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METHODS DEVELOPMENT FOR SAMPLING AND ANALYSIS OF CHLORINE, CHLORINE DIOXIDE, BROMINE, AND IODINE

Research Report for Chlorine Dioxide

to

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
National Institute for Occupational Safety and Health

Project 4558-R1

Southern Research Institute

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to

Ms. Mary Ellen Cassinelli, Project Officer

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service, Centers for Disease Control
National Institute for Occupational Safety and Health
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Contract 210-80-0067

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ABSTRACT

This report describes an unsuccessful attempt to develop a personal air sampling and analysis method for the determination of chlorine dioxide in workplace air. To take advantage of the relatively high inherent reactivity of chlorine dioxide, candidate reactive solids were screened for their potential utility as sampling media. In contrast to chlorine dioxide's well-known solution reactivity, however, its reactivity in the gas phase with solid sorbents was found to be rather poor and to be confined largely to the formation of ionic salts or complexes. Hence, no suitable solid-state sampling medium was found. An impinger-type spectrophotometric method based on the decolorization of chlorophenol red (CPR) by chlorine dioxide was then investigated. The precision, sampling capacity, storability, specificity, sensitivity, and analyte slippage rates associated with this method appeared to be quite acceptable for validation, but the accuracy of the method could not be established within the remaining contract budget and period of performance. The method exhibited a systematic bias relative to the reference method, which was based on dual-pH iodometry, and our attempts to determine which method was at fault were not successful.

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ACKNOWLEDGMENTS

The concientious attention given to our work by NIOSH personnel--including Ms. Mary Ellen Cassinelli and Ms. Doris V. Sweet, Project Officers, Dr. Peter M. Eller, Alternate Project Officer, and Dr. David G. Taylor, Chief, Inorganic Methods Section of the Methods Research Branch--facilitated the planning and completion of our research efforts. These individuals were meticulous in their analysis of our experimental protocol and progress reports and often made suggestions that were advantageous to the directions and outcome of experiments. Through meetings with our staff and periodic telephone conversations, they kept abreast of our work.

Overall supervision of the project was the responsibility of Dr. Herbert C. Miller, Head, Analytical and Physical Chemistry Division. Ms. Martha L. Bryant, Associate Chemist, performed most of the experimental work under the direction of Dr. William K. Fowler, Program Manager, Chemical Detection Methodology, and Dr. H. Kenneth Dillon, Head, Industrial Hygiene Chemistry Section. Other Southern Research Institute personnel provided assistance in the execution of this work. These included Dr. Edward B. Dismukes, Senior Research Advisor, Merry B. Emory, Research Chemist, Marynoel M. Graham, Associate Chemist, John C. Harmon, Research Chemical Technician, Ruby H. James, Head, Environmental Analytical Chemistry Section, Marion C. Kirk, Research Chemist, Debra H. Love, Assistant Chemist, Sherri L. McCarthy, Technical Editor, David W. Mason, Associate Chemist, Richard J. Remy, Information Scientist, Lucy M. Rose, Research Chemist, and Lee Ann Wallace, Research Chemical Technician.

An additional source of valuable information during this project was Dr. Robert Fisher of the National Council of the Pulp and Paper Industry for Air and Stream Improvement (NCASI) in Gainesville, FL. Much of Dr. Fisher's recent research work was closely related to the objectives of this project. We remained in frequent contact with Dr. Fisher throughout the period of this project, and during this period, he cited several worthwhile publications and addressed a number of technical questions that arose in connection with our work.

METHODS DEVELOPMENT FOR SAMPLING AND ANALYSIS OF CHLORINE, CHLORINE DIOXIDE, BROMINE, AND IODINE

Research Report for Chlorine Dioxide

I. INTRODUCTION

This report describes our attempt to develop and validate a method for the sampling and analysis of chlorine dioxide in air at concentrations in the vicinity of the permissible exposure limit (PEL), 0.1 ppm (v/v). As stipulated by the contract Scope of Work, preference was given to solid-state sampling technology (as opposed to "wet" sampling techniques) during this project. Moreover, specificity with respect to chlorine dioxide was required of all candidate sampling and analysis methods because the vapors of chlorine and chlorine dioxide may occur jointly in certain industrial hygiene settings. Also emphasized in this work was the evaluation of reactive, rather than inert, sampling media; in view of the extraordinary chemical reactivity of chlorine dioxide, it seemed logical to take advantage of this reactivity rather than to attempt to avoid a reaction altogether. Hence, our plan was to identify a solid substance that would react specifically and quantitatively with chlorine dioxide vapor to form a unique product that was more stable and more amenable to determination than chlorine dioxide itself.

The first task to be addressed in this project was a search of the scientific and technical literature to acquire background information pertaining to the sampling and analysis of chlorine dioxide and other substances that fell within the scope of this contract. This search comprised, in part, a systematic perusal of the indices and tables of contents of certain reference works available in our technical library such as the Kirk-Othmer Encyclopedia of Chemical Technology and the multi-volume Treatise on Analytical Chemistry. Additionally, a computer search was executed by means of the facilities available through the Lockheed DIALOG Information Retrieval Service of the North Carolina Science and Technology Research Center. The data bases involved in this computer search were Chemical Abstracts (1967 to present) and the National Technical Information Service (NTIS, 1964 to present). Collectively, these procedures resulted in the accumulation of a large, comprehensive body of information on chlorine dioxide.

Much of the contract experimental work with chlorine dioxide entailed the preparation, evaluation, and calibration of chlorine dioxide test atmospheres and the screening and evaluation of candidate reactive sampling media. After no suitable candidate solid-state sampling media could be found, an aqueous impinger method based on the decolorization of chlorophenol red (CPR) by chlorine dioxide was subjected to an intensive investigation. These topics, along with our recommendations for future developmental work, are delineated in the remainder of this report.

II. PREPARATION, EVALUATION, AND CALIBRATION OF CHLORINE DIOXIDE TEST ATMOSPHERES

A. Construction and Operation of a Test-Atmosphere Generator

In the construction and operation of our test-atmosphere generator for chlorine dioxide, we relied heavily upon the experiment and advice of Dr. Robert Fisher of NCASI. The NCASI laboratory evaluated two basically similar methods of chlorine dioxide generation. One of these methods involved the passage of a dilute stream of chlorine vapor through a bed of solid sodium chlorite, while the other method entailed the passage of dilute chlorine vapor through a concentrated aqueous solution of sodium chlorite (specifically, 10 g of $NaClO_2$ in 25 mL of water). Of these two methods, only the latter produced a chlorine-free stream of chlorine dioxide vapor. Therefore, we used this method to generate chlorine dioxide in most of our work under this contract. The required source of chlorine vapor was a calibrated mixture of chlorine and nitrogen available from Matheson, Inc., Morrow, GA; the chlorine concentration in this mixture was approximately 100 ppm.

The generator was designed so that test atmospheres of chlorine in air could also be produced as required in interference tests (see Section IV.E). A regulated stream of the calibrated mixture of chlorine and nitrogen was simply diluted with filtered air to obtain chlorine concentrations of about 1 to 3 ppm (1 to 3 PEL).

A vapor-generation system intended to produce steady-state vapor concentrations of chlorine dioxide (and chlorine) at the appropriate test levels was constructed as depicted schematically in Figure 1. All components that were exposed to analyte vapor consisted of glass, Teflon, or other suitably inert materials. The entire apparatus was shielded from light and was operated beneath a laboratory fume hood. The main components of the system were as follows:

- separate primary generation sources for chlorine dioxide vapor and chlorine vapor (as described above),
- a dilution and mixing chamber for mixing the analytes with dilution air, and
- a sampling chamber for the exposure of sampling devices.

As can be seen in Figure 1, the carrier stream bearing the species of interest was diluted with filtered air that could be humidified as needed. The humidifier was merely an impinger that was filled with liquid water. The analyte dilution factor at this stage was adjusted to 100 or greater as required. Humidity levels were determined at the output port (sampling chamber) by sampling a known volume of the output air through a tared bed of desiccant (e.g., magnesium perchlorate or calcium sulfate) and weighing the collected water.

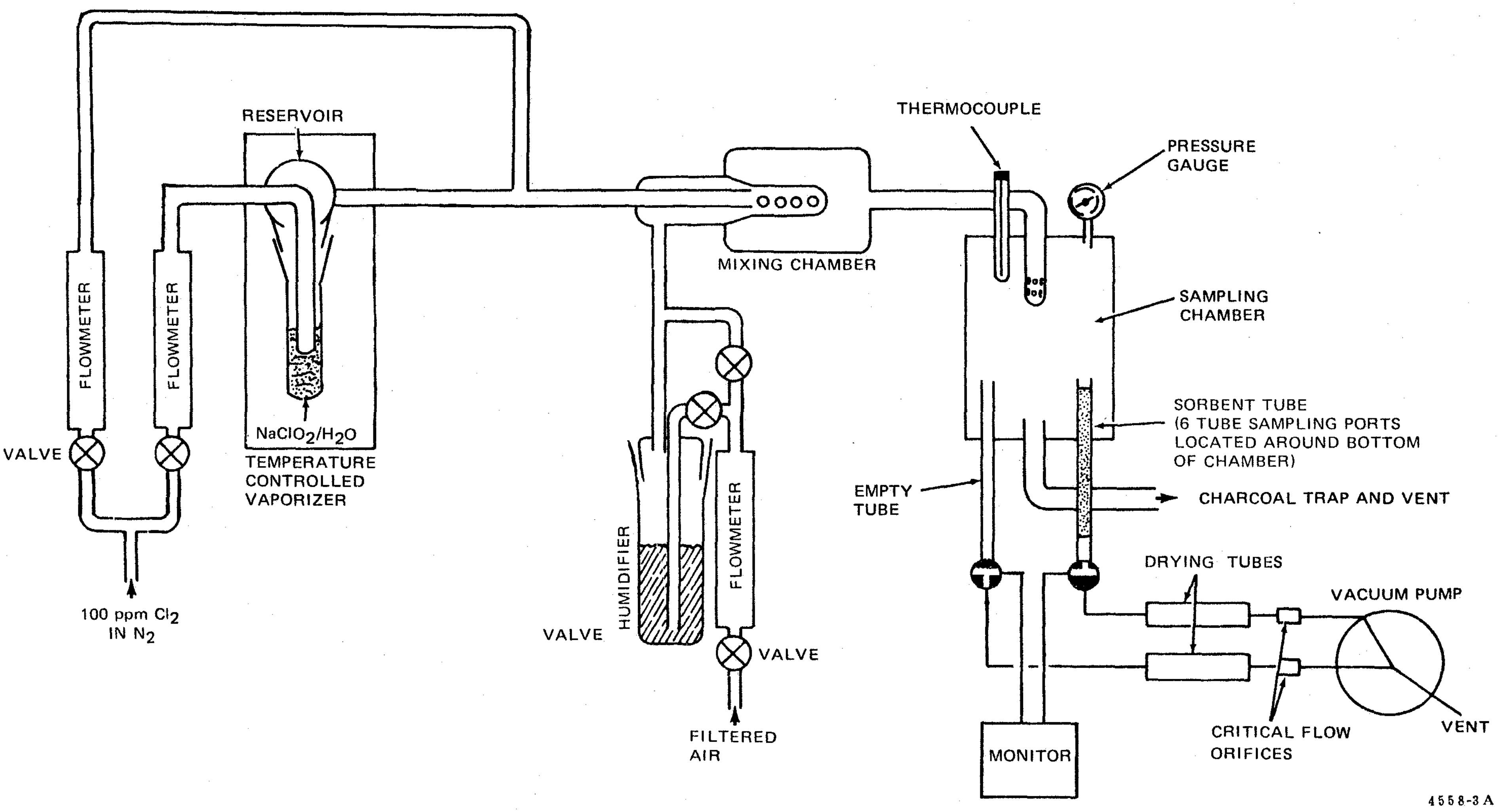

Figure 1. Schematic diagram of test-atmosphere generator and sampling system.

The effluent from the final dilution stage was fed directly into a sampling stage consisting of a cylindrical glass chamber about 15 cm in length and approximately 10 cm in diameter. Teflon endcaps for the cylinder contained appropriate openings and access ports for insertion of a thermometer, a sampling line for a continuous monitor, and several sampling devices. An additional opening was employed for venting the excess effluent through a charcoal trap and into a laboratory fume hood.

The chlorine dioxide vapor concentration in the generator output stream was monitored continuously with a Model 724-5 portable oxidant monitor from Mast Development Corp., Davenport, IA. This monitor provided the capability for the continuous detection of chlorine dioxide in air at concentrations down to approximately 0.1 ppm. The monitor's principle of operation is based on the oxidation of iodide ion to iodine, followed by the oxidation of hydrogen by the liberated iodine. The loss of hydrogen at the maximally polarized platinum cathode partially depolarizes the electrode, thereby permitting a polarization current to flow in the electrochemical cell. Unfortunately, the device is relatively nonspecific in that it responds to most oxidants. In addition, it is extremely intolerant of minor pressure differences between the sampled atmosphere and the ambient atmosphere. Both of these drawbacks limited significantly the usefulness of the Mast monitor in the work of this contract.

In operation, the generator provided a continuous volume output of about 5 L/min at a constant but adjustable concentration of chlorine dioxide in the parts-per-million and sub-parts-per-million range. The chlorine dioxide vapor concentration was adjusted to the desired level by altering the temperature of the sodium chlorite solution, the feed rate of chlorine passing into the sodium chlorite solution, or the flow rate of the dilution air. The generator effluent stream could be humidified to any desired level up to the saturation point, and because the mixing chamber and sampling chamber were wrapped with heating tape, the output vapor could be warmed above ambient temperature to approximately 45 °C.

