

STATE OF FLORIDA  
DEPARTMENT OF ENVIRONMENTAL REGULATION

TWIN TOWERS OFFICE BUILDING  
2600 BLAIR STONE ROAD  
TALLAHASSEE, FLORIDA 32399-2400



BOB MARTINEZ  
GOVERNOR  
DALE TWACHTMANN  
SECRETARY

April 10, 1987

Mr. David T. Arceneaux  
Environmental Control Supervisor  
Champion International Corporation  
P.O. Box 87  
Cantonment, Florida 32533-0087

Dear Mr. Arceneaux:

Re: Construction Permits Nos. AC 17-111195, -113551, -113552  
and -113553

The department is in receipt of your letter with attachments dated March 24, 1987, which requested an extension of the expiration date for the above referenced permits. Also requested was acceptability of an alternate test method for chlorine and chlorine dioxide specified in AC 17-113551. Based on a review of these requests, the following shall be changed and added:

A. Expiration Date:

From: July 1, 1987  
To: October 31, 1987

B. AC 17-113551

The proposal to use the alternate test method described in your submittal to test for chlorine and chlorine dioxide to show compliance with the emission limits is acceptable.

Attachment to be Incorporated:

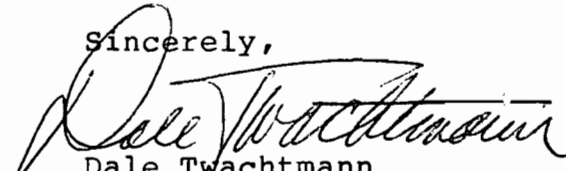
Affected Permits: AC 17-111195, -113551 and -113553  
7. Mr. David Arceneaux's letter and attachments dated 3/24/87.

Affected Permit: AC 17-113552  
8. Mr. David Arceneaux's letter and attachments dated 3/24/87.

Mr. David T. Arceneaux  
Page Two  
April 10, 1987

This letter must be attached to your construction permits  
Nos. AC 17-111195, -113551, -113552 and -113553, and shall become  
a part of those permits.

Sincerely,



Dale Twachtmann  
Secretary

DT/ks

cc: E. Middleswart  
J. Costas, Esq.

P.O. Box 87  
Cantonment, Florida 32533-0087  
904 968-2121

3-27-87  
Cantonment, FL

DER  
MAR 30 1987  
BAQM



March 24, 1987

Mr. C. H. Fancy, P.E.  
Bureau of Air Quality Management  
State of Florida  
DEPARTMENT OF ENVIRONMENTAL REGULATION  
Twin Towers Office Building  
2600 Blair Stone Road  
Tallahassee, Florida 32301-8241

Dear Mr. Fancy:

On February 11, 1986, Champion was granted air quality construction permits NOS: AC 17-111195, AC 17-113551, AC 17-113552, and AC 17-113553 as part of the Pensacola Conversion Project. At the time of application, Champion expected to have all construction complete by December, 1986, and to be in full operation by January, 1987. This schedule would then allow adequate time for compliance testing at the required full production rates.

Longer than expected construction and start-up problems with the paper machine have resulted in a delay in completing the required compliance testing. It has only been during the past few days that the bleach plants have operated at consistent production levels. Champion, therefore, requests an extension of the construction permits to October 1, 1987. This will allow three additional months to complete compliance testing and submit applications for operating permits.

In addition, Champion would like to request the approval to use an alternate test for chlorine and chlorine dioxide testing for compliance. The test method specified in Specific Condition 8 and 9 of Permit AC 17-113551 is the CPPA Standard Testing Method J.14P. This test is directly applicable only to very high concentration gas streams and is primarily used as a process control method. The test method we would like to use is one developed by NCASI, and is very similar to the CPPA method, differing in the sample volume and the addition of a buffer to the potassium iodide. A paper describing the NCASI method will be published in an upcoming issue to TAPPI JOURNAL, and will also be the subject of a NCASI technical bulletin. A copy of the TAPPI JOURNAL article is attached along with a copy of CPPA Method J.14P.

Mr. C. H. Fancy  
March 24, 1987  
Page 2

If you or your staff have any questions concerning these requests, please contact me at the Pensacola Mill.

Sincerely,



David T. Arceneaux  
Environmental Control Supervisor

DTA/dj  
Attachment

cc: Mr. Thomas W. Moody, FDER, Pensacola

## CHLORINE DIOXIDE PLANT ANALYSES

### SCOPE

Chlorine dioxide is widely used in the pulp and paper industry as a bleaching agent. It is manufactured as a gas on site from sodium chlorate in a strongly acidic solution by reduction with sulphur dioxide, methanol, hydrochloric acid or alkali metal chloride. The chlorine dioxide gas is stripped from the solution with air and dissolved in water for storage and use.

The following methods cover all the necessary tests for a chlorine dioxide plant regardless of the manufacturing process used.

1. Generator Feed Solution Concentrations
  - a) Chlorate
  - b) Chloride
2. Generator Liquor Concentrations
  - a) Chlorate
  - b) Acid and chloride
  - c) Chlorine dioxide and chlorine
  - d) Catalysts
3. Generator Gas Volume and Chlorine Dioxide Concentrations
4. Chlorine Dioxide Solution Concentrations
  - a) Chlorine dioxide and chlorine
  - b) Hydrochloric and sulphuric acid

### REAGENTS

1. **Sodium Hydroxide, 10 %.** Dissolve 100 g of reagent grade NaOH pellets in 1000 mL of distilled water.
2. **Sodium Hydroxide, 0.50 M.** Dissolve  $20.0 \pm 0.1$  g of reagent grade NaOH pellets in 1000 mL of distilled water. Standardize against reagent grade potassium biphthalate ( $C_6H_4(COOH)COOK$ ) to the nearest 0.01 M.
3. **Sodium Hydroxide, 0.10 M.** Dissolve  $4.0 \pm 0.1$  g of reagent grade NaOH pellets in 1000 mL of distilled water. Standardize against reagent grade potassium biphthalate to the nearest 0.01 M.
4. **Sodium Bromide, 10 %.** Dissolve 100 g reagent grade NaBr in 1000 mL of distilled water.
5. **Potassium Dichromate, 0.0167 M.** Dissolve 4.903 g of dry reagent grade  $K_2Cr_2O_7$  in 1000 mL of distilled water.
6. **Sodium Thiosulphate, 0.10 M.** Dissolve  $25.0 \pm 0.1$  g of reagent grade  $Na_2S_2O_3 \cdot 5H_2O$  in freshly boiled and cooled distilled water, add 0.1 g of sodium bicarbonate and make up to 1000 mL. Standardize against 25.0 mL of

standard 0.0167 M potassium dichromate solution, to which has been added 10 mL of 10 % potassium iodide and 10 mL of 1 M sulphuric acid, using starch indicator.

