

File Copy

PM
3-29-93
Atlanta, Ga.



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION IV

345 COURTLAND STREET, N.E.
ATLANTA, GEORGIA 30365

RECEIVED

4APT-AEB

APR 01 1993

Mr. Clair H. Fancy, P.E., Chief
Bureau of Air Regulation
Florida Department of Environmental
Regulation
Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Division of Air
Resources Management

RE: Champion International Corporation (PSD-FL-200)

Dear Mr. Fancy:

This is to acknowledge receipt of your preliminary determination and draft Prevention of Significant Deterioration (PSD) permit for the above referenced facility by letter dated February 25, 1993. The proposed project includes the construction of a new gas-fired power boiler, the modification of the existing lime kiln, and the modification of the existing bleach lines. The project is subject to PSD review for the emissions of NO_x, CO, and VOC.

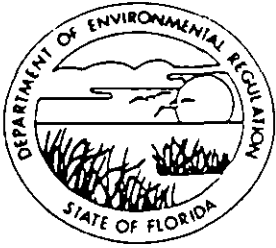
We have reviewed the package as requested and have no adverse comments. If you have any questions or comments, please contact Mr. Gregg Worley of my staff at (404) 347-5014.

Sincerely yours,

Brian L. Beals, Chief
Source Evaluation Unit
Air Enforcement Branch
Air, Pesticides and Toxics
Management Division

cc: E. Middelwart, NWD
F. Bungak, NPS
T. Cole, OHE/C
G. Golson, ADEM
K. Moore, CLE
(HF/Brown/Alford)

} 4-9-93 BRL



Florida Department of Environmental Regulation

Twin Towers Office Bldg. • 2600 Blair Stone Road • Tallahassee, Florida 32399-2400

Lawton Chiles, Governor

Virginia B. Wetherell, Secretary

FAX TRANSMITTAL SHEET

TO: Kyle Moore

DATE: 3-10-93 PHONE: 904-968-3068

TOTAL NUMBER OF PAGES, INCLUDING COVER PAGE: 2

FROM: Champion

DIVISION OF AIR RESOURCES MANAGEMENT

COMMENTS: Page 7 of 12; Permit PSD-FL-200

AC 17-223343

Sorry for the omission!

RR

PHONE: 904-444-1344

FAX NUMBER: 904/922-6979

If there are any problems with this fax transmittal, please call the above phone number.

MESSAGE CONFIRMATION

MAR-10-'93 WED 17:52

TERM ID: DIV OF AIR RES MGMT F-9539

TEL NO: 904-922-6979

NO.	DATE	ST. TIME	TOTAL TIME	ID	DEPT CODE	OK	NG
754	03-10	17:51	00:01:23	9049583068		02	00

PERMITTEE:

Permit Number: AC 17-223343

PSD-FL-200

Champion International Corp. Expiration Date: Dec. 31, 1995

SPECIFIC CONDITIONS:

g. the pollutant emissions from the LK-MDS shall not exceed:

NOx*	No. 6 fuel oil: 200 ppmvd @ 10% O ₂ (49.3 lbs/hr, 215.9 TPY)
	Natural Gas: 175 ppmvd @ 10% O ₂ (43.1 lbs/hr, 188.8 TPY)
PM/PM ₁₀	10.9 lbs/hr, 47.7 TPY
CO*	45 ppmvd @ 10% O ₂ (6.75 lbs/hr, 29.6 TPY)
VOC*	104 ppmvd @ 10% O ₂ (as propane) (24.5 lbs/hr, 107.3 TPY)
TRS**	8 ppmvd @ 10% O ₂ (1.46 lbs/hr, 6.4 TPY)
SO ₂	6.49 lbs/hr, 28.4 TPY
VE	< 20% opacity

* 24-hour average

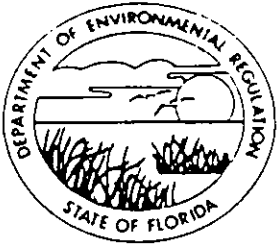
** 12-hour average

Note: o Maximum of 500 tons/day lime product (90% CaO);
o Maximum sulfur content of the No. 6 Fuel Oil is 1.0%, by weight; and,
o Concentration limits and allowable pound per hour emission rates are based on a maximum design volumetric flowrate of 34,383 dscfm.

h. while firing No. 6 fuel oil, initial and subsequent annual compliance tests shall be conducted using the following test methods in accordance with F.A.C. Rule 17-297 and 40 CFR 60, Appendix A (July, 1991 version):

- 1) EPA Method 5, Determination of Particulate Emissions from Stationary Sources.
- 2) EPA Method 7D or 7E, for Determining Nitrogen Oxide Concentrations at Fossil Fuel Fired Steam Generators.
- 3) EPA Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources; or, EPA Method 6C, Determination of Sulfur Dioxide Emissions from Stationary Sources, may be used;
- 4) EPA Method 9, Visual Determination of the Opacity of Emissions from Stationary Sources.
- 5) EPA Method 10, Determination of Carbon Monoxide Emissions from Stationary Sources.
- 6) EPA Method 25A, Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer.

Note: Other reference methods may be used with prior written approval received from the Department in accordance with F.A.C. Rule 17-297.620.



Florida Department of Environmental Regulation

Twin Towers Office Bldg. • 2600 Blair Stone Road • Tallahassee, Florida 32399-2400

Lawton Chiles, Governor

Virginia B. Wetherell, Secretary

FAX TRANSMITTAL SHEET

TO: Bill Strank

DATE: 03/10/93

PHONE: 215-344-3661

FAX: 215-430-7401

TOTAL NUMBER OF PAGES, INCLUDING COVER PAGE: 2

FROM: Weston

DIVISION OF AIR RESOURCES MANAGEMENT

COMMENTS: Page 7 of 12: Permit P30-FL-200
AC 17-22343

Sorry for the omission!

BAW

PHONE: 904-488-1344

FAX NUMBER: 904/922-6979

If there are any problems with this fax transmittal, please call the above phone number.

MESSAGE CONFIRMATION

MAR-10-1993 WED 17:50

TERM ID: DIV OF AIR RES MGMT P-9999

TEL NO: 904-933-8979

NO.	DATE	ST. TIME	TOTAL TIME	ID	DEPT CODE	OK	HS
753	03-10	17:48	00'01'21	315 430 7401		02	00

PERMITTEE:

Permit Number: AC 17-223343

PSD-FL-200

Champion International Corp. Expiration Date: Dec. 31, 1995

SPECIFIC CONDITIONS:

g. the pollutant emissions from the LK-MDS shall not exceed:

NOx*	No. 6 fuel oil: 200 ppmvd @ 10% O ₂ (49.3 lbs/hr, 215.9 TPY)
	Natural Gas: 175 ppmvd @ 10% O ₂ (43.1 lbs/hr, 188.8 TPY)
PM/PM ₁₀	10.9 lbs/hr, 47.7 TPY
CO*	45 ppmvd @ 10% O ₂ (6.75 lbs/hr, 29.6 TPY)
VOC*	104 ppmvd @ 10% O ₂ (as propane) (24.5 lbs/hr, 107.3 TPY)
TRS**	8 ppmvd @ 10% O ₂ (1.46 lbs/hr, 6.4 TPY)
SO ₂	6.49 lbs/hr, 28.4 TPY
VE	< 20% opacity

* 24-hour average

** 12-hour average

Note: o Maximum of 500 tons/day lime product (90% CaO);
o Maximum sulfur content of the No. 6 Fuel Oil is 1.0%, by weight; and,
o Concentration limits and allowable pound per hour emission rates are based on a maximum design volumetric flowrate of 34,383 dscfm.

h. while firing No. 6 fuel oil, initial and subsequent annual compliance tests shall be conducted using the following test methods in accordance with F.A.C. Rule 17-297 and 40 CFR 60, Appendix A (July, 1991 version):

- 1) EPA Method 5, Determination of Particulate Emissions from Stationary Sources.
- 2) EPA Method 7D or 7E, for Determining Nitrogen Oxide Concentrations at Fossil Fuel Fired Steam Generators.
- 3) EPA Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources; or, EPA Method 6C, Determination of Sulfur Dioxide Emissions from Stationary Sources, may be used;
- 4) EPA Method 9, Visual Determination of the Opacity of Emissions from Stationary Sources.
- 5) EPA Method 10, Determination of Carbon Monoxide Emissions from Stationary Sources.
- 6) EPA Method 25A, Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer.

Note: Other reference methods may be used with prior written approval received from the Department in accordance with F.A.C. Rule 17-297.620.



1 WESTON WAY
WEST CHESTER, PA 19380-1449
PHONE: 215-692-3030
FAX: 215-430-3124

RECEIVED

MAR 9 1993

8 March 1993

Division of Air
Resources Management

Mr. Bruce Mitchell
Florida DER, Division of Air Resources Management
Twin Towers Office Building
2600 Blair Stone Rd.
Tallahassee, FL 32399-2400

Work Order No. 02246-056-001

Re: Champion International- Pensacola Mill

Dear Mr. Mitchell:

Per your request to Kyle Moore at Champion International's Pensacola Mill, enclosed is a copy of the NCASI Technical Bulletin which discusses the test method (EPA Modified Method 6) for chlorine, chlorine dioxide, and chloroform. Also enclosed is the quality assurance document which pertains to this sampling procedure. Champion proposed to use this method for determining emissions from the applicable sources identified in the pending PSD permit application.

This information is being submitted by Weston on behalf of Champion. This submittal is supporting documentation for Champion's Mill Modification Project (permit number AC 17-223343). Should you have any questions, please contact Kyle Moore of Champion at (904) 968-2121 or John Barone of Weston at (215) 430-7218.

Very truly yours,

ROY F. WESTON, INC.

William V. Straub
Assistant Engineer II

wvs

Enclosures

cc: Kyle Moore Champion
 John Egan Weston
 John Barone Weston

ncasi

ATC 413
technical bulletin

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC., 280 MADISON AVENUE, NEW YORK, N.Y. 10016

RECEIVED

MAR 9 1993

Division of Air
Resources Management

OPTIMIZATION AND EVALUATION OF AN IMPINGER
CAPTURE METHOD FOR MEASURING CHLORINE AND
CHLORINE DIOXIDE IN PULP BLEACH PLANT VENTS

TECHNICAL BULLETIN NO. 520

APRIL 1987

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.
260 MADISON AVE. NEW YORK, N.Y. 10016 (212) 532-9000

April 1, 1987

Russell O. Blosser
Technical Director
(212) 532 9001

TECHNICAL BULLETIN NO. 520

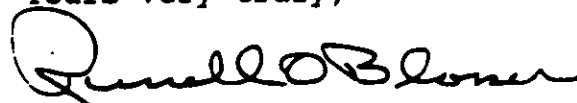
OPTIMIZATION AND EVALUATION OF AN IMPINGER
CAPTURE METHOD FOR MEASURING CHLORINE AND
CHLORINE DIOXIDE IN PULP BLEACH PLANT VENTS

The evaluation and, where necessary, the development and evaluation, of analysis methods for substances of environmental and/or regulatory concern, has been a component of many NCASI studies. The measurement of concentrations of chlorine and chlorine dioxide in pulp bleach plant vent gases is a requirement of an ongoing NCASI study of non criteria pollutant emissions and emission control strategies, and it is a requirement of many mill programs addressing bleach plant emissions and control device effectiveness. Yet, techniques for measuring chlorine and chlorine dioxide in these vent gases either have not been developed (e.g., continuous instrumental monitoring methods), or they have not been evaluated (e.g., impinger capture grab sampling method).

This report describes results of an NCASI study of an impinger capture dual pH potassium iodide method for measuring chlorine and chlorine dioxide in bleach plant vent gases. Although the technique is in wide use for this purpose, its performance apparently has never been evaluated. This study showed that pH buffering of the capture solution was necessary to avoid the formation of falsely high chlorine levels. Other features of the performance of the method were evaluated, and a method for removing a sulfur dioxide interference was developed.

The studies reported in this bulletin were carried out at the NCASI Southern Regional Center in Gainesville, Florida. The work was performed by Michael D. Marks and Steven W. Jett, both research technical associates, under the direction of Robert P. Fisher, Investigative Programs Manager. Dr. Fisher also prepared the report upon which this bulletin is based. Persons with questions on this bulletin should contact Dr. Fisher at P.O. Box 14483, Gainesville, FL 32604 or telephone (904-377-4708), or this office.

Yours very truly,



Russell O. Blosser
Technical Director

ROB:mh
Attach.

TABLE OF CONTENTS

	<u>Page</u>
I INTRODUCTION	1
II ANALYSIS METHOD STUDIES	2
A. Method Background	2
B. Method Testing and Modification	3
III DEVELOPMENT AND EVALUATION OF A CHEMICALLY REACTIVE FILTER FOR REMOVING SULFUR DIOXIDE	9
A. Background	9
B. Sulfur Dioxide Removal Experiments	13
C. Chlorine and Chlorine Dioxide Recovery Experiments	16
IV ONGOING STUDIES	20
V CONCLUSION	20
VIII LITERATURE REFERENCES	21
APPENDICES	
APPENDIX A - METHOD FOR MEASURING CHLORINE AND CHLORINE DIOXIDE GASEOUS EMISSIONS	A1
APPENDIX B - PREPARATION OF CHEMICAL FILTERS FOR REMOVAL OF SULFUR DIOXIDE	B1

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:

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

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

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

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

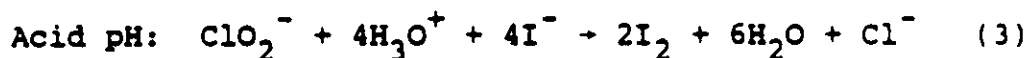
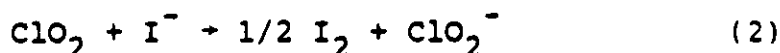
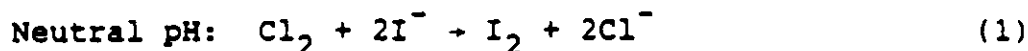
where EqI_2N and EqI_2A are equivalents of iodine determined in the neutral and (total) acid titrations, respectively, and \bar{N} is the normality of the sodium thiosulfate solution. Calculate gas phase concentrations of ClO_2 and Cl_2 employing standard EPA calculations. Assume gas phase water saturation in most vents.

NCASI is conducting a study of bleach plant emissions of Cl_2 and 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.

II ANALYSIS METHOD STUDIES

A. 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 sampling practice within the industry has been to use two impingers in series, each containing 2 percent unbuffered 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 Cl_2 and ClO_2 on the basis of the neutral and total acid titration equivalents.

The origin of this test is not widely known, but the method has been formalized by the Canadian Pulp and Paper Association. CPPA Standard J.14P(4) includes methods for analyzing ClO_2 production plant liquors, plus generator gas ClO_2 concentrations in the system after the generator and before the cold water absorption tower. These gas phase concentrations are much higher than those encountered in process vents. To the knowledge of NCASI staff, this method had not been evaluated for the determination of lower Cl_2 and ClO_2 concentrations, prior to this NCASI study.