B. Reference Analytical Methods

To calibrate the continuous monitor, a reference analytical method for chlorine dioxide was selected and evaluated following the literature survey. The method was expected to display high specificity for the species of interest and adequate sensitivity for all anticipated work. In addition, a method was desired that could be standardized with reagents other than the analytes themselves. Other factors that were considered included cost, analysis time, simplicity of execution, and linear dynamic range.

The analytical method that was chosen as the reference method for chlorine dioxide was the chlorophenol red (CPR) colorimetric method of Wheeler et al (1). According to the authors, this method is not readily susceptible to interference from other active chlorine compounds (including Cl_2), and the CPR reagent may be standardized by titration against potassium dichromate.

However, several problems surfaced as we attempted to duplicate the published procedure. First, we found that the published stoichiometry for the dichromate standardization titration could not be duplicated and, further, that replicate determinations showed poor reproducibility. Moreover, the text of the paper published by Wheeler et al. (1) contained apparently contradictory statements with regard to the dichromate/CPR reaction stoichiometry. Subsequently, we determined that the chlorine dioxide/CPR molar reaction ratio of 2:1, as given on the first page of the paper, was inconsistent with the 3:1 ratio implicit in the calibration data of Table 3 of the paper. Consequently, a series of informal calibration experiments was conducted in our laboratory in which the chlorine dioxide/CPR molar reaction of 3:1 was verified empirically. Moreover, an "accurate" value of 97% (2/2) for the purity of the CPR reagent, was obtained from the supplier of the reagent, Eastman Organic Chemicals, Inc. (Rochester, NY). The CPR method was then modified to exclude the standardization step by using the CPR reagent powder as a primary standard.

In the modified CPR method, 4 mL of a 3.33×10^{-4} M CPR solution was combined with 100 mL of water and 2 mL of pH 7.0 phosphate buffer (1.76 g KH_2PO_4 and 3.64 g of $Na_2HPO_4 \cdot 2H_2O$ per 100 mL of water), and a 10- or 20-mL aliquot of this solution was placed in each of two standard midget impingers. The impingers were then connected in series and exposed to the generator effluent at 0.5 to 1.2 L/min for 5 to 45 min. After the completion of the sampling step, the contents of the two impingers were combined, and the absorbances of the resulting "sample" solution and of the original unexposed impinger medium were determined at 575 nm. The "sample" absorbance was subtracted from the absorbance of the unexposed impinger medium to obtain the absorbance change caused by exposure to chlorine dioxide; this absorbance change was then related to the chlorine dioxide concentration by means of the known 3:1 reaction ratio described earlier and the known concentration of CPR in the solution.

In experiments designed to test for slippage of chlorine dioxide through the CPR impinger, we discovered that approximately 12% of the chlorine dioxide that entered the first impinger was swept into the back-up impinger. Moreover, this percentage was relatively unaffected by changes in impinger sampling rate within the range from 0.5 to 1.2 L/min and by variations in impinger liquid volume between 10 and 20 mL. Thus, tandem impingers were employed as described above for all CPR analyses.

In other informal experiments, the CPR impinger medium was challenged with chlorine vapor, and the CPR method was found to be only about 3 times less sensitive to chlorine than to chlorine dioxide. However, a color change (i.e., an apparent shift in the absorbance maximum) occurred in the CPR solution on exposure to chlorine, as opposed to the bleaching of color caused by chlorine dioxide. Hence, it is possible that the relative sensitivity to chlorine may be a function of sample volume or chlorine concentration.

For total-oxidant analyses of chlorine dioxide-containing atmospheres, the dual-pH version of the iodometric titration method was employed. This method is capable of quantifying both chlorine and chlorine dioxide in atmospheres where they occur concomitantly, provided that other oxidants are not present in significant amounts. In this procedure, each of two impingers was charged with 15 mL of a 2% aqueous solution of potassium iodide at approximately neutral pH. The impingers were connected in series and allowed to sample from the generator at 1.2 L/min for 30 min. The contents of the two impingers were then combined and titrated with standard (0.01 or 0.001 N) sodium thiosulfate solution and with the use of Thyodene indicator, a proprietary product of Magnus Chemical Company that is marketed by Fisher Scientific Company, Fair Lawn, NJ. Next, the impinger solution was acidified with sulfuric acid to a pH of about 1.5 and titrated again with thiosulfate to a second endpoint. Prior to its use in this titration, the thiosulfate solution was standardized against the primary standard, potassium iodate. (The iodate ion reacts with iodide ion in acid solution to form iodine, which then reacts with thiosulfate.)

The first titration consumed the iodine that was formed as follows:

$$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^- \qquad (1)$$

$$2ClO_2 + 2I^- \longrightarrow I_2 + 2ClO_2^- \qquad (2)$$

The second titration consumed iodine formed in the further reduction of chlorite to chloride:

$$ClO_2^- + 4I^- + 4H^+ \longrightarrow 2I_2 + Cl^- + 2H_2O \qquad (3)$$

Hence, the chlorine and chlorine dioxide contents of the impinger solutions were determined algebraically from the second titers. Note that when chlorine dioxide was the only oxidant present in the sampled air, the second titration consumed exactly four times the amount of titrant required for the first titration.

In slippage experiments performed with the iodometric method, we determined that, although slippage of chlorine dioxide was minor (≃5%), the sparging of iodine was quite significant under certain circumstances (i.e., when large amounts of iodine were present in the primary impinger or when prolonged sampling was conducted). Thus, all formal iodometric sampling experiments involving chlorine dioxide test atmospheres were carried out with two impingers connected in series to minimize sparging losses.

Throughout this work, the generator was tested for both chlorine and chlorine dioxide with the halogen detector tube marketed by Mine Safety Appliances, Inc. (MSA, Pittsburgh, PA). Values of chlorine and chlorine dioxide concentrations determined in this manner were found to be invariably higher than the corresponding iodometric and reference-method values by factors ranging from 2 to 10 or more. Consequently, the MSA tube was considered to be unreliable for quantification; however, the tube was still used for informal, qualitative testing for the presence or absence of the vapors of interest.

In the preparation of reagent solutions for the CPR method, the dual-pH iodometric method, and for all other wet-chemical methods used for the determination of chlorine dioxide, we generally used chlorine demand-free water. Although chlorine demand-free water may not be fully equivalent to chlorine dioxide demand-free water, the demand-free water produced as subsequently described appeared to yield satisfactory results when used in experiments with chlorine dioxide.

To produce a reservoir of chlorine demand-free water, approximately 4 L of distilled, deionized water contained in a large foil-covered Erlenmeyer flask was chlorinated by the addition of a sufficient quantity of Chlorox bleach to create a 2- to 3-ppm chlorine solution. A 450-W high-pressure mercury vapor lamp was then placed in a large Pyrex test tube and the tube lowered into the chlorine solution. During the ensuing irradiation step, the heat evolved from the lamp raised the temperature of the water to its boiling point, although the rate of boiling was too low to cause a significant loss of water. After 30 min of irradiation, a sample of the water was tested for the absence of chlorine by treatment with an iodide-Thyodene (starch indicator) mixture, and the Erlenmeyer flask was then capped with aluminum foil and set aside for later use. Other less drastic irradiation schemes, such as exposure to direct sunlight, were evaluated without success.

C. Calibration of the Continuous Monitor for Chlorine Dioxide

In order to make use of the continuous monitor in the characterization of chlorine dioxide test atmospheres, the monitor was calibrated against the CPR colorimetric reference method over a range of chlorine dioxide concentrations. Because this concentration range spanned nearly 3 orders of magnitude (from 0.007 to 5.75 ppm chlorine dioxide), the data were divided into lower and upper ranges, which were subjected to separate linear regression analysis. In the upper range (0.064 to 5.75 ppm chlorine dioxide), the least-squares fit of CPR results (y) to monitor readings (x) yielded a slope of 4.12, an intercept of -0.060 ppm, and a correlation coefficient (r) of 0.9977. Analysis of the lower range (0.007 to 0.064 ppm chlorine dioxide) yielded a slope of 3.14, an intercept of -0.010 ppm, and r = 0.9942.

The data for the upper range are plotted in Figure 2, and the low-range data are plotted in Figure 3. Each plotted data point represents the average of duplicate reference (i.e., CPR) determinations. Following this work, the calibration of the monitor was checked informally every day.

D. Characterization of Chlorine Dioxide Test Atmospheres

In the characterization of chlorine dioxide test atmospheres, the concentration of the analyte in the test atmospheres was determined under different conditions of temperature, humidity, and elapsed time. Both the CPR and the dual-pH iodometric analytical methods were employed. Concurrent readings were also taken with the calibrated Mast monitor. Specifically, duplicate determinations were performed with each method under each set of experimental conditions, and the results were compared. The purpose of the dual-pH iodometric method was to demonstrate that no oxidant other than chlorine dioxide was present in the generated test atmospheres.

The chlorine dioxide generator characterization data are summarized in Table 1. The CPR value in Test 3 and the iodometric value in Test 4 were not consistent with the pattern established by the remainder of the data, and moreover, neither value agreed closely with its partner in the duplicate pair. Accordingly, this portion of the experimental matrix was repeated under very similar conditions, as shown for Tests 9 and 10. The data of Tests 9 and 10 contained no anomalies of the type noted above for Tests 3 and 4.

Between the experiments carried out on February 3 and on February 23, 1981, the general maintenance of the Mast monitor required that its electrolyte solution be replaced with a fresh solution. A slight but significant shift in the monitor's response to chlorine dioxide was noted immediately thereafter, and hence the monitor was recalibrated over a limited concentration range so that we would obtain accurate readings in the remaining tests. Once calibrated, the instrument provided a stable, consistent response throughout the rest of the work.

Of major concern was the ≈25% bias between the CPR results and the iodometric results. Several attempts were made to elucidate the cause of this discrepancy and to circumvent the difficulty. All reagent solutions employed in either analytical method were discarded and prepared again. Moreover, a third analytical method, i.e., the colorimetric method based on <u>N</u>,<u>N</u>-diethyl-<u>p</u>-phenylenediamine (DPD), was introduced to ascertain which of the other two methods (CPR or iodometric) contained the bias; however, the DPD results were inconsistent and were not closely aligned with results from either of the other two methods. Finally, the CPR reagent was analyzed by high-pressure liquid chromatography (HPLC) in search for impurities. If the purity of the CPR had been less than the reported value of 99.9%, the apparent determinations of chlorine dioxide concentration by the CPR method would have overestimated the actual concentrations. In the HPLC analysis, at least two chromatographic

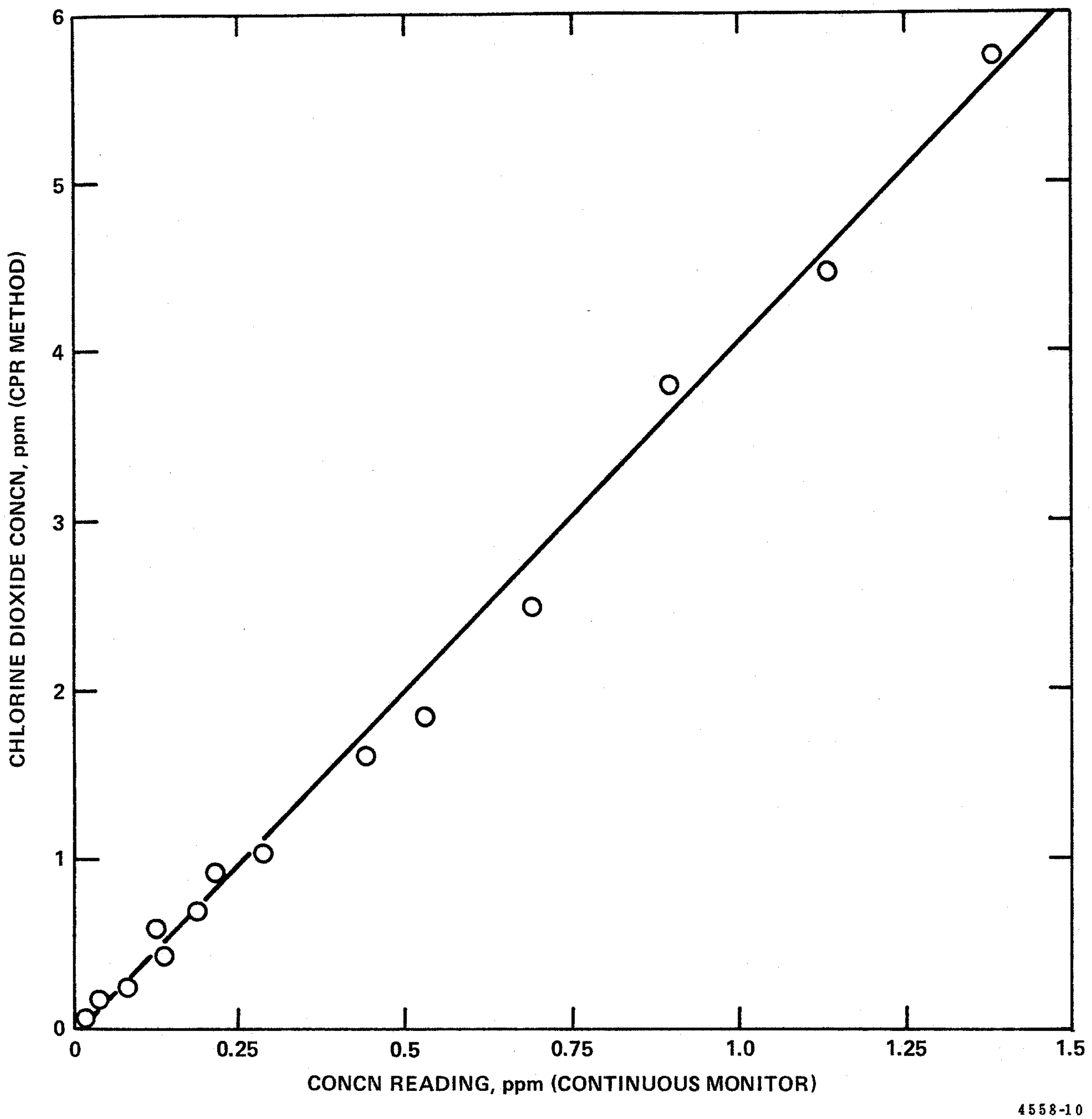

Figure 2. Plot of chlorine dioxide concentration as determined by the CPR method versus the corresponding concentration readings given by the continuous monitor (upper concentration range).