7. **Silver Nitrate, 0.02 M.** Dissolve 3.398 g of dry reagent grade  $AgNO_3$  crystals in 1000 mL of distilled water.
8. **Sulphuric Acid, 1 M.** Pour 55 mL of reagent grade 96 %  $H_2SO_4$  carefully into 500 mL of distilled water and make up to one litre. (Caution: do not pour water into acid).
9. **Sodium Arsenite, 0.0025 M.** Dissolve 0.2473 g of dry reagent grade arsenious oxide,  $As_2O_3$ , in 20 mL of 1 M sodium hydroxide solution. Add 1 M sulphuric or hydrochloric acid to the solution until neutral or slightly acidic. Transfer to a 500 mL volumetric flask and make up to the mark with distilled water.
10. **Sodium Bicarbonate, dry reagent grade  $NaHCO_3$ .**
11. **Hydrochloric Acid, conc. HCl.**
12. **Acetic Acid, 3 %.** Pour 30 mL glacial  $CH_3COOH$  into 500 mL of distilled water and make up to 1000 mL.
13. **Phenolphthalein, 0.1 %.** Dissolve 0.1 g of phenolphthalein into 60 mL of ethanol and make up to 100 mL with distilled water.
14. **Starch Indicator, 0.5 %.** Make 5 g of soluble reagent grade starch into a smooth paste with water. Pour it into a litre of boiling water. Make up fresh each time since it deteriorates on standing.
15. **Potassium Chromate, 5 %.** Dissolve 5 g of reagent grade  $K_2CrO_4$  in 100 mL of distilled water.
16. **Potassium Iodide, 10 %.** Dissolve 100 g of reagent grade KI in 100 mL of distilled water and make up to 1000 mL.

### APPARATUS

Each procedure is accompanied by a diagram of the apparatus set-up necessary to perform the test. The apparatus can be assembled from standard lab glassware.

## 1. GENERATOR FEED SOLUTION

### SAMPLING

Pipette 10 mL of feed solution into a 500 mL volumetric flask and dilute to volume with distilled water. Mix thoroughly.

be adjusted to prevent excessive bubbling of the sample into the top sections of the apparatus. Any liberated gases are absorbed in 200 mL of 10 % KI.

When all of the colour has disappeared from the sample, transfer the vacuum line from the stripper to the suction flask and draw the sample into the flask. Wash down the walls of the stripper thoroughly, passing at least 100 mL of distilled water through the fritted disc.

Titrate the sample with 0.5 M NaOH using phenolphthalein indicator. Call this titration "Na".

Add a drop or two of 3 % acetic acid to decolorize the solution and then add 2 mL of 5 % potassium chromate. Titrate with 0.020 M AgNO<sub>3</sub> to the first appearance of a permanent reddish tinge. Call this titration "Ag".

### c) Chlorine Dioxide and Chlorine Concentration

Transfer the contents of the KI trap quantitatively to a 1000 mL flask and titrate the solution to a colourless end point with 0.10 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. DO NOT USE STARCH and do not refill the burette. Call this titration "N".

Add 10 mL of 1 M H<sub>2</sub>SO<sub>4</sub> and continue the titration with 0.10 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> using starch indicator near the end point. Call this titration "T". Let "A" = T-N (Note 7, 8, 9, 10).

### CALCULATIONS

$$\text{Chlorate, Molarity} = \frac{T_1 - T_2}{15 \times \text{Aliquot, mL}}$$

$$\text{Chlorate, as NaClO}_3, \text{ g/L} = 106.5 \times \text{Molarity}$$

$$\text{Acid, as HCl Molarity} = \frac{\text{Na}}{5}$$

$$\text{Chloride, Molarity} = \frac{\text{Ag}}{125}$$

$$\text{Chloride, as NaCl g/L} = 58.5 \times \text{Molarity}$$

$$\text{Chlorine Dioxide, g/L} = 0.675 \times A$$

$$\text{Chlorine, g/L} = 1.42 \times (T - 1.25 A)$$

### d) Catalyst Levels

Certain chlorine dioxide manufacturing processes require the use of catalysts in order to reach peak efficiency. Because of the variety of catalysts in use it is recommended that the manufacturers' instructions for the selection of proper testing conditions be carefully followed.

## 3. GENERATOR GAS VOLUME AND CHLORINE DIOXIDE

### SAMPLING

The sample is obtained by drawing gas from the line

between the generator and absorption tower into the gas pipette shown in Fig. 3.

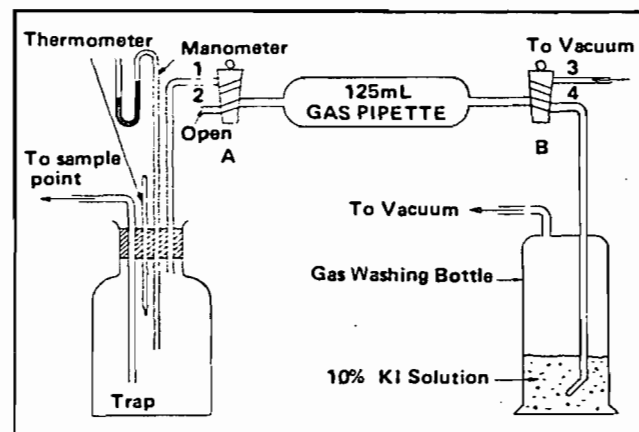


Figure 3. Gas Sampling Apparatus

The gas pipette shall be calibrated by weighing to the nearest 10 mg when completely filled with water at a known temperature. Drain the pipette and rinse well with acetone. Draw air through the pipette by attaching it to a source of vacuum to dry, and reweigh. The volume is then calculated as follows:

$$\text{Volume, mL} = \frac{W_w - W_d}{d_t}$$

Where:

$W_w$  = Weight when filled with water, g

$W_d$  = Weight when dry, g

$d_t$  = Density of water at the temperature used, g/mL

### PROCEDURE

Add enough 10 % KI solution to the gas washing bottle to cover the bubbler to a depth of about 4 cm. Open stopcocks A and B so that gas is drawn from the sample line through the pipette leaving via line 3, and allow to run for about 5 min. Close stopcock B, record temperature and pressure, then close stopcock A.

Open stopcock B so that vacuum is applied to the pipette via the gas washing bottle, then open stopcock A so that air is drawn in through line 2. Do not allow the bubbling to become too violent in the gas washing bottle. Allow about 5 min for the sample to be thoroughly drawn out of the pipette.

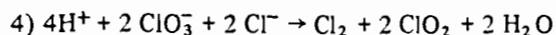
Remove the gas washing bottle and transfer its contents quantitatively into a 1000 mL flask. Titrate the iodine released with 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to a colourless end point. Do not use starch and do not refill the burette. Call this titration "N".

Add 10 mL of 1 M H<sub>2</sub>SO<sub>4</sub> and continue the titration using starch indicator near the end point. Call this titration "T". Let "A" = T - N (Notes 10, 11).

The quantities of reagents and sequence of addition remain exactly as above. The calculation is also unchanged.

3. Care must be taken that a vacuum does not develop, otherwise the contents of the trap may be sucked back into the flask. This can be prevented by opening the dropping funnel stopcock briefly, taking care to avoid any loss of gases.

4. Since the reaction:

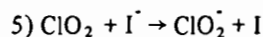


will proceed after the sample is removed from the reactor, it is essential that the sample be diluted promptly.

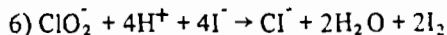
5. Use 5.0 mL where the chlorate concentration is expected to be above 0.10 Molar, and 10 mL where the concentration is expected to be below 0.10 Molar.

6. The chlorate concentration is determined in the same manner as for the chlorate feed. However, since the generator liquor contains dissolved chlorine dioxide and chlorine, this must be determined separately and a correction made.

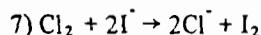
7. The analysis of chlorine dioxide in mixtures containing chlorine is based on the observation that in neutral solutions the reduction of  $\text{ClO}_2$  by iodide proceeds as follows:



then on acidification the reduction is completed:



Chlorine in either neutral or acid solution is rapidly reduced by iodide:



Therefore, by absorbing the mixture in neutral KI solution, reactions (5) and (7) occur and the titration with thiosulphate represents all of the chlorine plus 1/5 of the oxidizing power of chlorine dioxide. On acidification of the mixture, reaction (6) occurs and the subsequent titration represents 4/5 of the oxidizing power of the chlorine dioxide present.

