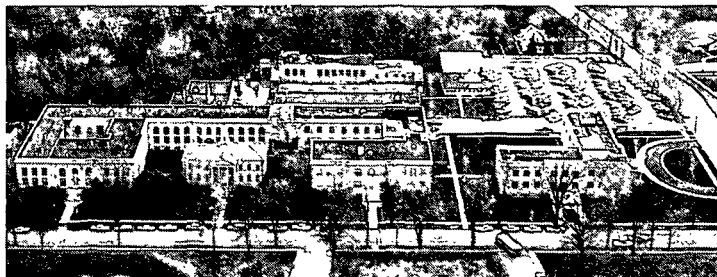


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**ANALYSIS OF BLEACHING LIQUORS BY ION
CHROMATOGRAPHY**

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Analysis of bleaching liquors by ion chromatography

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ABSTRACT

An ion chromatographic (IC) method for determining chlorine dioxide has been developed, and IC procedures for measuring chlorite, chlorate, chlorine (as hypochlorite) and oxalate have been evaluated. A chlorite response in the IC, proportional to the chlorine dioxide injected, is the basis for the chlorine dioxide method. Chlorite originally present in the liquor is measured in a separate aliquot of sample from which chlorine dioxide has been removed by sparging. Chlorine is converted to hypochlorite in the alkaline eluent and measured with the electrochemical detector. Quantitative spike recoveries and/or agreement of IC results with those from other methods demonstrate the validity of IC for measuring chlorine dioxide, chlorine, chlorine-containing anions, and oxalate in bleach liquors.

for bleach liquor analysis are described below. The ion chromatograph is a dual-channel Model 2020i equipped with electrolytic conductivity and electrochemical (amperometric) detectors (Dionex Corporation, Sunnyvale, CA, U.S.A.). Bleach liquor analysis was performed on an HPIC AS-3 column followed by an anion fiber suppressor. Eluent used for chlorine-containing species was 0.002M Na₂CO₃; for oxalate the eluent was 0.003M NaHCO₃, 0.0024M Na₂CO₃. All ions except hypochlorite were detected by electrolytic conductivity; hypochlorite was detected with the electrochemical detector with a platinum electrode, applied potential -0.20V. The electrochemical detector was placed ahead of the separator column to avoid loss of hypochlorite due to its decomposition by the ion-exchange resin.

Because distilled water produced an interference equivalent to about 0.7 ppm hypochlorite at the hypochlorite retention time, eluent rather than water was used to dilute samples in which hypochlorite was determined. Use of formaldehyde solution (1 mL/L) as diluent has been suggested in T 699 for preserving hypochlorite samples and standards. This was found to produce a negative interference equivalent to about 2.5 ppm hypochlorite. Therefore, formaldehyde was not used to preserve hypochlorite.

Iodometric and spectrometric methods

Determinations of chlorine-containing oxidants in water and bleach liquors by iodometry have been reported by several authors (2-4). Aleta's procedure (4), which employs five iodometric titrations, was used in this study for measuring chlorine dioxide, chlorine, chlorite, and chlorate. The strength of hypochlorite solutions was determined by iodometric titration at pH 2.

Spectrometric and other procedures for determining chlorine dioxide have been reviewed by Masschelein (5-6). Methods employing a UV spectrometer (7) and

a flow calorimeter (8) have been published recently. The tyrosine method was used for determining chlorine dioxide in the current investigation. In this procedure, chlorine dioxide oxidizes tyrosine to dopaquinone, measurable at 490 nm (5,9). Interference due to chlorine was removed by reaction with ethylamine.

RESULTS AND DISCUSSION

Chlorine dioxide

Bleach liquors are known to change in composition during storage, and ion chromatography should be able to characterize the decomposition by simultaneous determination of chlorine-containing anions. To test this ability, a laboratory-prepared chlorine dioxide liquor was diluted 1:2500 with distilled water, and aliquots of dilute liquor were injected into the IC as a function of storage time at room temperature. Results are shown in Fig. 1. Initial data points suggest that the chlorine dioxide was converted to chlorite upon injection into the IC, presumably by reaction with the ion-exchange resin. Data obtained after several hours' storage indicate that the chlorine dioxide had decomposed to chlorate and chloride prior to injection.