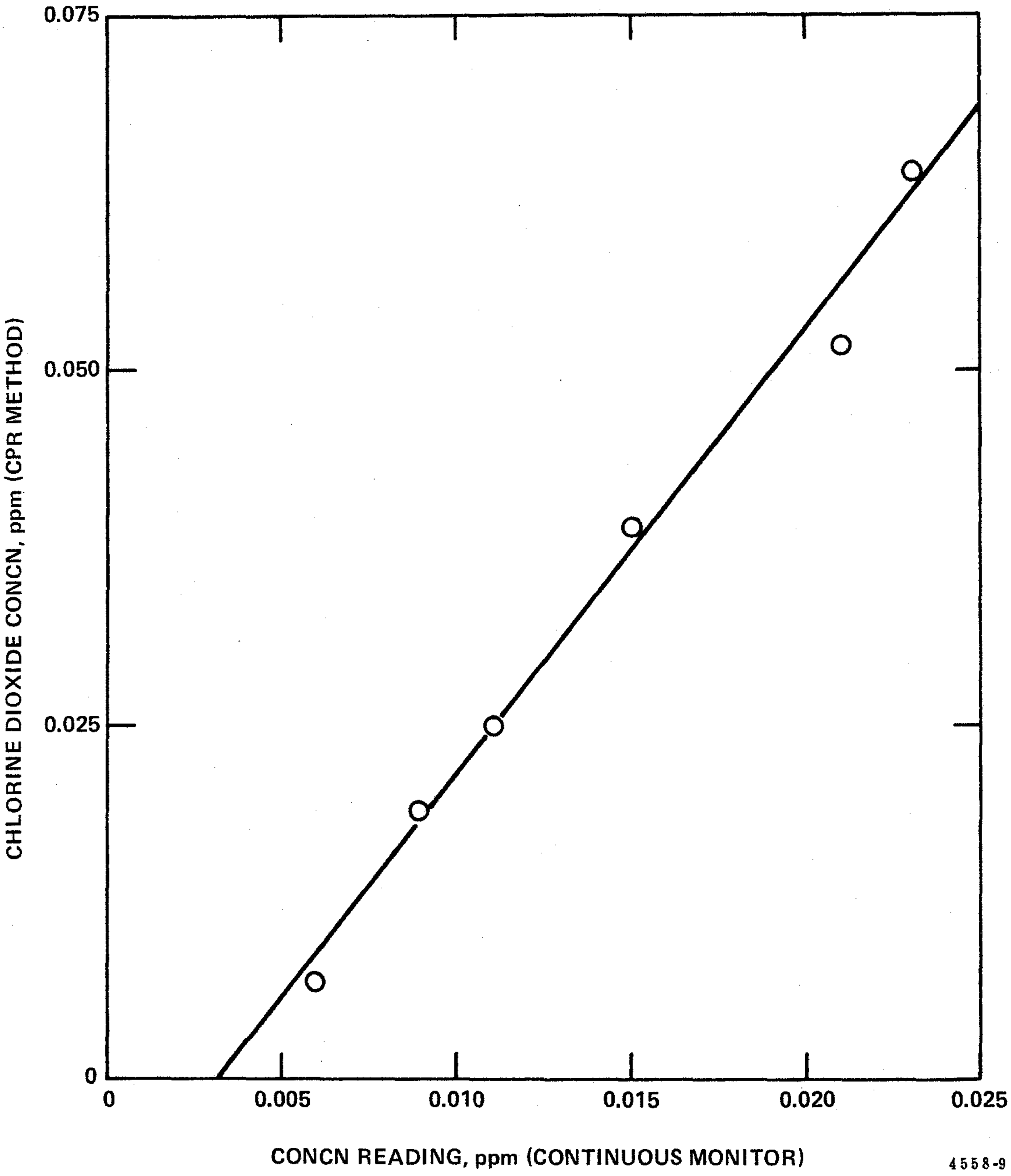

Figure 3. Plot of chlorine dioxide concentration as determined by the CPR method versus the corresponding concentration readings given by the continuous monitor (lower concentration range).

Table 1. Influence of Temperature, Humidity, and Time on the Oxidant Content of Chlorine Dioxide Test Atmospheres

Test No.	Date	Generator temp, °C	RH,[a] %	Chlorine dioxide or total oxidant concn (as ClO_2), ppm			$\frac{\text{CPR - IODO}}{\text{CPR}}$ x 100, %	$\frac{\text{CPR - MON}}{\text{CPR}}$ x 100, %
				CPR[b]	IODO[c]	MON[d]		
1	2/2/81	27	5	1.74	1.40	1.84	20	-6
2	2/2/81	27	5	1.80	1.40	1.84	22	-2
3	2/3/81	45	5	0.89[e]	0.80	1.06	10	-19
4	2/3/81	45	5	1.14	0.64[e]	1.06	44	7
5	2/3/81	27	80	1.10	0.83	1.02	25	7
6	2/3/81	27	80	1.17	0.81	1.02	31	13
7[f]	2/20/81	27	5	1.03	0.82	1.06	20	-3
8[f]	2/20/81	27	5	1.21	0.83	1.25	31	-3
9	2/23/81	42	5	1.03	0.79	1.06	23	-3
10	2/23/81	42	5	1.13	0.89	1.18	21	-4
							Avg 25	Avg -1

[a] RH = relative humidity.

[b] These values are chlorine dioxide vapor concentrations determined by the CPR colorimetric method.

[c] These values are total oxidant concentrations (as ClO_2) determined by the dual-pH iodometric method.

[d] These values are total oxidant concentrations (as ClO_2) determined by the Mast continuous monitor.

[e] These values are suspect (see text).

[f] Tests 7 and 8 were performed only after the chlorine dioxide vapor generator had been operated continuously for more than 4 h.

peaks, presumably due to impurities, were perceptibly resolved from the CPR chromatographic peak. However, the impurity peaks were not sufficiently well resolved for us to obtain their UV absorption spectra or to collect them separately from the CPR in a fraction of eluate for identification or quantification. Hence, we can offer no explanation for the discrepancy between the two methods.

Although we recognized that a continued effort to resolve this matter might eventually prove to be fruitful, we decided instead to proceed with the screening of reactive sampling media. In view of the systematic nature of the discrepancy, it was not expected to impede the search for a suitable sampling medium for chlorine dioxide. In any event, even though firm conclusions could not be drawn from the results of the generator characterization experiment for chlorine dioxide, there nevertheless appeared to be no evidence of a change in the content of the test atmosphere due to the effects of temperature, humidity, or elapsed time. Moreover, the continuous monitor appeared to be entirely satisfactory for use with chlorine dioxide, providing that it was recalibrated daily and especially whenever the electrolyte was replaced.

III. SCREENING OF CANDIDATE REACTIVE SAMPLING MEDIA

A. Selection and Preparation of Candidate Sampling Materials

Based on specific information in the literature concerning the reactivity of the halogens and their oxides, a preliminary list was compiled of candidate reactive sampling media (i.e., substrates) as shown in Table 2. A silver/mercury amalgam membrane was also considered, but was eventually set aside because of the toxicity hazard associated with the handling of mercury. Although literature references to a given candidate substrate typically involved only one of the three analytes of interest in this work, all candidates were tested with all three analytes, including chlorine dioxide. The available literature describing the reactivity of chlorine dioxide and the other analytes typically referred to reactions in the solution phase rather than in the gas-solid phase. Gas-solid reactivity is generally far less vigorous than solution-phase reactivity because the solvent often lowers the activation energy of the reaction by facilitating the formation of the activated complex or a related intermediate species. Accordingly, we made plans to evaluate as many candidate substrates as possible within the allotted time and budget.

Three solid supports for the reactive substrates were selected for preliminary consideration in this work: a carbonaceous sorbent, a porous silica material, and a silica gel. The carbonaceous support was a petroleum-based charcoal (20/40-mesh, Lot No. 104) from SKC, Inc., Eighty Four, PA (Catalog No. 226-38-01). Relative to the other charcoals, this material has typically exhibited low capacity but high desorption efficiency for organic compounds. The porous silica used in this work was Porasil A, a high-surface-area product from Supelco, Inc., Bellefonte, PA (80/100-mesh, Catalog No. 2-0310, Batch No. 329). This material was unavailable in a large particle size, but preliminary tests indicated that the pressure drop across a 100-mg bed of the uncoated beads (packed in a standard 0.25-in.-OD, 0.15-in. ID glass tube) was not excessive. Finally, the silica gel was a 20/40-mesh material from SKC, Inc., Catalog No. 226-10-01.

In subsequent tests involving the substrate-coated support materials, attempts were made to strip the substrate coatings off the supports with suitable solvents. However, it was visually evident that quantitative extractions could not be achieved for any of the most promising substrates, even after exhaustive treatment in an ultrasonic bath and with a number of different solvents. We hypothesized that this extraction problem was related to the inherent porosity of the silica gel and porous glass supports. In other words, it seemed likely that the relatively massive surface areas of these supports resulted in a correspondingly massive adsorptive interaction with the coated substrates. For this reason, we decided to incorporate into the testing program two additional candidate support materials that were essentially non-porous in nature. The supports that were chosen were 60/80-mesh solid glass

Table 2. List of Candidate Reactive Substrates Selected for Evaluation as Sampling Media for Chlorine Dioxide

Br^-/fluorescein
Triethylamine
Diphenylamine
Vanillin
o-Dianisidine
N-vinylcarbazole
Br^-/phenol
Phenol red
Chlorophenol red
Bromocresol purple
N,*N*-diethyl-*p*-phenylenediamine
Br^-/CN^-
Glycine
Malonic acid
Sulfamic acid
Silver metal membrane[a]

[a] The silver metal membrane was a 37-mm-diameter filter membrane with 8-μm-diameter pores; it is marketed by Flotronics Division, Selas Corporation of America, Huntingdon Valley, PA, Catalog No. FM-37.

beads (Applied Science Laboratories, Inc., State College, PA) and 20/40-mesh Fluoropak 80 (The Fluorocarbon Co., Anaheim, CA). The latter material consists of irregularly shaped particles of Teflon. Both materials feature smooth, nonporous, and relatively inert surfaces. No extraction difficulties were experienced with these nonporous supports.

The candidate support materials were tested for their inertness toward chlorine dioxide. Briefly, 7-cm lengths of 0.25-in.-OD, 0.15-in.-ID glass tubing were each packed with 100 mg of the support material to be tested. Each tube was then challenged with chlorine dioxide from the test atmosphere generator at a rate of about 0.2 L/min until breakthrough of chlorine dioxide was observed. The effluent from the tube was monitored for breakthrough with an MSA halogen detector tube (Catalog No. 82399) located immediately downstream from the test device. Although the MSA detector tube was shown in earlier tests to be inaccurate, its tube-to-tube reproducibility seemed to be quite satisfactory at a given concentration level, and it never failed to respond sensitively to the presence of chlorine dioxide. Hence, even though the MSA tube might not have been suitable for definitive measurements of breakthrough volume, it was used with apparent success in these preliminary studies where indications of only the approximate relative capacities of the candidate support materials were required. The criterion for breakthrough was the formation of a 1-mm tan stain in the MSA tube; the manufacturer's literature states that this occurs when 100 mL of air containing 0.05 ppm chlorine dioxide has been sampled.

Breakthrough was observed from silica gel, Porasil A (porous glass beads), Fluoropak 80, and nonporous glass beads after only 40 mL (or less) of air containing chlorine dioxide vapor had been sampled; hence, each of these materials was considered to be suitably inert. Breakthrough from charcoal,on the other hand, was not obtained even after sampling approximately 11 L of chlorine dioxide from the generator. In this work, the chlorine dioxide concentration varied from about 8 to 5 ppm. Because of the relative ease with which the various substrate coatings could be stripped from the nonporous supports (Fluoropak 80 and nonporous glass beads), these supports were chosen for use in the evaluation of the substrates. The pressure drop across the nonporous supports during the challenge tests was about 2.6 in.H_2O for each material; this level is well within the capabilities of most portable sampling pumps.

Each of the candidate substrates was coated onto the support material by mixing 1.9 g of the support with approximately 10 mL of a solution containing 100 mg of the dissolved substrate. The resulting mixture was placed in a watchglass, and the solvent was allowed to evaporate, thereby depositing most of the substrate onto the surface of the support. Because a minor portion of the substrate was invariably precipitated onto the wall of the watchglass rather than onto the surface of the support material, the amount of the coating actually deposited on the support was in each case somewhat less than 5% by weight. The resulting candidate sampling materials were packed into 7-cm lengths of 0.25-in.-OD, 0.15-in.-ID glass tubing in the amount of 100 mg of sampling material per tube. The beds of sorbent were held in place within the tubes by plugs of silanized glass wool. Thus prepared, the candidate sampling media were then ready to be challenged with chlorine dioxide vapor and assigned an approximate breakthrough volume.

B. Testing of Candidate Substrates for Retention of Chlorine Dioxide

The breadboard sampling devices, prepared as described above, were attached to the chlorine dioxide test-atmosphere generator, and the generator effluent was pumped through the devices until breakthrough of chlorine dioxide was observed in an MSA tube located downstream from the test device. The criterion for breakthrough was, once again, the formation of a 1-mm tan stain within the MSA tube. During the test interval, the chlorine dioxide concentration in the generator was monitored by the portable continuous monitor to ensure that the concentration remained at least approximately constant. Sampling was conducted at about 0.2 L/min through each test sampler; the generator was operated at room temperature and at less than 10% relative humidity (RH).