8. As with the feed solution, the use of the dropping funnel and trap assembly may be eliminated from the chlorate determination for routine testing with only slight sacrifice of accuracy. A solid rubber stopper is substituted. Reagent quantities, sequences of addition and calculations remain the same.

9. The acidity and chloride determinations may be simplified for routine testing by substituting the stripping apparatus shown in Fig. 4. The sample is introduced into the flask and stripped to complete disappearance of the yellow colour by drawing air through the capillary tube. Subsequent dilution, titrations and calculations remain the same. Care must be taken to ensure that the capillary tube is close to the bottom of the flask and that the bottom of the stopper and the capillary are rinsed with water into the flask.

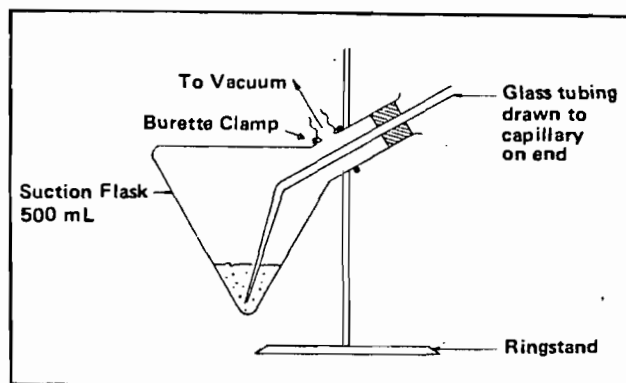


Figure 4. Stripping Apparatus

10. The total gas ( $\text{ClO}_2 + \text{Cl}_2$ ) in the generator liquor may be calculated from the  $\text{Na}_2\text{S}_2\text{O}_3$  titration  $T_2$  obtained in the chlorate analysis as follows:

$$\text{Total gas (as } \text{ClO}_2) \text{ g/L} = 0.54 T_2$$

11. This test is necessary for the processes using chloride or methanol as the reducing agent.

12. For purposes of routine control the manometer and the thermometer are often eliminated from the apparatus. It is then assumed in the calculation that  $V_S = V_O$ .

13. When working with neutral solutions,  $\text{ClO}_2$  and  $\text{Cl}_2$  can be determined using a neutral and acid titration as described under the determination of these constituents in Generator Liquor. Chlorine dioxide solution produced in the plant invariably contains some acidity which interferes with the neutral titration. For this reason the  $\text{Cl}_2$  content is determined accurately and independently using sodium arsenite with the system buffered to a pH at which only the chlorine is titrated.

14. For convenience, the chlorine dioxide content in mixtures with chlorine is usually expressed as Gram Atom percent chlorine dioxide, defined as:

$$\text{GA \%} = \left[ \frac{\text{ClO}_2}{\text{ClO}_2 + \text{Cl}_2} \right] \times 100$$

where  $\text{ClO}_2$  represents moles of  $\text{ClO}_2$  in the mixture and  $\text{Cl}$  represents atoms of chlorine in the mixture. (This is not to imply that the chlorine is present as atomic chlorine).

## REFERENCES

1. Electric Reduction Company of Canada, Limited, Technical Service Bulletin, T-6-1, October 1961.
2. Allied Chemical Corporation, Solvay Process Division, Technical Service Report No. 9, 55 R, January 1958.

STUDIES OF MEASUREMENT METHODS FOR CHLORINE AND CHLORINE DIOXIDE  
EMISSIONS FROM PULP BLEACH PLANT OPERATIONS

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ABSTRACT

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Methods for determining chlorine and chlorine dioxide emissions from pulp bleaching facilities are employed in control device efficiency studies and in determining compliance with non-criteria pollutant regulations. The dual pH potassium iodide impinger capture method was investigated in laboratory and field studies, and an optimized method was developed and tested.

An instrumental method for continually measuring total oxidants of chlorine and chlorine dioxide was developed via modification of a commercial electrochemical chlorine monitor. Comparison testing with the dual pH potassium iodide method demonstrated the utility of the instrumental method for survey purposes.

INTRODUCTION

Non-criteria pollutant regulations are being established by state regulatory agencies for the purpose of regulating ambient concentrations of substances released to the atmosphere by industrial operations. These substances are typically chemicals which are recognized as having adverse health effects at higher concentrations, and are usually limited in workplace atmospheres by regulation (Occupational Safety and Health Act Permissible Exposure Levels - PELs) or by recommendation (American Conference of Governmental Industrial Hygienists Threshold Limit Values - TLVs). The emerging state regulations generally specify a maximum ambient concentration of a regulated substance as a fraction of a workplace limit (e.g., 1/50 of the TLV), and mathematical source emission modelling is employed to calculate the maximum allowable quantity of that substance which may be emitted.

Because of their ability to produce respiratory tract and eye irritation (1), chlorine ( $Cl_2$ ) and chlorine dioxide ( $ClO_2$ ) are assigned 8-hour TLVs of 1 and 0.1 ppm, respectively. They are included in many state non-criteria pollutant regulations, and because of their use in the bleaching of pulp, their atmospheric emissions are of concern to the pulp and paper industry.



The various pulp bleaching sequences involve several stages of bleaching and extraction of solubilized organic material. Each stage typically includes reaction with bleaching chemical or caustic extraction solution in a retention tower, washing of the product pulp on a rotary vacuum drum washer prior to subsequent operations, and removal of the filtrate via a seal tank. The vents to the atmosphere from the towers, washer hoods, and seal tanks, may or may not be fan driven, ducted together to common vents, or ducted to gas-liquid scrubbers for emission control. Because chlorine dioxide is always generated on-site, there is a  $\text{ClO}_2$  generator vent which may be a source of emissions of  $\text{Cl}_2$  and  $\text{ClO}_2$ , and which may or may not be ducted to a gas-liquid scrubbing device for emission control.

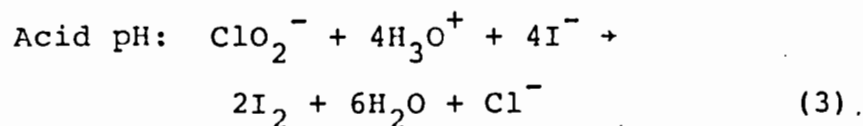
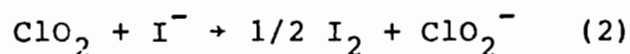
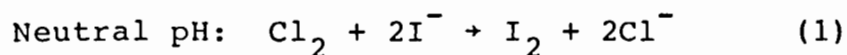
The pulp and paper industry in the United States is in various stages of reducing chlorine and chlorine dioxide atmospheric emissions. In those circumstances where non-criteria pollutant regulations do not impose restrictions on  $\text{Cl}_2$  and  $\text{ClO}_2$  release, emission control may be undertaken primarily for workplace considerations, if necessary. This control may take the form of reduction in vat residuals of aqueous  $\text{Cl}_2$  and  $\text{ClO}_2$  (where this is possible), it may involve the use of tall vent stacks, or it may include gas-liquid scrubbing. Scrubbers may utilize sodium hydroxide, cold water, extraction-stage filtrate, weak wash, or aqueous sulfur dioxide solutions. (2,3)

NCASI is conducting a study of bleach plant emissions of  $\text{Cl}_2$  and  $\text{ClO}_2$ , in order to (a) document uncontrolled emission levels, (b) examine the relationship of process operation variables to emission levels, and (c) determine the effectiveness of in place control devices. This activity has required the examination of methods for measuring chlorine and chlorine dioxide emissions.