(Fig. 1 here)

The unanticipated behavior of chlorine dioxide in the IC was tested further by injecting a series of chlorine dioxide solutions and measuring the chlorite response. As shown in Fig. 2, the chlorite response was proportional to the chlorine dioxide injected. This provides the basis for an IC method for determining chlorine dioxide in bleach liquors. In this procedure, chlorite serves as a surrogate for chlorine dioxide, and Fig. 2 shows the calibration line. Data in Table I show that chlorine dioxide contents determined by IC were in excellent agreement with values from the tyrosine and iodometric methods.

(Fig. 2 here)

(Table I here)

A liquor's chlorite response reflects chlorite originally present in the liquor plus chlorine dioxide. The original chlorite may be determined by injecting a second aliquot of sample from which the chlorine dioxide has been removed by nitrogen sparging. This technique was used to obtain the data in Table II, in which measured chlorine dioxide and chlorite concentrations match well the known contents of prepared mixtures.

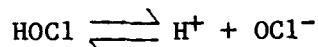
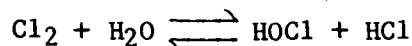
(Table II here)

Because chlorine and chlorine dioxide are often used in the same bleaching stage, possible interference by chlorine in the chlorine dioxide determination was a concern. Values in Table III did not reveal any interference, even when chlorine was present in a ten-fold excess. Note that chlorine dioxide (chlorite) is determined with the conductivity detector, which does not respond to chlorine (hypochlorite).

(Table III here)

Chlorine

The sodium carbonate eluent used for IC analysis of bleach liquors has a pH of 10.8. At that pH the hypochlorous acid formed by the hydrolysis of chlorine in water would be essentially all converted to hypochlorite:



These equations are the basis for an IC method for the determination of chlorine in bleach liquors. Tables IV and V indicate that the IC and iodometric analysis of chlorine water and tap water yielded comparable results. Because the chlorine (hypochlorite) was measured with the electrochemical detector, there was no interference from chlorine dioxide (Table V). Solutions containing chlorine dioxide, chlorite, chlorate, and chloride were run through the electrochemical detector to confirm that these species were not electroactive under the conditions of this analysis.

(Tables IV and V here)

Chlorate and chlorite

Values for chlorate in bleach liquors determined by IC are compared with those from the iodometric method in Table VI. Results are similar from the two methods. The iodometric method for chlorate also detects chlorine, chlorine dioxide, and chlorite. Accurate chlorate values depend, therefore, on accurate determination of and correction for these other chlorine-containing species. Thus, use of IC rather than iodometry for measuring chlorate should lead to enhanced speed, ease, specificity, and accuracy in the determination.

(Table VI here)

A spike recovery study was performed to confirm the validity of the IC method for determining chlorate and chlorite. The chlorine dioxide liquor studied earlier (Fig. 1) was diluted 1:2500 and allowed to stabilize overnight. Spiking solution containing chlorate and chlorite was added, and six replicate determinations of these ions were performed by IC. Results shown in Table VII indicate nearly quantitative spike recoveries.

(Table VII here)

Oxalate

The formation of oxalic acid during bleaching of kraft pulp has been demonstrated (10). In that study the oxalic acid was esterified and measured by gas chromatography. Oxalate was determined in the current work by ion chromatography without derivatization. Spent liquors from chlorine and chlorine dioxide stages were diluted, and their oxalate contents were measured before and after addition of oxalate spikes. Quantitative spike recovery values in Table VIII document the value of IC for this analysis.

(Table VIII here)

CONCLUSIONS

Because it produces a chlorite response, chlorine dioxide may be determined by ion chromatography. Chlorite can be measured in a separate aliquot of sample from which chlorine dioxide has been removed by nitrogen sparging. Chlorine does not interfere in the determination. In alkaline eluent, chlorine is converted to hypochlorite, which may be measured with the electrochemical detector. Ion chromatographic determination of chlorate is easier and more specific than the iodometric method. Oxalate in spent bleaching liquors may also be determined by ion chromatography.

