Influence of organic impurities on chlorine concentration in chlorine dioxide solutions

M. F. Hoq and W. R. Ernst*

ABSTRACT: Both methanol and formic acid are impurities found in chlorine dioxide solutions produced industrially by the reaction of methanol and sodium chlorate. This work shows that each of these impurities influences the apparent concentration of chlorine in these solutions. (1) Formic acid reacts with chlorine; and (2) methanol interferes with the "arsenite titration" procedure commonly used for chlorine analysis. Rates of reaction of chlorine with formic acid were measured in chlorine dioxide solutions prepared in the laboratory. The reaction is approximately first order in chlorine and in formic acid. The activation energy is 15 kcal/mol. Rates of reaction of chlorine with methanol were comparatively less significant under similar experimental conditions; however, methanol reacted very rapidly under basic conditions of the arsenite titration procedure, leading to false measurements of chlorine concentration.

KEYWORDS: Chlorine, chlorine compounds, chlorine dioxide, concentration, formic acid, impurities, interference, measurement, methanol, organic compounds, solutions.

Chlorine dioxide is an oxidizing chemical that is used in water purification and is replacing chlorine in bleaching processes of pulp and paper mills because of environmental concerns. This work continues a study of reactions that may be important in the commercial production of chlorine dioxide *(1–9)*.

Most chlorine dioxide used in pulp bleaching is generated by reducing sodium chlorate with methanol in sulfuric acid solution *(10–13)*. These processes have replaced the chloride–chlorate process which yields chlorine as a major by-product *(2, 14)*. The methanol–chlorate process substantially reduces the measured chlorine concentration in chlorine dioxide absorber solutions. Even at relatively low concentrations, chlorine is a concern to paper manufacturers. The detection and elimination of chlorine are therefore important issues in the industry. Other impurities—unreacted methanol and byproduct formic acid—are also present in chlorine dioxide absorber solutions produced by this process *(3)*. It is important to understand whether, and to what extent, these organics influence the presence, as well as the determination, of chlorine in these solutions.

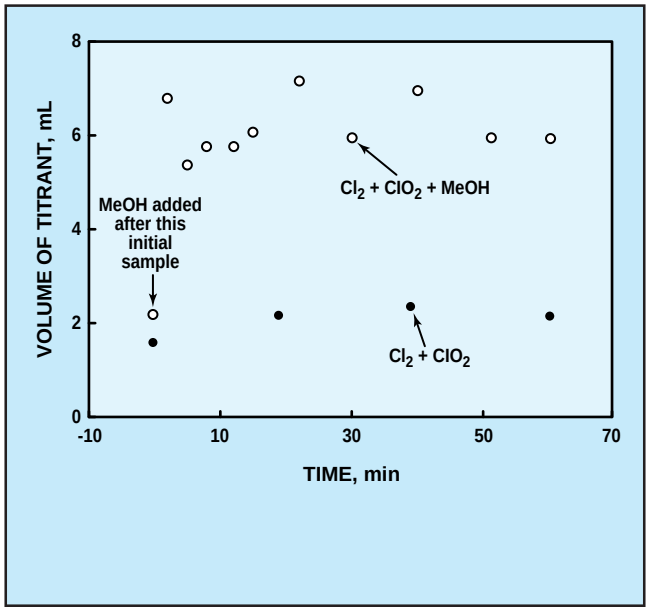
There are two titrimetric methods of measuring chlorine that are routinely practiced in the pulp and paper industry. They are referred to as the thiosulfate method and the arsenite method *(15–17)*. The thiosulfate method involves adding potassium iodide to the chlorine–chlorine dioxide solution and titrating the released iodine with thiosulfate. Two titrations are required—one at neutral condition, and one under acidic condition. This method measures both chlorine and chlorine dioxide; however, the method yields true results only if no acidic gases, such as HCl, HCOOH, or SO_2 are present in the ClO_2–Cl_2 mixture *(16)*.

The arsenite method involves adding sodium hydroxide to the chlorine–chlorine dioxide solution to convert chlorine dioxide to sodium chlorite and sodium chlorate, and to convert chlorine to sodium hypochlorite and sodium chloride followed by the addition of excess of sodium bicarbonate to neutralize the unreacted sodium hydroxide. Buffered potassium iodide solution is

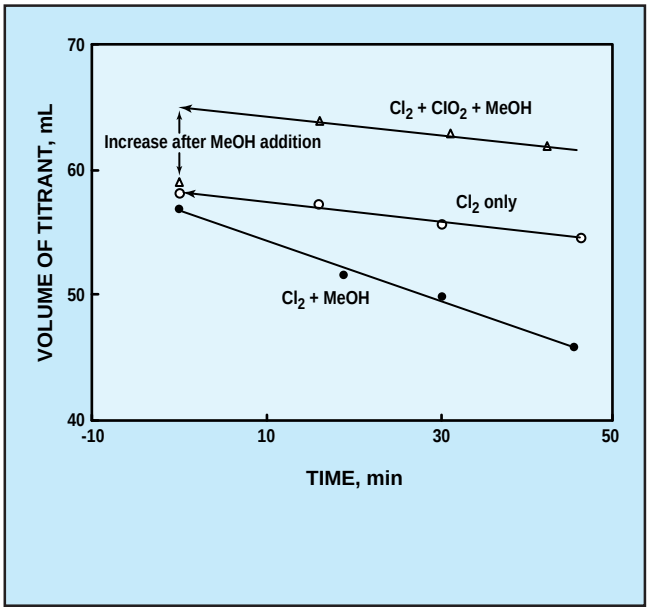
Hoq and Ernst are, respectively, research scientist and professor, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332.