#### ANALYSIS METHODS DEVELOPMENT

##### Grab Sampling Method

Background. Gas phase chlorine and chlorine dioxide may be captured in neutral potassium iodide solution in impingers in an extractive sampling system. Because of the dependence of the reactivity of chlorine dioxide with iodide upon solution pH, the post-sampling determination of iodine formed at neutral and acidic pH permits the quantitative measurement of both chlorine and chlorine dioxide:



Standard practice within the industry has been to use two impingers in series, each containing 2 percent potassium iodide, to sample at a rate of from 1 to 5 L/min, and to collect a sample over a period of from 5 to 30 minutes (using shorter sampling times if the color in the second impinger turns from straw yellow to orange). After sampling, the contents of the impingers are combined and titrated with 0.1 N sodium thiosulfate solution. After the first endpoint, the solution is acidified with sulfuric acid solution, and the titration is continued to the second endpoint. Algebraic manipulation of equations (1) through (3) permits the calculation of gas phase concentrations of  $\text{Cl}_2$  and  $\text{ClO}_2$  on the basis of the neutral and total acid titration equivalents.

Method Testing and Modification. The evaluation of this method included study of the following: the effect of capture solution pH, and the necessity for capture solution pH buffering; the precision of the optimized method; the effect of potassium iodide concentrations; and the effect of capture solution temperature.

Capture Solution pH. Although reaction (2) above is for calculation purposes regarded as the full extent of the reaction of  $\text{ClO}_2$  with iodide at other than acidic pH values, there is a dependence of the rate of reaction of chlorite with iodide on solution pH, such that at slightly acidic pH values the reaction can proceed to an extent appreciable enough to cause (1) deviation from the 5:1 (total acid:neutral) ratio of equivalents of iodine expected upon titration of a capture solution obtained from  $\text{ClO}_2$  only, and (2) an erroneously high calculated concentration of chlorine. Because drawing a bleach plant vent sample through an unbuffered potassium iodide solution may lower the pH of the solution, this phenomenon was investigated.

The sampling equipment described in the appendix was employed to sample gaseous emissions from a chlorine dioxide bleaching tower vent. A manifold was constructed from FEP and PFA Teflon<sup>R</sup> which permitted the collection of six gas samples simultaneously. Twenty mL of 2 percent unbuffered potassium iodide (KI) solution were placed in each first impinger, and a gas sample was drawn at ca. 500 mL/min through each impinger. The pH of the solutions was measured electrometrically. Twelve samples (two sets) were taken, representing a sampling time of from 5 seconds to 4 minutes. The solution pH dropped from an initial value of 6.7 to 6.1, at 30 seconds, then returned to ca. 6.6 at 4 minutes. This was taken as evidence that the pH of unbuffered KI solution could drop during sampling to a level low enough to permit the reaction of chlorite with iodide. This was confirmed in subsequent testing.

A sample was withdrawn from a chlorine dioxide bleaching tower vent into a 30 L Tedlar<sup>R</sup> gas bag (Pollution Measurement Corporation, Oak Park, IL). To determine that the chlorine and chlorine dioxide were stable with time, analyses of the bag contents by the method of the appendix were carried out. Over a period of

one hour, the measured chlorine and chlorine dioxide varied randomly with an average of 66 and 148 ppm, with standard deviations of 12 and 40 ppm, respectively, for five measurements. Another sample was placed in a Tedlar bag, and using the method of the appendix with 1 minute sampling and potassium iodide solutions buffered with borate and phosphate buffers, the data of Figure 1 were obtained. (The  $\text{ClO}_2$  concentration remained constant as a function of pH, averaging 1490 ppm with a standard deviation of 43 ppm, except for pH 4.3 and 5.3 tests, where the  $\text{ClO}_2$  concentration decreased.)

Insert  
Fig. 1  
here

Two experiments were conducted to test the hypothesis that the concentration of chlorine formed by conversion of captured chlorite depends upon the initial concentration of  $\text{ClO}_2$ , as well as upon the pH of the capture solution. In the laboratory, dynamic  $\text{ClO}_2$  test gases containing very low concentrations of chlorine were prepared by passing air through a room temperature solution of aqueous  $\text{ClO}_2$  (from a pulp bleach plant), then passing this gas through an impinger containing aqueous 0.1% sulfamic acid to remove chlorine, then blending this gas with humidified air to produce the desired concentration of  $\text{ClO}_2$  (determined by analysis using the method of the appendix). The results of tests at 500 ppm and at 4000 ppm  $\text{ClO}_2$ , shown in Figure 2, clearly illustrate the effect of pH and of  $\text{ClO}_2$  concentration upon artifact chlorine formation.

Insert  
Fig. 2  
here

Experiments were also conducted at a pulp bleach plant in which a sampling manifold, fabricated from FEP and PFA Teflon, was employed, which permitted collection of four samples simultaneously, employing trains as described in the appendix. Each impinger pair contained two percent KI solution, buffered essentially as per the appendix formula, but buffered at pH values of 6.4, 7.5, 8.5, and 9.5. Samples were withdrawn from a chlorine dioxide bleaching tower vent over a period of time such that normal variations in bleaching conditions produced variations in chlorine and chlorine dioxide gaseous emission concentrations. The data of Figure 3 were collected, and these data support the hypothesis.

Insert  
Fig. 3  
here

In order to demonstrate the combined effect on recovery and precision of buffered versus unbuffered sampling, an experiment was performed in which a Tedlar bag containing a gas sample drawn from a chlorine dioxide bleaching tower vent was sampled via the method of the appendix, using a manifold which permitted collection of six simultaneous samples. The experiment was conducted with three sets of impingers containing unbuffered 2 percent KI, and three sets containing pH 7.5 buffered 2 percent KI, and was repeated once to obtain 12 tests. Results are indicated in Figure 4. The average concentrations of chlorine and chlorine dioxide obtained using the unbuffered system were 354 and 1400 ppm, with standard deviations of 63 and 71 ppm, respectively. The average  $\text{Cl}_2$  and  $\text{ClO}_2$  concentrations obtained employing buffered sampling were 228 and 1440 ppm, with standard deviations of 25 and 22 ppm, respectively.

Insert  
Fig. 4  
here

On the basis of the information obtained in these experiments, it was concluded that use of an iodide solution buffered between pH 7.0 and 7.5 would minimize the formation of "phantom" chlorine due apparently to the reaction of chlorite with iodide at low pH values, but would not cause losses in apparently valid finite chlorine concentrations. Such losses appear at high pH values (e.g., greater than pH 8), and may be due to the reaction of iodine with base to form hypoiodite. The selection of pH 7.0 as the buffer pH of choice was based upon the apparent equivalence of recoveries at pH 7.0 and at 7.5, plus the knowledge that the buffering capacity of a given concentration of a dihydrogen phosphate buffer is greater at pH 7.0 than at pH 7.5.

Precision. Laboratory generated mixtures of chlorine and chlorine dioxide at three different analyte concentrations were analyzed by testing six simultaneously withdrawn samples from each mixture by the method of the appendix. Results are indicated in Figure 5. For the range of concentrations examined, relative standard deviation values were all less than 6 percent.