APPENDIX A

METHOD FOR MEASURING CHLORINE AND
CHLORINE DIOXIDE GASEOUS EMISSIONS

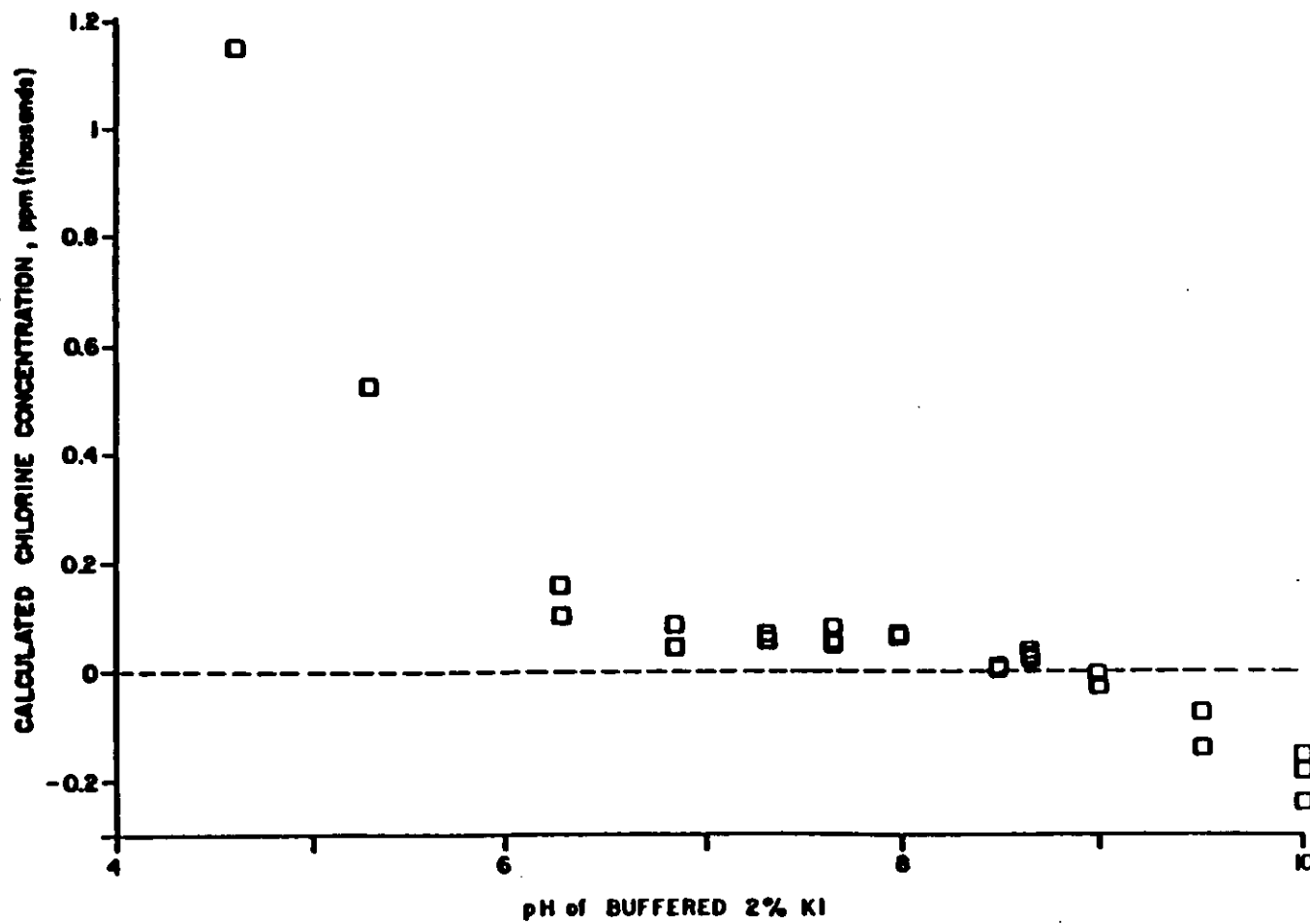


FIGURE 1

EFFECT OF CAPTURE SOLUTION pH ON CALCULATED CHLORINE CONCENTRATION.

this gas through an impinger containing aqueous 0.1 percent sulfamic acid to remove chlorine, then blending this gas with humidified air to produce the desired concentration of ClO_2 (determined by analysis using the method of Appendix A). The results of tests at 500 ppm and at 4000 ppm ClO_2 , shown in Figure 2, clearly illustrate the effect of pH and of ClO_2 concentration upon artifact chlorine formation.

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 Appendix A. Each impinger pair contained two percent KI solution, buffered essentially as per the Appendix A 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.

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 Appendix A, 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 Cl_2 and ClO_2 concentrations obtained employing buffered sampling were 228 and 1440 ppm, with standard deviations of 25 and 22 ppm, respectively.

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.

(2) Precision of the pH Buffered Method - 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

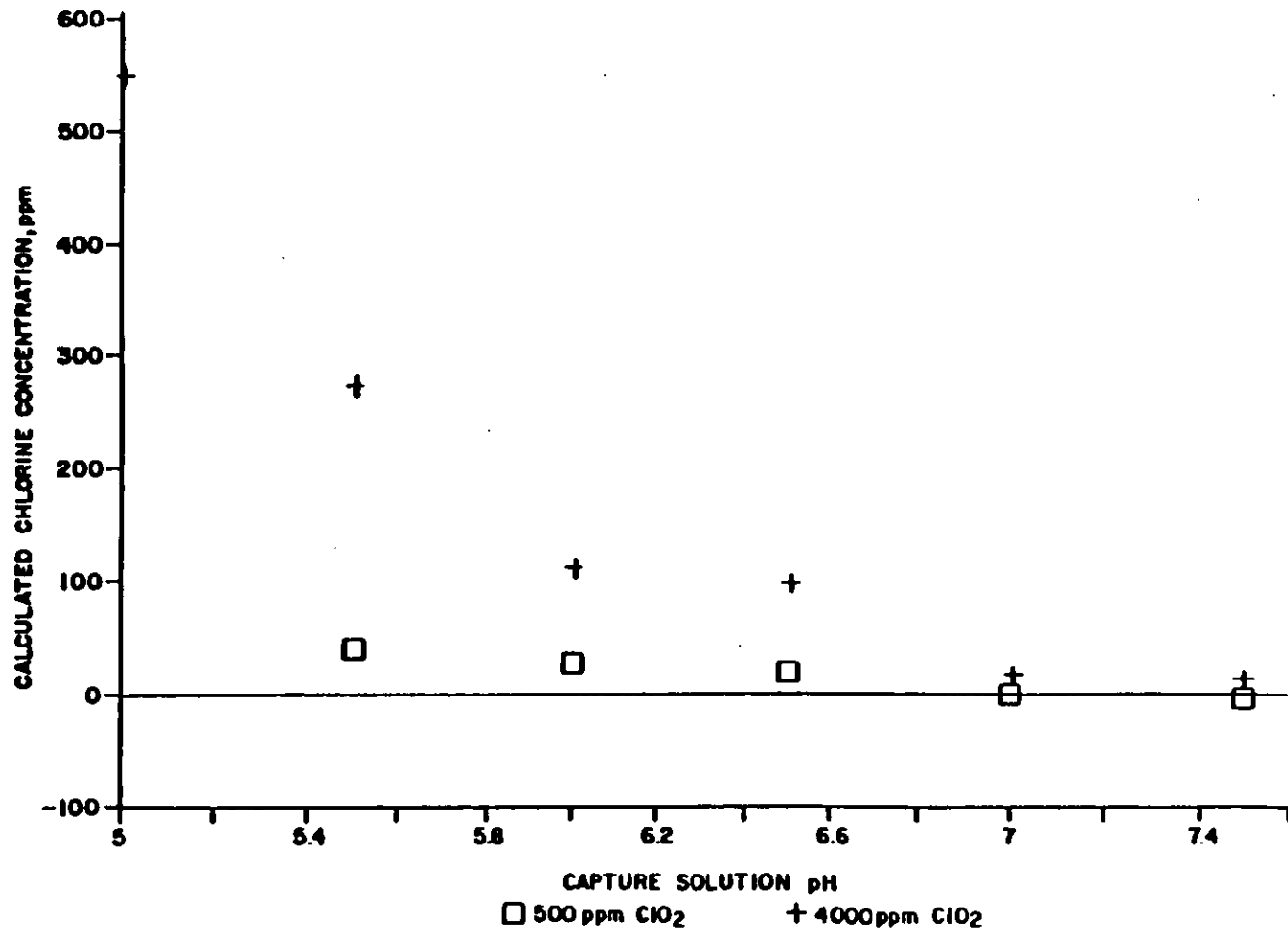


FIGURE 2

**EFFECT OF CHLORINE DIOXIDE CONCENTRATION AND pH
ON CALCULATED CHLORINE CONCENTRATION -
LABORATORY TESTING**

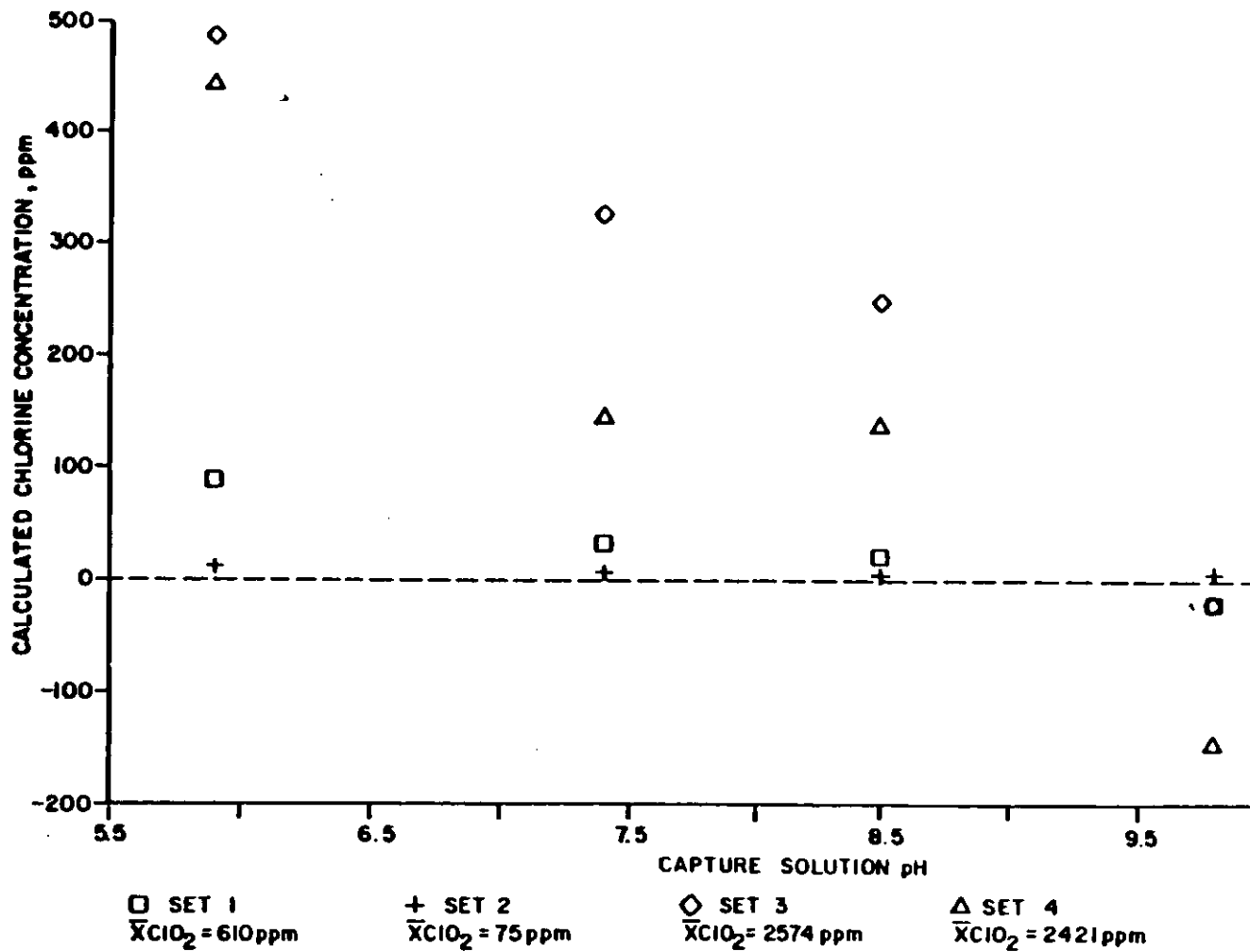


FIGURE 3 EFFECT OF CHLORINE DIOXIDE CONCENTRATION AND pH ON CALCULATED CHLORINE CONCENTRATION - FIELD TESTING

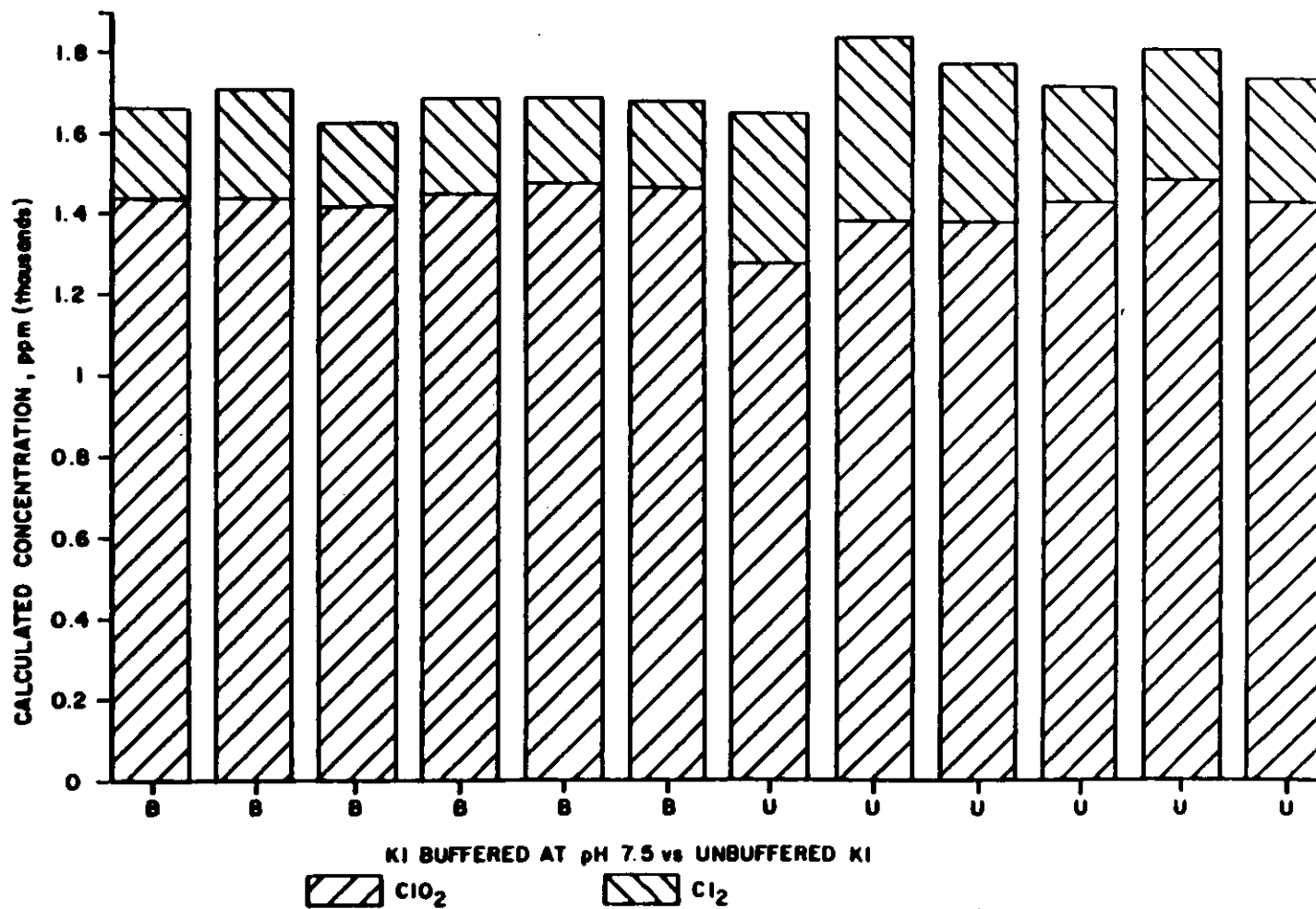


FIGURE 4 EFFECT OF BUFFERED (B) VS. UNBUFFERED (U) pH CAPTURE SOLUTIONS ON CALCULATED CHLORINE AND CHLORINE DIOXIDE CONCENTRATIONS

of Appendix A. Results are indicated in Figure 5. For the range of concentrations examined, relative standard deviation values were all less than 6 percent.

