\text{I}_3^- + \text{I}_2(\text{aq.})]$ . With a tenfold increase in KI concentration (0.0241 to 0.241*M*) the absorbances of  $9.659 \times 10^{-6}M$   $\text{I}_2$  at 287 and 351  $m\mu$  increased only by 4%, arising largely from increased  $\text{I}_3^-$  concentration (28, 29). The equilibrium constant as well as  $\epsilon \text{I}_3^-$  was then determined from the observed change in absorbance and the reagent concentrations of the solutions. Thus, a value of  $9.4 \times 10^2$  liter mole $^{-1}$  was obtained for  $K$  at room temperature, which is comparable to the value of  $7.14 \times 10^2$  liters mole $^{-1}$  at 25°C reported by Jones and Kaplan (30) as  $1/K = 0.00140M$ . The values for  $\epsilon \text{I}_3^-$  at pH 8.3 ( $3.5 \times 10^{-3}M$   $\text{NaHCO}_3$ ) are  $3.99 \times 10^4$  at 287  $m\mu$ ,  $2.62 \times 10^4$  at 351  $m\mu$ ; at pH 3.1 ( $8 \times 10^{-4}N$   $\text{H}_2\text{SO}_4$ ),  $4.02 \times 10^4$  at 287  $m\mu$ ,  $2.65 \times 10^4$  liters mole $^{-1}$  cm $^{-1}$  at 351  $m\mu$  (Figure 5). These values agree well with those of Autrey and Connick (29) ( $\epsilon_{\text{I}_3^-}^{288 m\mu} = 40,000$ ,  $\epsilon_{\text{I}_3^-}^{353 m\mu} = 26,400$  liters mole $^{-1}$  cm $^{-1}$ ). In  $2.41 \times 10^{-2}M$  KI,  $\epsilon [\text{I}_3^- + \text{I}_2(\text{aq.})] \cong 0.96 \epsilon \text{I}_3^-$ . The slightly lower values of  $\epsilon \text{I}_3^-$  at pH 8.3 than at pH 3.1 might be attributed to the slight conversion of  $\text{I}_2$  to  $\text{IO}^-$  and subsequent disproportionations of the latter and its hydrolysis product  $\text{HOI}$  to  $\text{IO}_3^-$  in a weakly alkaline medium (15*b*, 18*f*, *g*, 27*b*, 31*a*).

**Absorption of Sodium Chlorite, Chlorine Dioxide, and Sodium Hypochlorite in Aqueous Solution.** Aqueous sodium chlorite, chlorine dioxide, and sodium hypochlorite have rather weak characteristic absorptions compared with that of  $\text{I}_3^-$  (Figure 5). The molar absorptivities of these species at the wavelengths of maximum absorption are:  $\epsilon_{\text{ClO}_2^-}^{261 m\mu} = (1.62 \pm 0.02) \times 10^3$ ,  $\epsilon_{\text{ClO}_2}^{360 m\mu} = (1.26 \pm 0.03) \times 10^3$ ,  $\epsilon_{\text{ClO}_2^-}^{292 m\mu} = (3.62 \pm 0.02) \times 10^2$  liters mole $^{-1}$  cm $^{-1}$ . The first value is in excellent agreement with that of Friedman ( $\epsilon_{\text{ClO}_2^-}^{261 m\mu} = 1.62 \times 10^3$  liters mole $^{-1}$  cm $^{-1}$ ) (32), while the last is about 10% higher than his value ( $\epsilon_{\text{ClO}_2^-}^{292 m\mu} = 3.28 \times 10^2$  liters mole $^{-1}$  cm $^{-1}$ ). In the determinations of  $\epsilon \text{ClO}_2(\text{aq.})$ , the concentrations of  $\text{ClO}_2(\text{aq.})$  were determined by the iodide

(27) N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, p. 1348 (a), p. 1223 (b), p. 1215 (c), p. 1213 (d), Oxford University Press, London, 1950.

(28) B. Zak, in "Colorimetric Determination of Nonmetals," D. F. Boltz, ed., p. 219, Interscience, New York, 1958.

(29) A. D. Autrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951).

(30) G. Jones and B. B. Kaplan, *J. Am. Chem. Soc.*, **50**, 1845 (1928).

(31) Fritz Ephraim, "Inorganic Chemistry," 6th English ed., p. 388 (a), p. 386 (b), P. C. L. Thorne and E. R. Roberts, Interscience, New York, 1954.