* Author to whom correspondence should be addressed.

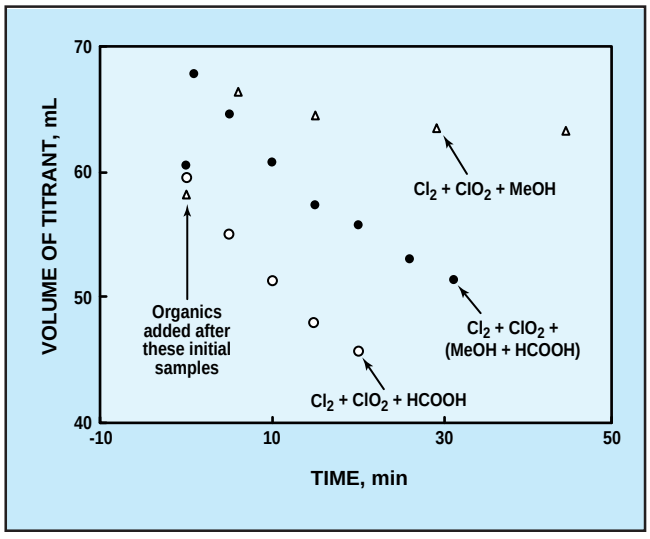
1. Influence of methanol addition on apparent chlorine concentration in a chlorine–chlorine dioxide solution. Conditions: 10°C, pH 2.4, 0.085 *M* chlorine dioxide, 0.00067 *M* initial chlorine in each solution. Symbols: solid—no methanol added; open—0.05 *M* methanol added immediately after initial sample was taken.



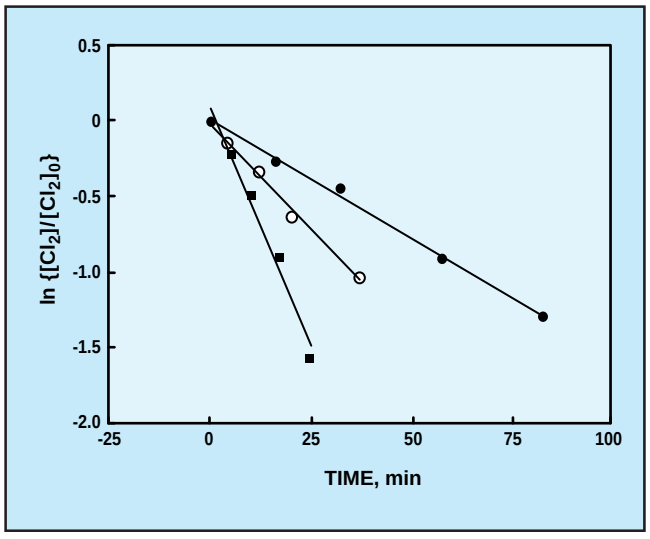
2. Influence of methanol and chlorine dioxide on apparent chlorine concentration. Conditions: 10°C, pH 3, 0.0067 *M* initial chlorine in each solution. Symbols: open circles—chlorine solution, no methanol added; solid circles—0.1 *M* methanol added to chlorine solution immediately after initial sample was taken; triangles—0.1 *M* methanol added to 0.11 *M* chlorine dioxide solution containing chlorine immediately after initial sample was taken.



3. Influence of methanol and formic acid on apparent chlorine concentration in a chlorine–chlorine dioxide solution. Conditions: 10°C, pH 3, 0.11 *M* chlorine dioxide, 0.0046 *M* initial chlorine in each solution; methanol and/or formic acid added immediately after initial sample was taken. Symbols: open circles—0.08 *M* formic acid added; triangles—0.1*M* methanol added; solid circles—methanol and formic acid added.



4. First-order plots of rate data. Symbols refer to experiments and conditions in Table III: Experiment No. 2 (solid circles); No. 4 (open circles); and No. 16 (squares).



added and iodine forms only by reaction with hypochlorite ions. Chlorine is measured by titrating the released iodine with sodium arsenite solution. This method is independent of acidity *(16)*.

This work further investigates the influence of both methanol and formic acid on the stability and measurement of chlorine in chlorine–chlorine dioxide solutions. It addresses the specific questions: (a) Does methanol, formic acid, or both species interfere with the arsenite