(3) 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 percent, sampling of high concentrations of gaseous Cl_2 and ClO_2 with midget impingers can deplete 2 percent 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 percent KI and three were taken in 2 percent KI. Both capture solutions were buffered at a pH of 7.0. In set one the average measured Cl_2 was 3.4 percent higher, and the average measured ClO_2 was 7.7 percent lower in the 10 percent KI than in the 2 percent KI. In set two the average Cl_2 was 4.0 percent higher, and the average ClO_2 was 7.9 percent lower in the 10 percent 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 percent, 5 percent, 7 percent, 10 percent, 12 percent, and a 15 percent 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 percent strength.

(4) 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 Appendix A. The results, indicated in Table 1, show that iced 2 percent buffered KI is no more effective at capturing chlorine and chlorine dioxide than is 2 percent buffered KI maintained at 24°C.

III DEVELOPMENT AND EVALUATION OF A CHEMICALLY REACTIVE FILTER FOR REMOVING SULFUR DIOXIDE

A. Background

The sampling of bleach plant vents by both grab sampling and continuous sampling methods is in some cases complicated by the

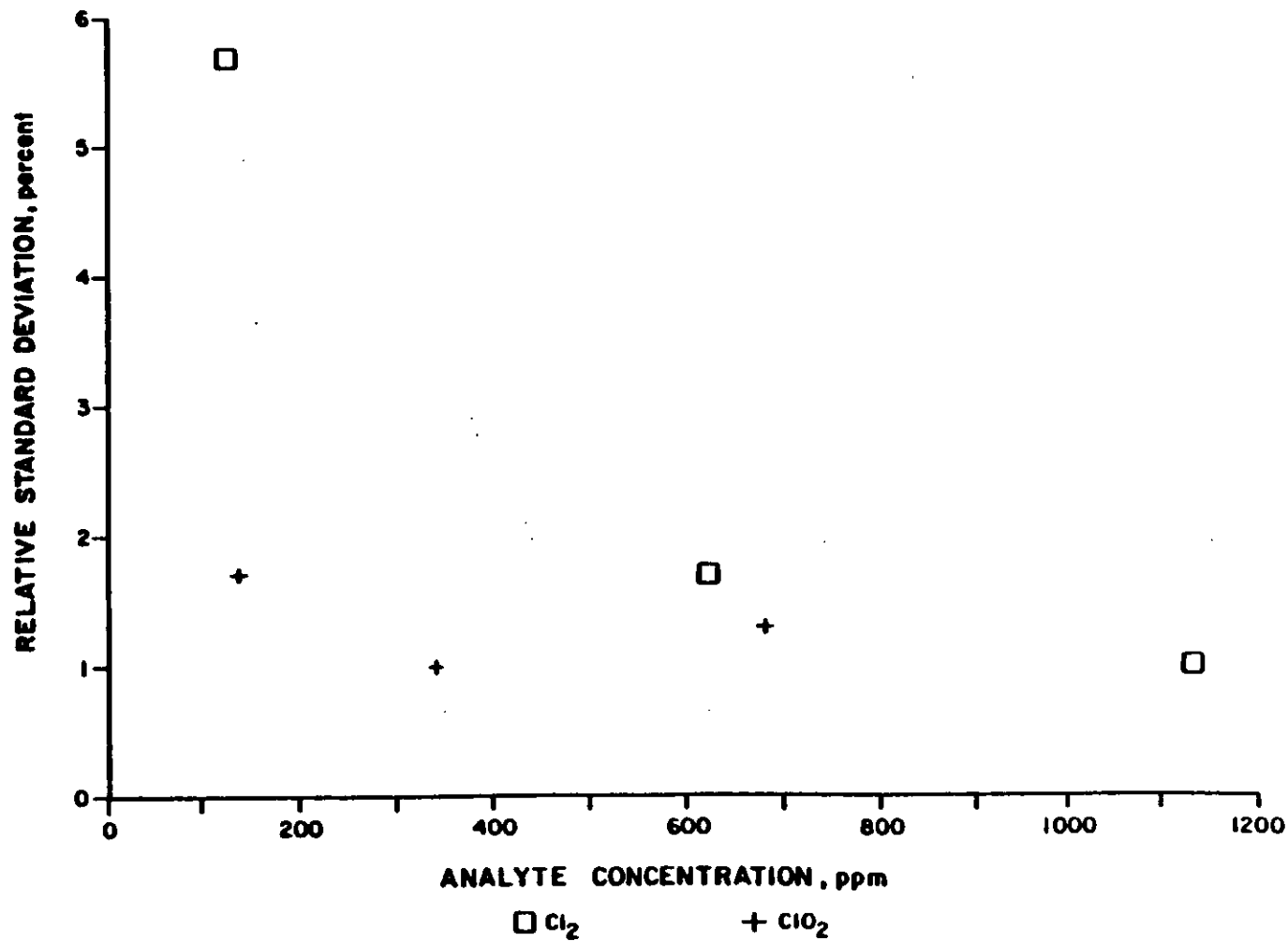


FIGURE 5 PRECISION OF CHLORINE AND CHLORINE DIOXIDE MIXTURE ANALYSES EMPLOYING pH 7.0 BUFFERED CAPTURE SOLUTIONS

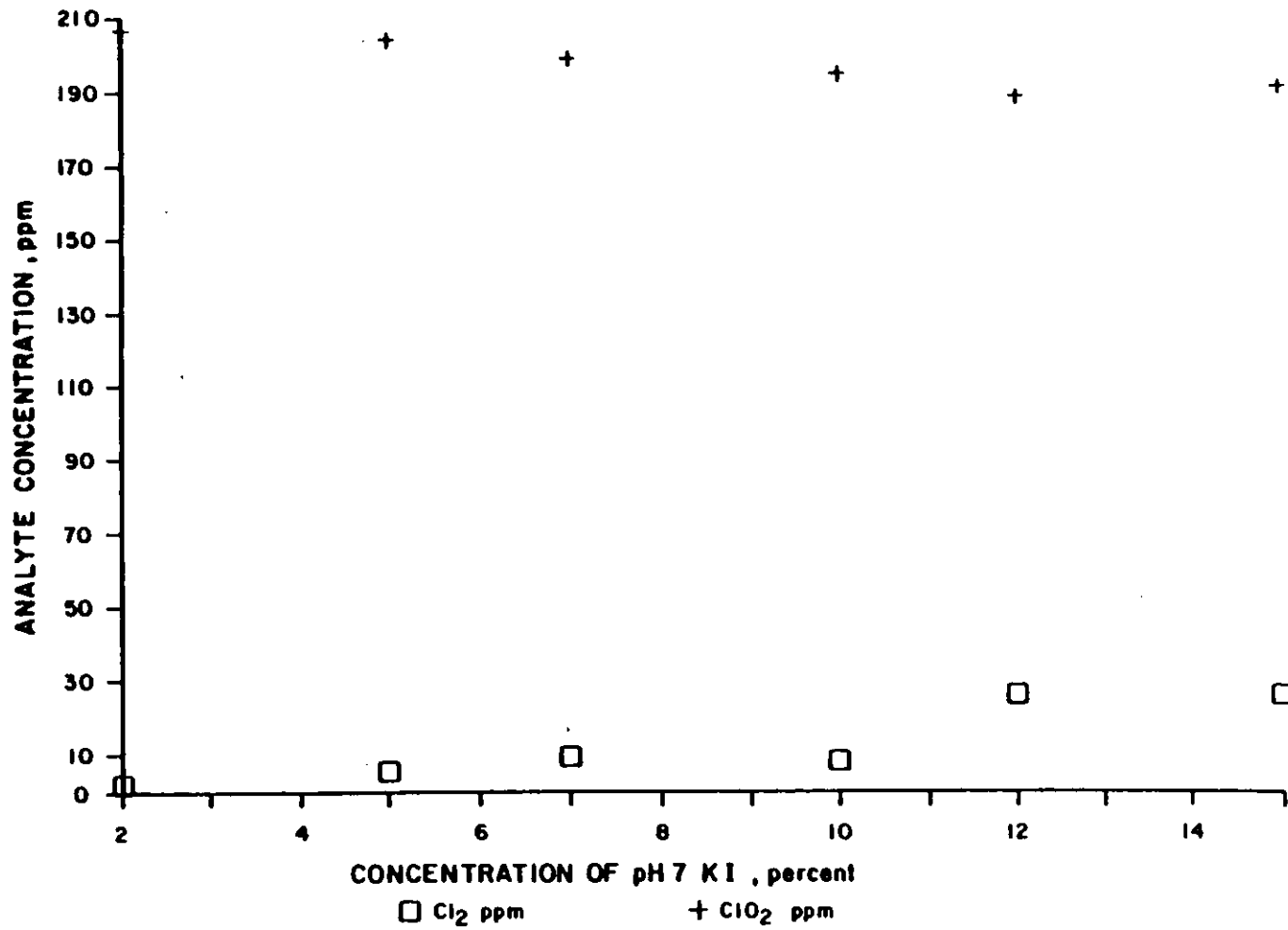


FIGURE 6 EFFECT OF POTASSIUM IODIDE CONCENTRATION ON APPARENT ANALYTE CONCENTRATION, ClO₂ ONLY SAMPLED

TABLE 1 **COMPARISON OF RESULTS OF ICED AND UNICED IMPINGER SAMPLING
OF GAS MIXTURES OF CHLORINE AND CHLORINE DIOXIDE**

<u>SET 1 (n = 3)</u>		<u>SET 2 (n = 3)</u>	
<u>Iced</u>	<u>Uniced</u>	<u>Iced</u>	<u>Uniced</u>
$\bar{x} \text{ ClO}_2 = 600 \text{ ppm}$ RSD = 2.1%	$\bar{x} \text{ ClO}_2 = 594 \text{ ppm}$ RSD = 0.74%	$\bar{x} \text{ ClO}_2 = 598 \text{ ppm}$ RSD = 1.5%	$\bar{x} \text{ ClO}_2 = 596 \text{ ppm}$ RSD = 2.3%
$\bar{x} \text{ Cl}_2 = 720 \text{ ppm}$ RSD = 1.0%	$\bar{x} \text{ Cl}_2 = 726 \text{ ppm}$ RSD = 1.0%	$\bar{x} \text{ Cl}_2 = 755 \text{ ppm}$ RSD = 1.7%	$\bar{x} \text{ Cl}_2 = 755 \text{ ppm}$ RSD = 1.7%

presence of sulfur dioxide (SO_2) in the gas being sampled. SO_2 is an interferent to the dual pH potassium iodide method (it reduces formed iodine to iodide) and to most instrumental methods for chlorine and chlorine dioxide. SO_2 is employed at some bleach plants as an antichlor for reducing oxidant residuals after bleaching, and it is also employed in some control devices for reducing chlorine and chlorine dioxide.

A method for removing the sulfur dioxide interference from workplace atmospheres being sampled for chlorine and chlorine dioxide was reported in NCASI Technical Bulletin No. 412 (5). This method is based upon the passage of gases to be analyzed through a glass fiber filter previously soaked in a solution of chromium trioxide and sulfuric acid, prior to their being analyzed for chlorine and chlorine dioxide. This technique was shown to provide adequate removal of sulfur dioxide at a ca. 5 ppm inlet concentration, and to provide adequate passage of Cl_2 and ClO_2 at 1 and 0.1 ppm inlet concentrations, respectively. SO_2 removal was found to be effective only when the filters were moist, however.

Because the concentrations of SO_2 of concern in bleach plant vent testing may be much higher than those encountered in workplace atmosphere testing, experiments were conducted to test at higher concentrations of SO_2 the efficiency of SO_2 removal of one form of the SO_2 chemical filters evaluated in the study reported in Technical Bulletin No. 412 (5). Significant breakthrough of SO_2 was observed, consequently a modification of the filter with greater capacity was constructed and tested. This testing showed adequate removal of SO_2 , after which experiments the ability of the modified filter to pass Cl_2 and ClO_2 was studied. These experiments are discussed in the following sections.

B. Sulfur Dioxide Removal Experiments

A single chromium trioxide/sulfuric acid impregnated glass fiber filter was prepared according to the method of Appendix B, and installed in a ca. $\frac{1}{2}$ in od x 8 in long FEP Teflon tube, forming a chemical filter similar to the Mast SO_2 filter of Figure 1 of Technical Bulletin No. 412 (5). The filter was moistened prior to testing, and inspection afterwards revealed that it had remained moist. The All-Teflon equipment illustrated in Figure 7 was assembled, and the ITT Barton Model 411 SO_2 analyzer was calibrated with cylinder gas SO_2 in nitrogen, which concentration was verified by analysis with a permeation tube calibrated gas chromatograph with a flame photometric detector. SO_2 (in nitrogen) at 500 ppm and 1.2 L/min was passed through the filter. Breakthrough to ca. 50 ppm SO_2 occurred in less than 2 minutes. This was not acceptable performance, consequently a larger capacity filter was constructed as described in Appendix B. This filter is illustrated in Figure 8.