Insert  
Fig. 5 >  
here

Effect of Potassium Iodide Concentration. Although the concentration of potassium iodide (KI) to be employed in impinger sampling of gaseous oxidants is generally specified as 2%, sampling of high concentrations of gaseous  $\text{Cl}_2$  and  $\text{ClO}_2$  with midget impingers can deplete 2% KI with as little as 15 minutes of sampling at 200 mL/min. Because of this, higher concentrations of KI have been proposed for use in bleach plant vent sampling. Two sets of six simultaneous samples were taken at a pulp bleach plant from a combined EHD seal tank vent. In each set, three of the samples were taken in 10% KI and three were taken in 2% KI. Both capture solutions were buffered at a pH of 7.0. In set one the average measured  $\text{Cl}_2$  was 3.4% higher, and the average measured  $\text{ClO}_2$  was 7.7% lower<sup>2</sup> in the 10% KI than in the 2% KI. In set two the average  $\text{Cl}_2$  was 4.0% higher, and the average  $\text{ClO}_2$  was 7.9% lower in the 10% KI capture solution. A laboratory experiment was designed to elucidate this effect.

A chlorine dioxide test gas at ca. 210 ppm was generated and scrubbed of chlorine in the manner described above. Two sets of six simultaneous samples were taken, with each set consisting of a 2%, 5%, 7%, 10%, 12%, and a 15% solution of buffered KI. Figure 6 illustrates the results of that experiment, and indicates that chlorine and chlorine dioxide should be sampled with KI capture solutions of less than 5% strength.

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Fig. 6 >  
here

Effect of Temperature. Because some field use of potassium iodide impinger sampling has been conducted with the impingers immersed in a water ice bath, an experiment was conducted to identify any advantage to reduced temperature sampling. In the laboratory, two sets of six simultaneous samples were taken from a Tedlar bag containing roughly equal concentrations of chlorine and chlorine dioxide. In each set, three impinger pairs were immersed in ice and three pairs were used at ambient temperature (approximately 24°C). Analyses were performed by the method of

On the basis of the information obtained in these experiments, it was concluded that use of an iodide solution buffered between pH 7.0 and 7.5 would minimize the formation of "phantom" chlorine due apparently to the reaction of chlorite with iodide at low pH values, but would not cause losses in apparently valid finite chlorine concentrations. Such losses appear at high pH values (e.g., greater than pH 8), and may be due to the reaction of iodine with base to form hypoiodite. The selection of pH 7.0 as the buffer pH of choice was based upon the apparent equivalence of recoveries at pH 7.0 and at 7.5, plus the knowledge that the buffering capacity of a given concentration of a dihydrogen phosphate buffer is greater at pH 7.0 than at pH 7.5.

Precision. Laboratory generated mixtures of chlorine and chlorine dioxide at three different analyte concentrations were analyzed by testing six simultaneously withdrawn samples from each mixture by the method of the appendix. Results are indicated in Figure 5. For the range of concentrations examined, relative standard deviation values were all less than 6 percent.

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Fig. 5  
here

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the appendix. The results, indicated in Table 1, show that iced 2% buffered KI is little, if any, more effective at capturing chlorine and chlorine dioxide than is 2% buffered KI maintained at 24°C.

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Table 1  
here >

#### Instrumental Analysis Method

Background. Field testing employing the method of the appendix indicated that several bleach plant sources were at some mills highly variable in the concentrations of chlorine and chlorine dioxide emitted. This prompted consideration of the use of continuous monitoring devices for high concentrations (as opposed to workplace level concentrations) of chlorine and chlorine dioxide. Of the several devices available commercially, two were chosen for study. An Anacon (Anacon, Marlborough, MA) electrochemical diffusion based workplace chlorine monitor was fitted by the manufacturer with a Teflon barrier around the sensing electrode, which caused the response to chlorine to be reduced such that high concentrations of chlorine could be measured. (This was designated a 0 to 500 ppm probe by Anacon.) Laboratory testing of this instrument with gases analyzed by the method of the appendix showed a linear response to chlorine from 0 to 500 ppm, but very low response to chlorine dioxide.

A Delta Model 964 (Delta/Xertex Corporation, Hauppauge, NY) diffusion based electrochemical high concentration chlorine monitor with a Delta-supplied nominal 0.25 mm (0.010 in) thickness Silastic (Dow Chemical, Midland, Michigan) membrane separating the electrochemical sensor from the test gas was tested in the laboratory for response to chlorine and chlorine dioxide. The data of Figure 7 indicate that the response to  $Cl_2$  was linear to ca. 400 ppm, and the response to  $ClO_2$  was linear to ca. 250 ppm. Below 250 ppm, the response ratio of  $Cl_2:ClO_2$  was near 1:1.

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Fig. 7  
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The Delta Model 964 was tested for time of response to changes in chlorine concentrations. The time response of the system to a pulse of 250 ppm chlorine of a duration of two minutes was satisfactory, as indicated in Figure 8. However, a pulse of 250 ppm chlorine of 14 minute duration produced an unusably long fall time, as indicated in Figure 9.

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A modification was made to the Model 964, as diagrammed in Figure 10. Teflon solenoids were configured so that source gas and potassium iodide-scrubbed ambient air could be alternately provided to the Teflon chamber in which the sensor was mounted. A cycle time of 2 minutes on source gas and 4 minutes on air proved satisfactory, as indicated in Figure 11.

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Figs.  
10+11  
here >

In earlier studies of measurement methods for workplace atmosphere chlorine and chlorine dioxide (4,5), NCASI determined that aqueous solutions of sulfamic acid in midget impingers would trap chlorine, but would quantitatively pass chlorine dioxide, at concentrations in the 0.05 to 2 ppm range. This prompted further modification of the Delta Model 964 system, as indicated in

Table 1 Comparison of results of iced and uniced impinger sampling of gas monitors of chlorine and chlorine dioxide

Set 1 (n = 3)		Set 2 (n = 3)	
Iced	Uniced	Iced	Uniced
$\bar{x}$ ClO <sub>2</sub> = 600 ppm RSD = 2.1%	$\bar{x}$ ClO <sub>2</sub> = 594 ppm RSD = 0.74%	$\bar{x}$ ClO <sub>2</sub> = 598 ppm RSD = 1.5%	$\bar{x}$ ClO <sub>2</sub> = 596 ppm RSD = 2.3%
$\bar{x}$ Cl <sub>2</sub> = 720 ppm RSD = 1.0%	$\bar{x}$ Cl <sub>2</sub> = 726 ppm RSD = 1.0%	$\bar{x}$ Cl <sub>2</sub> = 755 ppm RSD = 1.7%	$\bar{x}$ Cl <sub>2</sub> = 755 ppm RSD = 1.7%

Figure 12. By providing to the sensor timed sequential pulses of source gas ( $\text{Cl}_2 + \text{ClO}_2$ ), air, source gas passed through sulfamic acid ( $\text{ClO}_2$  only), and air, the output indicated in general form in Figure 13 was obtained. Testing with mixtures of gaseous  $\text{Cl}_2$  and  $\text{ClO}_2$  produced the recovery results indicated in Table 2.

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Figs 12  
& 13  
here

Table 2 Gas phase  $\text{Cl}_2$  and  $\text{ClO}_2$  measurements, laboratory mixture analysis results, modified Delta 964

True Concentration, ppm		Recovery, Percent	
$\text{Cl}_2$	$\text{ClO}_2$	$\text{Cl}_2$	$\text{ClO}_2$
106	300	78	100
100	298	80	101
107	58	106	132
65	320	86	141

Upon testing with mixtures of chlorine and chlorine dioxide, neither of the configurations of the modified Delta Model 964 systems yields data which are accurate enough for non-criteria pollutant analysis reporting purposes. The equipment has proven very useful, however, in continuous monitoring during field studies of factors influencing  $\text{Cl}_2$  and  $\text{ClO}_2$  emission rates.

#### CONCLUSIONS

The buffered dual pH potassium iodide impinger capture method yields good precision upon analysis of gaseous chlorine and chlorine dioxide mixtures, and buffering at pH 7.0 appears to reduce the chance of obtaining falsely high chlorine concentrations in the presence of high concentrations of chlorine dioxide.