(32) H. L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953).

procedure (Procedure III D6) both immediately prior to and immediately after filling the 1-cm stoppered cylindrical absorption cell for absorbance measurement at the 360-m $\mu$  band head, the mean value being taken as that of the solution in the cell. This precaution is essential to compensate for the loss of ClO<sub>2</sub>(g) from the aqueous solution during the sample transfer. The absorptions of ClO<sub>2</sub><sup>-</sup>, ClO<sub>2</sub>(aq.), and ClO<sup>-</sup> have limited analytical applications to the mixture analysis on account of their low absorptivities and significant overlapping absorptions. They, nevertheless, offer a rapid and simple method of determining  $5 \times 10^{-5}$  to  $4 \times 10^{-4}M$  (using a 10-cm cell) and  $4 \times 10^{-4}$  to  $2 \times 10^{-3}M$  (using a 1-cm cell) alkali chlorite,  $1 \times 10^{-3}$  to  $2.3 \times 10^{-3}M$  alkali hypochlorite, and  $10^{-3}M$  to  $10^{-6}M$  (using a 10-cm cell) chlorine dioxide. In these concentration ranges, ClO<sup>-</sup> and ClO<sub>2</sub><sup>-</sup> followed Beer's law closely. The absorption of ClO<sub>2</sub>(aq.) was not investigated as a function of concentration. In mixture analysis, the absorption of ClO<sub>2</sub>(aq.) at the 360-m $\mu$  band head could be used to determine the ClO<sub>2</sub> content after correcting for the slight absorption of ClO<sup>-</sup> ( $\epsilon_{\text{ClO}^-}^{360 \text{ m}\mu} = 10 \text{ liters mole}^{-1} \text{ cm}^{-1}$ ). The ClO<sup>-</sup> correction can be eliminated if the absorbance measurement is made at the 390-m $\mu$  band head, although this will also reduce the sensitivity of ClO<sub>2</sub> determination by about 34%.

Below  $1 \times 10^{-3}M$ , the absorption of hypochlorite solution shows a negative Beer's law deviation, and this becomes progressively serious as the dilution factor increases. Moreover, below  $5 \times 10^{-5}M$  where the measured pH values begin to decrease sharply, a new broad absorption peak centering at about 225 m $\mu$  appears concurrently with the marked decrease in the absorption intensity at 292 m $\mu$  (Figure 5), indicating the formation of other absorbing species. In fact, the absorption near 225 m $\mu$  becomes more prominent than that at 292 m $\mu$  in highly diluted solutions. Evaluation of the equilibrium concentrations of HClO, ClO<sup>-</sup>, Cl<sub>2</sub>O, and Cl<sub>2</sub> from various equilibrium constants involving these species (17b, 18b,h, 27c,d, 31b) and the experimentally determined pH and Cl<sup>-</sup> concentration led to the conclusion that the new absorption is due to HClO and that the deviation from Beer's law is caused by conversion of ClO<sup>-</sup> to HOCl which absorbs weakly at 290 m $\mu$  ( $\epsilon_{\text{HOCl}}^{290 \text{ m}\mu} = 28 \text{ liters mole}^{-1} \text{ cm}^{-1}$ ) (32, 33) because of pH decrease in dilute solutions. This conclusion was confirmed by the fact that the deviation from Beer's law can be quantitatively related to the extent of ClO<sup>-</sup> conversion to HClO in the equilibrium mixture, and was further substantiated by investigation of the 292-m $\mu$  absorption maximum as a function of pH, and the general agreement of the spectrum of  $3.7 \times 10^{-5}M$  ClO<sup>-</sup> in Figure 5 with the HOCl spectra of Friedman (32) and Fergusson *et al.* (33), taking into consideration the contribution of the strong ClO<sup>-</sup> absorption at 292 m $\mu$ .

Obviously, for the analytical application of ClO<sup>-</sup> absorption at 292 m $\mu$ , the solution should be buffered at pH 10. At this pH, the absorption of ClO<sup>-</sup> should conform to Beer's law in the wide range of concentrations. Also, the absorptivities of ClO<sup>-</sup> near 290 m $\mu$  (Figure 5) are estimated to be about 8% lower than the true values.