I. Influence of component concentrations on determination of chlorine in solutions containing methanol

Expt.	Initial concentrations, M x 10^2			Vol. of 0.0022 M arsenite, mL			%Error
no.	$[ClO_2]$	[MeOH]	$[Cl_2]$	With MeOH	No MeOH	Difference	in $[Cl_2]$
41	15	8	0.97	46.0	44.0	2.0	4.5
42	15	8	0.95	44.0	43.0	1.0	2.3
43	15	8	0.62	38.6	28.4	10.2	36.2
44	15	8	0.62	39.0	27.6	11.4	40.5
45	15	8	0.37	26.5	16.7	9.8	58.7
46	15	8	0.35	24.0	16.0	8.0	50.0
47	15	2	1.10	48.0	50.0	-2.0	-4.0
48	15	2	1.08	50.0	49.0	1.0	2.0
49	15	2	0.64	31.4	29.4	2.0	6.9
50	15	2	0.64	30.0	28.4	1.6	5.5
51	15	2	0.45	22.6	20.4	2.2	10.8
52	15	2	0.42	23.4	19.2	4.2	21.9
53	11	8	1.00	47.2	46.0	1.2	2.6
54	11	8	1.00	46.0	45.0	1.0	2.2
55	11	2	1.05	46.1	47.4	-1.3	-2.7
56	11	2	1.05	47.7	47.6	0.1	0.2
57	11	2	0.94	38.2	42.0	-3.8	-8.9
58	11	2	0.94	40.0	43.0	-3.0	-7.0
59	11	2	0.28	19.0	12.8	6.2	48.7
60	11	2	0.28	18.3	13.0	5.3	41.6
61	7	8	1.08	47.0	49.0	-2.0	-4.1
62	6	8	0.99	42.4	45.0	-2.6	-5.8
63	7	8	1.12	45.0	51.0	-6.0	-11.8
64	6	8	0.99	42.4	45.0	-2.6	-5.8
65	8	8	0.60	28.0	27.6	0.4	1.5
66	8	8	0.60	29.0	27.0	2.0	7.3
67	7	8	0.20	13.6	9.2	4.4	47.8
68	7	8	0.22	14.4	9.8	4.6	46.9
69	7	2	1.14	50.0	52.0	-2.0	-3.8
70	7	2	1.04	42.8	47.0	-4.2	-8.9
71	7	2	1.17	48.0	53.0	-5.0	-9.4
72	7	2	1.04	43.2	47.2	-4.0	-8.5
73	8	2	0.58	25.2	26.4	-1.2	-4.6
74	8	2	0.58	25.8	26.2	-0.4	-1.5
75	1	8	0.85	27.8	38.2	-10.4	-26.9
76	1	8	0.85	27.4	38.8	-11.4	-29.5
77	1	2	0.87	35.7	40.4	-4.7	-11.9
78	1	2	0.87	35.2	38.6	-3.4	-8.6
79	0	8	0.82	33.4	37.2	-3.8	-10.2
80	0	8	0.82	33.3	37.3	-4.0	-10.7
81	0	2	0.78	34.4	35.4	-1.0	-2.8
82	0	2	0.78	34.0	35.6	-1.6	-4.5

titration method for chlorine in chlorine dioxide solutions, leading to inaccurate measurements of concentration? (b) Does chlorine in chlorine dioxide solutions react with the organic species? If chlorine does react at a substantial rate, how fast is the reaction, and how do concentrations and temperature influence the rate?

Experimental

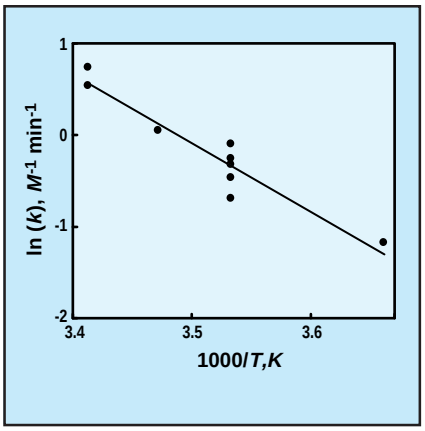
For each reaction experiment, 50 mL of reaction mixture was prepared by adding appropriate amounts of stock solutions of chlorine dioxide (0.19 *M* ClO_2 at pH 6), 0.033 *M* chlorine and phosphate buffer (0.5 *M* at pH 3), and allowing the temperature to equilibrate in a closed cylindrical flask partly immersed in a constant temperature bath. The mixture was continuously stirred using a magnetic bar while temperature was monitored by a mercury thermometer. Five mL of this mixture was analyzed for chlorine prior to addition of methanol and formic acid. This datum point served as the initial chlorine concentration. The reaction was started by adding an appropriate volume of stock solutions of formic acid (5 *M* at pH 3) or methanol to the flask.

II. Sequence of reagent addition and titration results

Expt. no.	*Sequence of reagent addition prior to titration*	*Titrant volume, mL 0.00116 N arsenite*
I	a. Cl_2 + ClO_2 added to NaOH b. $NaHCO_3$ + KI added	39, 37, 40
II	a. Cl_2 + ClO_2 + MeOH added to NaOH b. $NaHCO_3$ + KI added	55, 53
III	a. Cl_2 + ClO_2 added to NaOH b. $NaHCO_3$ + KI added c. MeOH added	40
IV	a. MeOH added to NaOH b. Cl_2 + ClO_2 added c. $NaHCO_3$ + KI	61

Key:
Cl_2 + ClO_2 = 5 mL of 0.11*M* chlorine dioxide solution containing chlorine as noted by the arsenite titrant volume.
MeOH = methanol at 0.08*M* concentration
NaOH = 25 mL of 1*M* sodium hydroxide
$NaHCO_3$ + KI = 5 g sodium bicarbonate, 75 mL water and 5 mL of 10 wt % potassium iodide.