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Table I. Comparison of methods for determination of chlorine dioxide.

| Method | Result, g/L |
|------------|-----------------|
| IC | 3.87 ± 0.04 |
| Tyrosine | 3.85 ± 0.03 |
| Iodometric | 3.78 |

^a95% confidence limits for the mean of eight determinations.

^bIodometric determinations were performed daily. Result decreased from 4.30 to 3.78 g/L in two weeks due to slow decomposition of the ClO₂ stock solution.

Table II. Ion chromatographic analysis of chlorine dioxide-chlorite mixtures.

| <u>Prepared Mixture, ppm</u> | | <u>Measured Concentration, ppm</u> | |
|------------------------------|-----------------|------------------------------------|-----------------|
| <u>ClO₂</u> | <u>Chlorite</u> | <u>ClO₂</u> | <u>Chlorite</u> |
| 1.93 | 1.00 | 1.92 | 1.00 |
| 1.93 | 1.00 | 1.95 | 1.00 |
| 1.93 | 2.00 | 1.92 | 2.00 |
| 1.93 | 2.00 | 1.95 | 1.97 |
| 0.96 | 3.00 | 0.96 | 2.97 |
| 0.96 | 3.00 | 0.98 | 2.94 |

Table III. Analysis of chlorine-chlorine dioxide mixture.

| Time, min ^a | Method | ClO ₂ , g/L | Cl ₂ , g/L |
|------------------------|-------------------|------------------------|-----------------------|
| - | Prepared conc. | 0.100 | 1.00 |
| 2 | IC (conductivity) | 0.101 | -- |
| 30 | Tyrosine | 0.102 | -- |
| 90 | Iodometric | 0.099 | 0.99 |
| 150 | IC (conductivity) | 0.100 | -- |

^aMinutes after preparing sample. Sample pH 1.98.

Table IV. Determination of chlorine.

| Method | Chlorine Water Samples | | Tap Water, mg/L |
|-------------------|------------------------|--------|-----------------|
| | A, g/L | B, g/L | |
| IC (electrochem.) | 0.75 | 0.81 | 1.3 |
| Iodometric | 0.77 | 0.80 | 1.2 |

Table V. Analysis of chlorine-chlorine dioxide mixtures.

| Method | ClO ₂ , g/L | Cl ₂ , g/L |
|-------------------|------------------------|-----------------------|
| Prepared conc. | 0.050 | 0.50 |
| IC (electrochem.) | -- | 0.50 |
| Iodometric | 0.049 | 0.50 |
| Approx. conc. | 0.50 | 0.50 |
| IC (electrochem.) | -- | 0.44 |
| Iodometric | 0.50 | 0.44 |

Table VI.: Determination of chlorate in bleach liquors.

| | Chlorate, mg/L | |
|-------------------------|----------------|-----|
| | Iodometry | IC |
| C _D influent | N.D. | 16 |
| C _D effluent | 49 | 66 |
| D ₁ influent | 331 | 260 |
| D ₁ effluent | 307 | 294 |
| D ₂ influent | 50 | 52 |
| D ₂ effluent | 78 | 93 |

N.D. = none detected.

Table VII. Recovery of chlorite and chlorate added to a chlorine dioxide liquor.

| | Original, ppm | Added, ppm | Expected, ^a ppm | Found, ^b ppm | Recovery, % |
|----------|-------------------|---------------|-------------------------------|----------------------------|----------------|
| Chlorite | N.D. ^c | 1.00 | 0.50 | 0.495 | 99 |
| Chlorate | 1.18 | 1.00 | 1.09 | 1.06 | 97 |

^aSpiked sample prepared by mixing 1 part spiking standard plus 1 part diluted ClO₂ liquor.

^bMean of six replicate determinations.

^cNone detected.