Prior to the performance of these tests, we had hoped to employ the continuous monitor in the effluent stream from the test sampling device to check for breakthrough. The plan was to switch the monitor's intake line periodically back and forth between the effluent stream and the output port of the generator so that the chlorine dioxide concentration could be monitored at both locations. However, the pressure difference between the effluent stream and the ambient atmosphere (on the order of 2 to 3 in.H_2O for most tubes) proved to be highly detrimental to the performance of the monitor. Consequently, the MSA tube was the only means available for the continuous, real-time detection of analyte breakthrough.

The results of the substrate capacity tests are summarized in Table 3. It is apparent from these data that none of the candidates included in the table provided satisfactory retentivity for chlorine dioxide. In addition to the candidates listed in Table 3, a silver metal membrane was also challenged with chlorine dioxide. The membrane, mounted in a 37-mm polystyrene filter holder, was exposed to about 0.84 ppm chlorine dioxide at a rate of 0.175 L/min. Breakthrough was obtained after about 2 L of air had been sampled, but because this membrane exhibited a very similar degree of reactivity toward chlorine, it was not considered further in this testing program. Hence, of the candidate reactive media, none presented itself as a likely prospect for continued evaluation in the solid state.

Upon completion of the substrate capacity tests for all three analytes, we learned that certain types of chemical substances stood out as being generally more reactive in the solid state than most of the other types of substances that were represented in our primary list of candidate reagents. For example, three of the most reactive compounds (in general) were _N_-vinylcarbazole, _o_-dianisidine, and diphenylamine. All three compounds are aromatic amines, and _N_-vinylcarbazole is the only candidate that contains an unconjugated double bond. These are, of course, merely empirical correlations that

Table 3. Approximate Breakthrough Volumes for Chlorine Dioxide in Sampling Tubes Containing Candidate Substrates Coated onto Nonporous Supports

Substrate	Fluoropak 80		Glass beads	
	Avg ClO_2 test concn, ppm	Approx breakthrough vol, L	Avg ClO_2 test concn, ppm	Approx breakthrough vol, L
Diphenylamine	6.70	<0.04	6.70	<0.04
	1.89	0.10	1.89	0.05
N-Vinylcarbazole	6.49	<0.04	6.49	<0.04
	1.89	0.05	--[a]	--
Triethylamine	6.33	<0.04	6.33	<0.04
	1.09	<0.05	1.09	0.15
o-Dianisidine	6.24	<0.04	6.24	<0.04
	1.09	0.05	1.09	0.05
Glycine	6.12	<0.04	6.12	<0.04
	1.09	<0.05	1.09	<0.05
N,*N*-Diethyl-*p*-phenylenediamine	5.99	<0.04	5.99	<0.05
	1.09	0.05	1.09	0.25
Br^-/phenol	6.16	<0.04	6.16	<0.04
	1.09	<0.05	1.09	0.05
Chlorophenol red	1.01	<0.04	0.88	<0.04
Sulfamic acid	0.84	<0.04	0.84	<0.04
Br^-/fluorescein	0.92	0.07	--	--
Phenol red	0.92	0.43	1.22	<0.05
Malonic acid	0.84	<0.04	1.17	<0.04
Bromocresol purple	0.96	0.15	1.22	0.05
Vanillin	1.18	0.05	1.01	0.05
Br^-/CN^-	0.97	0.06	1.01	0.12

[a] "--" = these tests were inadvertently omitted.

may or may not bear upon the observed reactivity of these candidates. However, correlations of this type were used in the selection of several additional candidate reactive substrates for evaluation under this contract. The new list of candidate substrates is given in Table 4. This list includes several inorganic candidate substrates that were also evaluated during this period.

The procedures for the evaluation of this secondary group of candidate sampling substrates were essentially identical to those already described in connection with the primary candidates. However, certain of the inorganic substrates were applied to the support materials as coatings whose weights were nominally 10%, rather than 5%, of the combined weight of substrate and support. Moreover, these 10% coatings were applied by deposition from aqueous solution with the aid of a rotary vacuum evaporator. Table 5 summarizes the results of the substrate capacity tests for the new candidate substrates. Those substrates that were employed as 10% coatings are indicated in the table.

It is apparent from the data of Table 5 that only *o*-aminophenol revealed a significant capacity for the trapping of chlorine dioxide vapor. Therefore, plans were made for a continued evaluation of this compound as a prospective sampling medium for chlorine dioxide.

C. Analysis of Analyte-Exposed *o*-Aminophenol by HPLC

The first step in the continued investigation of *o*-aminophenol was to analyze the material for the presence of a reaction product following its exposure to chlorine dioxide vapor. Accordingly, a sampling tube containing 100 mg of the *o*-aminophenol sampling medium, which consisted of 5% by weight of *o*-aminophenol on 20/40-mesh Fluoropak 80, was exposed to 0.91 ppm of chlorine dioxide at a sampling rate of approximately 0.2 L/min for 15 min. The sampling medium was then extracted into 4.0 mL of methanol, and the extract was analyzed by HPLC.

The HPLC analysis was conducted with the use of a C_{18} reversed-phase column marketed by Perkin-Elmer Corporation, Norwalk, CT (ODS-SIL-X-1), which proved slightly superior to other similar columns marketed by Waters Associates, Inc. (Milford, MA) and by Varian Associates, Inc. (Palo Alto, CA) in tests performed with the sample extract. The chromatographic elutions were carried out isocratically with 2% acetonitrile and 98% water. The solvent flow rate was 1 mL/min, and the detector, a UV absorption unit, was set at 280 nm.

Table 4. New Candidate Solid Reagents

Butadiene sulfone
Hydroquinone
2,6-Di-*tert*-butyl-4-methylphenol
Catechol
o-Aminophenol
m-Aminophenol
1-Adamantanamine
Maleimide
Potassium hydroxide
Sulfamic acid/sodium hydroxide[a]
Potassium iodide/potassium hydroxide

[a] Because of the presence of an excess of sodium hydroxide in this mixture, the sulfamate ion was actually present in the mixture as the sodium salt, not as the acid. The term "sulfamic acid" is used here only because the coating weight subsequently applied to an inert support was based on the weight of the intact acid.

Table 5. Approximate Breakthrough Volumes for Chlorine Dioxide in Sampling Tubes Containing Additional Candidate Sampling Media

Candidate substrate	Avg ClO_2 test concn, ppm	Approx breakthrough vol, L	
		Fluoropak 80	Glass beads
Butadiene sulfone	0.96	<0.05	<0.05
Hydroquinone	1.01	0.13	0.13
2,6-Di-*tert*-butyl-4-methylphenol	1.05	0.05	0.05
Catechol	1.09	0.50	0.85
o-Aminophenol	0.71	3.80	1.60
m-Aminophenol	0.88	0.61	0.48
1-Adamantanamine	0.88	<0.05	<0.05
Maleimide	1.05	<0.05	<0.05
Potassium hydroxide	1.09	0.05[a]	
Sulfamic acid (10%)/ sodium hydroxide (10%)	1.60	<0.05	
Potassium iodide (10%)/ Potassium hydroxide (10%)	1.60	0.09	

[a] This candidate reactive substrate was coated onto silica gel rather than onto glass beads or Fluoropak 80.

When introduced into the chromatograph, the o-aminophenol extract produced only a single chromatographic peak, corresponding to the unreacted substrate, at a retention time of 5.5 min. It was postulated that the products of the reaction between o-aminophenol and chlorine dioxide were ionic salts or other species that were not amenable to separation and detection by HPLC. (Evidence for the presence of such salts was not found in this work, but was found in other HPLC analyses in our laboratory involving bromine-exposed substrates, particularly the aminophenols.)

No further evaluations of solid-state sampling media for chlorine dioxide were performed under this contract.

IV. EVALUATION OF THE CHLOROPHENOL RED SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF CHLORINE DIOXIDE

During a conference held at Cincinnati, OH, on September 29, 1981, representatives of NIOSH and of Southern Research Institute agreed mutually that an attempt be made to develop a sampling and analysis method for chlorine dioxide based on an impinger sampler containing the spectrophotometric reagent, chlorophenol red (CPR). As a reference method for the determination of chlorine dioxide in test atmospheres, the CPR method seemed to have performed satisfactorily except that no accurate, convenient means of standardizing the CPR reagent solution appeared to exist. Wheeler et al. (1), however, had performed a standardization with an aqueous solution of chlorine dioxide, and Harp et al (2) had recently employed a more convenient variation of this standardization that incorporated a simple method for preparing uncontaminated chlorine dioxide solutions (3). Consequently, we endeavored to adapt the procedure of Harp et al (2), which was intended for the determination of chlorine dioxide in water, to the determination of this species in air.

A. CPR Calibration Curve

The CPR method adapted from the method of Harp et al. (2) differed in certain respects from the CPR method described previously in this report as the reference method for chlorine dioxide. (The reference method had been adapted from the work of Wheeler et al. (1)). Thus, to prepare CPR calibration standards, we combined 10 mL of each chlorine dioxide standard solution with 0.2 mL of pH 5.2 citrate/citric acid buffer, 0.2 mL of 4.73×10^{-4} M CPR solution, and 0.2 mL of pH 10 borate/boric acid buffer. The absorbances of these solutions were then read at 570 nm in a 1-cm spectrophotometric cuvette.

The standard solutions of chlorine dioxide were obtained by dilution of an approximately 300-mg/L chlorine dioxide stock solution, which was prepared by first reacting 3.2 g of acetic anhydride with 1.0 g of sodium chlorite (80%) dissolved in 900 mL of distilled water and then diluting the resulting mixture to 1 L. This procedure has been reported to yield a chlorine dioxide solution that is free of chlorine (and its hydrolysis products) and free of excess chlorite ion (3). Once prepared, the stock solution was stored in a refrigerator in the absence of light and with minimum headspace above the liquid.

In diluting the stock solution, we took care first to chill the dilution water to approximately 5 °C. The working standards were then prepared by dispensing the cold stock solution underneath the surface of cold distilled water and diluting to volume. All glassware that contacted chlorine dioxide was first soaked overnight in a 0.5% solution of sodium hyperchlorite, which was prepared from Clorox.

The concentration of chlorine dioxide in the stock solution was determined by measuring its absorbance at 360 nm in a 1-cm spectrophotometric cuvette. Throughout this work, the standardization was based on a molar absorptivity value of 1100 L/mol•cm for chlorine dioxide (1). Other reference sources, however, indicated that the true value may be somewhat higher (4); the average of six independent determinations of molar absorptivity was 1196 L/mol•cm, with a standard deviation of 65 L/mol•cm and a relative standard deviation of 5.4%.

Because of the uncertainty in the value of the molar absorptivity of chlorine dioxide, we decided to measure the molar absorptivity ourselves in the laboratory. As a first step, we recorded the chlorine dioxide absorption spectrum. An aqueous solution of chlorine dioxide was prepared with the use of sodium chlorite and acetic anhydride as described above. This solution was diluted by a factor of 25 with distilled water, and its absorbance was recorded between 300 and 400 nm on a Cary Model 17 UV-visible recording spectrophotometer. A "blank" solution was prepared by the addition of appropriate amounts of acetic anhydride, sodium hydroxide, sodium chloride, and acetic acid to distilled water; however, this solution produced no measurable absorption between 300 and 400 nm.

The absorption spectrum is reproduced in Figure 4. Although the actual absorbance maximum occurred at 358 nm, the absorbance at this wavelength did not differ substantially from the absorbance at 360 nm.

The measured excess of acetic anhydride employed in the production of chlorine dioxide virtually ensures the quantitative conversion of sodium chlorite to chlorine dioxide. The reaction generates 1 mol of chlorine dioxide from 2 mol of sodium chlorite. Hence, it should be possible to calculate the concentration of chlorine dioxide in a stock solution from the concentration of sodium chlorite used in the reaction. With a known chlorine dioxide concentration, a simple absorbance measurement of 360 nm can be converted to the molar absorptivity through Beer's Law.

When the above-described experiment was conducted, the absorbances of five different dilutions of the stock chlorine dioxide solution were measured at 360 nm and recorded. The average value of molar absorptivity resulting from these measurements was about 1250 L/mol•cm. Unfortunately, we still had no reason to believe that this value was any more accurate than the previously available values. However, it constituted an extra datum to be considered in deciding upon a "best" value for ultimate use in the validated CPR method. In any event, no firm decisions were made with regard to the suitability of any given molar absorptivity value pending the accumulation of additional information.