Instrumental methods for continuously measuring gaseous chlorine and chlorine dioxide in bleach plant vents were studied, and modifications made to one commercially available system permitted the observation of short term concentration fluctuations in total  $\text{Cl}_2$  and  $\text{ClO}_2$ . A further modification to provide separate continuous quantitation of  $\text{Cl}_2$  and  $\text{ClO}_2$  proved sufficiently accurate for survey purposes.



## APPENDIX - METHOD FOR MEASURING CHLORINE AND CHLORINE DIOXIDE GASEOUS EMISSIONS

This method is based upon extractive sampling using midget impingers, sampling at a low sampling rate, ca. 200 mL/min. Greater sampling rates may be used with larger impingers.

The sampling train includes a sample probe and withdrawal line which is an appropriate length, e.g., 3 m of 0.64 cm (0.25 in) od FEP Teflon tubing. This is connected at one end via either Galtek (Chaska, MN) 0.64 cm unions or short pieces of silicone tubing to a tapered stem 30 mL capacity midget impinger with 0.64 cm od inlet and outlet tubulatures (Southern Scientific, Micanopy, FL). Two identical impingers are connected in series behind the first. The third impinger contains silica gel as a dessicant, and its outlet tubulature is connected to the flow control/prime mover equipment.

Two methods may be employed for low flow rate sampling flow control. One method utilizes a dessicant column and a critical orifice downstream of the second impinger, followed by a vacuum pump capable of providing ca. 64 cm (25 in) of mercury vacuum. The orifice is calibrated prior to use, the vacuum at which critical flow is achieved is noted, and in use the high vacuum side of the orifice is always maintained at at least 13 cm (5 in) of mercury vacuum greater than this value. The flow rate at the probe tip is measured before and after sampling with a bubble tube flow meter, as impingers or other restrictive devices upstream of the critical orifice will cause the system flow rate to change from the value obtained during calibration with atmospheric pressure at the orifice inlet.

A second means of controlling flow during low flow rate sampling is to utilize EPA Method 25 evacuated sampling tanks to draw the sample and, via pre- and post-sampling pressure measurements, to measure its volume.

The first two impingers each contain 20 mL of potassium iodide (KI) solution, buffered with potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) and sodium hydroxide (NaOH), as follows:

Dissolve 20 g KI in ca. 900 mL deionized water  
Add 50 mL of 1 M  $\text{KH}_2\text{PO}_4$   
Add 30 mL of 1 M NaOH

Measure pH of solution electrometrically and add 1 M NaOH to bring pH to between 6.95 and 7.05.

When sampling, measure the temperature and pressure in the vent being sampled. Assuming critical orifice flow controls, activate the sample draw equipment and measure the sampling flow rate at the probe tip with a bubble tube flow meter. Insert the probe into the sample port and start a stopwatch. End the sampling (stop the watch) after 30 minutes, or after the color in the

second impinger turns from pale yellow to a deeper straw color. After sampling, remove the probe from the vent, and with the probe tip elevated above the impingers, add ca. 5 mL deionized water to the probe so that this drains into the first impinger. Combine the contents of the impingers in a 100 mL beaker, and titrate with sodium thiosulfate solution (0.100 N or less concentrated, depending upon the quantity of iodine being titrated). Record the volume of titrant to the first endpoint ( $T_N$ , mL). Add 5 mL of 10 percent sulfuric acid solution, and continue the titration to the second endpoint. Record the total volume of titrant required to go through the first and to the second endpoint ( $T_A$ , mL).

To calculate moles of chlorine and moles of chlorine dioxide captured employ the formulas:

$$\text{EqI}_2\text{N} = (T_N) (10^{-3}) (\bar{N})$$

$$\text{EqI}_2\text{A} = (T_A) (10^{-3}) (\bar{N})$$

$$\text{ClO}_2 \text{ moles} = 1/4 \text{ EqI}_2\text{A} - 1/4 \text{ EqI}_2\text{N}$$

$$\text{Cl}_2 \text{ moles} = 1/8 (5 \text{ EqI}_2\text{N} - \text{EqI}_2\text{A}),$$

where  $\text{EqI}_2\text{N}$  and  $\text{EqI}_2\text{A}$  are equivalents of iodine determined in the neutral and (total) acid titrations, respectively, and  $\bar{N}$  is the normality of the sodium thiosulfate solution. Calculate gas phase concentrations of  $\text{ClO}_2$  and  $\text{Cl}_2$  employing standard EPA calculations. Assume gas phase water saturation in most vents.