Table VIII. Recovery of oxalate added to bleaching effluents.

| Sample | Original, ppm | Added, ppm | Total Found, ppm | Recovery, % |
|------------------------|---------------|------------|------------------|-------------|
| C Stage, Diluted 1:10 | 0.20 | 1.0 | 1.20 | 100 |
| | 0.20 | 1.0 | 1.20 | 100 |
| | 0.20 | 2.0 | 2.15 | 98 |
| | 0.20 | 2.0 | 2.15 | 98 |
| D Stage, Diluted 1:100 | 0.20 | 2.0 | 2.19 | 99 |
| | 0.20 | 2.0 | 2.10 | 95 |
| | 0.20 | 3.0 | 3.20 | 100 |
| | 0.20 | 3.0 | 3.30 | 103 |

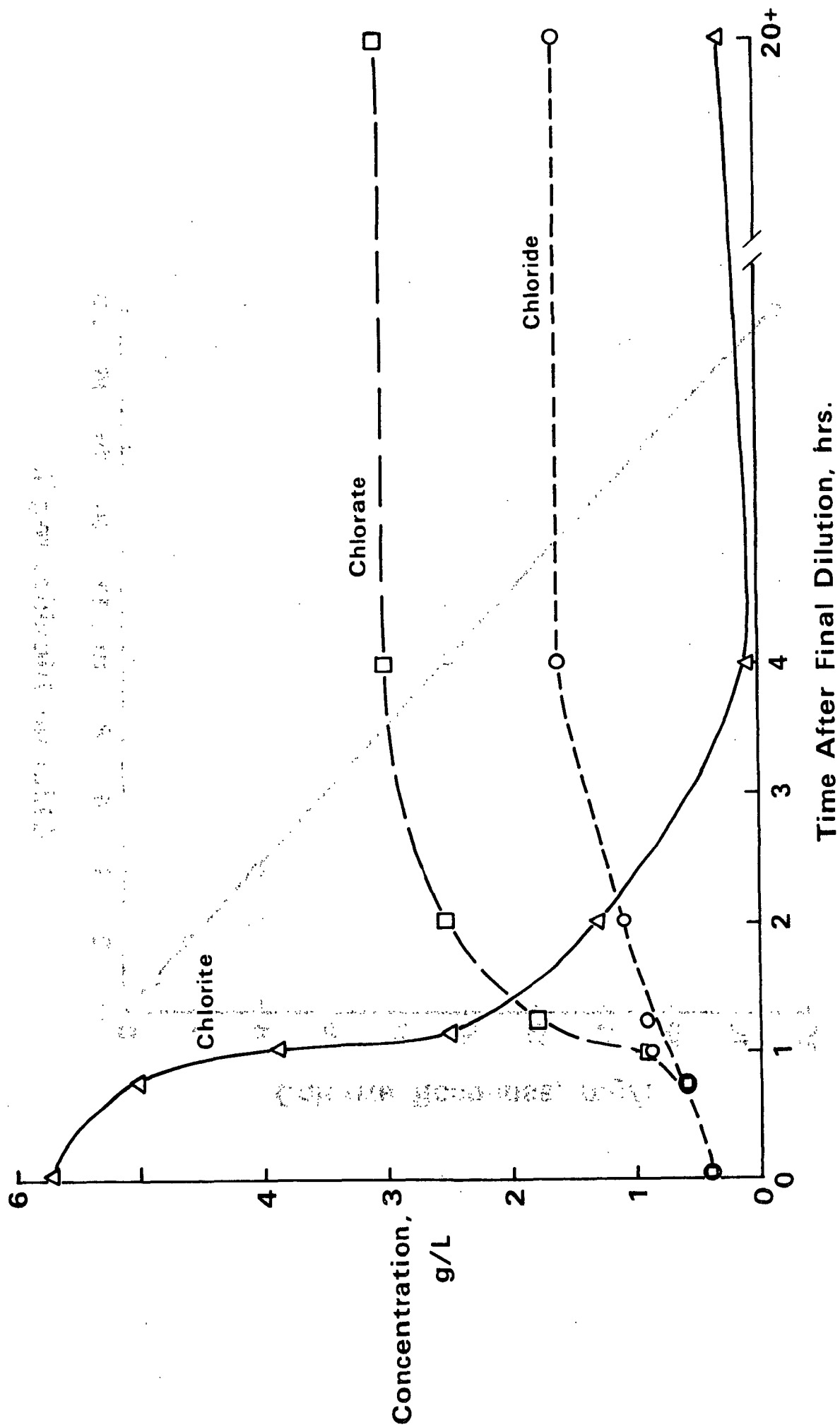


Figure 1. Ions determined in diluted chlorine dioxide liquor injected into the ion chromatograph.