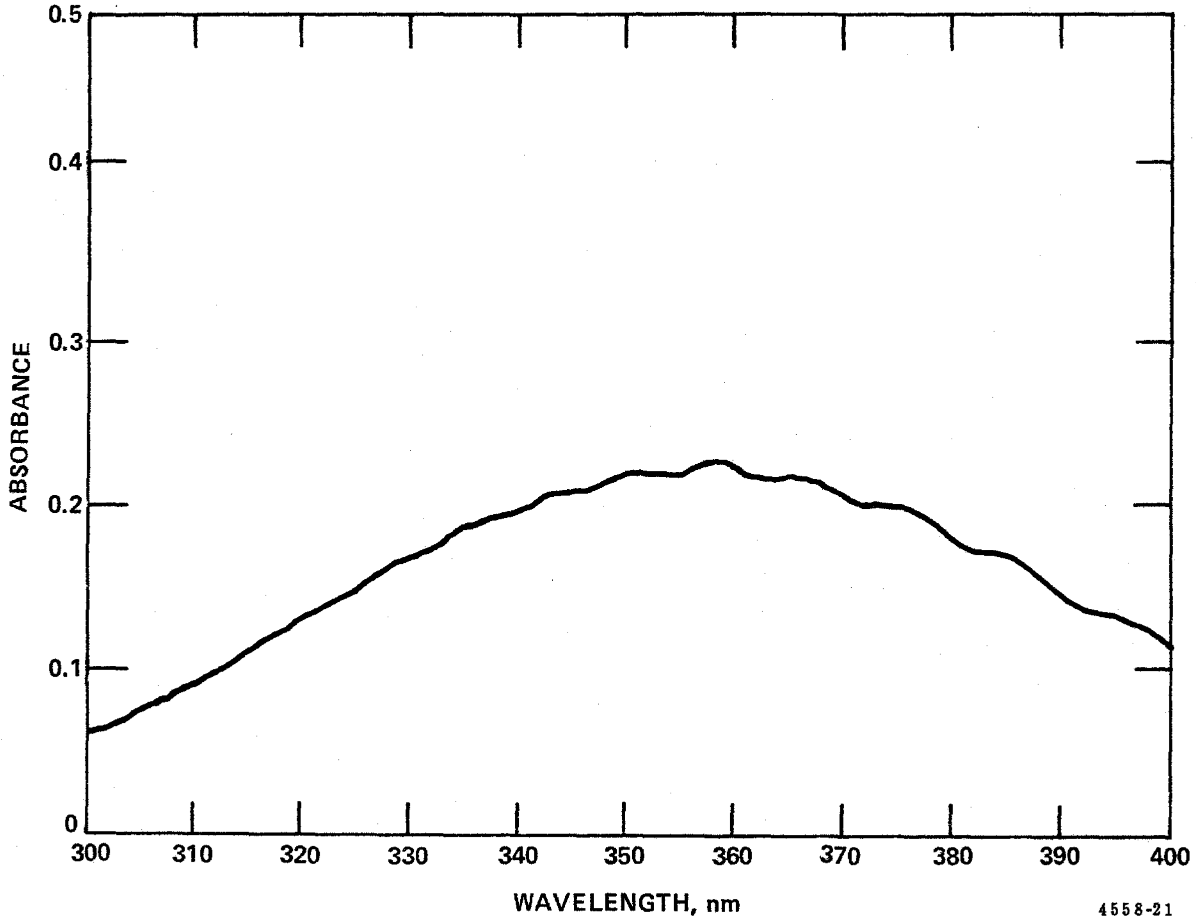

Figure 4. UV absorption band of chlorine dioxide in aqueous solution.

Because Harp et al. (2) provided very little information about the composition of their buffers, we formulated the requisite buffers empirically in the laboratory. The pH 5.2 citrate/citric acid buffer was prepared by combining 50 mL of 0.02 M citric acid with 20 mL of 0.1 M sodium hydroxide and diluting the mixture to 100 mL with distilled water. The pH 10 borate/boric acid buffer was made by mixing 50 mL of 0.125 M borax with 10 mL of 0.5 M sodium hydroxide and then diluting to 100 mL with distilled water. The pH 10 buffer was intended to be strong enough to exceed the capacity of the pH 5.2 buffer in the standard solutions. In practice, therefore, the chlorine dioxide was reacted with the CPR at pH 5.2, and the CPR absorbance was then read at pH 10.

The first chlorine dioxide calibration curve that was generated in this manner is shown in Figure 5. The least-squares fit of absorbance (y) as a function of the quantity of chlorine dioxide (x) in micrograms (in 10 mL of solution) obeyed the following linear relationship:

$$y = (-0.035 \pm 0.003)\chi + (0.670 \pm 0.015) \tag{4}$$

where the uncertainties in the slope and intercept correspond to 95% confidence limits. The correlation coefficient (r) was -0.9981, and the standard error of estimate ($s_y \cdot x$) was 0.008.

Additional statistical calculations revealed that the determination of unknown quantities of chlorine dioxide could be estimated with a high degree of confidence if a CPR solution were exposed to enough chlorine dioxide to reduce the absorbance by about 0.3. Given a final solution absorbance (y_0) of 0.360, the 95% confidence interval for the predicted quantity of chlorine dioxide (x_0) was computed to be as follows:

$$x_0 = (8.93 \pm 0.80)\ \mu g \tag{5}$$

Thus, the calibration of the CPR method was considered to be acceptable for preliminary experimentation.

B. Preliminary CPR Sampling Experiments

In the first series of sampling experiments involving the CPR method, standard midget impingers charged with 10 mL of distilled water, 0.2 mL of pH 5.2 buffer, and 0.2 mL of 4.73×10^{-4} M CPR solution were each connected in tandem with another similarly charged impinger, and the two impingers were then allowed to sample from the chlorine dioxide test-atmosphere generator at 0.7 L/min for 20 min. Following the sampling period, 0.2 mL of pH 10 buffer was added to each impinger solution, and the absorbance was measured at 570 nm. Two sets or pairs of impingers were used in each of three sampling experiments of this type.

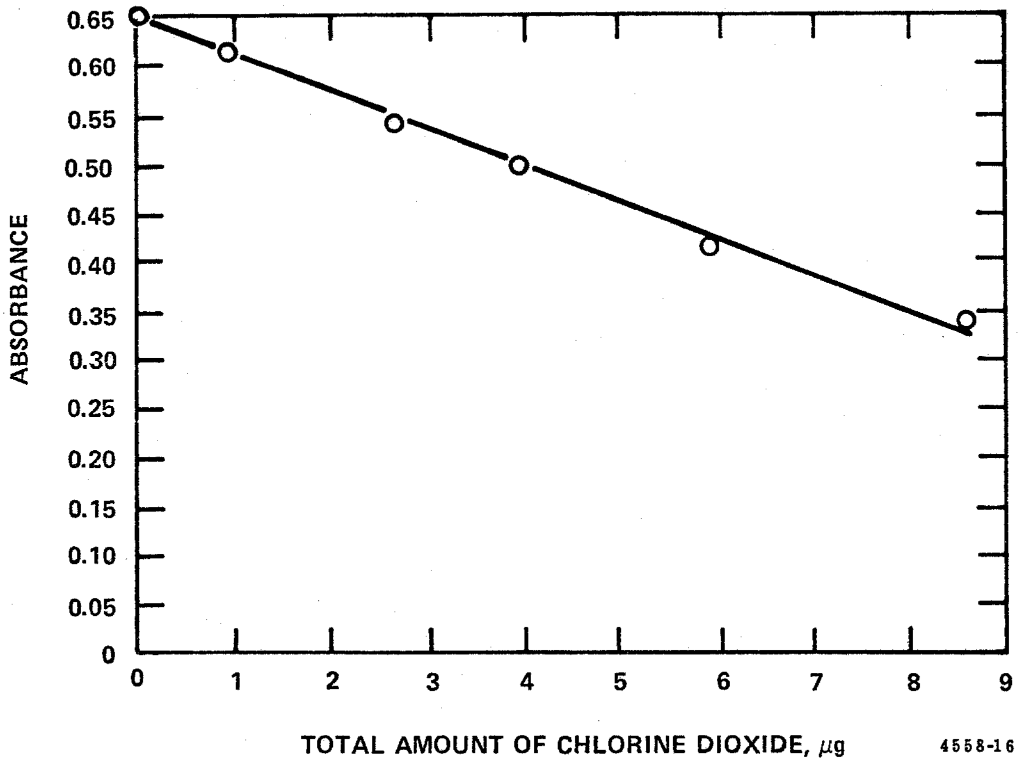

Figure 5. Plot of CPR absorbance versus the amount of chlorine dioxide to which the CPR was exposed.

The results of these experiments are summarized in Table 6. Because the actual amounts of chlorine dioxide found in the back-up impingers were typically quite low, the estimates of slippage given in the table can be considered only as rough approximations. They are sufficiently consistent, however, to indicate that slippage on the order of 25 to 30% occurred systematically under these conditions. This level of slippage constituted a serious drawback to the CPR method as performed here. Another equally serious difficulty was the apparent bias between the chlorine dioxide concentration values obtained by the continuous monitor and those obtained by the CPR method. Note that this bias might have been diminished somewhat, but not altogether eliminated, by the use of 1200 L/mol•cm rather than 1100 L/mol•cm as the molar absorptivity of chlorine dioxide at 360 nm.

Both the slippage problem and the bias problem were addressed in the next sampling experiment. As stated previously, our earlier work with the CPR method, in which the method was used as a reference analytical method for the evaluation of chlorine dioxide test atmospheres, was based on the method of Wheeler et al. (1). Because those investigators specified a pH of 7 for the reaction between CPR and chlorine dioxide, we also employed this pH level during our early work, and at that time, we found a slippage rate of only about 12%. Hence, we reasoned that the present 25 to 30% slippage rate might be substantially reduced by adopting a higher reaction pH. Largely as a matter of convenience, we chose a pH of 10 as the reaction pH for the next experiment.

With regard to the bias problem observed in the previous sampling experiments, we suspected that the difficulty might have been caused by an inaccurately calibrated continuous monitor. Therefore, we included in the next experiment another set of primary and back-up impingers, each containing 10 mL of 2% potassium iodide solution. The contents of these impingers were subsequently combined, then split and analyzed by two iodometric analysis procedures: one based on the dual-pH titration and one based on a spectrophotometric determination of the starch/iodine complex. The dual-pH titration permitted separate determinations of chlorine and chlorine dioxide, whereas the spectrophotometric method provided a single result in response to both chlorine and chlorine dioxide.

The above-mentioned spectrophotometric procedure, based on the oxidation of iodide ion to iodine and the subsequent formation of the blue starch/iodine complex, proved to be a sensitive procedure for the determination of oxidant species in solution (5). In acidic solution iodate ion reacts with iodide ion to form iodine by the following reaction:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \qquad (6)$$

We found experimentally that this reaction was driven essentially to completion only at a pH of less than about 3.

Table 6. Results of Preliminary Sampling Experiments with CPR Impingers

	Chlorine dioxide concn, ppm			Degree of chlorine dioxide slippage, %	
Test No.	Continuous monitor	First pair of CPR impingers[a]	Second pair of CPR impingers[a]	First pair of CPR impingers	Second pair of CRP impingers
1	0.20	0.27	0.28	24	27
2	0.24	0.40	0.41	34	30
3	0.20	0.28	0.27	22	30

[a] The amounts of chlorine dioxide found in the primary impinger and in the back-up impinger were combined in order to obtain each of these concentration values.

To carry out this method, we acidified 10 mL of the potassium iodide-containing impinger solution to a pH of about 1.5 with a convenient mineral acid. We then added 3 mL of 0.5% (w/v) Thyodene solution and measured the solution absorbance at 345 nm. Spectrophotometric standards were prepared and treated in much the same manner except that known amounts of a 25-µg/mL solution of standardized potassium iodate (typically 0.1, 0.2, 0.4, 0.6, and 0.8 mL) were added to each of several 10-mL aliquots of unexposed impinger solution, and the volumes of the standards (and samples) were equalized with distilled water. A spectrophotometric blank was prepared without the use of iodate ion, and its absorbance was subtracted from those of the standards and samples.

In the next sampling experiment, the primary CPR impinger and the primary iodometric impingers were each connected to identical back-up impingers and then attached to the sampling chamber of the chlorine dioxide test-atmosphere generator. Each set or pair of impingers sampled from the generator at about 0.8 L/min for 30 min. In contrast to the CPR impingers of the previous sampling experiments, these CPR impingers each contained 0.2 mL of the pH 10 buffer rather than 0.2 mL of pH 5.2 buffer. After the sampling interval, moreover, these CPR impingers were analyzed immediately (by measurement of their absorbances at 570 nm) without the addition of any other buffer.

The dual-pH iodometric results indicated a chlorine dioxide vapor concentration of 0.30 ppm and a chlorine vapor concentration of about 0.04 ppm in the test atmosphere. The spectrophotometric version of this iodometric method yielded a single concentration of 0.33 ppm (as chlorine dioxide); this value undoubtedly contained a contribution from chlorine and was therefore considered to be in close agreement with the dual-pH results. The CPR result, determined by combining the analysis results from both the primary and the back-up bubblers, was 0.27 ppm, which is only 10% below the dual-pH result for chlorine dioxide concentration. In addition, the slippage of chlorine dioxide into the back-up CPR impinger was only about 15%, a significant improvement over that observed at pH 5.2.

One disturbing aspect of the above experimental outcome was the finding that not all of the chlorine used in the generation of chlorine dioxide had been converted to chlorine dioxide. Consequently, we performed a series of experiments with the chlorine dioxide vapor generator in an attempt to rid the system of unreacted chlorine vapor. In each experiment, the dual-pH iodometric method was employed to establish the presence or absence of chlorine in the generator. The pH and temperature of the generator's sodium chlorite reaction solution as well as the rate of flow of chlorine into the solution were varied in these experiments to achieve essentially quantitative consumption of chlorine. Our data from these tests suggested that the reaction was quantitative at the pH naturally established by the sodium chlorite in the solution and at a temperature of 60 °C; however, the problem appeared to persist in subsequent sampling experiments even under these conditions.

The sampling experiment involving both the CPR and the iodometric impingers was repeated twice, except that the volume of the CPR sample collection medium was increased from 10 to 15 mL in each impinger in an effort to further reduce the degree of slippage of chlorine dioxide. As done previously, sampling was conducted for 30 min at a rate of about 0.8 L/min through each pair of impingers. All other parameters also remained essentially the same as those given for the previous CPR sampling experiment.

The results of these experiments are given in Table 7. The CPR results agreed closely with the dual-pH results and were apparently unaffected by the presence of a small amount of chlorine. Additionally, the degree of slippage of chlorine dioxide from the primary to the back-up CPR impinger in the two experiments was 11% and 16%, respectively. The spectrophotometric results from the iodometric impingers, however, agreed to be systematically high relative to the results from the other two methods. Spectrophotometric calibration data generated with both chlorine dioxide-containing standards and potassium iodate-containing standards were reasonably similar, which suggested that the problem did not arise from faulty calibration of the method. We investigated this problem no further.