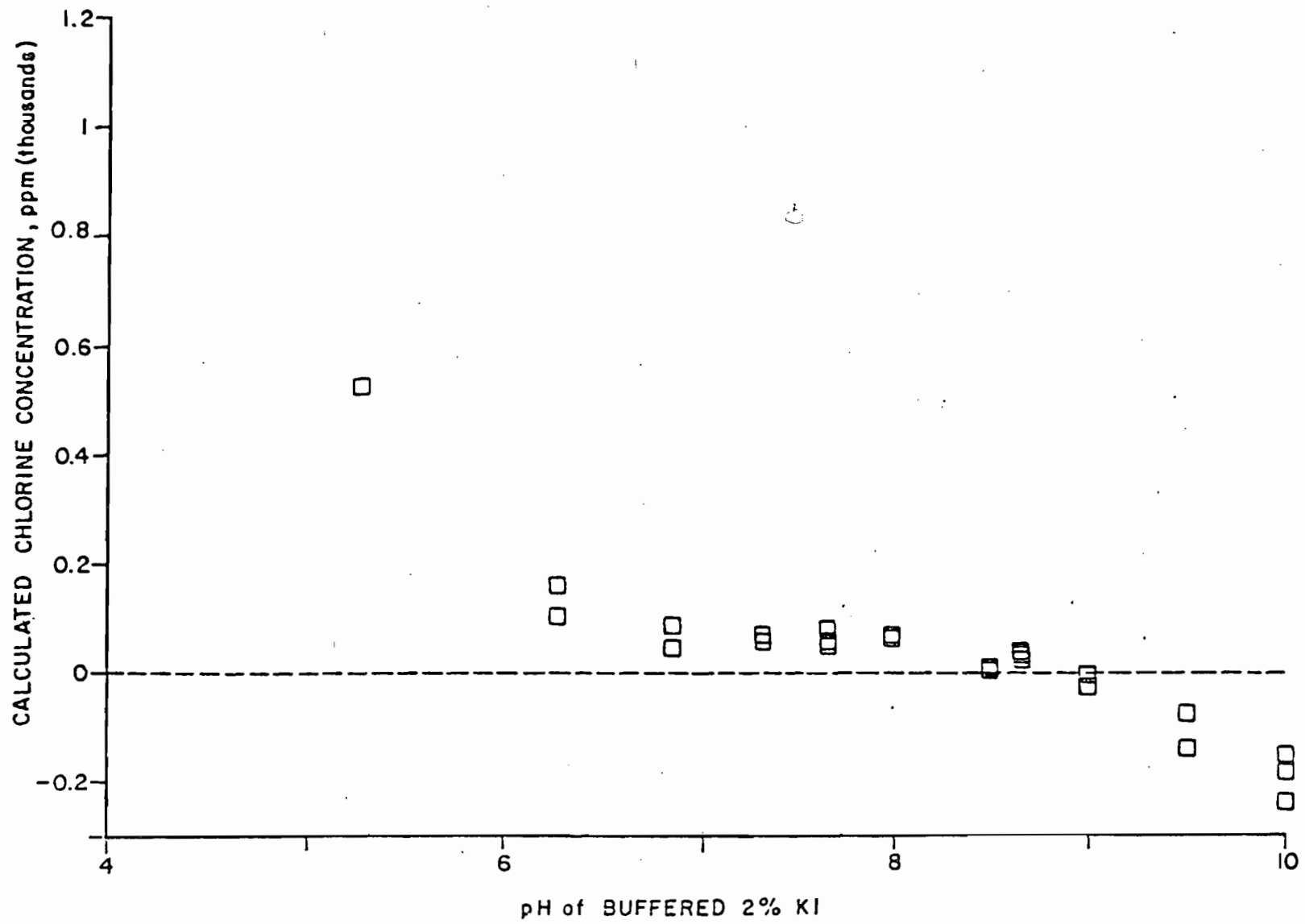
#### LITERATURE CITED

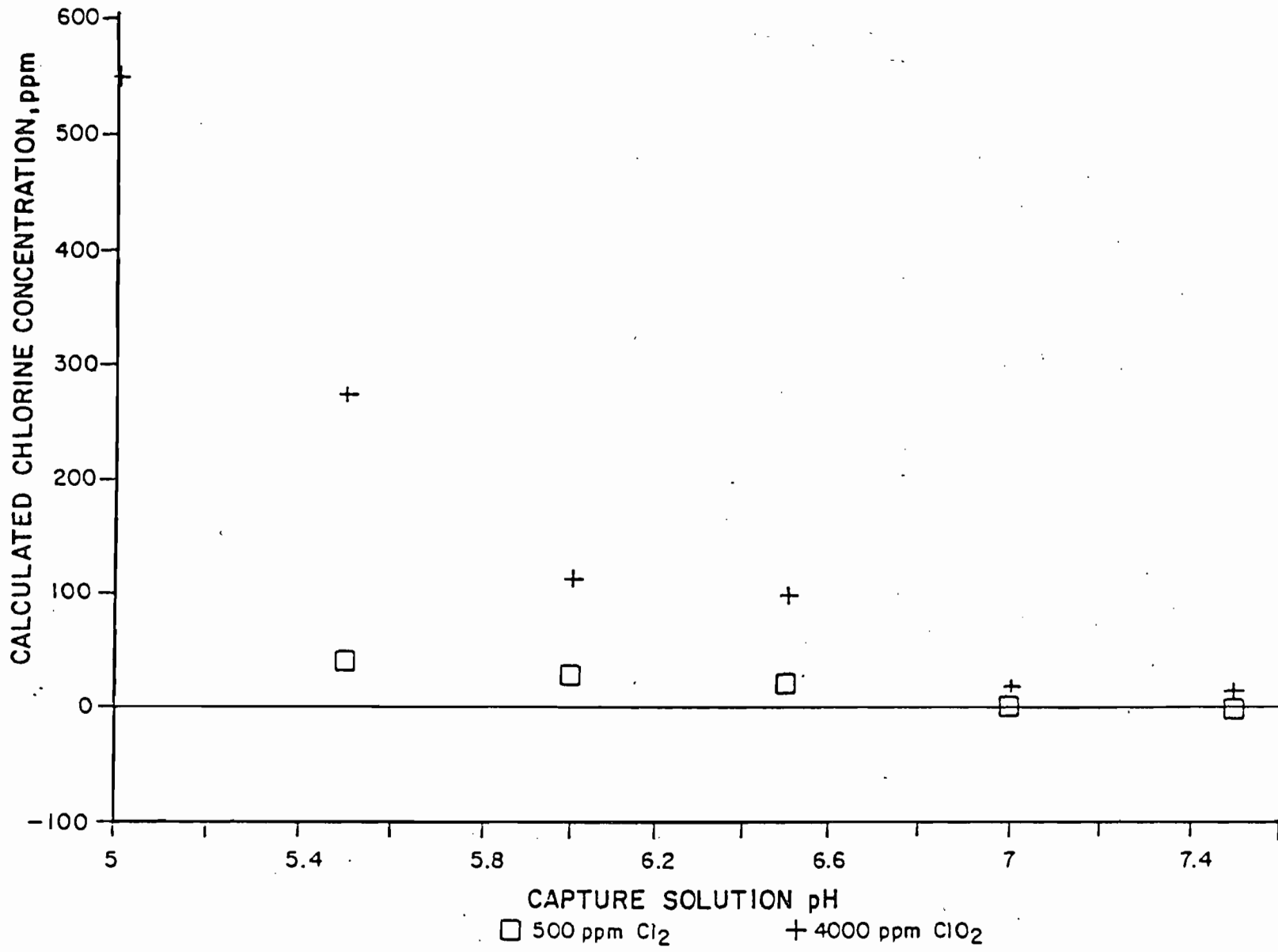
1. American Conference of Governmental Industrial Hygienists (ACGIH), Documentation of the Threshold Limit Values, 4th ed., ACGIH, Cincinnati. 1980, pp. 80-81.
2. G. Y. Pan, J. J. Renard, and J. F. DeGraw, "Scrubbing Chlorine Dioxide from Bleach Plant Waste Gases," Tappi Journal, 66 (7): p. 55 (1983).
3. N. Manley, "Control of Chlorine and Chlorine Dioxide Emissions," Proceedings of the 1985 NCASI Northeast Regional Meeting, Special Report No. 86-01, NCASI, New York, pp. 124-34 (1986).
4. "A Laboratory Investigation of Techniques for Instrumentally Measuring Chlorine and Chlorine Dioxide in the Pulp Bleaching Area Workplace," Technical Bulletin No. 412, NCASI, New York (1983).
5. "A Laboratory Evaluation of the Sulfamic Acid-Iodometric Method for Determining Chlorine in Pulp Bleaching Area Workplace Atmospheres," Special Report No. 82-02, NCASI, New York (1982).