5. Arrhenius plot of second-order rate constants (pH 3–3.2)



At regular time intervals, a 5-mL aliquot was removed from the flask and quickly poured into 25 mL of 1 *M* sodium hydroxide solution. Caustic converts chlorine dioxide to chlorite and chlorate ions, and converts chlorine to chloride and hypochlorite ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \quad (1)$$

$$Cl_2 + 2OH^- \rightarrow Cl^- + OCl^- + H_2O \quad (2)$$

Reaction 2 is very rapid. The completion of reaction 1 is indicated by the complete disappearance of the yellow color of chlorine dioxide.

After this solution became colorless, 5 g of sodium bicarbonate, 75 mL water, and 5 mL of (10 wt.%) potassium iodide solution were added, resulting in a solution pH of 8.0–8.5. Under these conditions, only the hypochlorite reacts with iodide, liberating iodine according to the reaction:

$$NaOCl + 2\,KI + H_2O \rightarrow I_2 + 2KOH + NaCl \quad (3)$$

The amount of liberated iodine is determined by titrating with 1–2 m*N* standard arsenite solution according to the stoichiometry of the reaction:

$$I_2 + AsO_3^{-3} + H_2O \rightarrow 2H^+ + 2I^- + AsO_4^{-3} \quad (4)$$

Experiments were conducted to investigate the influence of methanol on the arsenite titration procedure. In each of these experiments, the solutions were prepared as before; however, only two samples were analyzed and compared—one sample prior to methanol addition, and one sample after adding methanol. Since the titration results were somewhat time-dependent in the experiments with added methanol, the samples from these experiments were added to the 1 *M* sodium hydroxide solution within 1 min after the solutions were prepared. (The analytical procedure deviates somewhat from a standard method *(17)*, although both are based on the same chemistry. For example, to tailor the method to the scale of our experiments, we changed the relative proportions of some reagents. The changes did not reduce the accuracy and reproducibility of the analyses.)

In several other experiments, also aimed at studying the influence of methanol on the arsenite titration procedure, the solutions were prepared by adding ingredients in different sequences. These solutions were then titrated for chlorine.

Results and discussion

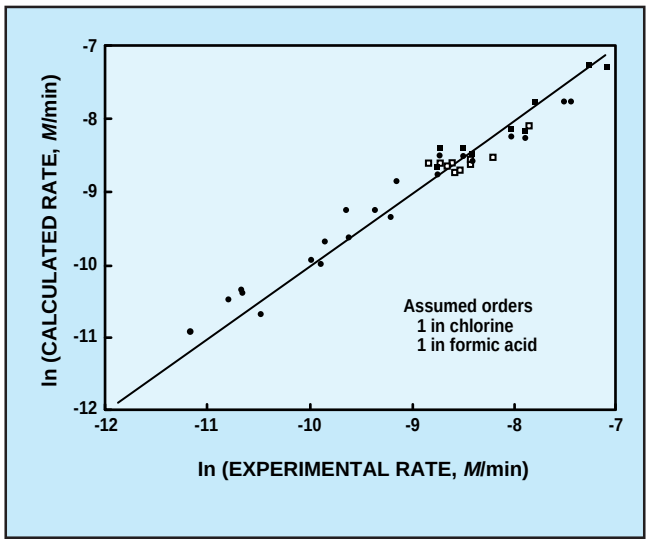
Influence of organics on chlorine analysis

Figures 1 through 3 show the influence of methanol and formic acid on the "apparent chlorine concentration," which is defined as the volume of arsenite solution required to titrate chlorine in 5-mL samples removed from the reactor at various times. Figure 1 shows results of two experiments involving chlorine–chlorine dioxide solutions that contained 0.085 *M* chlorine dioxide. In one experiment (open circles), methanol was added at a concentration of 0.05 *M* immediately after the first sample (data point at t = 0) was withdrawn from the reactor for analysis. In the other experiment, no methanol was added (solid circles). The figure shows that at the beginning of the experiment both solutions required about 2 mL of 0.00333 *N* arsenite solution, which is equivalent to a chlorine concentration of 0.00067 *M*. After the methanol was added in the

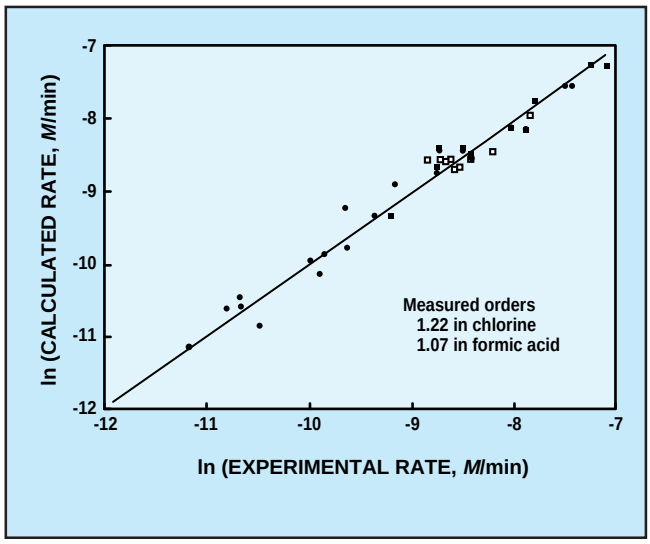
III. Reaction data and rate coefficients