**REACTION OF CHLORATE WITH IODIDE.** As in the case of the Fe<sup>+2</sup> system, chlorate was found to be unreactive. Thus, about  $7.6 \times 10^{-6}M$  ClO<sub>3</sub><sup>-</sup> remains unchanged even after 22 hours in  $2.4 \times 10^{-2}M$  KI in the presence of  $8 \times 10^{-4}N$  H<sub>2</sub>SO<sub>4</sub>. Increasing the acidity of this reaction medium to 0.11N results only in the serious air oxidation of iodide with-

out affecting the reaction between ClO<sub>3</sub><sup>-</sup> and I<sup>-</sup> to any measurable degree. In the absence of a suitable catalyst, the reaction of ClO<sub>3</sub><sup>-</sup> and I<sup>-</sup> is therefore too slow for analytical purposes. On the other hand, the inertness of chlorate makes it possible to determine chlorite and hypochlorite in the mixture containing chlorate.

**REACTION OF CHLORITE WITH IODIDE.** In contrast with the Fe<sup>+2</sup> system (Procedure III A), the reaction of chlorite with iodide follows the pattern expected from the chlorine potential diagram considerations—i.e., the reactivity of ClO<sub>2</sub><sup>-</sup> toward I<sup>-</sup> increases progressively with the acidity increase of the reaction medium. Thus, in a series of experiments, chlorite was found to be completely inert at pH 8.3, only 46.8% reduced even after 17 hours near pH 6, and quantitatively reduced to Cl<sup>-</sup> while oxidizing I<sup>-</sup> to I<sub>2</sub> after 15 minutes and in less than 3 minutes at pH 3.1 and above pH 2.4, respectively, in the concentration ranges studied [ $I^- = 2.41 \times 10^{-2}M$ ,  $(\text{ClO}_2^-) = 4.90 \times 10^{-6}M$  to  $14.70 \times 10^{-6}M$ , in  $3.5 \times 10^{-3}M$  NaHCO<sub>3</sub> (pH = 8.3), neutral, and  $8 \times 10^{-4}N$  to  $2 \times 10^{-2}N$  H<sub>2</sub>SO<sub>4</sub> media]. For analytical applications, the optimum acidity was determined to be about  $5 \times 10^{-3}N$  (pH 2.3). At this acidity, the air oxidation of reagent blank corresponds to only about  $1 \times 10^{-7}M$  ClO<sub>2</sub><sup>-</sup> even after a 1-hour standing period.

**REACTION OF HYPOCHLORITE WITH IODIDE.** The oxidation of iodide to iodine by hypochlorite was studied in weakly alkaline and acidic media. In the concentration ranges studied [ $I^- = 2.41 \times 10^{-2}M$ ,  $(\text{ClO}^-) = 7.15 \times 10^{-6}$  to  $2.81 \times 10^{-5}M$ , in  $3.5 \times 10^{-3}M$  NaHCO<sub>3</sub> (pH = 8.3), neutral, 0.1M HAC + 0.1M NaAC (pH = 4.75),  $8 \times 10^{-4}N$  H<sub>2</sub>SO<sub>4</sub> media], the reaction was found to be quantitative within 3 minutes. The results at pH 8.3 were slightly lower (2 to 3%), however. This was attributed to the chlorite contamination in hypochlorite, as no further reaction was observed even after 83 minutes' standing. The difference in reactivity of chlorite and hypochlorite toward iodide constitutes the basis of the analytical scheme for the determination of these species in the same mixture. In hypochlorite analysis of the mixture, high alkalinity (above pH 8.3) should be avoided to minimize the possibility of partial conversion of I<sub>2</sub> into other species (Procedure III B).

**Procedure III C. Mercuric Chloranilate System.** The procedure of Bertolacini and Barney (9) for the indirect spectrophotometric determination of Cl<sup>-</sup> was examined to determine the interferences of other oxygen-chlorine species in mixture analysis. Although not serious, the absorption of reagent blank at 307 m $\mu$  prepared according to their procedure was considerable [0.56 absorbance unit (*vs.* H<sub>2</sub>O) in a 1-cm cell]. This is largely due to the superimposing absorption of NO<sub>3</sub><sup>-</sup> ( $\epsilon_{\text{NO}_3^-}^{302 \text{ m}\mu} = 7.22 \text{ liters mole}^{-1} \text{ cm}^{-1}$ ) and can be reduced to about 0.2 absorbance unit by the use of either H<sub>2</sub>SO<sub>4</sub> or HClO<sub>4</sub> instead of HNO<sub>3</sub>. Moreover, the liberation of chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone) from mercuric chloranilate was found to depend on the temperature of the mixture and the standing period after mixing. Thus, the relative absorbance change,  $(\Delta A/A) \times 100$ , increases about 1.5% per °C temperature rise and 13 and 58% after 140-minute and 66-hour standing periods, respectively. The reagent blank and sample solutions should therefore be prepared in the same manner and at the same time to compensate for these effects. Chloranilic acid, once separated from its salt, however, is very stable and its absorption is independent of the temperature of the solution. Thus, overnight standing of this solution causes only a 2 to 3% decrease in the absorption intensity at 307 m $\mu$ .