The larger capacity filter was tested for SO_2 removal in two experiments, again employing the equipment indicated in Figure 7. The filter was moistened as described in Appendix B, and it

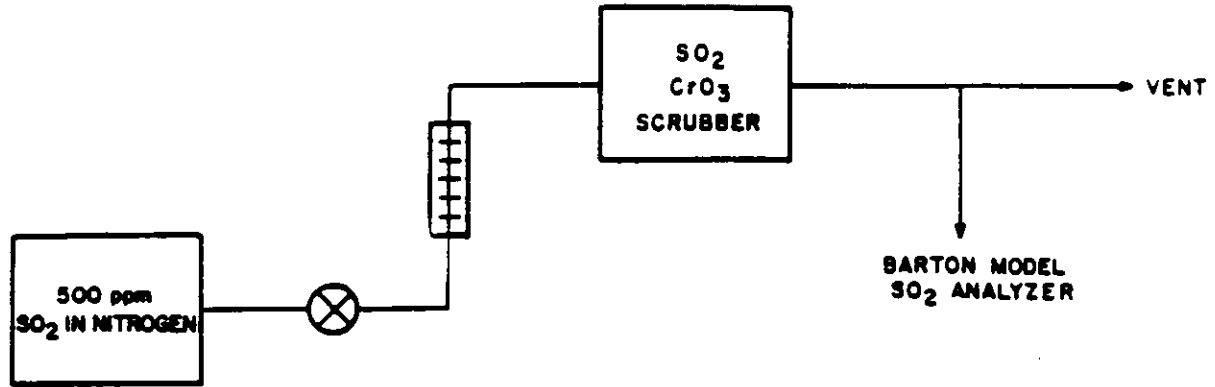
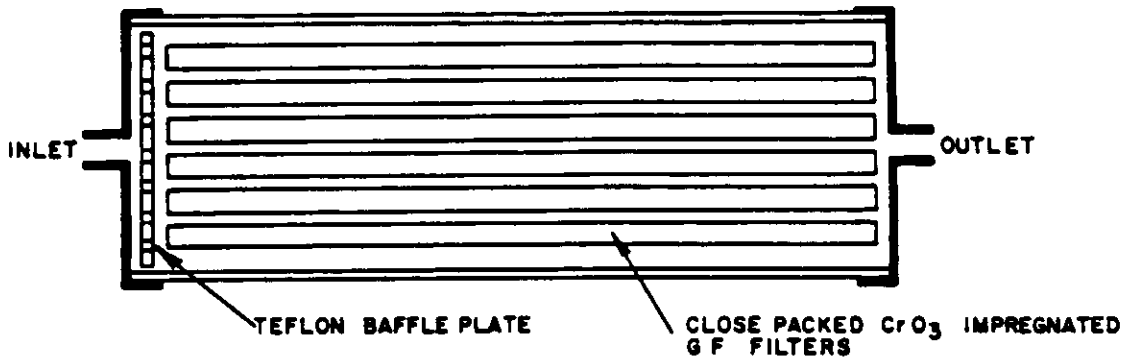
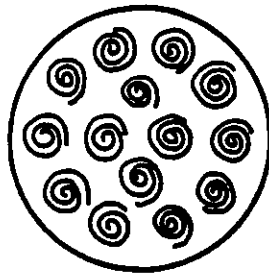


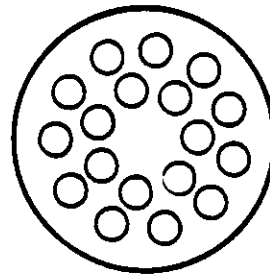
FIGURE 7 SCHEMATIC OF TEST APPARATUS EMPLOYED FOR
SO₂ REACTIVE FILTER BREAKTHROUGH STUDIES



SIDE VIEW



OPEN CHAMBER
SHOWING GF
FILTERS



BAFFLE PLATE

END VIEW

FIGURE 8

DIAGRAM OF REACTIVE FILTER DESCRIBED
IN APPENDIX B

remained moist throughout the experiments. SO_2 at 500 ppm in nitrogen was passed through the filter at 1.2 L/min. This represented an extreme in terms of testing the ability of the filter to remove SO_2 , in that (1) air-oxygen oxidation of SO_2 sorbed to the filter would be minimal in the nitrogen atmosphere, and (2) this represented the highest sampling rate which would be employed for bleach plant vent sampling, and lower rates should result in longer retention times within the filter, hence longer times to breakthrough.

Both experiments indicated no detectable breakthrough (less than 1 ppm SO_2) for four hours. Results from one of the experiments are plotted in Figure 9. This was taken to indicate that the filter assembly of Figure 8/Appendix B is suitable for removing the SO_2 interference in bleach plant vent sampling.

C. Chlorine and Chlorine Dioxide Recovery Experiments

Several factors were considered in designing the Cl_2 and ClO_2 recovery experiments. First, it was postulated that the ability of the reactive filter to pass Cl_2 and ClO_2 could be altered by the presence of SO_2 , either in terms of (1) gas phase reactions of SO_2 with Cl_2 and ClO_2 , and/or (2) reaction products of SO_2 and CrO_3 reacting with Cl_2 and ClO_2 in a gas/liquid or gas/solid reaction. The former point was not investigated (one function of an SO_2 removal device installed as near the analyte source as practical in an extractive system is to reduce the possibility of gas phase reactions of SO_2 with analyte in the sampling line). The second point was included in the studies of Cl_2 and ClO_2 recovery by pre-exposing the filters undergoing testing to SO_2 just prior to commencing the recovery studies.

A second factor important to Cl_2 and ClO_2 recoveries concerns the possibility that there may exist reactive sites within the filter which will attenuate Cl_2 and ClO_2 , but which may be filled by purging the filter with gas to be analyzed prior to beginning an actual analysis. Pre-purging was included in many of the recovery experiments conducted in this study.

Also expected to affect recoveries of Cl_2 and ClO_2 through the reactive filters are the flow rates of the Cl_2 and ClO_2 containing gases, and the gas phase concentrations of Cl_2 and ClO_2 . NCASI bleach plant studies require sampling at 1 and 0.2 L/min, and recoveries at these flow rates were investigated. The concentrations of Cl_2 and ClO_2 studied for the majority of the experiments were fixed at ca. 20 ppm, so as to provide a difficult but realistic test of the ability of the filter to pass Cl_2 and ClO_2 .

The recovery experiments were conducted employing the equipment indicated in Figure 10. All materials coming into contact with Cl_2 , ClO_2 , and SO_2 were FEP, TFE, or PFA Teflon. Results of these experiments are presented in Table 2.

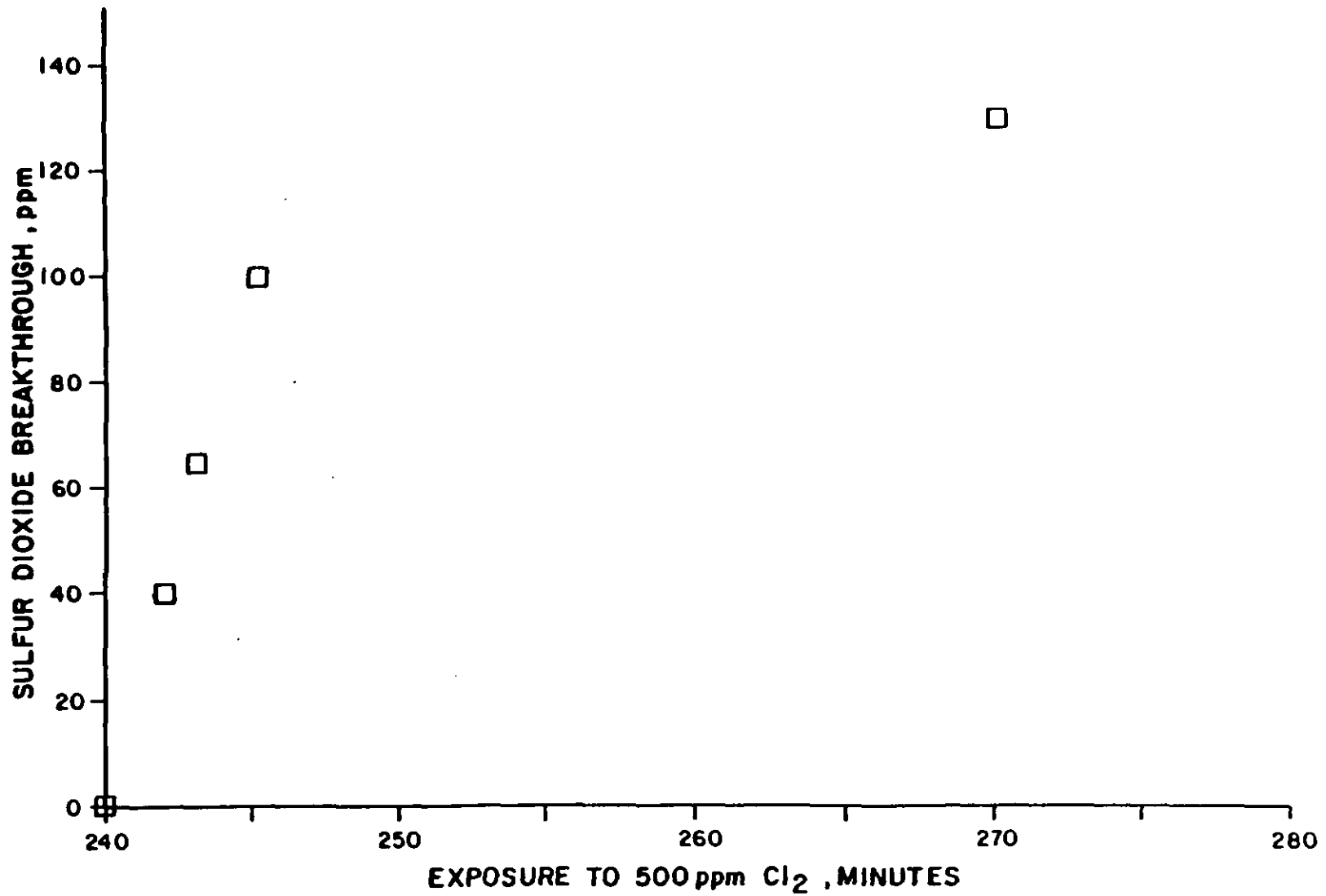


FIGURE 9 RESULTS OF REACTIVE FILTER SO₂ BREAKTHROUGH EXPERIMENT

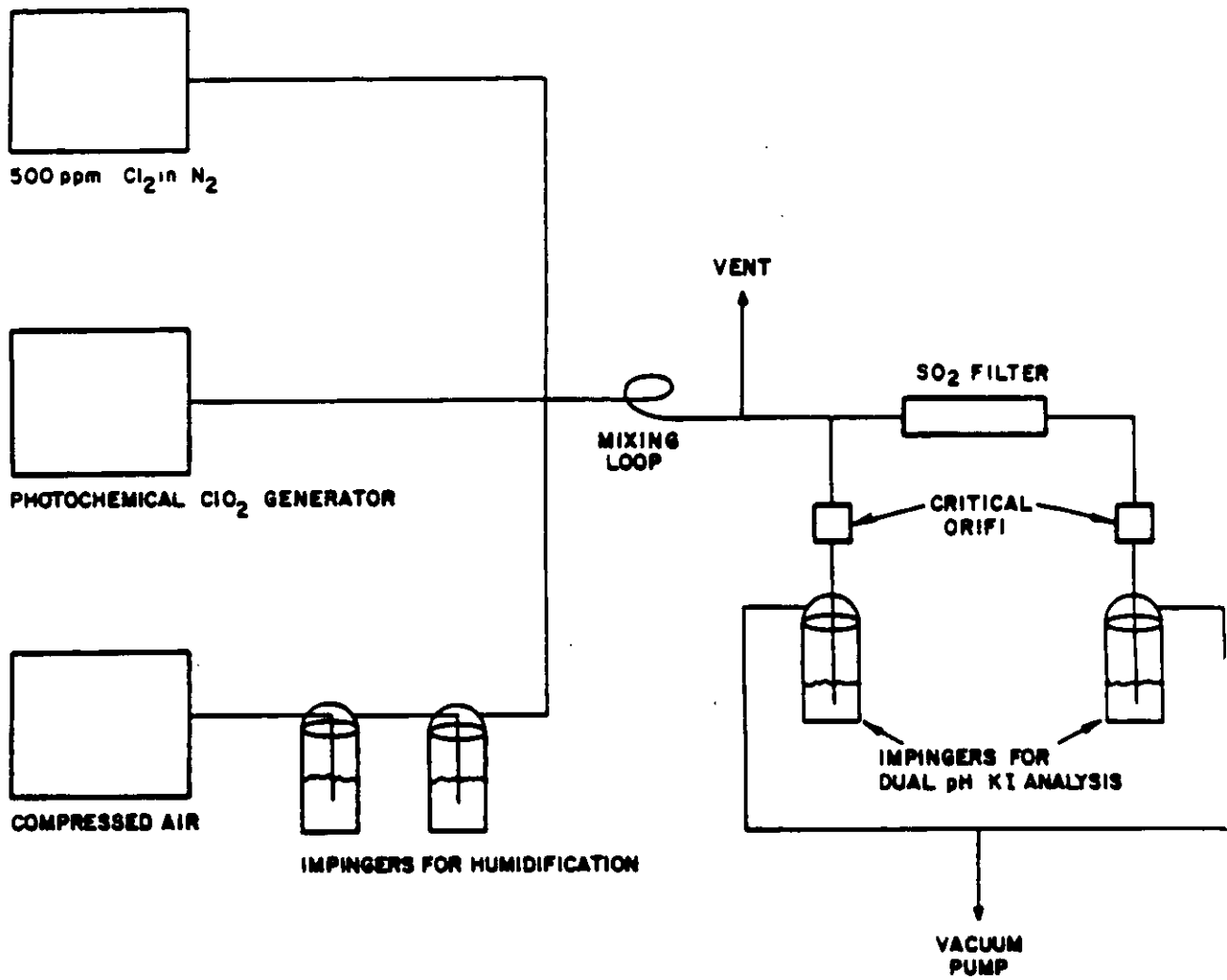


FIGURE 10

SCHEMATIC OF APPARATUS EMPLOYED FOR REACTIVE
FILTER Cl₂ AND ClO₂ RECOVERY EXPERIMENTS

TABLE 2 RESULTS OF LABORATORY DETERMINATION OF CHLORINE AND CHLORINE DIOXIDE RECOVERIES THROUGH CHEMICAL FILTERS FOR SO₂ REMOVAL

<u>GAS FLOW RATE, L/MIN</u>	<u>TOTAL GAS VOLUME, L</u>	<u>TIME EXPOSED TO 500 PPM SO₂ AT 1.3 L/MIN²</u>	<u>INITIAL Cl₂ PPM</u>	<u>INITIAL ClO₂ PPM²</u>	<u>Cl₂ RECOVERY, PERCENT</u>	<u>ClO₂ RECOVERY, PERCENT</u>	<u>PRE-ANALYSIS FILTER PURGE TIME, MIN</u>
1	2	3 hrs	32	-	91	-	No Purge
1	3	3 hrs	61	-	89	-	No Purge
1	3	3 hrs	108	-	88	-	No Purge
1	1	3 hrs	271	-	86	-	No Purge
1	1	3 hrs	272	-	98	-	1
1	8	3 hrs	-	8.6	-	73	1
1	9.5	3 hrs	-	19.4	-	69	1
1	7	3 hrs	-	19.6	-	94	1
1	7	3 hrs	-	19.6	-	96	1
1	13	0	-	20.6	-	83	1
1	10	0	-	21.8	-	88	1
1	10	0	-	21.9	-	86	1
1	10	0	29.4	22.1	95	84	1
1	10	0	27.1	22.3	99	86	1
1	10.5	1 hr	24.2	22.7	96	84	1
1	10	1 hr	23.9	22.2	96	86	1
1	10	2 hrs	27.9	20.8	96	83	1
1	10	2 hrs	27.3	21	96	81	1
1	10	3 hrs	25.8	20.5	93	82	1
1	10	3 hrs	25.1	21	96	84	1
1	10	3.5 hrs	30.1	21.6	95	84	1
1	10	3.5 hrs	32.2	20.7	99	84	1
0.2	4	3.5 hrs	29.3	21.6	99	57	2
0.2	4	3.5 hrs	30.1	21.3	103	57	5
0.2	4	3.5 hrs	22.9	20.3	96	61	2

Referring to the data of Table 2, the following conclusions are important:

- (1) Chlorine recoveries were acceptable (86 to 103 percent) under all conditions of the testing;
- (2) Chlorine dioxide recoveries were dependent upon the rate of gas flow through the filter, with low recoveries observed at 0.2 L/min, with no improvement effected by increasing the pre-analysis purge time;
- (3) Exposure of the filters to SO₂ prior to conducting the recovery experiments did not influence the recovery values obtained; and
- (4) In the laboratory tests of recoveries of a mixture of an average of 25 ppm Cl₂ and 22 ppm ClO₂, the recovery of Cl₂ through the high capacity filter averaged 96 percent (2 percent RSD), and the recovery of ClO₂ through the high capacity filter averaged 84 percent (2 percent RSD). Gas flow rates in these tests were 1 L/min.