Expt. no.	Temp., °C	pH	Initial concentrations, M x 10^2 Chlorine	Formic acid	Rate x 10^5, M/min	k 1st Order	k opt Order
Experiments at constant temperature and pH							
1	10	3.0	0.18	2.0	2.8	0.78	3.5
2	10	3.0	0.25	2.0	2.3	0.46	1.9
3	10	3.0	0.22	2.0	2.0	0.46	2.0
4	10	3.0	0.18	4.0	5.0	0.70	3.0
5	10	3.0	0.19	8.0	8.6	0.56	2.3
6	10	3.0	0.19	12.0	10.5	0.46	1.8
7	10	3.0	0.38	2.0	4.6	0.61	2.3
8	10	3.0	0.38	4.0	6.5	0.43	1.6
9	10	3.0	0.40	8.0	20.1	0.63	2.2
10	10	3.0	0.31	8.0	15.6	0.63	2.3
11	10	3.0	0.37	8.0	21.7	0.73	2.6
12	10	3.0	0.12	4.0	2.3	0.48	2.2
13	10	3.0	0.14	2.0	1.4	0.51	2.4
14	10	3.0	0.13	8.0	6.6	0.63	2.8
15	10	3.0	0.12	8.0	5.2	0.54	2.4
16	10	3.0	0.40	8.0	16.0	0.50	1.8
17	10	3.0	0.52	8.0	32.2	0.78	2.6
18	10	3.0	0.51	8.0	36.9	0.91	3.0
19	10	3.0	0.84	8.0	58.5	0.87	2.6
20	10	3.0	0.84	8.0	54.9	0.82	2.5
			Average *k* of runs 1 to 20 =			0.62	2.4
Effect of pH							
21	10	0.8	0.60	8.0	38.7	0.81	2.6
22	10	1.2	0.32	8.0	18.6	0.73	2.7
23	10	1.5	0.36	8.0	18.0	0.63	2.2
24	10	1.7	0.38	8.0	21.7	0.71	2.5
25	10	2.2	0.36	8.0	21.6	0.75	2.7
26	10	2.3	0.39	8.0	26.9	0.86	3.0
27	10	2.3	0.33	8.0	19.5	0.74	2.7
28	10	2.5	0.36	8.0	14.4	0.50	1.8
29	10	2.7	0.35	8.0	17.2	0.61	2.2
30	10	2.9	0.36	8.0	16.2	0.56	2.0
					Average *k* of runs 21 to 30 =	0.69	2.4
					Average *k* of runs 1 to 30 =	0.65	2.4
					Standard deviation =	0.14	0.4
					Percent deviation =	21.3	17.6
Effect of temperature							
31	20	3.2	0.50	8.0	83.5	2.09	7.0
32	20	3.0	0.51	8.0	70.4	1.73	5.8
33	15	3.0	0.48	8.0	40.8	1.06	3.6
34	10	3.0	0.40	8.0	20.1	0.63	2.2
35	10	3.0	0.31	8.0	15.6	0.63	2.3
36	10	3.0	0.37	8.0	21.7	0.73	2.6
37	10	3.1	0.40	8.0	16.0	0.50	1.8
38	10	3.2	0.52	8.0	32.2	0.78	2.6
39	10	3.0	0.51	8.0	36.9	0.91	3.0
40	0	3.0	0.41	8.0	10.0	0.30	1.1

6. Calculated versus measured rate of chlorine disappearance assuming second-order kinetics. Symbols refer to data in Table III: Experiment Nos. 1 to 20 (circles), Nos. 21 to 30 (open squares), and Nos. 31 to 40 (solid squares).



7. Calculated versus measured rate of chlorine disappearance assuming statistically determined reaction orders. Symbols refer to data in Table III: experiment Nos. 1 to 20 (circles), Nos. 21 to 30 (open squares), and Nos. 31 to 40 (solid squares).



one experiment, the volume of arsenite solution required for titration immediately increased to about 6 mL, while it remained at 2 mL for samples of the solution which did not contain methanol. This increase in titrant is equivalent to an increase in chlorine concentration of 0.00133 *M*, or 200%.

An increase in "apparent chlorine concentration" was also observed immediately after adding methanol to chlorine–chlorine dioxide solution in one experiment at higher initial chlorine concentration (see Fig. 2—triangles). In this experiment, the chlorine dioxide concentration was 0.11 *M*. The figure shows that at the beginning of the experiment, prior to methanol addition, the solution required about 58 mL of 0.00116 *N* arsenite titrant, which is equivalent to a chlorine concentration of 0.0067 *M*. After methanol was added to the solution, the required volume of arsenite solution increased to a higher level. That level was estimated to be about 65 mL by extending a line through the three data points (triangles) after the initial point, and extrapolating the line to zero time. This represents an increase of about 7 mL, which is equivalent to an increase in chlorine concentration of 0.0008 *M* or 12%.