C. Evaluation of CPR Sampling Capacity

After completing the above sampling experiments, we performed two additional tests of a similar nature to expand our data base and to estimate the capacity of the CPR impinger as a sampler for chlorine dioxide. In these tests, each set of impingers was allowed to sample at a rate of 0.23 L/min for either 60 min or 120 min. Two sets of CPR impingers, each set consisting of a primary and a back-up impinger, were used in each test to obtain duplicate CPR responses from each test.

Table 8 summarizes the results of each test. One of the CPR data points was unexpectedly low; this phenomenon was probably due to a leak in the sampling line leading from the test-atmosphere generator to the primary impinger. Except for this anomaly, however, the CPR results appeared to correspond satisfactorily with the dual-pH iodometric results. The spectrophotometric/iodometric results, on the other hand, appeared once again to be positively biased with respect to the rest of the data, although the bias was less severe in these tests than in the previous experiments. The slippage rates among the CPR impinger sets varied from 8 to 13%, with an average of 10%.

Because the second test (see Table 8) involved the sampling of 27.6 L of air, the sampling capacity of the CPR impinger must have been at least 27.6 L. Based on the CPR spectrophotometric absorbance value obtained in the test, we estimated that the impinger could have sampled at least 30 L of air without a loss of response linearity. Furthermore, a reduction in the chlorine dioxide vapor concentration from 0.23 ppm to 0.20 ppm—i.e., to two times the permissible exposure limit (PEL) for chlorine dioxide—probably would have further increased the sampling capacity of the CPR impinger. Accordingly, we concluded that the sampling capacity of the CPR impinger under these conditions is at least 30 L over the chlorine dioxide vapor concentration range from 0.5 to 2 PEL.

Table 7. Results of Additional CPR Sampling Experiments

Expt No.	Chlorine dioxide concn, ppm Dual-pH iodometry	 Spectrophotometric iodometry	 CPR method	Chlorine concn,[a] ppm
1	0.33	0.55	0.31	0.07
2	0.29	0.41	0.29	0

[a] Determinations of chlorine under these conditions probably were not very accurate because of very small volumes of titrant employed to reach the first endpoint in the dual-pH titrations.

Table 8. Results of Sampling Experiments Conducted to Estimate the Sampling Capacity of the CPR Impinger

Test No.	Sampling interval, min	Sample vol, L	Chlorine dioxide concn, ppm				Chlorine concn,[a] ppm
			Iodometry		CPR method		
			Dual-pH iodometry	Spectrophotometric iodometry	First pair of CPR impingers	Second pair of CPR impingers	
1	60	13.8	0.25	0.27	0.25	0.25	0.04
2	120	27.6	0.23	0.30	0.15[b]	0.26	0

[a] Determinations of chlorine under these conditions probably were not very accurate because of the very small volumes of titrant employed to reach the first endpoint in the dual-pH titrations.

[b] This value was probably affected by a leak in the sampling line.

D. Evaluation of CPR Storage Stability

To perform this experiment, we charged each of six impingers with 15 mL of the usual pH 10 CPR impinger medium and then used them to sample chlorine dioxide vapor from the test-atmosphere generator at approximately 0.18 L/min for 120 min. During the sampling process, the generator effluent was maintained at greater than 80% relative humidity and at 26 °C (room temperature). At the end of the sampling interval, the impingers were detached from the generator, sealed with a ground-glass stopper, and stored in the dark at room temperature. They were then analyzed in the usual manner (i.e., absorbances were measured at 570 nm and compared to a standard curve) later that same day (Day 0) and again on Day 1, Day 8, and Day 14 of the 2-week storage period. The results were recorded as parts per million by volume of chlorine dioxide. Although the true chlorine dioxide concentration in the generator effluent was not known (because no reference determinations were made), the absorbances of the CPR solutions were reduced by approximately 50% during the sampling interval, which qualitatively indicated that the chlorine dioxide concentration was quite ample for this experiment.

The results of this experiment are given in Table 9. On each of the four test days, the average of the six results was 0.25 ppm of chlorine dioxide, and the standard deviation was 0.02 ppm, which is 6.1% of the average. These results indicate that both the precision of replicate results and the storage stability associated with the CPR method were well within acceptable limits for validation as a NIOSH method.

E. Evaluation of Chlorine as an Interferent in the CPR Method

Before attempting to validate the CPR method, we evaluated chlorine as a potential source of interference in the CPR determination of chlorine dioxide. Chlorine vapor could conceivably exist in an industrial atmosphere at concentrations as high as 2 or 3 ppm (2 or 3 PEL). For the testing of chlorine as a potential interferent, therefore, the test-atmosphere generator was adjusted to provide concentrations of both chlorine dioxide and chlorine in the general vicinity of 2 or 3 PEL for each substance. In the first experiment, a primary impinger and a back-up impinger, each charged with 15 mL of the pH 10 CPR sample collection medium, were exposed to the generator effluent at 0.7 L/min for 30 min. A set of primary and back-up iodometric impingers was also exposed to the test atmosphere at the same rate and time. At the end of the sampling interval, the iodometric impingers were combined and analyzed by the dual-pH titration method, and the CPR impingers were analyzed in the usual manner.

The iodometric analysis indicated a chlorine dioxide concentration of 0.26 ppm and a chlorine concentration of 3.2 ppm, but the CPR analysis yielded a concentration value of 0.42 ppm as chlorine dioxide. Moreover, 24% of the total CPR analytical signal response (i.e., absorbance change) occurred in the back-up impinger solution. These results suggested that chlorine vapor produced a significant positive interference under these conditions and that much of the chlorine slipped through the primary impinger into the back-up impinger. During the sampling interval, the CPR solution changed from wine red to deep purple, presumably upon reaction with chlorine.

Table 9. Results of the Storage Stability Evaluation of the CPR Method

Impinger No.	Chlorine dioxide concn, ppm					
	Day 0	Day 1	Day 8	Day 14	Avg	SD[a]
1	0.26	0.26	0.26	0.26	0.26	0
2	0.25	0.25	0.25	0.25	0.25	0
3	0.24	0.24	0.24	0.24	0.24	0
4	0.25	0.25	0.25	0.25	0.25	0
5	0.22	0.22	0.22	0.22	0.22	0
6	0.26	0.26	0.26	0.26	0.26	0
Avg	0.25	0.25	0.25	0.25		
SD	0.02	0.02	0.02	0.02		
RSD[b] %	6.1	6.1	6.1	6.1		

[a] SD = standard deviation.

[b] RSD = relative standard deviation.

Both of the available reference sources of the CPR method for chlorine dioxide (1,2) state that no interference is obtained from hypochlorite ion. Moreover, Harp et al. (2) found that hypochlorous acid is nonreactive with CPR. Because both groups of researchers performed their studies at pH levels below 10, we repeated the chlorine interference test described above using 15 mL of CPR solution buffered at pH 5.2 (rather than at pH 10) in each CPR impinger. In addition, the sampling rate and duration were changed to 0.23 L/min and 120 min, respectively. In this experiment, however, the CPR solution in the primary impinger turned deep purple after only 20 min of sampling, and it then turned colorless after an additional 35 min of sampling. Consequently, the CPR solution was not analyzed. The dual-pH iodometric method yielded a chlorine concentration of 2.8 ppm and a chlorine dioxide concentration of 0.14 ppm. It is possible that undissociated molecular chlorine (i.e., Cl_2), rather than hypochlorite or hypochlorous acid, was responsible for the reaction with CPR.

Both glycine and malonic acid have been used to neutralize chlorine selectively in solutions containing both chlorine and chlorine dioxide (6). Thus, we decided to assess the effect of adding glycine or malonic acid (≃1%, w/v) to the CPR sample collection medium. However, these reagents were found to reduce the slope sensitivity associated with the spectrophotometric calibration curves greatly, and this approach was therefore abandoned.

Earlier in the experimental program for this contract, we discovered several solid reagents that effectively removed chlorine vapor from air, but did not appear to interact significantly with chlorine dioxide vapor. These reagents were members of the group of candidate solid-state sampling media that were evaluated in the form of coatings on inert, porous, or nonporous surfaces. We hypothesized that such reagents might be of considerable value in diminishing or wholly eliminating the chlorine interference problem in the CPR method for chlorine dioxide. Thus, several of these materials were packed into the glass inlet stems of the CPR and iodometric impingers to serve as prefilters for the selective removal of chlorine from the sampled airstream. Again, a set of 15-mL, pH-10 CPR impingers (both primary and back-up) were used to sample the test-atmosphere generator in parallel with a set of iodometric impingers in each experiment. Generator effluent was sampled into the impingers at approximately 0.2 L/min for 120 min.

Four separate experiments of this type were performed, and the results are summarized in Table 10. By the end of the third experiment, it was clear that the sulfamic acid/sodium hydroxide/silica gel material permitted the closest correspondence between chlorine dioxide concentrations found by the CPR method and those found by the dual-pH iodometric method. The fourth experiment was conducted primarily to demonstrate that good agreement among the different methods could also be obtained at a lower chlorine dioxide concentration. Hence, the use of a 150-mg bed of 10% sulfamic acid and 10% sodium hydroxide on silica gel as a prefilter for the selective removal of chlorine from sampled air appeared to be a promising approach for use in the development of a sampling and analysis method for chlorine dioxide.

Table 10. Evaluation of Solid-State Reagents for the Selective Removal of Chlorine from Air Containing both Chlorine and Chlorine Dioxide

Expt No.	Analytical method	Prefilter material	Chlorine dioxide concn, ppm	Chlorine concn, ppm
1	CPR	100 mg of 5% diphenylamine on Fluoropak 80	0	ND[a]
	CPR	100 mg of 10% sulfamic acid/10% sodium hydroxide on Fluoropak 80	0.43	ND
	dual-pH iodometry	None	0.14	3.6
2	CPR	100 mg of 5% *N*-vinylcarbazole on Fluoropak 80	0.30	ND
	CPR	100 mg of 10% sulfamic acid/10% sodium hydroxide on silica gel	0.27	ND
	dual-pH	None	0.22	2.2
3	CPR	150 mg of 10% sulfamic acid/10% sodium hydroxide on silica gel	0.21	ND
	dual-pH iodometry	150 mg of 10% sulfamic acid/10% sodium hydroxide on silica gel	0.25	0.03
	dual-pH iodometry	None	0.25	2.7
4	CPR	150 mg of 10% sulfamic acid/10% sodium hydroxide on silica gel	0.05	ND
	spectro-photometric iodometry	150 mg of 10% sulfamic acid/10% sodium hydroxide on silica gel	0.05	ND
	dual-pH iodometry	150 mg of 10% sulfamic acid/10% sodium hydroxide on silica gel	0.05	0
	dual-pH iodometry	None	0	3.0

[a] ND = not determined.

It was recognized, however, that a far simpler approach to chlorine removal would be to dissolve the sulfamic acid in the CPR impinger medium immediately prior to sampling. To evaluate this prospect, we prepared a CPR calibration curve in the usual manner except that the CPR standards contained 0.12% (w/v) sulfamic acid (adjusted to pH 10). The resulting calibration curve was exceedingly flat, revealing only very little change in absorbance with a change in chlorine dioxide concentration. Accordingly, this approach was abandoned.

The ability of the sulfamic acid/sodium hydroxide prefilter to trap chlorine vapor while passing chlorine dioxide vapor was next evaluated under different conditions of RH, chlorine concentration, and chlorine dioxide concentration. Each of several glass impingers was charged with 15 mL of CPR solution (buffered at pH 10) and allowed to sample chlorine dioxide vapor at approximately 0.2 L/min through a 150-mg bed of sulfamic acid/sodium hydroxide prefilter material. In each test, the prefilter material was packed into the inlet stem of each primary impinger.

Each test also included one or more additional impingers charged with 10 mL of 2% (w/v) potassium iodide solution. As with the CPR impingers, test air was drawn into the iodometric impingers at about 0.2 L/min. In most instances, the iodometric impingers also bore prefilters as described above. At the conclusion of the sampling intervals, the iodometric impinger solutions were titrated by the dual-pH method to obtain reference values for chlorine dioxide concentration and, in cases where a prefilter was not used, values for chlorine concentration.

In addition to chlorine dioxide vapor, the test atmospheres contained either high (>60% RH) or low (<15% RH) concentrations of water vapor and either high (>1 ppm) or low (<0.1 ppm) concentrations of chlorine. All primary CPR and iodometric impingers employed in these experiments were paired with identical back-up impingers to ensure that excessive slippage did not occur. Other experimental details were as given previously or were as noted subsequently in this report.

Table 11 summarizes the results of six separate experiments of this type. Note that two of the iodometric impingers did not employ prefilters for the removal of chlorine vapor from the sampled air stream, and therefore, these impingers permitted iodometric determinations of the chlorine concentration. In the presence of high concentrations of both chlorine and water vapor (i.e., in the first four experiments), the chlorine dioxide concentrations obtained by the CPR method were markedly lower than those obtained by the dual-pH iodometric titration. Moreover, within experimental error, this phenomenon was not observed at high RH levels (Experiment 5) or at high chlorine concentrations (Experiment 6, as well as Experiments 3 and 4 of Table 10).

Table 11. Results of Tests Performed to Determine the Effects of Humidity and Chlorine Vapor upon the Performance of Sulfamic Acid/Sodium Hydroxide Prefilters

Expt No.	Sampling period, min	RH, %	Chlorine dioxide concn, ppm		Chlorine concn, ppm
			CPR method	Dual-pH iodometry	
1	120	>60	0.06	0.22	
				0.25[a]	1.5[b]
2	120	>60	0.14	0.24	
				0.28[a]	2.5[b]
3	75	>60	0.50	0.58	2.5
			0.53	0.69	
4	60	>60	0.29	0.40	1.1
			0.30	0.41	
5	112	>60	0.39	0.36	<0.1
			0.37	0.42	
6	120	<15	0.25	0.29	1.3
				0.29	

[a] These values were determined without the use of a prefilter for the selective removal of chlorine from the sampled air stream.