IV ONGOING STUDIES

As this is written, experimental work is ongoing by NCASI addressing the measurement of chlorine and chlorine dioxide in bleach plant vents via instrumental, continuous methods. One study includes modification and testing of a commercially available high concentration electrochemical sensor based chlorine monitor (Delta Model 964, Delta Xertex, Hauppauge NY). A second study involves testing of a commercially available ultraviolet absorption based instrument for measuring gas phase ClO₂ (Mooney Analytical Systems, Burlington MA). Results of this work will be reported in the near future.

V CONCLUSION

- (1) The buffered dual pH potassium iodide impinger capture method showed good precision upon analysis of gaseous chlorine and chlorine dioxide mixtures. Buffering at pH 7.0 appeared to reduce the chance of obtaining falsely high chlorine concentrations in the presence of high concentrations of chlorine dioxide. A procedure for employing this method is printed in Appendix A.
- (2) A method for removing the sulfur dioxide interference from this and other extractive sampling methods for Cl₂ and ClO₂ was developed. Its performance in removing sulfur dioxide was shown to be acceptable. Its performance in passing chlorine and chlorine dioxide was shown to be dependent upon the rate of gas flow, so that higher flow rates (e.g., 1 L/min) should be employed, rather than lower flow rates (e.g., 0.2 L/min).

VI LITERATURE REFERENCES

- (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) "Chlorine Dioxide Plant Analyses," Canadian Pulp and Paper Association Standard J.14P, May, 1984.
- (5) "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).

APPENDIX A

METHOD FOR MEASURING CHLORINE AND
CHLORINE DIOXIDE GASEOUS EMISSIONS

APPENDIX A

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 (KH_2PO_4) and sodium hydroxide (NaOH), as follows:

Dissolve 20 g KI in ca. 900 mL deionized water
Add 50 mL of 1 M KH_2PO_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 EqI_2N and EqI_2A 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 ClO_2 and Cl_2 employing standard EPA calculations. Assume gas phase water saturation in most vents.

APPENDIX B

PREPARATION OF CHEMICAL FILTERS FOR REMOVAL OF SULFUR DIOXIDE

APPENDIX B

PREPARATION OF CHEMICAL FILTERS FOR REMOVAL OF SULFUR DIOXIDE

PROCEDURE:

1. To prepare 75 mL chromium trioxide solution, add 3.5 mL concentrated H_2SO_4 and 12.5 g CrO_3 to 71.5 mL H_2O .
2. Roll the 12.5 cm glass fiber filters as tightly as possible and dip into the CrO_3 solution. Use gloves and work in an exhaust hood.
3. Place the filters in a drying oven for one hour at 90°C.
4. Assemble the Teflon chamber as shown in Figure 8 of the text. Open the chamber from the end opposite the baffle plate and place the dried filters in the chamber parallel to the bore. The filters should be packed as tight as possible without crushing.
5. Moisten the filters by holding the canister with the open end up and adding 15 to 20 mL H_2O drop by drop at several points on the exposed cross section. Leave in this position for approximately one hour so that the water can be uniformly absorbed in the filter material, and add a few drops more at the end of this time if not completely saturated.
6. Replace the endcap and tighten securely.

MATERIALS:

1. Whatman 12.5 cm glass microfiber filters 934-AH. (Fisher Scientific catalog no. 1827-125)
2. PFA Teflon chamber, 12 cm long, 5 cm diameter. (Galtek Corp., Chaska, MN)
3. Teflon baffle plate, 2 mm thick, 4.5 cm diameter, locally fabricated.
4. Concentrated sulfuric acid.
5. Chromium trioxide (CrO_3), Reagent ACS. (EM Science, Gibbston, NJ)

RECEIVED

MAR 9 1993

Division of Air
Resources Management

**QUALITY ASSURANCE AND MEASUREMENT OF
CHLOROFORM, CHLORINE, AND CHLORINE DIOXIDE
RELEASES FROM BLEACH PLANTS**

SEPTEMBER 1990

TABLE OF CONTENTS

	<u>PAGE</u>
Program for Sampling Bleach Plant Chloroform, Chlorine, and Chlorine Dioxide Emissions	1
Method for Measurement of Chloroform in Bleach Plant Vent Emissions	4
Quality Assurance for the Measurement of Chloroform Emissions from Bleach Plant Vents Via Solid Sorbent Adsorption	14
Methods for Collection of Bleach Plant Effluent Samples for Chloroform Analysis	17
Liquid Sample pH Adjustment and Hexane Extraction	19
Quality Assurance for Measurement of Chloroform in Bleach Plant Effluents and Mill Sewers	20
Analysis Method for Chloroform in Hexane Extracts	22
Method for Measuring Chlorine and Chlorine Dioxide Gaseous Emissions	23
Validation of the Method for Measuring Chlorine and Chlorine Dioxide in Bleach Plant Vents	25
Field and Laboratory Quality Control Check Methods for Use with the Iodometric Method for Measuring Chlorine and Chlorine Dioxide in Pulp Bleach Plant Vents	28

PROGRAM FOR SAMPLING BLEACH PLANT CHLOROFORM,
CHLORINE, AND CHLORINE DIOXIDE EMISSIONS

I INTRODUCTION

NCASI member company representatives in Alabama requested that NCASI staff assemble this program to use as guidance for determining where, when, and how many samples should be collected during testing of bleach plant releases of chloroform, chlorine, and chlorine dioxide. In addition to the sampling information, this program describes the bleach plant operating information that should be collected concurrently with the samples.

II SAMPLE COLLECTION FREQUENCY

A minimum of six samples must be collected from every vent and effluent source. Two samples per day should be collected from each source with a minimum of four hours between each sample for three days. The three sampling days for each source do not have to be concurrent. All of the sources do not have to be sampled on the same days.

III VENT GAS SAMPLING LOCATIONS

Sampling for chloroform emissions must be conducted in each bleach plant vent. Locations where measurements of chloroform from pulp bleach plant vents are needed to determine total releases can be visualized in a much-simplified diagram (Figure 1). Direct gas phase emissions may be contained in each stage's tower, washer hood, and seal tank vent. A CEHD bleach plant which does not provide for common venting could thus have $4 \times 3 = 12$ emission points which would require testing in a bleach plant emission survey. At facilities that have the individual vents ducted together for oxidant scrubbing or some other purpose, the number of vent sampling locations may be reduced significantly. In the simplest situation, all of the bleach vents would be ducted together, thus requiring only one vent sample to be collected.

Sampling for chlorine and chlorine dioxide emissions must be conducted in all bleach plant vents except those containing only extraction stage vent gases.

To calculate mass emissions from the vents, the vent temperature, velocity, moisture content (usually saturated), diameter, pressure, and ambient temperature must be recorded.

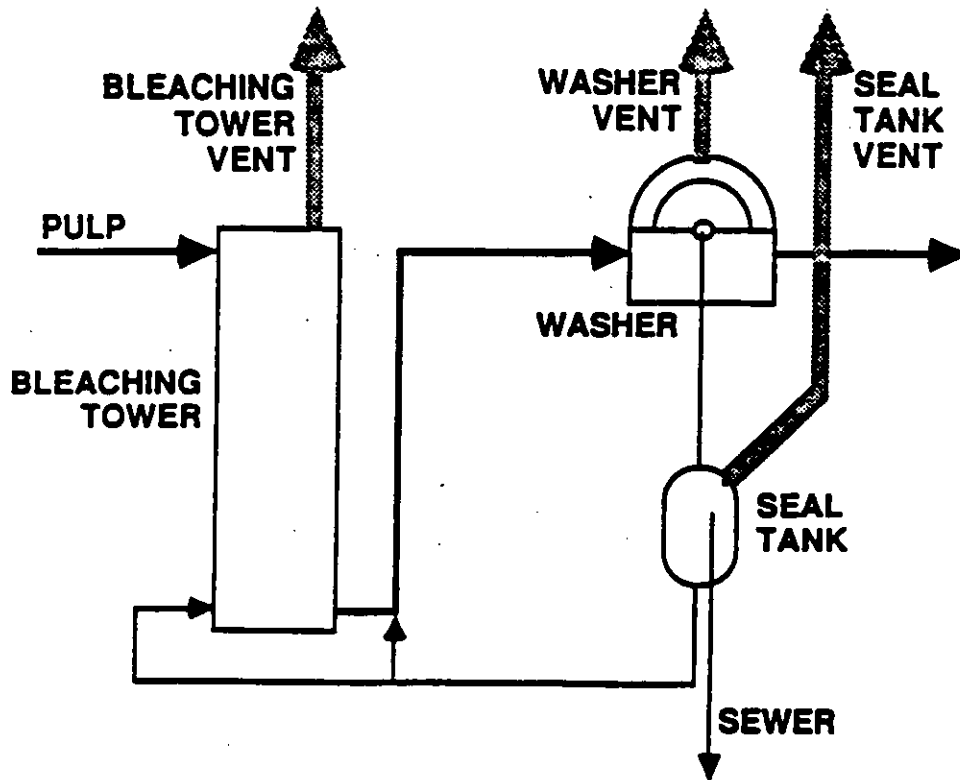


FIGURE 1 TYPICAL VENTING FROM A BLEACHING STAGE

IV LIQUID EFFLUENT SAMPLING

A. Locations to Sample

In addition to the vent gas samples, the bleach plant discharges to effluent treatment must be collected to analyze for chloroform. The bleach plant discharges may be sampled at any point before they reach a tank or channel open to the atmosphere. In the simplest situation, either the combined bleach plant effluent or whole mill effluent could be sampled from an enclosed sewer.

In the next most simple case, samples of the bleach plant alkaline and acid sewers could be collected separately from pipes or enclosed sewers. At some bleach plants, only the first (chlorination) and second (extraction) stage seal tanks overflow to the sewer. In this case, samples of these filtrates would be representative of the bleach plant alkaline and acid sewers. In the most difficult situation where none of the filtrates could be sampled together before they are exposed to the atmosphere, samples of each individual filtrate would have to be collected.

The mass releases of chloroform with the bleach plant effluent must be calculated. Depending on where the liquid samples are collected, e.g., from sewers or filtrate tanks, either the sewer flows must be known from flow measurement or the seal tank filtrate overflows must be calculated via a bleach plant water balance.

B. Sample pH Adjustment

It is known that the chloroform concentration of acidic bleach plant effluents increases when the pH is increased upon mixing with alkaline mill effluent streams. Thus, to obtain the most accurate measurement of the amount of chloroform released to effluent treatment, samples of acidic bleach plant discharges should be adjusted to pH 7 before analysis. Whole mill effluent samples need not have their pH adjusted even if the natural pH is less than 7 since the bleach plant discharges in the whole mill effluent have reached the highest pH that they will encounter.

V PROCESS INFORMATION

Concurrent with sample collection, the values of the following process operating parameters should be collected.

- Brownstock Kappa or K No.
- CE Kappa or K No.
- Pulp Production Rate
- Product Brightness
- Chemical Application Rates (in all stages)
- Tower Temperatures
- Tower pH Values
- Tower Retention Times
- Residuals in Chlorination and Hypochlorite Stages
- Water Reuse Practices

METHOD FOR MEASUREMENT OF CHLOROFORM
IN BLEACH PLANT VENT EMISSIONS

I INTRODUCTION

The method discussed here is very similar to the solid sorbent method reported in NCASI Technical Bulletin No. 531, "Development, Evaluation, and Protocol of Methods for Source Sampling and Analysis for Chloroform in the Presence of Chlorine and Chlorine Dioxide." Several changes have been made to decouple the method for chloroform from the method for chlorine and chlorine dioxide. These changes make the chloroform method much easier to use and allow the sampling train to be constructed entirely glass-free. Additional validation studies on the changed method have been conducted and the results are reported herein. These studies addressed the bias and precision of the method as suggested by a draft EPA protocol for method validation (EPA Contract No. 69-02-4550, Work Assignment 300, June 1990). The method was found to be acceptable by the draft standards.

II METHOD DESCRIPTION

A. Sampling Apparatus

Figure 1 shows a block drawing of the sampling train. The major components of the sampling train are a sampling line, an ambient temperature moisture dropout bottle, a scrubber for removing chlorine and chlorine dioxide from the stack gas, a sorbent tube for capturing the chloroform from the gas stream, and finally apparatus for drawing a constant gas flow through the sample train.

The sample line is composed of $\frac{1}{4}$ inch O.D. Teflon tubing which is also used to connect the various components of the sampling train. The dropout bottle is a 4 oz. Teflon transfer container with $\frac{1}{4}$ inch Teflon compression fittings. The oxidant scrubber is physically similar to the primary sorbent tube shown in Figure 2, except it is packed with solid sodium thiosulfate crystals ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) instead of Tenax sorbent and it has $\frac{1}{4}$ inch to $\frac{1}{2}$ inch reducing compression tube fittings on both ends. The scrubber tube must be repacked when the crystals have melted significantly or turned yellow for more than one-half the length of the tube.

Two sorbent tubes are used in series so that any breakthrough from the front tube will be detected from the analysis of the backup tube. As shown in Figure 2, adsorbent tube housings were prepared entirely from $\frac{1}{4}$ inch O.D. Teflon tubing and fittings. The primary side is 23.5 cm long; whereas