A calibration curve was subsequently constructed employing

(33) W. C. Fergusson, L. Slotin, and D. W. G. Style, *Trans. Faraday Soc.*, **32**, 956 (1936).

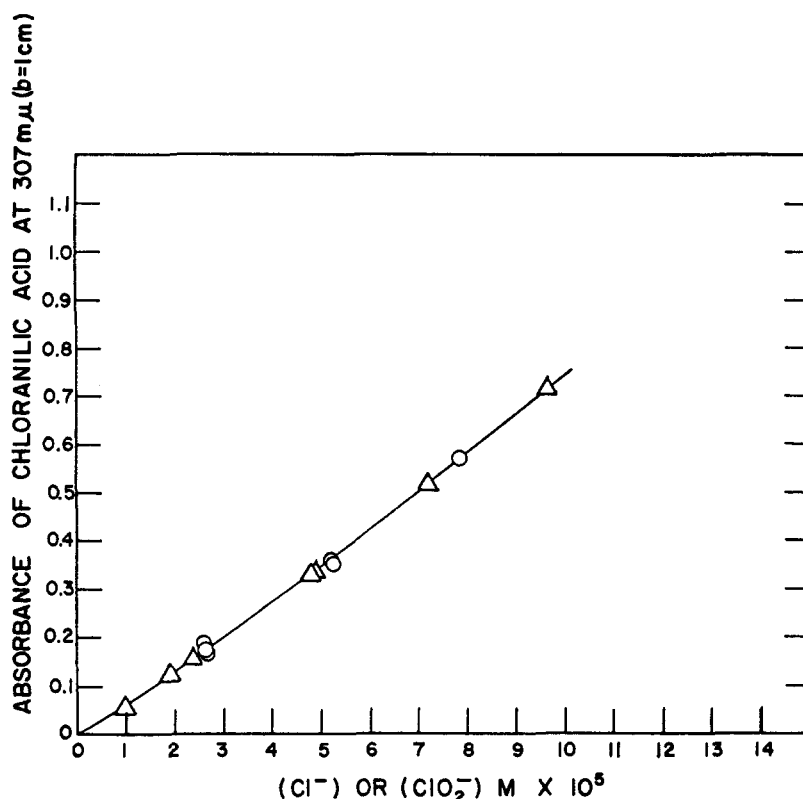


Figure 6. Calibration curve for  $ClO_2^-$  determination

○  $Cl^-$   
△  $ClO_2^-$

standard KCl solutions in  $H_2SO_4$  medium. This shows a significant positive deviation from Beer's law (ca. 10%) in the concentration range studied (up to  $1.3 \times 10^{-4}M Cl^-$ ). The addition of  $9.2 \times 10^{-3}M KClO_4$ ,  $9.5 \times 10^{-3}M KClO_3$ ,  $10^{-3}M As_2O_3$ , or  $10^{-3}M As_2O_5$ , or a  $\pm 20\%$  change in the acidity of the medium (0.05*N*) caused no interference or change in the sensitivity of the procedure.

Chlorite, however, interfered with the mercuric chloranilate method by liberating chloranilic acid in a nonquantitative way. Thus, about  $2.4 \times 10^{-5}M ClO_2^-$  liberates chloranilic acid corresponding only to 60% of its chlorine content. Further studies under various conditions to determine  $ClO_2^-$  by the chloranilate procedure were unsuccessful, and it then became necessary to eliminate  $ClO_2^-$  and  $ClO^-$  for analytical application of the chloranilate procedure to the chloride determination in the presence of these species. For this purpose, chemical elimination methods were chosen to reduce these oxidizing species to chloride. As a result of this modification in the procedure, only the total chlorine content of chlorite, hypochlorite, and chloride could be determined. However, because chlorite and hypochlorite can be determined separately (Procedures III B and III D) the chloride content can be determined by difference.

For the reduction of chlorite and hypochlorite, weakly alkaline hydrogen peroxide (15c) and neutral arsenious oxide (15d) solutions have been used. The reduction of hypochlorite to chloride by arsenious oxide solution is apparently complete in a very short time, for the strong absorption of  $ClO^-$  at 292  $m\mu$  disappears completely immediately upon the addition of the reducing agent. Table I shows that the total chlorine content of hypochlorite and chloride can be satisfactorily determined, provided that arsenious oxide is used as

the reducing agent. A correction for 63.5 mole %  $Cl^-$  contamination of the  $ClO^-$  solutions has been applied in this table.