[b] These values were determined iodometrically; all other values in this column were estimated from the response of the continuous monitor.

The results of this series of experiments prompted speculation about losses of chlorine dioxide in a degradative side-reaction. Because the iodometric values of chlorine dioxide concentration obtained without the use of a prefilter were quite similar to the corresponding results obtained with the use of a prefilter, the prefilter seemed not to have been involved in the problem. Moreover, if the chlorine dioxide was partially consumed in a side-reaction, then this reaction apparently required the presence of both water and chlorine in the vapor state, since water was readily available in the CPR impinger, yet no analyte losses occurred when only chlorine was present with the analyte in the vapor state.

Consequently, it was hypothesized that chlorine was partially destroyed in a gas-phase reaction involving both chlorine and water and that a product of this reaction produced a positive interference in the iodometric determination (but not in the CPR determination) of chlorine dioxide. Although the reaction could have occurred in the prefilter and not in the vapor state, the prefilter would not likely have produced a volatile oxidative reaction product that caused a positive interference in the iodometric analysis. Hence, we concluded that the sulfamic acid/sodium hydroxide prefilter satisfactorily eliminated the interference due to chlorine, without simultaneously causing losses of chlorine dioxide, under all conditions of RH.

At this point in the experimental program, we performed an experiment to provide additional evidence that the loss of chlorine dioxide referred to above did not occur in the CPR impinger solution. The conditions of this experiment were identical to those of Experiment 2, Table 11, except that the test atmosphere contained no chlorine dioxide. Instead, an appropriate portion of chlorine dioxide was introduced as an aqueous solution into each of two impingers (one CPR and one iodometric) that sampled from the generator. As a control measure, two additional impingers (again, one CPR and one iodometric) were also allowed to sample from the generator, but were not spiked with chlorine dioxide. Finally, two more impingers (i.e., "reference" impingers) were spiked with chlorine dioxide, but were not exposed to the test atmosphere. Hence, a total of three CPR and three iodometric impingers were carried through this experiment, and all six impingers contained sulfamic acid/sodium hydroxide prefilters.

The results of this experiment are summarized in Table 12. These data confirmed that no reaction involving chlorine dioxide occurred when the chlorine dioxide was not present as a vapor. This conclusion therefore supported the hypothesis that a gas-phase reaction involving chlorine dioxide, chlorine, and water took place when all three vapors were present concomitantly in air.

In speculating further about the nature of the hypothesized gas-phase reaction, we devoted particular attention to the following well-characterized solution equilibrium reaction:

Table 12. Results Obtained from Impingers Spiked with Chlorine Dioxide and Allowed to Sample Chlorine Vapor at High RH

	Amt of chlorine dioxide spiked, μg		Amt of chlorine dioxide found, μg	
	CPR	Dual-pH iodometry	CPR	Dual-pH iodometry
Spiked sample impingers	17.2	34.4	16.5	33.8
Spiked reference impingers	17.2	34.4	16.8	35.6
Unspiked control impingers	0	0	0	0

$$2ClO_2 + Cl_2 + 2H_2O \rightleftharpoons 2ClO_3^- + 2Cl^- + 4H^+ \quad (7)$$

$$(K_{eq} = 10.3)$$

If this reaction had occurred in our test-atmosphere generator within submicrometer-sized airborne droplets of water, then the chlorate ion that appeared as a product of the reaction could have interfered positively in the iodometric analysis. (Although the glass wool plugs of the experimental prefilters would have filtered large aerosol particles out of the sampled air stream, the plugs may not have retained very small aerosol particles appreciably. Hence, we carried out a simple, informal experiment in which an iodometric impinger solution was spiked with 80 µg of sodium chlorate and then titrated as if to determine its chlorine dioxide content; however, the iodometric method was found not to respond to the spiked sodium chlorate.

Nevertheless, the experimental evidence accumulated up to this point suggested that a gas-phase reaction involving chlorine dioxide occurred under certain conditions and that the lack of agreement between the CPR method and the dual-pH iodometric method may not have been due to an inherent deficiency in the CPR method. Because we lacked the time to pursue this matter further, we decided to proceed to the validation of the CPR method on the strength of the available evidence, however incomplete, for the validity of this method. We reasoned that if the CPR method survived the validation process, then there might be sufficient justification for continuing to address the question of chlorine dioxide loss at a later date.

F. Final Optimization of the CPR Method Prior to Validation

In an effort to optimize the accuracy and precision of the CPR method, our procedures for the preparation, mixing, and dilution of the necessary reagents and buffer were altered to eliminate the measurement of very small (i.e., <1 mL) but critical solution volumes and to minimize the total number of critical volume measurements to be performed in a given experimental run. In the resulting optimized method, a CPR impinger concentrate was prepared by mixing 100 mL of 4.73×10^{-4} M CPR stock solution with 100 mL of the original pH 10 borax buffer solution and diluting to 2 L. A 400-mL aliquot of the 2.36×10^{-5} M CPR solution was then diluted to 1 L prior to the addition of 15 mL of the 9.46×10^{-6} M CPR solution to each impinger. The CPR spectrophotometric standards were each prepared by combining 20 mL of the 2.36×10^{-5} M CPR solution with an appropriate volume (>1 mL) of a dilute chlorine dioxide solution and diluting to 50 mL.

As a test of the optimized procedure, a CPR calibration curve was generated, and the data were subjected to least-squares analysis. The experimental data points and least-squares curve are plotted in Figure 6. The least-squares fit is described by the following equation with absorbance as the dependent variable (y) and with the quantity of chlorine dioxide in micrograms (in a 15-mL portion of the CPR impinger solution) as the independent variable (x):

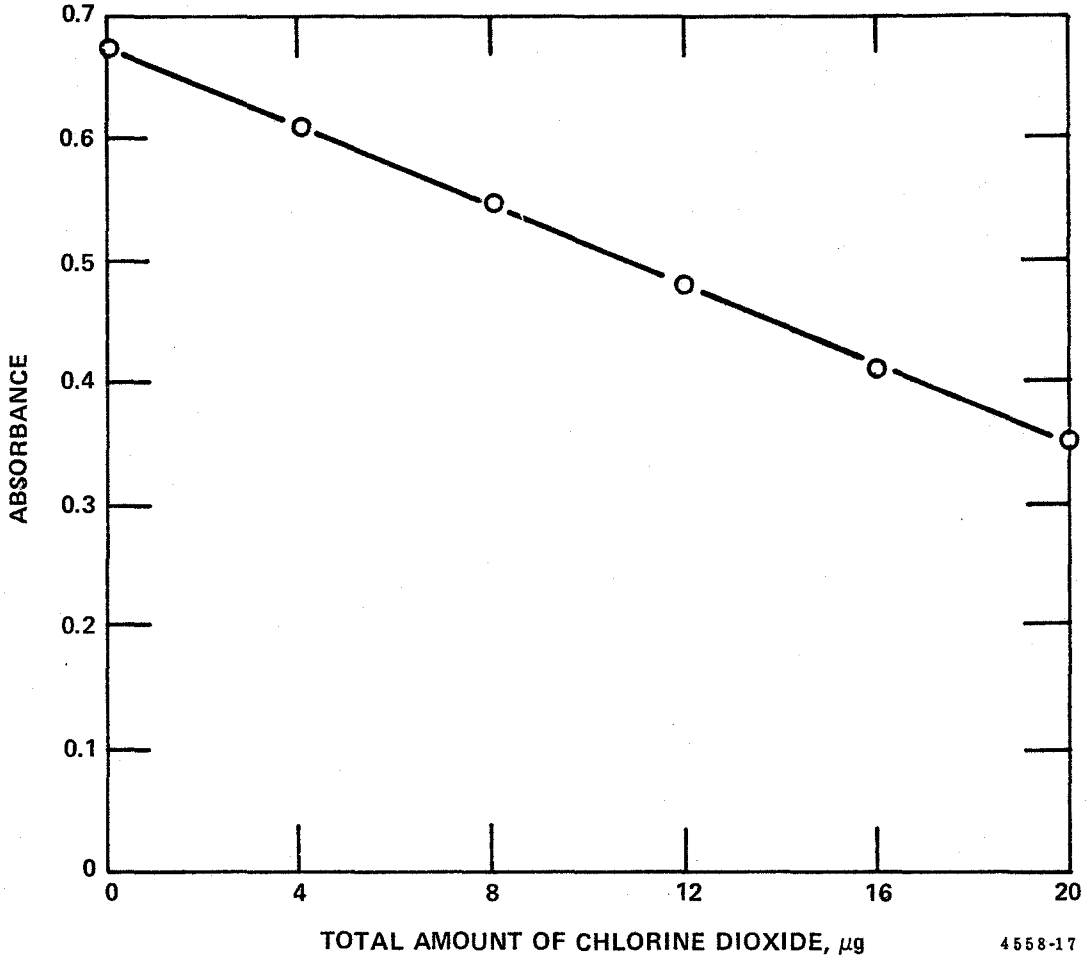

Figure 6. CPR spectrophotometric calibration curve generated after optimization of the procedures for the preparation of solutions.

$$y = (-0.0164 \pm 0.0006)x + (0.678 \pm 0.007) \qquad (8)$$

where the uncertainties in the slope and intercept are 95% confidence limits. The correlation coefficient (r) was -0.9996, and the standard error of the estimate ($s_y \cdot x$) was 0.004.

Calculations of the uncertainty in quantities of chlorine dioxide (x) predicted from measured absorbances (y) indicated that approximately 4 µg of chlorine dioxide could be determined with an estimated error of ±10%, 95% of the time, for six replicate determinations (i.e., the number of replicates determined in subsequent accuracy and precision tests). Four micrograms correspond to the quantity of chlorine dioxide that would be sampled in 29 L of air containing 0.05 ppm chlorine dioxide (0.5 PEL).

G. Accuracy and Precision Studies

As required for the validation of the CPR method, we initiated a series of formal sampling experiments, involving statistically significant numbers of CPR and iodometric impingers, to permit a determination of the accuracy and precision of the CPR method. Test atmospheres containing water vapor at concentrations corresponding to at least 80% RH and chlorine dioxide at concentrations corresponding roughly to 0.5, 1.0, or 2.0 PEL were sampled through each impinger at approximately 0.22 L/min for 120 min (26.4 L). The CPR and iodometric impingers were prepared and analyzed as described previously in this report (i.e., the optimized CPR method and the dual-pH iodometric method). Both the primary CPR impingers and the primary iodometric impingers were connected in tandem with identical back-up impingers.

The validation regimen required that at least six separate determinations be performed with the experimental method at each of the three analyte concentration levels; however, our apparatus accommodated only four pairs of impingers in any given sampling experiment. Therefore, we intended that three sampling experiments, each involving two pairs of CPR impingers and two pairs of iodometric impingers, would be performed at each analyte concentration level. We encountered difficulties at the lower two concentration levels, however, and only two experiments were performed at each of these two levels.

The results of the experiments conducted at a chlorine dioxide concentration of 0.3 ppm are summarized in Table 13. The two primary CPR impingers and the two primary iodometric impingers of Experiment 1 contained sulfamic acid/sodium hydroxide prefilters for the removal of chlorine. Moreover, all sampling was conducted at room temperature, which was about 28 °C. The bias between the two methods was acceptable (i.e., within ±10%), and the relative standard deviation (RSD) of the CPR determinations was <10% as required.

Table 13. Accuracy and Precision Data for the CPR Method
at a Chlorine Dioxide Concentration
of About 0.3 ppm

Expt No.	Chlorine dioxide concn, ppm		
	CPR	Dual-pH iodometry	
1	0.29	0.27	
	0.29	0.29	
2	0.27	0.31	
	0.28	0.31	
3	0.33	0.33	
	0.29	0.33	
	Avg = 0.29	Avg = 0.31	Bias = -0.02
	RSD = 7.0%	RSD = 7.6%	Relative bias = -6.5%

The bias between the CPR method and the iodometric method was excessive in the four sampling experiments conducted at chlorine dioxide concentrations of about 0.1 and 0.05 ppm. The concentrations determined by the CPR method indicated that little or no chlorine dioxide was being generated. The results of the iodometric determinations indicated oxidant levels (calculated as chlorine dioxide) of 0.07 to 0.12 ppm. The iodometric results, however, could be obtained only from the second titration in the dual-pH iodometric titration scheme because no titrant was required to reach the first endpoint for any of these iodometric solutions. In principle, the first titer should have been exactly 1/5 of the total titer if chlorine dioxide were present exclusively. This 5:1 stoichiometric ratio prevailed in <u>all</u> of the iodometric titrations of the first three experiments (Table 13) and in <u>none</u> of the iodometric titrations of these last four experiments.

To confirm that the prefilters associated with the CPR impingers were not involved in the above-mentioned bias problem, we conducted a sampling experiment under the same conditions that prevailed in the last four experiments except that one of the CPR impingers was operated without the use of a prefilter. The results of this experiment were essentially the same as those of the four experiments in question, indicating that the outcome was, indeed, independent of the presence or absence of the prefilter.

Based on these observations, we surmised that the oxidant causing the iodometric response in the last four experiments was, for the most part, a species other than chlorine dioxide. It is possible that this extraneous species was chlorite ion, either as sodium chlorite or as chlorous acid. In other words, the interior surfaces of the test-atmosphere generator may have somehow become contaminated with chlorite ion, or the operating parameters of the chlorine dioxide generator may have somehow changed. Consequently, we disassembled our generator and thoroughly cleaned its components in preparation for further experimentation.