FIGURE 1 NCASI SOUTHERN REGIONAL CENTER SAMPLING TRAIN
FOR CHLOROFORM IN BLEACH PLANT VENTS

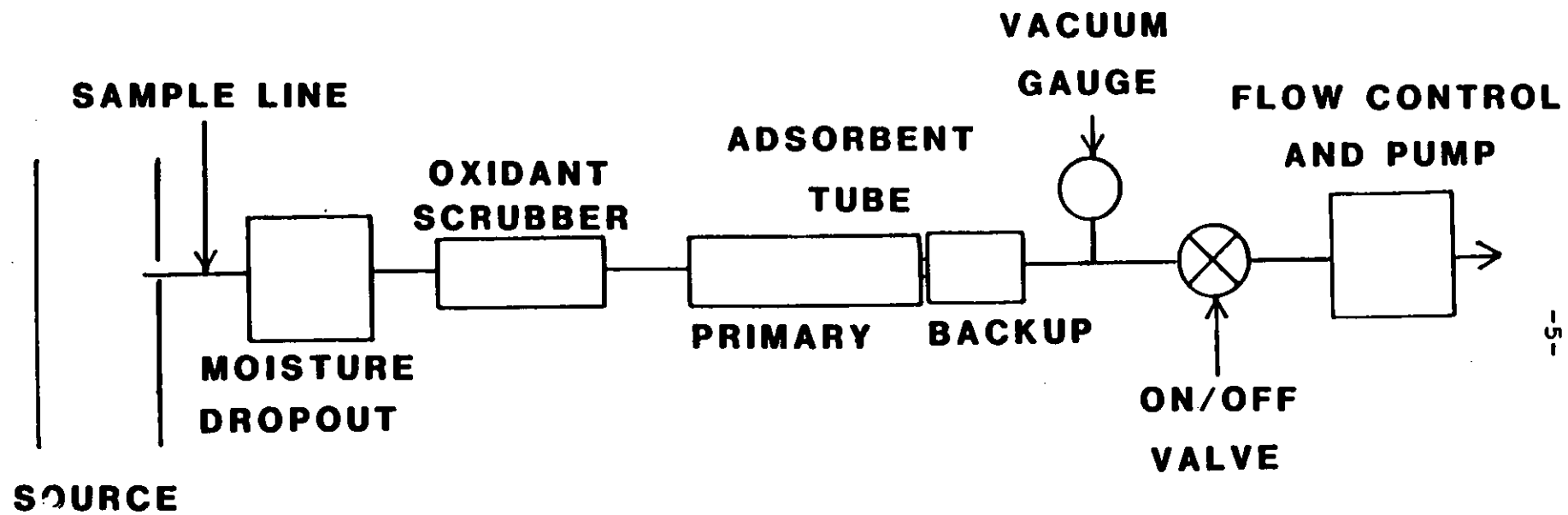
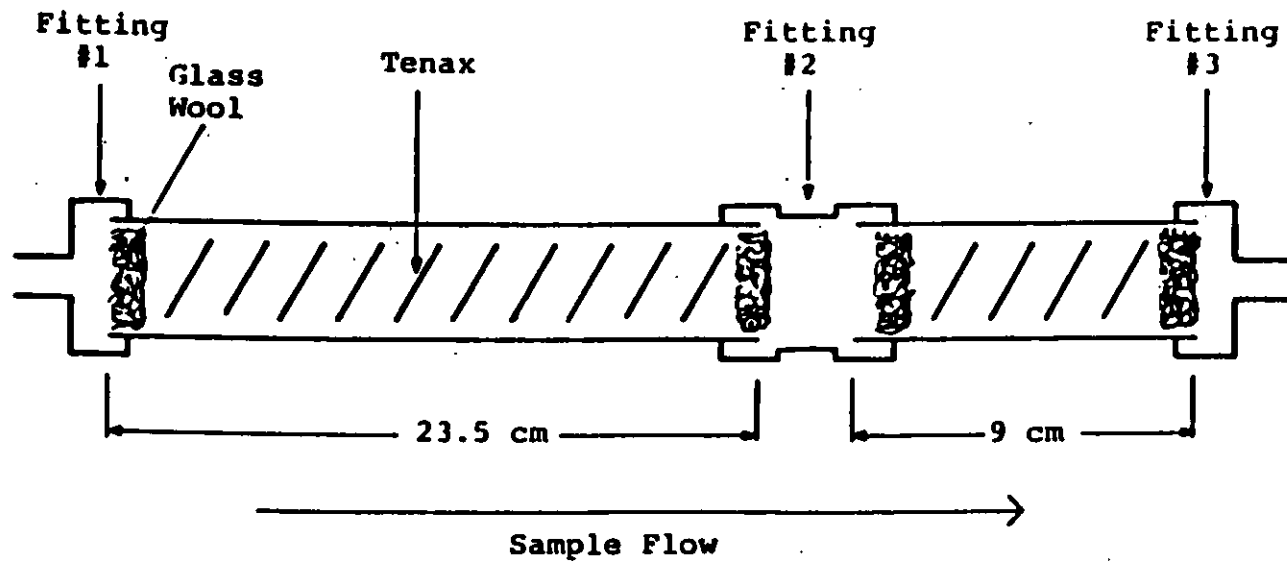


FIGURE 2 ADSORBENT TUBE CONSTRUCTION



the secondary side is 9 cm long. Fittings nos. 1 and 3 are $\frac{1}{4}$ inch to $\frac{1}{4}$ inch reducing unions, fitting no. 2 is a $\frac{1}{4}$ inch union. When the sorbent traps are not in use a $\frac{1}{4}$ inch cap is simply placed on each end, whereas during sampling the $\frac{1}{4}$ inch cap is replaced with a $\frac{1}{4}$ inch Teflon compression nut. A glass wool plug is used at each end of both the primary and secondary traps to retain the adsorbent. The primary end is packed with ca. 2.1 g Tenax TA 60/80 mesh adsorbent; whereas the secondary side is packed with ca. 0.7 g of this material. The tubes are numbered by etching with a vibration engraver. The primary and secondary parts of each tube are given the same number for convenience. Following the sorbent tubes are a vacuum gauge and a shutoff valve which are used in the leak check procedure.

The final components of the sampling train are a pump and flow control device capable of maintaining a constant sampling flow rate of ca. 170 mL/min. One example of appropriate apparatus for drawing the sample is a critical orifice followed by a vacuum pump; a procedure for using this particular scheme is discussed in NCASI Technical Bulletin No. 531.

B. Sampling Procedure

The method should not be used at ambient temperatures above 40°C for two reasons: the sodium thiosulfate crystals will begin to melt and the possibility of breakthrough from the primary Tenax tube increases. After the sampling train is assembled, it must be leak checked. Following the leak test, the flow rate into the end of the sample line (170 \pm 20 mL/min) is checked. The flow rate is checked again at the conclusion of the sampling period. The procedure for leak testing, flow rate testing, and sampling is listed below.

- (1) With the adsorbent tube in place, start the vacuum pump (on/off valve in on position).
- (2) Plug the end of the probe (a $\frac{1}{4}$ inch Teflon compression nut with a male Teflon plug is recommended).
- (3) Allow the pressure to drop so that vacuum gauge no. 1 reads a minimum of 15 in. Hg vacuum.
- (4) Turn the on/off valve to the off position.
- (5) If the vacuum does not rise more than 1 in. Hg on the vacuum gauge in 2 minutes, then the leak test is successful.
- (6) To release the vacuum in the system, remove the plug on the end of the probe.
- (7) With the sample line out of the vent to be sampled, measure the flow rate into the sample probe with an appropriate device. The flow must be 170 \pm 20 mL/min.

- (8) Turn the valve off.
- (9) Insert the sample line into the source and turn on the valve to begin sample collection.
- (10) At the completion of the 20 minute sampling period, remove the sample line from the stack and recheck the sampling flow rate. This flow rate must be within ± 5 percent of the presampling flow rate.
- (11) After the post sampling flow rate check, place a charcoal scrubber on the end of the sample line and continue to draw ambient air through the sampling train for 2 minutes. This procedure allows the sample gas remaining in the dead space ahead of the sorbent tube to be drawn through the tube. Charcoal sorbent tubes used for workplace sampling have been found to make good ambient air scrubbers for use during the post sampling dead space purge.
- (12) Remove the sorbent tube from the system, cap it, and store at 4°C until extraction (maximum storage time 7 days).
- (13) An example form for recording sampling information is shown in Figure 3.

C. Hexane Extraction

The procedure for performing the hexane extraction of the sorbent tubes is listed below.

- (1) Set up an elevated hexane reservoir with a ca. 4 ft long by $\frac{1}{4}$ inch O.D. Teflon line attached to the exit of the reservoir via a short piece of silicone tubing. A 2 L separatory funnel is suggested.
- (2) Disassemble the adsorbent tube at the $\frac{1}{4}$ inch Teflon union and attach the primary side (long side) of the tube to the $\frac{1}{4}$ inch Teflon line.
- (3) With the open end of the adsorbent tube pointed up, turn on the hexane and allow the adsorbent tube to fill. The adsorbent tube is inverted to avoid the possibility of hexane channelling through the adsorbent.
- (4) Just before the hexane reaches the top of the tube ($\frac{1}{4}$ inch), turn the stopcock off.
- (5) Carefully invert the tube over a glass funnel placed in a 100 mL volumetric flask.
- (6) Turn stopcock on and carefully rinse the end of the sorbent tube and funnel with hexane from a Teflon wash bottle.
- (7) Allow the volumetric flask to fill to near the top, turn off

FIGURE 3 EXAMPLE FORM FOR RECORDING SAMPLING INFORMATION

CHLOROFORM SOURCE SAMPLING FIELD DATA SHEET

Company: _____ Location: _____

Name of Sampler(s): _____ Date: _____

Source Description: _____

Adsorbent Tube Number: _____

Ambient Temperature: _____

LEAK TEST

	<u>Time</u>	<u>Vaccum</u>	
Start	_____	_____	Minimum 15 in. Hg
Stop	_____	_____	
Difference	_____	Minimum 2 min.	Maximum 1 in. Hg

RUN

	<u>Time</u>	<u>Flow Rate, mL/min</u>
Start	_____	_____
Stop	_____	_____
Rotometer I.D.:	_____	

the stopcock and add hexane from the wash bottle until the volumetric flask is filled to the mark.

- (8) After mixing the volumetric flask contents by inverting several times, an aliquot of the sample may be poured into a glass sample vial with a Teflon-faced septum. The sample vial should be filled to the top before sealing.
- (9) Repeat steps (2) through (8) with the secondary end of the adsorbent tube. The procedure is identical for the primary and secondary ends of the tube, with the exception that the secondary end is eluted with only 25 mL of hexane; therefore, a 25 mL volumetric flask is used in place of the 100 mL volumetric flask in steps 5 through 7.

D. Tube Cleanup

After extraction, the tubes are connected one at a time to a low pressure source of prepurified nitrogen to remove the liquid hexane from the tubes. The tubes are reassembled and then placed uncapped in an oven at approximately 180°C and left overnight. After baking, the tubes are removed from the oven one at a time and while still hot are again connected to the low pressure nitrogen source. The nitrogen is allowed to flow through the tube before it is capped. The tube is then ready for reuse.

E. List of Vendors

The following is a list of vendors and part numbers used by NCASI for the acquisition of components for sampling train construction, sorbent tube extraction, and gas calibration.

LIST OF VENDORS

<u>VENDOR</u>	<u>PART DESCRIPTION</u>	<u>PART NO.</u>
KNF Neuberger, Inc. P. O. Box 4060 Princeton, NJ 08543 609/799-4350	Pump	20 STP29A-AT
Savillex Corporation 5325 Highway 101 Minnetonka, MN 55343 612/935-4100	Teflon Moisture Dropout Containers, 180 mL	0104-4-2
Galtek Corporation Jonathan Industrial Center Chaska, MN 55318 612/448-6717	Teflon Tubing <u>and Fittings</u> ¼" Heavy Walled FEP Tubing	ET250-030

LIST OF VENDORS (Cont'd)

<u>VENDOR</u>	<u>PART DESCRIPTION</u>	<u>PART NO.</u>
Galtek (cont'd)	1/4" Heavy Walled FEP Tubing	ET500-062
	1/4" FEP Union	SU 8N
	1/4" to 1/4" Reducing Union	SU 8-4N
	1/4" Tube to 1/8" NPT Reducer (Fits in KNF Pump Inlet & Outlet)	C4-2N
Jax Valve & Fitting Co. 3633 Southside Blvd. Jacksonville, FL 32245 904/642-2093	<u>Brass Fittings & Valves</u>	
	1/4" Tube Ball Valve	B-4354
	Female Branch Tee	B-400-3-4TTF
VWR Scientific 1230 Kennestone Circle Marietta, GA 30066-0117 404/423-1354	Vacuum Gauge 0-30 in Hg	31749-006
Alltech Associates, Inc. 2051 Waukegan Road Deerfield, IL 60015 800/255-8324	Tenax TA Porous Polymer 60/80 mesh	049161
Baxter Healthcare Corp. Scientific Products Div. 1430 Waukegan Road McGaw Park, IL 60085-6787 312/689-8410 800/241-2022 (Atlanta)	Hexane, THM Grade, <1 ppb THM	215-235 DK
VWR Scientific 1230 Kennestone Circle Marietta, GA 30066-0017 404/423-1354 800/392-3338 (Dallas)	Hexane, Baker "Capillary Analyzed" (less pure than THM grade) but can be used for samples well above detection limit (with a reagent blank)	JT9126-2

LIST OF VENDORS (Cont'd)

<u>VENDOR</u>	<u>PART DESCRIPTION</u>	<u>PART NO.</u>
Scott Specialty Gases Route 611 Plumsteadville, PA 18949 215/766-8861	Chloroform-in-Air Cylinder Gases	

III VALIDATION TESTING

As referenced in the introduction, the method was tested for precision and bias as suggested by the Draft EPA Protocol for method validation. The results of bias and precision testing as per the protocol are summarized in Tables 1 and 2, respectively.

Table 1 summarizes the results of bias testing. The bias testing is performed by simultaneous sampling with four trains, two of which are dynamically spiked with a chloroform-in-air gas of known concentration. Spike recovery is calculated by comparing the results obtained from the two spiked trains to the two unspiked trains. The protocol specifies that the test be conducted at low, mid-range, and high chloroform concentrations. In this testing, the spike recoveries at the mid-range (59.6 ppm) and the high (320 ppm) concentrations were good at 98 percent and 106 percent, respectively. The chloroform concentration of the source gas used for the low range testing was about a factor of ten too high to obtain accurate quantitation of the spike recovery. Low range bias testing is currently being performed on a lower chloroform concentration source.

Table 2 summarizes the results of precision testing. The protocol specifies that three runs with four replicates be conducted on the same source. The overall method precision is calculated by pooling the relative standard deviations from the three runs. For single instead of replicate sample collection, the draft EPA protocol states that the relative standard deviation (RSD) of the method should be ≤ 15 percent. The highest percent RSD of the three sets is 1.9 percent which is excellent by these standards.

In summary, from the data currently at hand, this method is performing very well relative to bias and precision, as per the standards of the draft EPA protocol.

TABLE 1 CHLOROFORM SOURCE SAMPLING BIAS TESTING VIA DRAFT EPA PROTOCOL.
 NCASI SOLID SORBENT METHOD WITH SODIUM THIOSULFATE
 CRYSTAL OXIDANT SCRUBBER INSTEAD OF KI IMPINGERS.
160 mL/min SAMPLING FLOW RATE, 20 MINUTE SAMPLING PERIOD

SOURCE	CHLOROFORM, PPM							SPIKE RECOVERY, PERCENT
	Spike Level	Unspiked			Spiked			
		Duplicate 1	Duplicate 2	Average	Duplicate 1	Duplicate 2	Average	
D Washer Hood	0.83	5.00	5.10	5.05	6.02	6.06	6.04	121*
E Washer Hood	59.6	12.1	12.2	12.2	72.1	68.8	70.5	98
E Washer Hood	320	13.7	14.1	13.9	352	352	352	106

*Source chloroform concentration was too high for accurate determination of spike recovery.

TABLE 2 CHLOROFORM SOURCE SAMPLING PRECISION TESTING VIA EPA DRAFT PROTOCOL, H WASHER HOOD

REPLICATE ID	CHLOROFORM, PPM		
	Set 1	Set 2	Set 3
A	22.3	91.3	81.2
B	22.7	91.3	81.5
C	23.0	94.8	82.7
D	23.1	93.6	81.9
Average	22.7	92.8	81.8
Standard Deviation	0.36	1.74	0.65
Relative Standard Deviation, Percent	1.6	1.9	0.8

QUALITY ASSURANCE FOR THE MEASUREMENT OF
CHLOROFORM EMISSIONS FROM BLEACH PLANT
VENTS VIA SOLID SORBENT ADSORPTION

I INTRODUCTION

A quality control check procedure for solid sorbent methods for measuring chloroform in pulp bleach plant vents was requested by NCASI member company representatives. The resulting check method is an uncomplicated test which uses cylinders of chloroform in air or nitrogen as challenge gases. It allows mill staff or their contractors a means of checking the accuracy of their methodology.

Quality control testing should be carried out in two areas of method use: in-laboratory and in-field testing carried out prior to bleach plant vent analysis. The chloroform recovery method discussed here may be used identically for both areas.

Cylinder gas for in-laboratory testing must be provided by the contractor.

For the particular purpose for which this protocol was assembled, i.e., bleach plant vent testing by companies in Alabama, Research Triangle Institute (RTI) has agreed to provide cylinder gases to the mills, which they may utilize in their own testing or in contractor testing.