Difficulties were encountered, however, in the reduction of chlorite with either arsenious oxide or hydrogen peroxide. As in the case of hypochlorite, alkaline hydrogen peroxide treatment gave inconsistent results, varying from 73% to quantitative reduction of  $ClO_2^-$  in the  $10^{-5}M$  range. Equally unsatisfactory results were obtained when arsenious oxide was used to reduce chlorite. However, after detailed experimentation under varied conditions, a procedure was found which enables the satisfactory determination of chlorite by the chloranilate method. This consists of treating chlorite with  $10^{-3}M As_2O_3$  in a weakly acidic medium at 50° C for 5 minutes prior to the  $Cl^-$  determination (Procedure

Table I. Determination of Total Chlorine Content of Hypochlorite and Chloride by the Mercuric Chloranilate Method

( $Cl^-$ ) taken, $M \times 10^5$	( $ClO^-$ ), $M \times 10^5$			( $Cl^- + ClO^-$ ) found, <sup>b</sup> $M \times 10^5$
	Taken <sup>a</sup>	Found <sup>b</sup>	Found <sup>c</sup>	
2.62	0.796	0.82		3.48
	0.796	0.86		
5.24	0.796	0.72		5.98
5.24	1.59	1.48	0.96	
5.24	1.59	1.60	1.39	
	1.59	1.60	0.85	
	1.59	1.65	0.85	
2.62	3.18	2.92		5.54

<sup>a</sup> Based on iodometric titration.

<sup>b</sup>  $ClO^-$  reduced by  $10^{-3}M$  neutral  $As_2O_3$  solution.

<sup>c</sup>  $ClO^-$  reduced by excess  $H_2O_2$  in weakly alkaline medium.



III D). Except for a slight decrease in sensitivity (1 to 2%), Figure 6 duplicates the calibration curve for  $\text{Cl}^-$  mentioned above and shows excellent agreement among the results obtained from the standard KCl solutions and from the chlorite solutions treated by this procedure.

**Procedure III D. Procedure for Mixture Analysis and Application to the Analysis of Synthetic Mixtures.** Based on the results of the above studies, the following experimental procedures for mixture analysis are recommended.

**D1. HYPOCHLORITE.** In a 50-ml volumetric flask, dissolve 0.2 gram of KI in a small amount of distilled water. Add 5 ml of 0.035*M*  $\text{NaHCO}_3$  and a sample containing 0.4 to 2  $\mu\text{mole}$  (preferably about 0.7  $\mu\text{mole}$ ) of hypochlorite. Dilute to the mark with distilled water, and mix the solution thoroughly. Prepare the reagent blank in the same manner. Measure the absorbance (*vs.*  $\text{H}_2\text{O}$ ) of reagent blank and the sample solution at 287  $m\mu$  in 1-cm silica cells. Determine the hypochlorite content using  $\epsilon_{[\text{I}_3^- + \text{I}_2(\text{aq})]}^{287 m\mu} = 3.83 \times 10^4$  liters  $\text{mole}^{-1} \text{cm}^{-1}$ .

**D2. CHLORITE.** *a.* In a 50-ml volumetric flask, dissolve 0.2 gram of KI in a small amount of distilled water. Add a sample containing hypochlorite and chlorite corresponding to 0.4 to 2  $\mu\text{moles}$  of hypochlorite (preferably about 0.7  $\mu\text{mole}$ ), and adjust the volume to about 45 ml with distilled water. Then add 0.10 ml of 4*N*  $\text{H}_2\text{SO}_4$ , dilute to the mark with distilled water, and mix the solution thoroughly. Prepare the reagent blank in the same manner. Measure the absorbances (*vs.*  $\text{H}_2\text{O}$ ) of the reagent blank and the sample solution at 287  $m\mu$  in 1-cm silica cells. Determine the chlorite in the sample using  $\epsilon_{[\text{I}_3^- + \text{I}_2(\text{aq})]}^{287 m\mu} = 3.86 \times 10^4$  liters  $\text{mole}^{-1} \text{cm}^{-1}$  and the result obtained for hypochlorite in Procedure III D1.