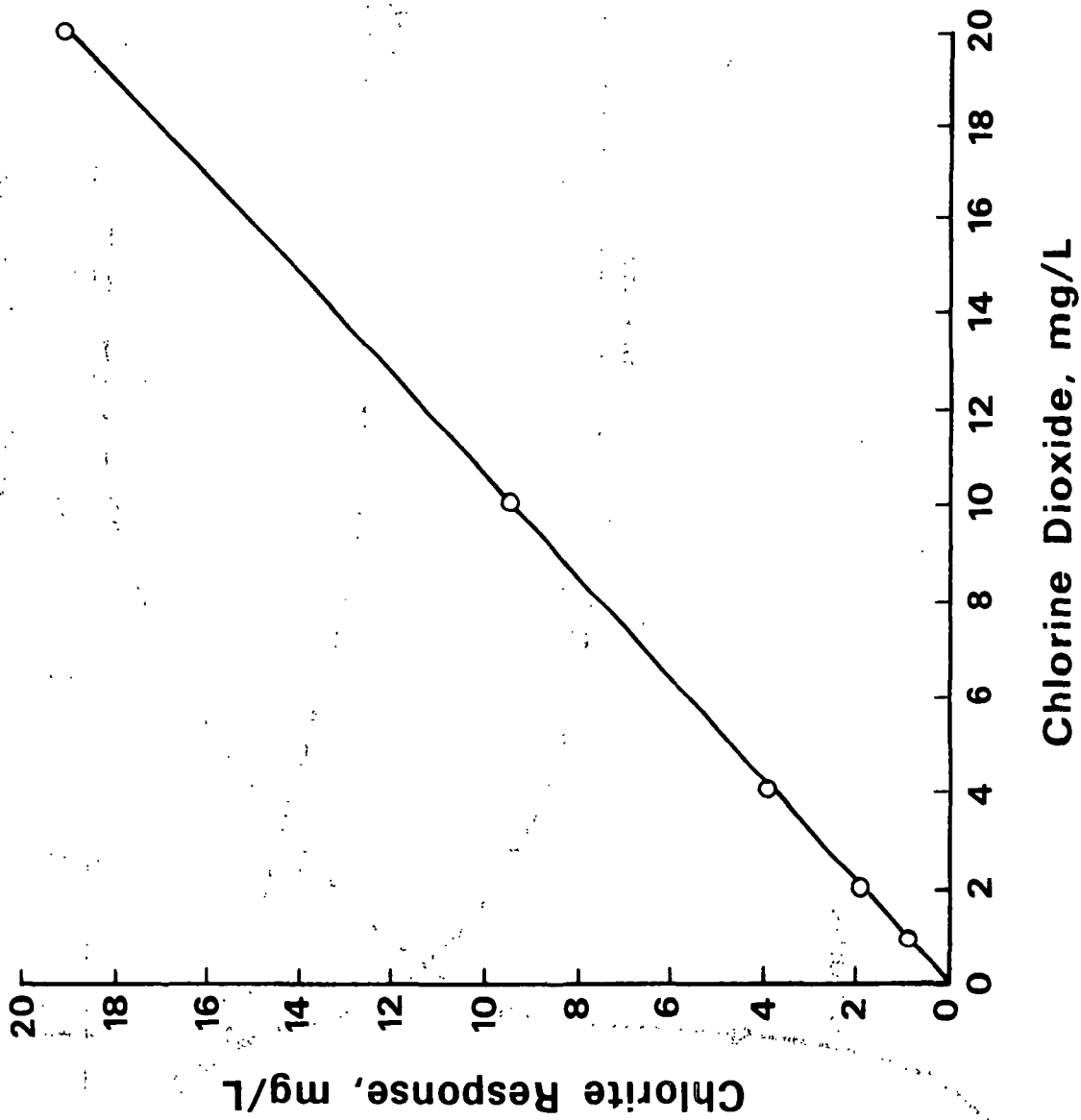


Figure 2. Chlorite response from injected chlorine dioxide solutions.