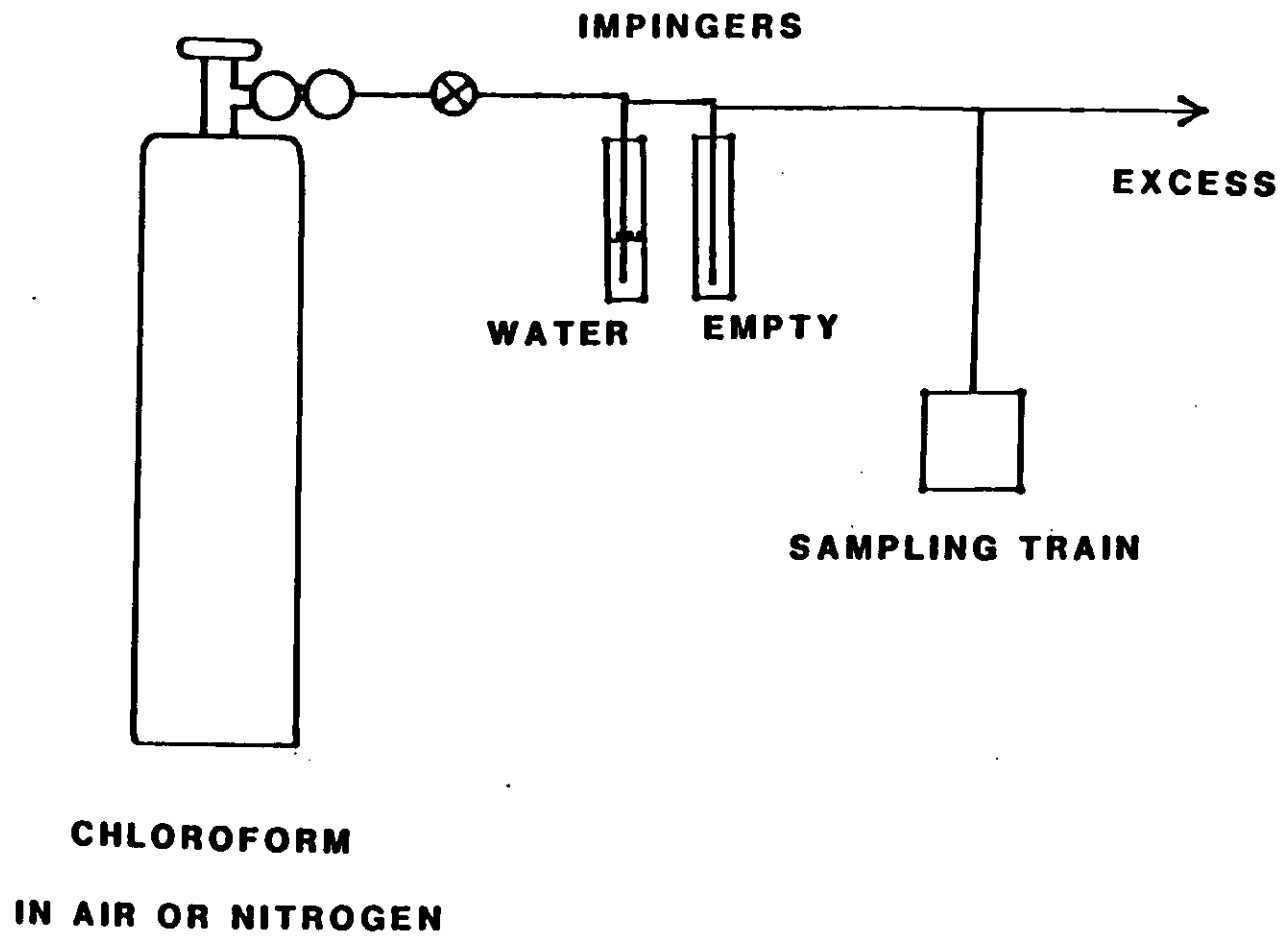
II LABORATORY DEMONSTRATION OF ABILITY

The laboratory must demonstrate its ability to accurately measure the chloroform concentration of laboratory-generated challenge gases. This is a one time demonstration.

The sorbent tubes used for sampling must have a primary and a backup section that are analyzed separately so that it will be known if chloroform breaks through the front section. If the amount of chloroform on the backup section is greater than 10 percent of the total collected, then the sample is voided.

As shown in Figure 1, to prepare challenge gases, a cylinder gas of chloroform in air or nitrogen of the appropriate concentration is passed through a midget impinger containing ca. 20 mL of water to humidify the gas stream. The gas flow rate through the impinger should be ca. 400 mL/min for a method that uses a 200 mL/min sampling flow rate. An empty impinger follows the water containing impinger to collect any liquid water that may leave with the gas stream from the first impinger. The sampling train is connected to a tee in the line exiting the

FIGURE 1 **AUDIT GAS PREPARATION**



second impinger. The gas stream should be allowed to pass through the impingers for five minutes before starting sampling to allow the water in the impinger to become saturated with chloroform.

The three chloroform concentrations used to prepare the challenge gases must be within ± 25 percent of 0.5, 50, and 300 ppm. From three replicates at each concentration, the percent relative standard deviation must be no greater than 10 percent and the average recovery at each concentration must be 100 ± 15 percent.

III FIELD QUALITY ASSURANCE

During each field sampling episode, the samplers must collect duplicate samples of low and high chloroform concentration audit gases. The field audit gas is prepared from cylinders in the same manner as for the laboratory tests. The low and high chloroform concentration audit gases will be in the ranges of 0.5 ppm to 10 ppm and 100 ppm to 300 ppm, respectively. The actual concentration of the audit gases will be unknown to the samplers. All sampling procedures and specifications such as sampling flow rate and sampling period must be the same in the field and laboratory tests. The difference between the results of duplicates must be no greater than 10 percent as defined by the following equation:

$$\text{difference, percent} = \left(\frac{|\text{duplicate 1} - \text{duplicate 2}|}{\text{average}} \right) \times 100$$

The average value of each set of duplicates must be within ± 15 percent of the true value.

METHODS FOR COLLECTION OF BLEACH PLANT
EFFLUENT SAMPLES FOR CHLOROFORM ANALYSIS

I INTRODUCTION

There are several inherent problems associated with obtaining an accurate sample from bleach plant filtrate streams and enclosed sewers for chloroform analysis. Chloroform is a volatile compound, and these sources are often hot and/or under pressure. Consequently, obtaining a sample without suffering significant chloroform loss to the atmosphere is not necessarily a straightforward process. Two methods of sample collection are presented here: one for pressurized and one for unpressurized filtrate and sewer pipes.

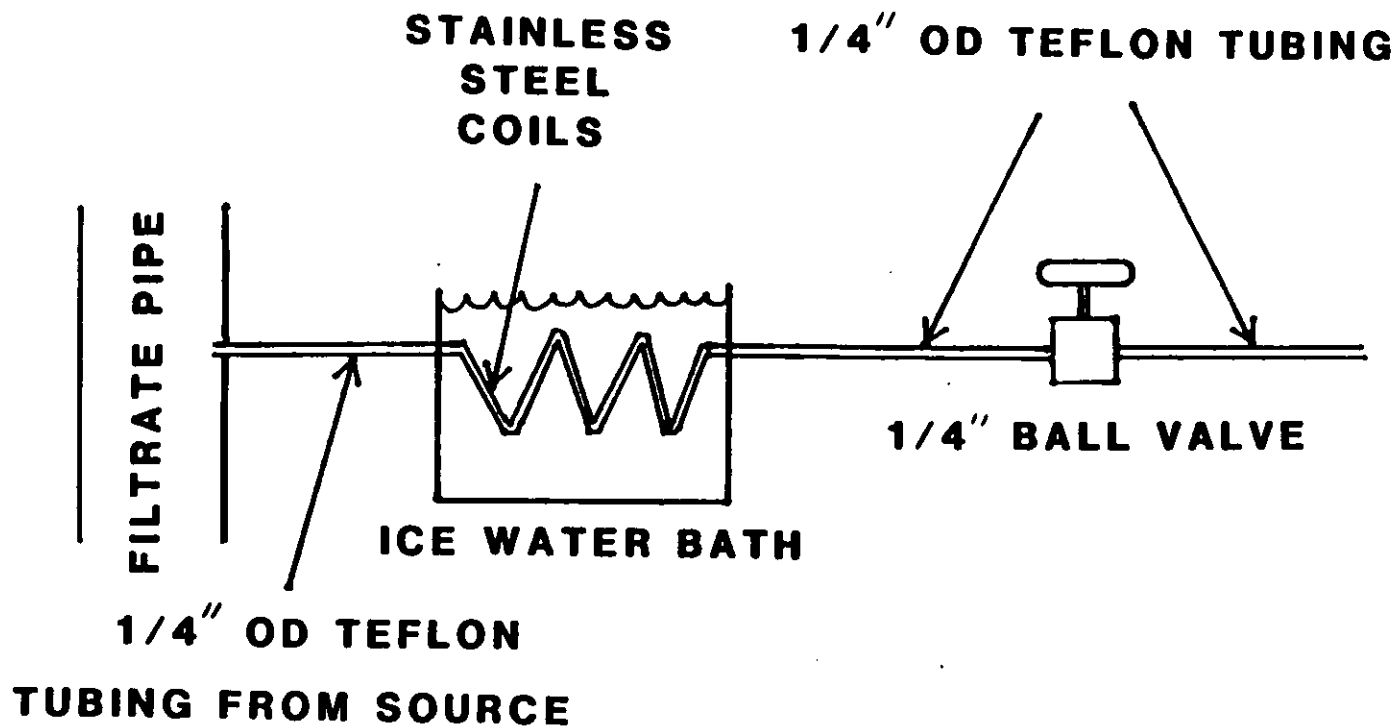
II PRESSURIZED FILTRATE AND SEWER PIPES

This method requires a valve outlet on the pipe of interest to be reduced to 1/4" Swagelok[®]. The basic scheme of this method involves removing a small stream from the filtrate pipe, cooling it under pressure, and filling a sample vial with the cooled stream. Figure 1 details the construction of the sampling system. The 1/4" ball valve is used to provide a slow flow of filtrate out of the system (ca. 0.5 L/min to 1 L/min). The temperature of the liquid leaving the system must be less than 20°C. Sample vials are filled with the tube inserted all of the way to the bottom of the vial; once the vial is overflowing, the tube is removed, the vial is topped off with the filtrate, ca. 0.2 g of sodium thiosulfate crystals ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) are added to the vial, and finally the vial is capped with as little headspace as possible. The samples must be stored at 4°C until they are analyzed. If the sample will require pH adjustment, then 125 mL bottles should be used for sample collection. For samples that will not be pH adjusted, 40 mL vials are adequate.

III UNPRESSURIZED FILTRATE AND SEWER PIPES

The procedure for the collection of samples from unpressurized sources is very similar to the procedure for pressurized sources. The only difference is that a peristaltic pump must be used to supply the sample to the cooling coils shown in Figure 2. A stainless steel sample line or a weighted Teflon line is inserted into the filtrate or sewer stream and connected to the pump. In NCASI studies a hand operated pump was used. The tubing going into and coming out of the pump must be Teflon. The only place that silicone tubing may be used is in the pump body.

FIGURE 1 SAMPLING PRESSURIZED FILTRATE AND SEWER PIPES



LIQUID SAMPLE pH ADJUSTMENT AND HEXANE EXTRACTION

I PROCEDURE WITHOUT pH ADJUSTMENT

The sample must be extracted with an equal volume of hexane before proceeding with the gas chromatographic (GC) analysis. The sample temperature must be less than 10°C when the vial is opened and during the sample withdrawal. The extraction procedure involves inserting a needle, that is attached to a 5 mL glass and Teflon syringe (Gastight[®]), into the sample vial and withdrawing a 5 mL aliquot of the liquid. The liquid sample is then injected through the septum into a previously sealed septum vial that contains an equal volume of hexane. The vial is well shaken, the aqueous and hexane phases are allowed to separate, aliquots of the hexane phase are withdrawn from the vial, and injected into the gas chromatograph (GC) with electron capture detection (ECD). If the extracted sample will be stored before analysis, then a syringe is used to remove the aqueous phase from the bottom of the septum vial and a new Teflon-lined septum is placed on the vial before it is stored.

II PROCEDURE WITH pH ADJUSTMENT

When the sample pH must be adjusted the following procedure is used:

- (1) Place 5.0 mL chilled aliquots via syringe into two sealed, empty 30 mL crimp-top vials with Teflon-lined septa. Two vials are prepared because one may be used as a duplicate or as a backup in the event of an unsatisfactory end pH.
- (2) In a 100-150 mL beaker, titrate 25 mL sample with 1 percent dipotassium phosphate (10 g/L K_2HPO_4) to pH 7.0 while stirring.
- (3) Via syringe, add an appropriate quantity of dipotassium phosphate (amount of 1 percent K_2HPO_4 used above + 5) to the sample aliquot in the vial and shake. Allow to stand for 5 minutes.
- (4) Add 5 mL hexane via syringe to vial, shake vigorously, and allow the aqueous and hexane phases to separate.
- (5) Remove lower aqueous layer with syringe (vial may need to be inverted) and test pH of same. If end pH is not within pH 6.5-7.5, check calculations and repeat.
- (6) Recap vial with new septa for storage prior to analysis to prevent contamination or leakage.

QUALITY ASSURANCE FOR THE MEASUREMENT OF CHLOROFORM
IN BLEACH PLANT EFFLUENTS AND MILL SEWERS

I INTRODUCTION

A quality control procedure for measuring chloroform in bleach plant effluents and mill sewers was requested by NCASI member company representatives. There are two elements to this quality control program: a laboratory demonstration of ability and analysis of unknown samples along with those collected in the field.

For the particular purpose for which this protocol was assembled, i.e., bleach plant effluent testing by NCASI member companies in Alabama, the NCASI Southern Regional Center will provide quality control check samples to be analyzed with the field samples. The individual laboratories or contractors must provide check samples for the laboratory demonstration of ability to accurately analyze for chloroform. Since some samples will need to be adjusted to pH 7 before analysis, all quality control check samples will be acidified and must be adjusted to pH 7.0 ± 0.5 before analysis.

II LABORATORY DEMONSTRATION OF ABILITY

The initial laboratory demonstration of ability requires that check samples of several known chloroform concentrations are prepared and run through the pH adjustment and analysis procedures. Check samples are prepared in triplicate at chloroform concentrations of 0.2 and 20 ppm. The check samples are prepared by acidifying water with HCl to a pH in the range of 1.5 to 2.0. Six sample bottles (125 mL with Teflon seals) are filled with the acidified water. The sample bottles are then spiked via a 25 mL syringe with a quantity of chloroform in methanol solution not to exceed 25 mL. The volume of the bottles must be accurately measured to determine the exact spike volume. For example, if the bottle volume is exactly 125 mL, then 16.9 μ L of 1:1000 (by volume) chloroform in methanol solution could be used for the preparation of 0.2 ppm check samples and 16.9 μ L of 1:10 (by volume) chloroform in methanol solution could be used for the preparation of the 20 ppm check samples. The needle is inserted all of its length into the bottle to inject the spike. Immediately after adding the spike the bottles are sealed and then chilled to 4°C before analysis.

Samples of the acidified water and methanol used to prepare the check samples must be analyzed along with the check samples. The chloroform concentrations of the blank acidified water and methanol must be less than 0.01 ppm and 10 ppm, respectively.

The pH of the check samples after adjustment must be between 6.5 and 7.5. The relative standard deviation of the measured chloroform concentration of each triplicate set of check samples must be less than 10 percent, and the average value must be within ± 15 percent of the spike concentration.