*b.* Add 0.10 ml of 4*N*  $\text{H}_2\text{SO}_4$  to the remaining solutions (not less than approximately 40 ml) used for hypochlorite determination in Procedure III D1 and repeat the absorbance measurements 3 minutes later at 287  $m\mu$  or at 351  $m\mu$  if the absorbance is above 1.0. If the concentration is still too high at 351  $m\mu$ , Procedure III D2*a* should be used. Determine the chlorite content as in III D2*a* ( $\epsilon_{[\text{I}_3^- + \text{I}_2(\text{aq})]}^{351 m\mu} = 2.54 \times 10^4$  liters  $\text{mole}^{-1} \text{cm}^{-1}$ ).

Though less sensitive and more time-consuming than the above procedures, the total chlorite and hypochlorite content can also be determined by the first part of Procedure III D3.

**D3. CHLORATE.** To a 50-ml volumetric flask, add 5 ml of  $1 \times 10^{-3}$  *M*  $\text{NaHCO}_3$  solution, 0.2 gram of uniformly pale green colored ferrous ammonium sulfate hexahydrate, and a small amount of water to dissolve the  $\text{Fe}^{+2}$  salt. At this point, the ferrous salt solution thus obtained should be free from the yellowish brown colloidal hydrous ferric oxide suspensions. Add a sample containing chlorate, chlorite, and hypochlorite corresponding to 1.2 to 3.8  $\mu\text{moles}$  (preferably about 3  $\mu\text{moles}$ ) of chlorate, and adjust the volume to about 40 ml with distilled water. Subsequently hold the flask in a 50° C water bath for 5 minutes, then cool to room temperature in a cold water bath. At this stage, the reagent blank should still remain clear. Acidify the solution with 5 ml of 1.1*N*  $\text{H}_2\text{SO}_4$  (3% by volume), dilute to the mark with distilled water, and mix the solution thoroughly. Measure the absorbances (*vs.*  $\text{H}_2\text{O}$ ) of both the reagent blank ( $A_s^0$ ) and the sample ( $(A_s^T)_t = 10 \text{ min.}$ ) solution at 305  $m\mu$  in 1-cm silica cells 10 minutes after acidification, and the temperatures of both solutions immediately following the absorbance measurements. Under these conditions, the reagent blank should be stable for 2 hours and its absorbance reading should not exceed about 0.050. Otherwise, a ferrous salt of higher grade should be employed. Ten minutes later, repeat the absorbance and temperature measurements ( $(A_s^T)_t = 20 \text{ min.}$ ). The small increase in sample absorption ( $<0.020$ ) arises from the slow reaction of chlorate with  $\text{Fe}^{+2}$ . Calculate

the total content of chlorite and hypochlorite by means of Equation 14:



$$\left\{ \frac{[(A_s)_t = 10 \text{ min.} - (A_s)_t = 20 \text{ min.}] - [(A_s)_t = 10 \text{ min.}]}{\epsilon_{\text{Fe}^{+2}}^{305 m\mu, 0.11N \text{ H}_2\text{SO}_4}} \right\} \quad (14)$$

where  $\text{ClO}^- + \text{ClO}_2^-$  is expressed in milliequivalents and the absorbances are normalized to 28.5° C, using

$\left[ \left( \frac{d\epsilon}{\epsilon} \right) / dT \right]_{0.11N \text{ H}_2\text{SO}_4} = +0.006$ —i.e., 0.6% absorbance increase per °C temperature rise, and  $\epsilon_{\text{Fe}^{+2}}^{305 m\mu, 0.11N \text{ H}_2\text{SO}_4} = 2238$  liters  $\text{mole}^{-1} \text{cm}^{-1}$  at 28.5° C. Following the absorbance measurements in 0.11*N*  $\text{H}_2\text{SO}_4$  medium, pipet a 5-ml sample solution into a 10-ml volumetric flask, and add 3 ml of concentrated  $\text{H}_2\text{SO}_4$  (98%) carefully from a 3-ml safety pipet by touching the tip of the pipet to the inside wall of the upper stem of the flask and releasing the acid slowly. Cool the solution to room temperature (Caution: Do not mix the solution before cooling). Dissolve 0.020 gram of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , dilute to the mark with distilled water, and mix the solution thoroughly. Prepare the reagent blank in the same manner. Measure the absorbances (*vs.*  $\text{H}_2\text{O}$ ) of the reagent blank and the sample solution at 301  $m\mu$  in 1-cm silica cells. The reagent blank is stable at least for one hour and its absorption should amount only to about 0.060 absorbance unit. Determine the chlorate content using  $\epsilon_{\text{Fe}^{+2}}^{301 m\mu, 10.0N \text{ H}_2\text{SO}_4} = 2.90 \times 10^3$  liter  $\text{mole}^{-1} \text{cm}^{-1}$  and the results of chlorite and hypochlorite determinations obtained by Procedures III D1 and III D2.