Figure 2 also shows results of experiments aimed at measuring the rate that chlorine disappears from an aqueous chlorine solution (open circles), from an aqueous chlorine solution after the addition of methanol at a concentration of 0.1 *M* (solid circles), and from an aqueous chlorine–chlorine dioxide solution after the addition of methanol at a concentration of 0.1 *M* (triangles). In all three experiments, the solutions had about the same initial chlorine concentration, 0.0067 *M*. The figure shows that after methanol was added to the chlorine solution (solid circles), the chlorine disappeared slightly faster than did chlorine in the solution with no methanol present (open circles). After methanol was added to the chlorine–chlorine dioxide solution, and after the initial "apparent" increase in chlorine concentration, the rate that chlorine disappeared was about equivalent to the rate that chlorine disappeared from a chlorine solution to which no methanol or formic acid was added. Figure 1, which includes data for experiments at much lower chlorine concentration, shows very little change in chlorine concentration with time.

Figure 3 compares rates of chlorine disappearance from chlorine–chlorine dioxide solutions containing 0.1 *M* methanol (triangles), 0.08 *M* formic acid (open circles), and 0.1 *M* methanol and 0.08 *M* formic acid (solid circles). In each experiment, the chlorine dioxide concentration was 0.11 *M*. The figure shows that at the beginning of the experiments, prior to methanol addition, all three solutions required about 40 mL of 0.00116 *N* arsenite solution, which is equivalent to a chlorine concentration of 0.0046 *M*. In the experiment in which both methanol and formic acid were added to the solution, the methanol was added first.

Figure 3 shows that the rates of chlorine disappearance were comparable in the two solutions in which formic acid was present, and much greater than the rate in the solution in which only methanol was present. In the two experiments in which methanol was added, there was again an abrupt increase in the volume of arsenite solution required to titrate the solutions. The increase in both experiments was about 15 mL of titrant, which would be equivalent to 0.0017 *M* chlorine or 37%.

Table I shows further evidence that solution composition influences results of arsenite titration of chlorine in chlorine dioxide solutions. It shows the volumes of arsenite required to titrate chlorine in 5-mL aliquots of solutions containing methanol and solutions containing no methanol (blank). It also shows that for all experiments these two volumes differ, indicating an apparent increase (positive error) or apparent decrease (negative error) in the chlorine concentration. In Table I, all experiments are reported in duplicate. There is reasonable agreement between duplicate runs.

Table I shows that for all concentrations of chlorine dioxide and methanol, the error in chlorine analyses increases in the positive direction as the concentration of chlorine in the blank decreases. At 0.15 *M* chlorine dioxide, and both 0.02 and 0.08 *M* methanol, the errors are positive, indicating an apparent increase in chlorine concentration after addition of methanol. At lower chlorine dioxide concentrations, the errors become negative, especially at higher chlorine concentrations, indicating an apparent decrease in chlorine concentration after methanol addition. Methanol also has an influence on the titration results in that the absolute error increases as methanol concentration increases.

Assuming that the differences between titration volumes for each experiment in Table I represent real changes in chlorine concentration, these data suggest that two processes may be occurring in the samples: (a) production of chlorine, possibly by reaction of chlorine dioxide with methanol; and (b) reaction of chlorine with methanol. The first process is apparent at high chlorine dioxide concentrations and increases in importance at lower chlorine concentrations. The second process predominates at low chlorine dioxide concentration.

To investigate further the influence of methanol on the arsenite titration procedure, we changed the sequence of combining reagents in the solutions prior to titration. **Table II** shows that four different sequences were used. In Sequence I, a chlorine–chlorine dioxide solution was added to sodium hydroxide solution followed by addition of sodium bicarbonate buffer and potassium iodide. This sequence represents a blank experiment since no methanol was added. The average titrant volume was 39 mL of 0.00116 *N* arsenite solution. Sequence II is identical to I, except that the initial solution also contains methanol. The average titrant volume was 54 mL, therefore indicating an apparent increase in chlorine concentration of about 39%. In Sequence III, the methanol was added after the other ingredients had been combined. The titrant volume is 40 mL, essentially identical to that for Sequence I. In Sequence IV, methanol was first added to sodium hydroxide, followed by the addition of the chlorine–chlorine dioxide solution, and subsequently by addition of the buffer and potassium iodide. The titrant volume is 61 mL, indicating an apparent increase in chlorine concentration similar to that of Sequence II.

We conclude from this latter set of experiments that methanol does not interfere with the titration step of the analytical procedure, but rather reacts with components of the solution after sodium hydroxide is added either producing more chlorine, possibly by reacting with chlorite, or reducing the amount of chlorine, possibly by reacting with hypochlorite.

IV. Kinetic parameters and statistical analysis results

Parameter	*Value*	*Standard deviation*	*t ratio*
ln *A*	26.89	2.89	9.29
-E/R	-7319	828	-8.84
a	1.22	0.07	18.2
b	1.07	0.06	16.43
Number of data points	40		
Standard model error	0.18		
Coeff. of determination	0.97		

Influence of formic acid on rate of chlorine reaction

Figures 1, 2 and 3 show that chlorine concentration in chlorine–chlorine dioxide solutions decreases relatively rapidly when formic acid is present; whereas, in the absence of formic acid, chlorine concentration is relatively stable even when methanol is present. In a series of 40 experiments, we measured the initial rate of chlorine disappearance from 0.11 to 0.12 *M* chlorine dioxide solutions containing various initial concentrations of chlorine and formic acid. Initial rates were determined by extrapolating concentration versus time graphs to zero time.