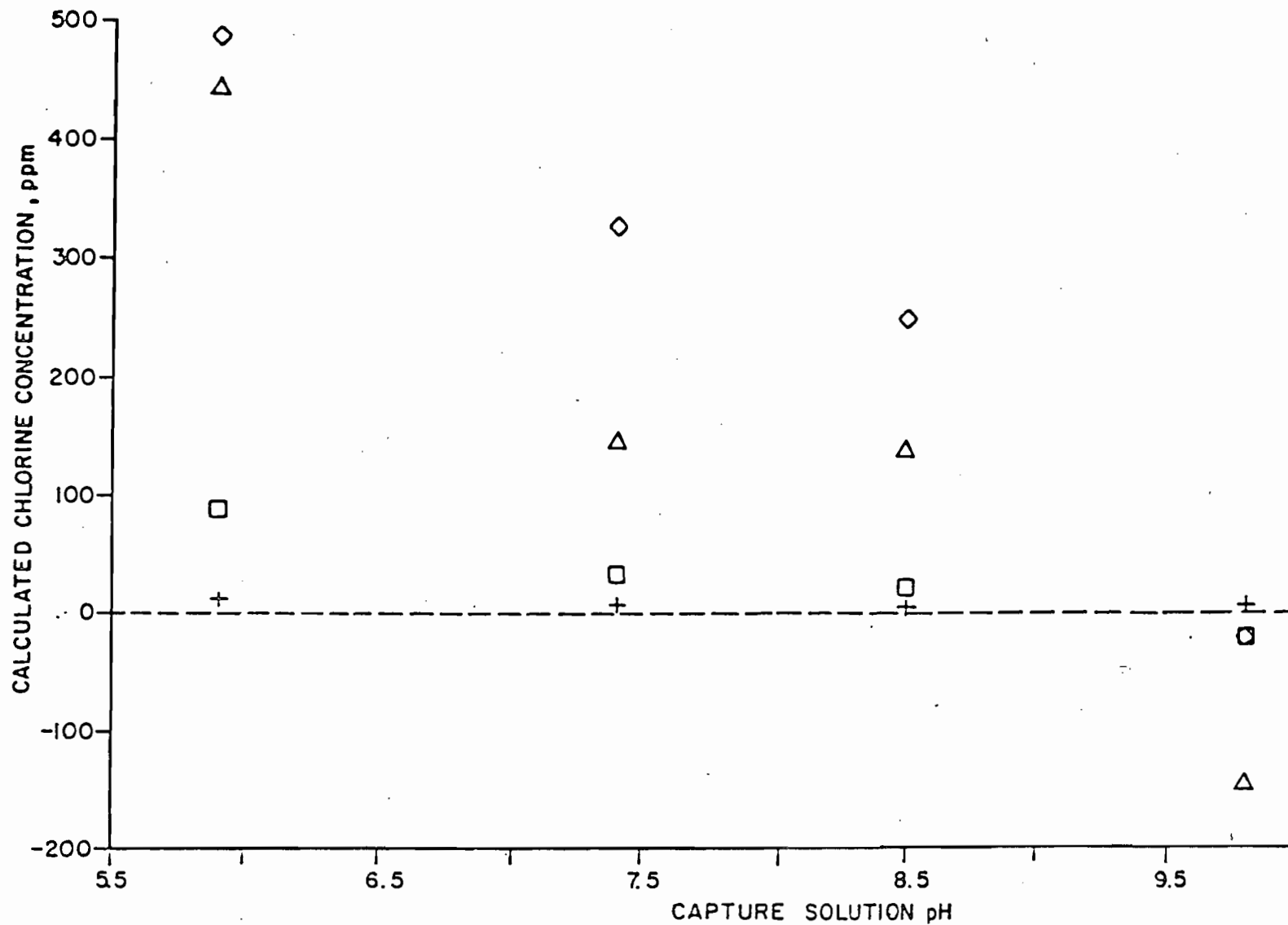
## FIGURE CAPTIONS

### Figure

- 1 Effect of capture solution pH on observed chlorine concentration.
- 2 Effect of chlorine dioxide concentration and pH on observed chlorine concentration - laboratory testing.
- 3 Effect of chlorine dioxide concentration and pH on observed chlorine concentration - field testing.
- 4 Effect of buffered vs. unbuffered pH capture solutions on calculated chlorine and chlorine dioxide concentrations.
- 5 Precision of chlorine and chlorine dioxide mixture analyses.
- 6 Effect of potassium iodide concentration on apparent oxidant concentration.
- 7 Response of Delta model 964 chlorine monitor to chlorine and chlorine dioxide.
- 8 Response of unmodified Delta 964 to a chlorine pulse of short duration.
- 9 Response of unmodified Delta 964 to a chlorine pulse of long duration.
- 10 Modified Delta model 964 sample system.
- 11 Response of modified Delta model 964 to a chlorine pulse of long duration.
- 12 Delta model 964 modified for chlorine dioxide speciation.
- 13 Response of the modified Delta model 964 to a mixture of chlorine and chlorine dioxide.





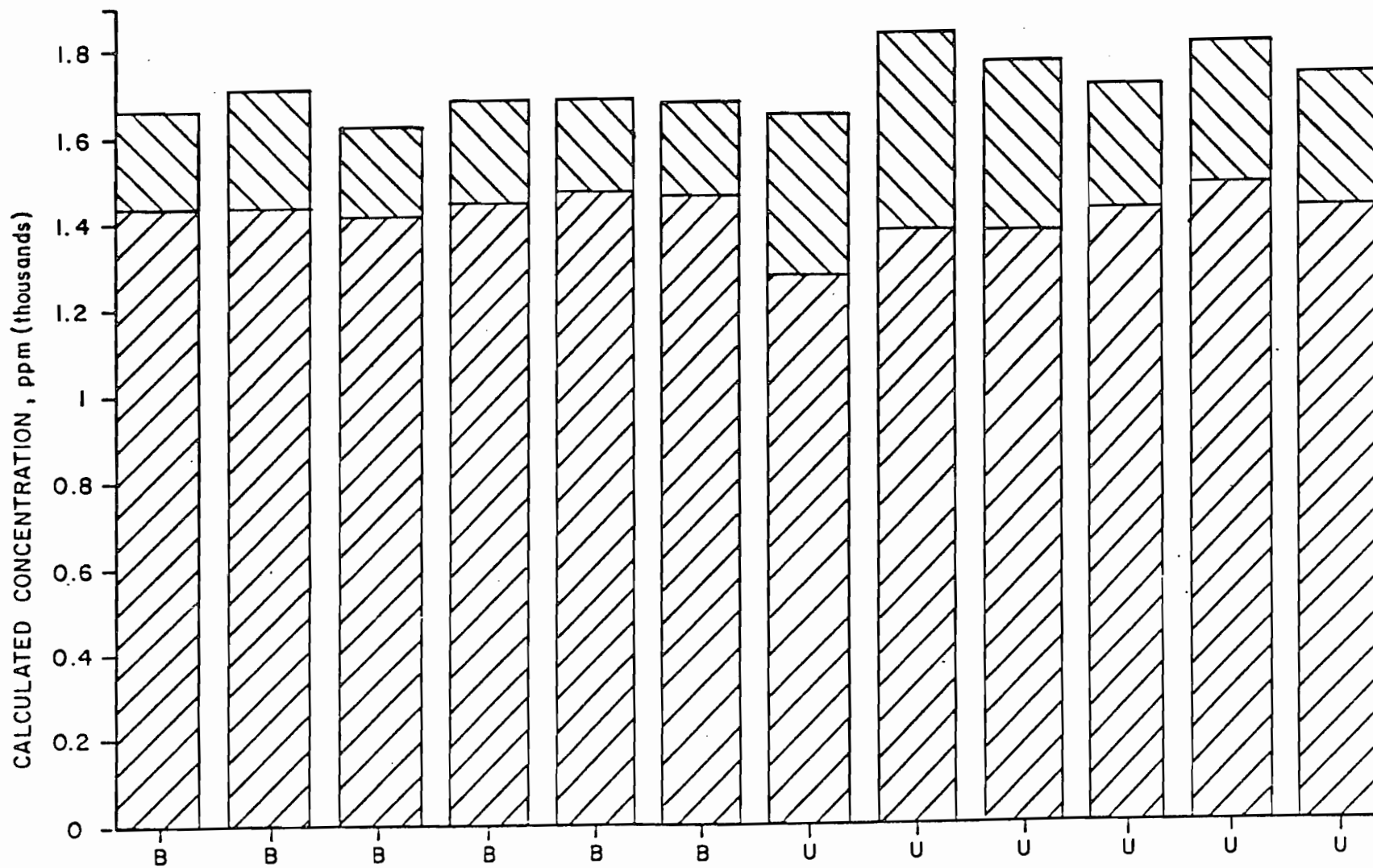


□ SET 1  
 $\bar{X}ClO_2 = 610 \text{ ppm}$

+ SET 2  
 $\bar{X}ClO_2 = 75 \text{ ppm}$

◇ SET 3  
 $\bar{X}ClO_2 = 2574 \text{ ppm}$

△ SET 4  
 $\bar{X}ClO_2 = 2421 \text{ ppm}$



KI BUFFERED AT pH 7.5 vs UNBUFFERED KI

  $\text{ClO}_2$

  $\text{Cl}_2$