**D4. CHLORIDE.** Prepare the sample and the reagent blank simultaneously according to the following procedure.

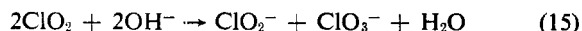
To a 50-ml volumetric flask, add 5 ml of  $10^{-2}$  *M* arsenious oxide solution, a sample containing 1.5 to 5  $\mu\text{moles}$  (preferably about 4  $\mu\text{moles}$ ) of total chlorite, hypochlorite, and chloride (less than 15 ml if added as solution), and 25 ml of methyl Cellosolve (ethylene glycol monomethyl ether). Mix the contents of the flask to dissolve the sample if added as solid. Add 2 ml of 0.02*N*  $\text{H}_2\text{SO}_4$  and adjust the volume to about 40 ml (less than 45 ml). Heat the flask for 5 minutes in a 50° C water bath and cool the solution to room temperature. Add 5 ml of 0.5*N*  $\text{H}_2\text{SO}_4$ , make up to the mark with distilled water, and mix the solution thoroughly. Then keep the flask in a water bath at about 20° C for 3 minutes and make up to the mark again if necessary. Add 0.1 gram of mercuric chloranilate and shake the mixture intermittently for 15 minutes (10-second shaking at 1-minute intervals, repeated 15 times). Centrifuge for 5 minutes to separate chloranilic acid from mercuric chloranilate suspensions within 15 minutes. Measure the absorbances (*vs.*  $\text{H}_2\text{O}$ ) of the supernatant solutions of reagent blank and sample at 307  $m\mu$  in 1-cm cells. Obtain the total chlorine content of chlorite, hypochlorite, and chloride from the calibration curve constructed by the same procedure using standard KCl solutions (Figure 6). Calculate the chloride content by subtracting from the total chlorine content the chlorite and hypochlorite contributions determined by Procedures III D1 and III D2.

**D5. ANALYSIS OF SYNTHETIC MIXTURES.** Satisfactory results (Table II) were obtained in the analysis of mixtures by the procedures described above. The mixtures consist of all the constituent species listed in Table II, and were prepared by mixing the proper species amount of the standard solution of each constituent, except for perchlorate which was added as crystals (between Standard sieve Nos. 50 and 60). To minimize the possible interactions among the component species, the mixtures were prepared immediately prior to the analysis.

# D6. ANALYSIS OF MIXTURES CONTAINING CHLORINE DIOXIDE.

The reaction of chlorine dioxide with iodide was studied under the conditions recommended for hypochlorite and chlorite determinations. The ratio of  $I_2$  liberated at pH 2.2 and 8.3 was found to be 5.01 (0.03 standard deviation), which corresponds to the reduction of  $ClO_2$  to  $Cl^-$  at pH 2.2 and to  $ClO_2^-$  at pH 8.3, respectively. This is in agreement with earlier results obtained under similar conditions (10, 34). Evidently, in the presence of  $ClO_2$ , the iodide procedures must be modified so that  $ClO^-$ ,  $ClO_2^-$ , and  $ClO_2$  can be determined. To this end, the  $ClO_2$  removal from the aqueous solution by bubbling with purified helium was examined as functions of pH and  $ClO_2$  concentration. Helium was purified by passing through acid dichromate, alkaline permanganate, and distilled water in the order mentioned. It was then dispersed uniformly into a 10-ml  $ClO_2$  aqueous solution contained in a 30-ml test tube at a flow rate of  $172 \pm 5$  ml per minute from a gas dispersion tube. One end of a dispersion tube consisting of a fritted glass disk of medium porosity (maximum pore diameter, 25 to 50 microns) was immersed near to the bottom of the test tube. With this arrangement, in the concentration range studied (up to  $5 \times 10^{-5} M$ ),  $ClO_2$  can be removed completely within 10 minutes from its neutral as well as alkaline aqueous solutions at pH 8.3 ( $3.5 \times 10^{-5} M NaHCO_3$ ) and pH 10.4 ( $3.5 \times 10^{-5} M Na_2CO_3$ ). The use of an efficient gas dispersion system is essential, or the  $ClO_2$  removal may not be complete. Thus, at pH 10.4, 17 and 9%  $ClO_2$  still remained in 40 ml of a  $1 \times 10^{-5} M$   $ClO_2$  solution contained in a 50-ml volumetric flask after 10 and 20 minutes of He bubbling, respectively, at the flow rate employed above, but without the use of a gas dispersion tube.