Table III is a summary of data gathered in these experiments. Experiment nos. 1–30 measured the influence of reactant concentrations on rate. In that series, chlorine concentration was varied from 0.0018 to 0.0084 *M*, and formic acid concentration was varied from 0.02 to 0.12 *M*. Experiment nos. 21–30 measured the influence of pH between 0.8 and 2.9. And experiment nos. 31–40 measured the influence of temperature between 0 and 20°C.

Figure 4 shows concentration–time data of three experiments plotted in semilogarithmic form. Straight lines could be reasonably fitted

through the data, indicating that the reaction is about first order in chlorine concentration. Rate coefficients for each experiment were calculated by dividing the initial rate by the product of chlorine and formic acid concentration. These values are shown in Column 7 of Table III. This method assumes that the reaction order is first in each species and second overall. These second order rate coefficients are reasonably constant for experiments 1–20, averaging 0.62 $M^{-1}min^{-1}$, and for experiments 21–30, averaging 0.69 $M^{-1}min^{-1}$. The overall average for the 30 runs is 0.65± 0.14 $M^{-1}min^{-1}$. From these results, we conclude that the reaction is approximately first-order in both chlorine and formic acid concentration, and is not pH-dependent within the accuracy of the data.

Figure 5 is an Arrhenius plot of the second-order rate coefficients in Column 7 of Table III. The activation energy and pre-exponential factor were obtained by fitting a straight line through the data. The resulting rate expression based on this analysis is:

$$-d[Cl_2]/dt = 2.5 \times 10^{11} \exp(-15{,}000/RT)\,[Cl_2]\,[HCOOH] \quad (5)$$

Figure 6 is a plot of rates of reaction predicted by Eq. 5 versus the experimental rates listed in Table III. On average, the difference between the experimental rates and those predicted by this model is 18%.

To check the assumption of first-order behavior of chlorine and formic acid, and the subsequently determined value of activation energy, we used an alternate approach in analyzing the data. This alternate approach involves a statistical analysis and is aimed at determining the reaction parameters, *a, b, A,* and *E*, that best fit all the data in Table III. We assumed that the reaction follows the power law expression, and correlated the data in terms of the expression,

$$-d[Cl_2]/dt = A \exp(-E/RT)(Cl_2)^a\,[HCOOH]^b \quad (6)$$

using a statistical software package *(18)*.

In applying the program, we fit the data to the logarithmic form of Eq. 7:

$$\ln(-d[Cl_2]/dt) = \ln A - E/RT + a \ln(Cl_2) + b \ln[HCOOH] \quad (7)$$

The input consisted of concentrations of chlorine and formic acid, reciprocal temperatures, and experimental rates. The program finds values of the parameters, *a, b,* ln *A,* and *E/R*, which minimize the difference between experimental and calculated values of ln (R_{ClO_2}) and performs a statistical analysis of the parameters.

The results are shown in **Table IV** and in **Fig. 7** for the 40 experiments reported in Table III. The reaction orders *a* and *b*, determined by this analysis, are respectively, 1.22 and 1.07, which are reasonably close to 1. The activation energy is 14.5 kcal/mol, which is reasonably close to the value 15 kcal/mol, reported in Eq. 5. A reasonably good fit was obtained in the analysis of all the data as shown in Table IV by the large *t*-ratios for each parameter and in the adjusted coefficient of determination near unity (R^2 = 0.97). When only the data of the isothermal runs were fit to the rate model using the statistical approach (Experiments 1–30), the resulting reaction orders *a* and *b* remained almost unchanged at 1.20 and 1.07, respectively. When only the data of Experiments 1–20 were fit to the rate model, the resulting reaction orders *a* and *b* again remained almost unchanged at 1.19 and 1.06. Figure 7 is a plot of rates of reaction predicted by Eq. 6 (and the parameters in Table IV) versus the experimental rates listed in Table III. Comparison of this plot with that of Fig. 6 shows that the statistical approach marginally improves the fit of the data. On average, the difference between the experimental rates and those predicted by this model is 14%.

Application

Depending upon the process, a chlorine dioxide solution produced at a pulp and paper facility has a chlorine dioxide concentration between 8 and 12 g/L and a temperature of about 10°C. We earlier examined commercial chlorine dioxide solutions produced by methanol–chlorate chemistry and showed that they contained formic acid concentrations typically between 0.02 and 0.04 *M (3)*. The chlorine concentration is usually undetectable and is most likely one or more orders of magnitude lower in concentration than formic acid.

The present work suggests that if chlorine is formed in these commercial processes and is present in the chlorine dioxide solution, the chlorine concentration should decline with time at a rate governed by either Eq. 6 (using the parameters in Table IV) or the simpler expression Eq. 5 (assuming second-order kinetics). We have shown that these expressions yield almost equivalent estimates of the rate behavior of the reaction; therefore, for simplicity we will continue this discussion by referring to Eq. 5.