III FIELD QUALITY ASSURANCE

Two quality control check samples with the chloroform concentrations unknown to the contractor or laboratory must be analyzed with each set of field samples. The check samples should be analyzed, and the results compared to the true values before proceeding with the analysis of the mill samples. These samples will be provided to the mills by the NCASI Southern Regional Center. These samples will be acidified and must be put through the pH adjustment and analysis procedures. One of the samples will have a low chloroform concentration (0.1 ppm to 1 ppm); the other sample will have a high chloroform concentration (10 ppm to 30 ppm). The measured pH of the samples after adjustment must be in the range of 6.5 to 7.5. The measured chloroform concentration of each sample must be within ± 15 percent of the true concentration.

ANALYSIS METHOD FOR CHLOROFORM IN HEXANE EXTRACTS

This method is used for the analysis of the hexane extracts from air and liquid sampling. The analysis is performed on a gas chromatograph (GC) with electron capture detection. The GC operating conditions are as follows:

Carrier Gas: Ar 90%/Methane 10% at 6 mL/min

Temperature Program:

Step 1: 30°C for 1 min; then 5°C/min to 60°C
Step 2: 70°C/min to 145°C for 30 sec

Retention Time: about 6.5 min

Injector Temperature: 200°C

Detector Temperature: ECD 300°C

Column: J and W DB-624 30 m x 0.53 mm

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 (KH_2PO_4) and sodium hydroxide (NaOH), as follows:

Dissolve 20 g KI in ca. 900 mL deionized water
Add 50 mL of 1 M KH_2PO_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 EqI_2N and EqI_2A 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 ClO_2 and Cl_2 employing standard EPA calculations. Assume gas phase water saturation in most vents.

VALIDATION OF THE METHOD FOR MEASURING CHLORINE
AND CHLORINE DIOXIDE IN BLEACH PLANT VENTS

The method was tested for precision and bias as suggested by the Draft EPA Protocol for method validation (EPA Contract No. 69-02-4550, Work Assignment 300, June 1990). The results of bias and precision testing as per the protocol are summarized in Tables 1 and 2, respectively.

Table 1 summarizes the results of bias testing. The bias testing is performed by simultaneous sampling with four trains, two of which are spiked prior to sampling with 2 mL of potassium iodate solution. Spike recovery is calculated by comparing the results obtained from the two spiked trains to the two unspiked trains. The protocol specifies that the test be conducted at low, mid-range, and high spike concentrations. In this testing, the spike recoveries at the low, mid-range, and high concentrations were good, with spike recoveries of 102, 100, and 101 percent, respectively. The average bias was +1 percent which compares very well to the draft EPA guidance of a maximum of ± 5 percent bias.

Table 2 summarizes the results of precision testing. The protocol specifies that three runs with four replicates be conducted on the same source. If the precision data are homogenous, the overall method precision is calculated by pooling the relative standard deviations from the three runs. If the data are not homogenous, the highest standard deviation is used as the precision of the method. In this case the precision data were not homogenous, so the precision of the method is the highest standard deviations which were 14.5 percent for chlorine and 1.4 percent for chlorine dioxide. These numbers fall into the category of the EPA protocol which says that if the relative standard deviation is ≤ 15 percent then a single sampling train is sufficient for the measurement.

In summary, this method is performing very well relative to bias and precision, as per the standards of the draft EPA protocol.

**TABLE 1 BIAS TESTING OF SOURCE CHLORINE AND
CHLORINE DIOXIDE MEASUREMENT METHOD**

<u>SOURCE</u>	<u>SPIKE LEVEL, EQ.</u>	<u>UNSPIKED SAMPLES</u>				<u>SPIKED SAMPLE ACID EQ.</u>	<u>SPIKE RECOVERY, PERCENT</u>
		<u>Neutral Eq.</u>	<u>Acid Eq.</u>	<u>Cl₂, ppm</u>	<u>ClO₂, ppm</u>		
E Washer Hood	0.00560	0	0	0	0	0.00569	102
#1 CEHD Seal Tank Vent	0.05600	0.01277	0.04862	10.1	47.8	0.10460	100
#2 CEHD Seal Tank Vent	0.5600	0.12472	0.35404	460	783	0.91689	101

TABLE 2 PRECISION TESTING OF SOURCE CHLORINE AND CHLORINE DIOXIDE MEASUREMENT METHOD

<u>REPLICATE ID</u>	<u>CHLORINE, ppm</u>			<u>CHLORINE DIOXIDE, ppm</u>		
	<u>Set 1</u>	<u>Set 2</u>	<u>Set 3</u>	<u>Set 1</u>	<u>Set 2</u>	<u>Set 3</u>
A	56.5	18.4	29.8	179	90.2	91.5
B	40.3	14.0	29.1	182	90.9	90.3
C	46.6	16.5	23.7	181	92.0	93.1
D	52.6	15.6	26.4	185	89.9	92.4
Mean	49.0	16.1	27.3	182	90.8	91.8
Standard Deviation	7.1	1.84	2.78	2.50	0.93	1.21
Relative Standard Deviation, Percent	14.5	11.4	10.2	1.4	1.0	1.3

FIELD AND LABORATORY QUALITY CONTROL CHECK METHODS FOR USE
WITH THE IODOMETRIC METHOD FOR MEASURING CHLORINE AND
CHLORINE DIOXIDE IN PULP BLEACH PLANT VENTS

I INTRODUCTION

A quality control check procedure for the iodometric method for measuring chlorine and/or chlorine dioxide in pulp bleach plant vents was requested by NCASI member company representatives. The resulting check method is an uncomplicated test which uses weighed potassium iodate in a known quantity, and utilizes the same reagents as the method for chlorine and chlorine dioxide vent sampling as described in NCASI Technical Bulletin No. 520 (1). It allows mill staff or their contractors a means of checking their methodology and reagent integrity.

Quality control testing should be carried out in two areas of method use: in-laboratory and in-field testing carried out prior to bleach plant vent analysis. The potassium iodate recovery method discussed here may be used identically for both areas. Because potassium iodate releases iodine only upon acidification, direct recovery calculations (e.g., as ppm ClO_2) cannot be made: instead, the number of equivalents of iodine measured is the quantity determined.

In-laboratory testing conducted prior to bleach plant vent analyses may utilize potassium iodate recovery check samples prepared by a mill laboratory, or by a contractor. For the particular purpose for which this protocol was assembled, i.e., bleach plant vent testing by NCASI member companies in Alabama, the Southern Regional Center of NCASI will provide potassium iodate field recovery check samples to the mills, which they may utilize in their own testing, or in contractor testing. When used for the latter, it is suggested that the concentration of the iodate solution remain unknown to the contractor prior to testing.

II SUMMARY OF QUALITY CONTROL CHECK PROCEDURE

The procedure for vent gas chlorine and chlorine dioxide analyses described in NCASI Technical Bulletin No. 520 employs sample collection in two midget impingers containing neutral, buffered potassium iodide solution. After sample collection, the contents of the impingers are combined and titrated with standard sodium thiosulfate solution to a colorless endpoint. After recording the volume of titrant to this first endpoint, the solution being analyzed is acidified with sulfuric acid solution, and the titration is continued to a second endpoint indicated by a colorless solution. (Starch solution may be employed to detect

the second endpoint.) The total titer (volume to first plus second endpoints) is recorded.

The equations employed to calculate moles of chlorine and moles of chlorine dioxide captured and titrated are as follows:

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

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

$$\text{ClO}_2 \text{ moles} = \frac{1}{2}\text{EqI}_2\text{A} - \frac{1}{2}\text{EqI}_2\text{N}$$

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

where T_N and T_A are the volumes of thiosulfate of normality \bar{N} required to reach the first and second (total) endpoints, respectively; and EqI_2A and EqI_2N are the number of equivalents of iodine titrated at acid (total acid and neutral titer) and neutral pH. For example, considering a dry vent and conditions such that 1 mole of gas = 24.0 L, collecting a gas sample for 30 minutes at 0.200 L/min, with $T_N = 1.25$ mL and $T_A = 6.25$ mL of 0.010 N sodium thiosulfate solution,

$$\text{EqI}_2\text{N} = (1.25)(10^{-3})(10^{-2}) = 1.25 \times 10^{-5}$$

$$\text{EqI}_2\text{A} = (6.25)(10^{-3})(10^{-2}) = 6.25 \times 10^{-5}$$

$$\text{ClO}_2 \text{ moles} = \frac{1}{2}(6.25 \times 10^{-5}) - \frac{1}{2}(1.25 \times 10^{-5}) = 1.25 \times 10^{-5}$$

$$\text{Cl}_2 \text{ moles} = \frac{1}{8}[5(1.25 \times 10^{-5}) - 6.25 \times 10^{-5}] = 0$$

$$\text{ppm ClO}_2 = \frac{(1.25 \times 10^{-5} \text{ moles})(24 \text{ L/mole}) \times 10^6}{(0.200 \text{ L/min})(30 \text{ min})} = 50$$

Employing this example to illustrate the quality control check procedure, a sampling train is assembled, and an aliquot of 2.0 mL of 0.028 N potassium iodate solution is added to the first impinger. The impinger contents are combined and acidified, and the total acid titer is recorded, in this example 5.5 mL of 0.010 N sodium thiosulfate solution. Recovery of the check standard is

$$\frac{(5.5)(10^{-3})(10^{-2})}{(2.0)(10^{-3})(2.8 \times 10^{-2})} \times 100 = 98\%$$

It should be pointed out that the total number of acid equivalents measured in the recovery check (5.5×10^{-5}), is

similar to the total number of acid equivalents measured in the analyses of the vent gas (6.25×10^5). If possible, recovery check samples should be used which contain the same order of magnitude of equivalents as the acid titer of the analyses to be carried out.

III PREPARATION AND ANALYSIS OF THE QUALITY CONTROL CHECK SAMPLE

The potassium iodate check sample is prepared and analyzed as follows:

Reagent Preparation

0.280 N Potassium Iodate - Dissolve 1.00 g KIO_3 , which has been dried at $103 \pm 2^\circ C$ for one hour, in 100 mL deionized H_2O . For field evaluation, take aliquots of this reagent, which can be stored in clean polypropylene bottles for one week.

Buffered Potassium Iodide - Dissolve 20 g potassium iodide in ca. 900 mL deionized water. Add 50 mL of 1 M potassium dihydrogen phosphate (1 M KH_2PO_4 = 13.6 g/100 mL) and 30 mL of 1 M sodium hydroxide (1 M $NaOH$ = 4.0 g/100 mL). Measure pH and add 1 M $NaOH$ to bring the pH to between 6.95 and 7.05.

0.100 N Sodium Thiosulfate - Normality may vary slightly, but must be standardized and recorded. Standardize as per Standard Methods, 17th ed., p. 4-49.

Starch Solution - Make a paste of ca. 5 g soluble starch and a few mL deionized water and grind as with a mortar and pestle. Add this to ca. 500 mL hot deionized water, and mix well. Cool before using.

10 percent sulfuric acid, by volume. (Add acid to water.)

Analysis Procedure Example

Add a 10.0 mL 0.280 N KIO_3 aliquot to 50 mL buffered KI in a 150 mL beaker. Rinse the KIO_3 container with a small amount of water and add to the beaker, to make sure it has all been transferred. Add 5 mL 10 percent H_2SO_4 , and titrate with 0.1 N sodium thiosulfate while stirring until the dark orange color turns medium yellow. Add a few mL of the starch solution, and slowly continue titrating until the blue color disappears. Solve the following equation:

(L titrant)(normality of titrant) = equivalents in QC sample titrated.

The result should be 2.80×10^{-3} equivalents.

Analysis Results

In laboratory trials, 27.90, 27.95, and 27.95 mL of 0.0999 N $\text{Na}_2\text{S}_2\text{O}_3$ were used to titrate a 10.0 mL aliquot of 0.280 N KIO_3 , for an average of 2.79×10^{-3} equivalents, which is 99.7 percent of the predicted recovery. In three trials in which the aliquots were stored five days in polypropylene bottles, the results were 28.0, 28.0, and 27.95 mL of 0.0999 N thiosulfate, an average of 2.795×10^{-3} equivalents, which is 99.8 percent recovery.

IV RECOVERY OF THE CHECK SAMPLE

Until more extensive field recovery data are available, acceptable recovery of the check sample should be 100 ± 10 percent.

V REFERENCE

(1) "Optimization and Evaluation of an Impinger Capture Method for Measuring Chlorine and Chlorine Dioxide in Pulp Bleach Plant Vents," NCASI Technical Bulletin No. 520, NCASI, 260 Madison Avenue, New York, NY 10016 (April, 1987).

APPENDIX A

METHOD FOR UTILIZING THE CHLORINE AND
CHLORINE DIOXIDE RECOVERY CHECK SAMPLE

Refer to Section II of this report for an example of the use of the recovery check sample.

Bleach plant vent gas sampling and analysis for chlorine and chlorine dioxide shall be conducted according to the method of NCASI Technical Bulletin No. 520. One analysis of the vent gas sample shall be conducted prior to the recovery demonstration to ascertain the approximate concentration of the vent gases. The total acid equivalents of the sample shall be determined under the conditions of sampling flow rate and time to be employed, and this information shall be provided to the mill's quality control representative responsible for providing the recovery check sample to the testing personnel.

The sampling train is assembled, and the recovery check sample is added to the potassium iodide solution in the first impinger in the train. The impinger contents are combined in the prescribed manner and analyzed by titration with sodium thiosulfate solution. The sample train contents containing the recovery check sample are acidified and titrated at acid pH only.

Calculate recovery of the check sample according to the following:

$$\frac{(\text{mL acid titer})(10^{-3})(\text{normality thiosulfate})}{(\text{mL QC check sample})(10^{-3})(\text{normality QC check sample})} \times 100$$

The BACT limits for the proposed modification of the Champion International Corporation's facility are thereby established as follows:

Source	Pollutant	Emission Standard/Limitation
#6 Power Boiler	NO _x *	0.06 lb/MMBtu (32.0 lbs/hr, 140.1 TPY)
	CO*	0.1 lb/MMBtu (53.3 lbs/hr, 233.5 TPY)
	VOCs*	0.01 lb/MMBtu (5.33 lbs/hr, 23.4 TPY)
		Combustion Control
		Combustion Control
Lime Kiln-Mud Dryer	NO _x *	#6 fuel oil: 200 ppmvd @ 10% O ₂
		(49.3 lbs/hr, 215.9 TPY)
	CO*	Natural Gas: 175 ppmvd @ 10% O ₂
		(43.1 lbs/hr, 188.8 TPY)
VOCs*	45 ppmvd @ 10% O ₂ (6.75 lbs/hr, 29.6 TPY)	
	104 ppmvd @ 10% O ₂ (as propane)	
		(24.5 lbs/hr, 107.3 TPY)

* 24-hour average

Note: The maximum sulfur content of the #6 fuel oil is 1.0%, by weight.

Details of the Analysis May be Obtained by Contacting:

Bruce Mitchell, Environmental Administrator
 Department of Environmental Protection
 Bureau of Air Regulation
 2600 Blair Stone Road
 Tallahassee, Florida 32399-2400

Recommended by:

Approved by:

C. H. Fancy
 C. H. Fancy, P.E., Chief
 Bureau of Air Regulation

Virginia B. Wetherell
 Virginia B. Wetherell, Secretary
 Dept. of Environmental Protection

3/28 1994
 Date

3-31 1994
 Date