During  $ClO_2$  removal, part of the  $ClO_2$  was converted into  $ClO_2^-$ , except in neutral medium where  $ClO_2^-$  formation amounts to only 0.9% of  $ClO_2$  content even after 4 months' standing in the dark. The  $ClO_2^-$  formation arising undoubtedly from the hydrolysis of  $ClO_2$  (Equation 15) increases from 2% at pH 8.3 to  $5.0 \pm 0.5\%$  of  $ClO_2$  content at pH 10.4.



Moreover,  $ClO_2^-$  formation was found to be, at least at pH 10.4, essentially directly proportional to  $ClO_2$  concentration.

The possible loss of hypochlorite was also studied under the conditions employed for  $ClO_2$  removal. With the use of even the low efficiency gas dispersion system described above, 30 and 5% hypochlorite were lost from  $1.7 \times 10^{-5} M$   $ClO^-$  at pH 7 and 8.3, respectively, after 10 minutes He bubbling. This is undoubtedly due to removal of  $HOCl$  in equilibrium with  $OCl^-$ , because the decrease of hypochlorite loss to one sixth associated with the change in pH from 7 to 8.3 coincides with the same decrease in  $HOCl$  concentration (from 77% to

Table II. Analysis of Synthetic Mixtures

Constituent species	Added		Found, <sup>a</sup> $\mu$ moles
	$\mu$ moles	Mole %	
KClO <sub>4</sub>	1440	99.6	
KClO <sub>3</sub>	3.80	0.263	3.87, 3.84 Av. 3.86
NaClO <sub>2</sub>	0.241	0.0167	0.245, <sup>b</sup> 0.241 <sup>c</sup> Av. 0.243
NaClO	0.404	0.0279	0.405, <sup>b</sup> 0.401 <sup>c</sup> 0.414, 0.388, 0.400 Av. 0.402 Std. dev. 0.008
KCl	1.31	0.0907	1.24, <sup>d</sup> 1.23 <sup>d</sup> Av. 1.24

<sup>a</sup> Except as noted below (<sup>b,c</sup>), one mixture was employed to obtain each result.

<sup>b,c</sup> One mixture employed for each pair of results.

<sup>d</sup> In addition to  $ClO^-$  and  $ClO_2^-$  corrections, correction for 63.5 mole %  $Cl^-$  contamination of  $ClO^-$  solutions made.

14% of total hypochlorite content). This conclusion is further supported by the fact that this loss is eliminated at pH 10.4 where  $HOCl$  concentration is reduced to only 0.1%.

In analysis of mixtures containing  $ClO_2$ , the iodine liberated at pH 8.3 and 2.2 corresponds to  $(ClO^- + \frac{1}{2} ClO_2) = a$  and  $(ClO^- + 2 ClO_2^- + \frac{5}{2} ClO_2) = b$ , respectively. However, if  $ClO_2$  is removed by He bubbling at pH 10.4 prior to analysis of mixtures, the iodine liberated at pH 8.3 and 2.2 corresponds to  $ClO^- = a'$  and  $[ClO^- + 2 ClO_2^- + (0.05 \times \frac{5}{2}) ClO_2] = b'$  where all quantities are expressed in moles. The hypochlorite, chlorite, and chlorine dioxide contents can then be calculated from these two sets of data. In the presence of  $ClO_2$ , therefore, the only modification required consists of additional  $I_2$  determinations to obtain  $a'$  and  $b'$ .

The possible interference of chlorine dioxide in chlorate determination can easily be eliminated by removing  $ClO_2$  in neutral medium by He bubbling prior to  $ClO_3^-$  determination. For  $ClO^-$  and  $ClO_2^-$  corrections, however, the results obtained from Equation 14 rather than those obtained by iodide procedures must be used because of partial loss of  $ClO^-$  as  $HOCl$  during  $ClO_2$  removal. In  $Cl^-$  determination, the possible interference of  $ClO_2$  can also be overcome by removing  $ClO_2$  by He bubbling at pH 10.4 prior to subsequent neutralization and  $Cl^-$  determination. In order to obtain  $Cl^-$  content, in addition to  $ClO^-$  and  $ClO_2^-$  corrections, the  $Cl^-$  contribution corresponding to 5%  $ClO_2$  content arising from the reduction of  $ClO_2^-$  formed by  $ClO_2$  hydrolysis must also be subtracted from the total chlorine content.

(34) Fritz Boehmlaender, *Vom Wasser*, **29**, 78 (1962); *C.A.*, **61**, 3692c (1964).

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