Since chlorine content decreases in chlorine dioxide solutions in the presence of formic acid, there may be some benefit in storing chlorine dioxide before use in a bleaching process so that any residual chlorine will have reacted. One can approximate the storage time that will have a significant impact on chlorine concentration by integrating Eq. 5. Assuming formic acid concentration is much greater than chlorine concentration and therefore essentially constant as chlorine reacts, and assuming constant storage temperature, the half-life of chlorine in the solution is found by integrating Eq. 5 from $[Cl_2]_0$ to $0.5[Cl_2]_0$:

$$t_{1/2}\,(min) = \ln(2)/k[HCOOH] \quad (8)$$

For example, the second-order rate constant in Eq. 8 at 10°C is 0.65 M^{-1} min^{-1}. Assuming a chlorine dioxide solution containing 0.03 *M* for-

Nomenclature

A	= pre-exponential Arrhenius parameter, $M^{1-a-b} \cdot min^{-1}$	R	= gas constant, 1.987 cal · mol^{-1} · $°K^{-1}$
a,b	= reaction orders, respectively, in chlorine and formic acid	t	= time, min
E	= activation energy, cal · mol^{-1}	$t_{1/2}$	= reaction half-life, min
		T	= temperature, $°K^{-1}$

mic acid, the pseudo first-order-rate coefficient, or 0.65 [HCOOH], would equal 0.02 min^{-1}. Equation 8 predicts a chlorine half life of 35 min, or approximately one-half hour. After 4 half-lives, or about 2 h, the chlorine concentration would have dropped below 6% of its initial value.

We might expect these results in an industrial plant only if other chlorine-producing reactions that we have not considered do not occur. For example, we have used reagent grade chemicals and de-ionized water in the laboratory experiments and conducted all experiments in laboratory glassware. We do not know whether contaminants in industrial process water, or metal surfaces and impurities associated with process equipment might interact with chlorine and chlorine dioxide in these processes.

Conclusions

We have shown that the arsenite titration procedure, when applied to chlorine dioxide solutions containing methanol, can yield chlorine concentration measurements that are either falsely high or falsely low, depending upon the relative concentrations of chlorine, chlorine dioxide, and to a lesser extent, methanol in the solutions. Methanol interferes with the procedure during the step in which the solution is made basic with sodium hydroxide. The results suggest that, under basic conditions, methanol participates in two competing processes: (a) production of chlorine—by reacting with chlorine dioxide in the sample (as shown by examination of Fig. 2), and (b) depletion of chlorine—probably by reacting with hypochlorite produced when base interacts with the chlorine in the sample.

We have shown that formic acid reacts with chlorine in chlorine dioxide solutions at a rate that is governed by approximate first-order kinetics in both reactants and by an activation energy of about 15 kcal/mol. The reaction may be significantly fast at normal industrial conditions to have an impact on industrial processing. At similar conditions, the rate of methanol with chlorine is much slower. ■

Literature cited

1. Burke, M., Tenney, J., Indu, B., *et al., Ind. Eng. Chem. Research* 32(7): 1449(1993).
2. Ernst, W. R., Shoaei, M., and Forney, L., *AIChE Journal* 34: 1927(1988).
3. Hoq, M. F., W. R. Ernst, and L. T. Gelbaum, *Tappi J.* 74: 217(1991).
4. Hoq, M. F., Indu, B., W. R. Ernst, *et al., J. Phys. Chem.* 95: 681(1991).
5. Hoq, M. F., Indu, B., Neumann, H.M., *et al., J. Phys. Chem.* 95(22): 9023(1991).
6. Hoq, M. F., Indu, B., Ernst, W.R., *et al., Ind. Eng. Chem. Research* 31(7): 1807(1992).
7. Indu, B., Hoq, M. F., Ernst, W.R., *et al., Ind. Eng. Chem. Research* 30(6): 1077(1991).
8. Indu, B., Hoq, M. F. and Ernst, W. R., *AIChE J.* 37(11): 1744 (1991). In this reference, there is an error in the caption to Fig. 4; it should read "Numbers refer to parameter a."
9. Indu, B., Ernst, W. R., and Gelbaum, L. T., *Ind. Eng. Chem. Research* 32(5): 981(1993).
10. Norell, M., U.S. pat. no. 4,770,868 (Sept. 13, 1987).
11. Norell, M. and Svedin, B. H., U.S. pat. no. 4,978,517 (Dec. 18, 1990).
12. Fredette, M.C.J., U. S. pat. no. 4,465,658 (Aug. 14, 1984).
13. Fredette, M.C.J., U.S. pat. no. 4,473,540 (Sept. 25, 1984).
14. Tenney, J., Shoaei, M., Obijeski, T., *et al., Ind. Eng. Chem. Research* 29(5): 912(1990).
15. Masschelein, W.J., *Chlorine Dioxide: Chemistry and Environmental Impact of Oxychlorine Compounds,* Ann Arbor Science, Ann Arbor, MI, 1979.
16. Owen, D., *TAPPI 1992 Bleach Plant Operations Short Course Notes,* TAPPI PRESS, Atlanta, p. 255.
17. Canadian Pulp and Paper Association, Montreal, Standard J.14P: Chlorine Dioxide Plant Analyses, Revised May 1984.
18. MINITAB release 6.2, (copyright 1990), Minitab Inc., 3081 Enterprise Dr., State College, PA 16801.

We gratefully acknowledge financial support from Eka Nobel, Inc. We thank the following persons from Eka Nobel: Joel Tenney, John Gray, Maria Norell, and Johan Landfors for helpful discussions regarding commercial chlorine dioxide processes.

Received for review April 19, 1994.

Accepted Aug. 8, 1995.