After the restoration of our generator's functionability, we resumed the sampling experiments that were required for validation of the accuracy and precision of the CPR method. Test atmospheres containing chlorine dioxide at approximately 0.1 ppm (as indicated by the iodometric method) and water vapor at a RH in excess of 80% were passed through iodometric and CPR impingers at approximately 0.22 L/min for 120 min. The CPR impingers each bore prefilters for the selective removal of chlorine from the sampled airstream; the prefilters were again composed of 150 mg of 10% (w/w) sulfamic acid and 10% (w/w) sodium hydroxide on silica gel. Both the primary CPR impingers and the primary iodometric impingers were connected in series with identical back-up impingers to test for slippage or breakthrough of the analyte. All impinger solutions were prepared and analyzed as described in connection with the previous accuracy and precision studies.

The results of these experiments are given in Table 14. As noted in connection with the analogous experiments performed previously, the CPR method produced significantly lower values of chlorine dioxide concentration than the dual-pH iodometric method. Moreover, all iodometric values of analyte concentration had to be computed from the results of the second, or acidic, titration step because no titrant was required to reach an endpoint in the first, or neutral, titration step in each case. In any event, the disassembly and decontamination of the generator that preceded these experiments seemed not to have rendered the desired improvement in experimental results.

This type of sampling experiment was repeated at various chlorine dioxide concentrations between 0.1 and 0.7 ppm (as given by the iodometric method). In these experiments, however, the RH was less than 10%. Moreover, a glass wool plug was installed in the generator immediately downstream from the sodium chlorite impinger, but upstream from the dilution air inlet, prior to the last of this series of experiments. Finally, none of the impingers of these experiments contained prefilters for the removal of chlorine vapor. All other experimental details were as described for the original experiments.

The experimental results are summarized in Table 15. Again, a systematic discrepancy between the iodometric method and the CPR method occurred at a low chlorine dioxide concentration (<0.3 ppm). Moreover, the iodometric determination of Experiments 1 and 3 again required no titrant to reach an endpoint in the respective first titrations. Hence, neither the prefilters nor the high RH levels that were used in the previous experiments (but that were absent in these experiments) seemed to be associated with the bias problem. However, the data of Table 15 are insufficient to establish whether the glass wool plug of Experiment 4 provided a beneficial effect.

Note that a portion of the observed discrepancy in these data probably can be attributed to evaporative losses of solvent (water) from the CPR impingers during sampling. Although such losses were not likely to have exceeded 0.5 mL (i.e., about 3% of the original solution volume of 15 mL), they could have caused a proportionately far greater error in the CPR results at low analyte concentrations. For example, a 3% reduction in the volume of the CPR impinger medium during sampling would have caused a 3% increase in the solution absorbance. If the simultaneous decrease in solution absorbance due to exposure to chlorine dioxide had been only 20% of the original solution absorbance, then the 3% evaporative loss would have caused a 15% negative bias in the CPR result. However, the discrepancy between the iodometric data and the CPR data in Experiment 1 of Table 15 was much too large to have been caused primarily by evaporation.

Table 16 contains the results of additional sampling experiments performed to evaluate the beneficial effects, if any, of the glass wool plug that was installed in the vapor generator as described previously. The experimental conditions were the same as noted above in connection with the experiments of Table 15 except as stated otherwise in Table 16. These results also reflect a systematic discrepancy between the two analytical methods, indicating that no significant improvement resulted from the installation of the glass wool filter.

Table 14. Results of Sampling Experiments Conducted at High RH and at a Chlorine Dioxide Concentration of Approximately 0.1 ppm

Expt No.	Chlorine dioxide concn, ppm	
	CPR	Dual-pH iodometry
1	0.08	0.12
2	0.04	0.11
	0.05	0.11
3	0.04	0.11
	0.04	0.11
4[a]	0.04	0.16

[a] In this experiment, sampling was performed for 60 min at approximately 0.45 L/min.

Table 15. Results of Additional Sampling Experiments

Expt No.	Chlorine dioxide concn, ppm	
	CPR	Dual-pH iodometry
1	0.05 0.05	0.10 0.11
2[a]	0.79	0.69
3[a]	0.33	0.51
4[b]	0.32 0.31	0.34 0.33

[a] In these experiments, sampling was carried out for only 15 min; in all other experiments the sampling period was 120 min.

[b] This experiment was performed after the installation of glass wool in the generator as described in the text.

Table 16. Results of Sampling Experiments Performed to Evaluate the Effect of a Glass Wool Plug Installed as a Particulate Filter in the Test-Atmosphere Generator

Expt No.	RH, %	Chlorine dioxide concn, ppm CPR	 Dual-pH iodometry
1	>80	0.04	0.14
		0.03	0.13
2	<10	0.04	0.14
		0.04	0.11[a]

[a] This iodometric result was obtained with the use of a prefilter for the selective removal of chlorine.

As in several previous experiments, moreover, no titrant was used in the first titrations of the iodometric determinations. This persistent phenomenon was interpreted as evidence for a fundamental problem or fault either in the iodometric determination itself or in the production of chlorine dioxide test atmospheres.

In another series of sampling experiments, the chlorine dioxide concentration in the test-atmosphere generator was varied slightly, but only by adjustment of the rate of flow of the dilution air, not by adjustment of the chlorine flow into the sodium chlorite impinger or by adjustment of the impinger temperature. Sampling was again conducted through iodometric and CPR impingers at approximately 0.22 L/min for 120 min; the RH of the test atmospheres was maintained at less than 10%. Some of the impingers were operated without sulfamic acid/sodium hydroxide prefilters, and some of the iodometric impingers contained none of the pH 7 phosphate buffer that had been added to the potassium iodide sampling solutions prior to the initiation of sampling in most of the previous sampling experiments.

The results of these experiments are presented in Table 17. The bias problem was observed once again in each of the experiments, which suggested that the problem was independent of the dilution air flow rate, the presence or absence of a sulfamic acid/sodium hydroxide prefilter, and the presence or absence of pH 7 phosphate buffer in the iodometric sampling medium. Interestingly, the phenomenon of "zero titrant required for the first titration" was observed in each of the buffered iodometric solutions but in none of the unbuffered iodometric solutions. However, results obtained both with and without the buffer agreed closely, suggesting that the phenomenon did not lead to a quantitative error, whatever its cause.

In preparation for a final series of sampling experiments, the test-atmosphere generator was modified by replacement of the aqueous sodium chlorite impinger with a column or tower packed with solid flakes of technical-grade (80%, w/w) sodium chlorite. (Chlorine gas reacts with solid sodium chlorite as well as sodium chlorite in aqueous solution to form chlorine dioxide.) The experiments were carried out in a manner similar to the immediately preceding experiments except that the sampling rates and sampling intervals were varied. Moreover, all of the CPR impingers and none of the iodometric impingers contained sulfamic acid/sodium hydroxide prefilters. In addition, both the dual-pH titration and the spectrophotometric versions of the iodometric analysis were employed in most of the experiments.

Table 18 contains the results of these experiments. Clearly, the alternative mode of chlorine dioxide generation, based on the use of solid sodium chlorite, failed to alleviate the bias problem. Hence, the problem was not likely to have depended on the way in which the chlorine dioxide vapor was produced. (The problem may, however, have been related to the way in which the vapor was diluted prior to sampling.) Once again, the "zero titrant/first titration" phenomenon occurred in the lone buffered iodometric sampler

Table 17. Results of Sampling Experiments Performed Under Various Sets of Experimental Conditions

Expt No.	Chlorine dioxide concn, ppm	
	CPR	Dual-pH iodometry
1	0.10[a] 0.07[a]	0.19[b] 0.13[b]
2	0.10[a] 0.10[a]	0.17 0.15[a]
3	0.12 0.12	0.19[b] 0.18

[a] These results were obtained with impingers that bore prefilters for the selective removal of chlorine from the sampled airstream; the remaining impingers employed no such prefilter.

[b] These results were obtained with iodometric impingers that contained a pH 7 phosphate buffer; the remaining iodometric impingers were treated with the buffer only after the completion of sampling.

Table 18. Results of Sampling Experiments Conducted After Modification of the Test-Atmosphere Generator

Expt No.	Sampling interval, min	Approx sampling rate, L/min	Chlorine dioxide concn, ppm		
			CPR	Dual-pH iodometry	Spectrophotometric iodometry
1	90	0.23	0.10	--[a]	--[a]
		0.23	0.09	0.21[b]	--[c]
2	120	0.41	0.02	0.09	0.08
		0.24	0.08	0.15	0.17
3	120[d]	0.41	0.03	0.12	0.15
		0.24	0.06	0.14	0.16

[a] Sample was lost.

[b] The iodometric sampling medium employed here contained the pH 7 phosphate buffer during the sampling interval.

[c] This analysis was not performed.

[d] In this experiment, the ratios of titrant required in the first and second titrations of the dual-pH iodometric determinations were such as to indicate the possible presence of chlorine in the sampled test atmosphere.

but not in the other (unbuffered) iodometric samplers. Curiously, both the CPR impingers and one of the two iodometric impingers that sampled at a relatively high rate (0.41 L/min) yielded much lower analyte concentration values than the corresponding impingers that sampled at a lower rate. The back-up impingers for these samplers did not provide evidence of breakthrough due to poor sampling efficiency, and hence we can offer no satisfactory explanation for this observation. Finally, the generally good agreement between the dual-pH titration and the spectrophotometric version of the iodometric determination implied that the dual-pH titration, exclusive of the sample collection step, was not a major source of error.

H. Experiments with Spiked Chlorine Dioxide

To obtain additional experimental data that were independent of the test-atmosphere generator, we performed a series of experiments involving the introduction of aqueous solutions of chlorine dioxide into the impinger solutions.

In prior related work with chlorine dioxide solutions, we learned that they were sufficiently acidic to reduce the pH of the unbuffered iodometric impinger medium to an unacceptably low level for the first or "neutral" titration step. Specifically, we observed that in the absence of the pH 7 buffer, the first titration consumed an excessive amount of titrant, and the second titration then consumed too little titrant. Apparently, the iodine consumed in the first titration was produced not only by the quantitative reduction of chlorine dioxide to chlorite ion (which normally occurs at neutral pH) but also by the partial reduction of chlorite ion to chloride ion (which normally occurs only at the lower pH of the second titration).

For this reason, the iodometric solutions of the following spiking experiments were buffered at pH 7 prior to the addition of chlorine dioxide solutions, even though an abnormal titration ratio had been observed in the preceding air sampling experiments involving buffered iodometric solutions. In these spiking experiments, however, an abnormal titration ratio was not observed.

In the first spiking experiments, CPR and iodometric impinger solutions were spiked with various amounts of chlorine dioxide and then analyzed in the usual manner without the sampling of any air. In other words, the CPR solutions were spiked with chlorine dioxide, their absorbances measured, and the absorbances compared to a previous calibration curve. Additionally, the spiked iodometric solutions were titrated with sodium thiosulfate according to the dual-pH method. Duplicate iodometric determinations were performed at each of three chlorine dioxide spike levels.

The results of this experiment appear in Table 19. Note that because the CPR method was standardized against solutions of chlorine dioxide, the CPR results in this table do not consitute an independent test of the actual level of spiked chlorine dioxide. Rather, the CPR results indicate only the reproducibility of the determination of CPR calibration standards. The iodometric results, on the other hand, were generated without the use of chlorine dioxide for standardization; therefore, the iodometric results constitute an independent measurement of the quantity of chlorine dioxide spiked.

The amounts of chlorine dioxide found by the iodometric method did not agree closely with the amounts believed to have been introduced into the iodometric solutions. The results were more than 20% higher than expected at the 4.3-μg spike level and were substantially below the expected values at the upper two spike levels.

Unfortunately, interpretation of these data was complicated by the possible existence of at least two separate sources of systematic error: (1) the loss of chlorine dioxide by volatilization or decomposition during its transfer from the stock solution to the impinger solutions, and (2) high results in the spectrophotometric determination of chlorine dioxide concentration in the stock solution from which the impingers were spiked. As discussed previously, the latter error could have been caused by the assumption of an inaccurate value for the molar absorptivity of chlorine dioxide. Information gathered prior to these experiments implied that our assumed value of 1100 L/mol•cm for the molar absorptivity of chlorine dioxide in water might not be accurate and that a higher value might be more nearly correct. With regard to analyte losses during the transfer of solutions, the CPR results (Table 19) by themselves suggest that at least some loss of chlorine dioxide might very well have occurred in this manner, since the results were generally slighly lower than expected.

Taken together, these two potential sources of error may have been sufficient to explain why the CPR results of Table 19 were not negatively biased with respect to the iodometric results, as was observed in the preceding experiments. Note that the postulated error due to losses of analyte would tend to depress the iodometric and CPR results, whereas the postulated error due to an incorrect value for molar absorptivity would tend to inflate only the CPR results and the values in the first column ("Amt of chlorine dioxide spiked"). If the magnitudes of the systematic errors were known and if the data could be corrected for them, the CPR results would probably still agree with the known spike levels nearly as well as the data of Table 19. However, the iodometric results would increase greatly (relative to the known spike levels), and the iodometric data would then reflect a large positive bias relative to both the CPR results and the known spike levels at low chlorine dioxide concentrations. In other words, if the postulated errors actually existed and could be eliminated from the data, the results of Table 19 might closely agree with the analogous results obtained in the preceding sampling experiments, except that the bias between the methods would be shown by these data to be clearly the fault of the iodometric method and not the CPR method. Of course, this conclusion was considered to be speculative, and our experiments to determine the cause of the bias problem were continued.

Table 19. Results of Chlorine Dioxide Spiking Experiments Involving CPR and Iodometric Sampling Media

Amt of chlorine dioxide spiked,[a] μg	Amt of chlorine dioxide found, μg	
	CPR	Dual-pH iodometry
0	0	0.0, 0.0
4.3[b]	4.3	5.0, 5.4
8.6	8.4	7.4, 7.9
17.2	16.0	14.1, 13.6

[a] As determined spectrophotometrically by the absorbance of chlorine dioxide at 360 nm with a reported molar absorptivity (ε) of 1100 L/mol•cm.

[b] An analyte spiked with 4.3 μg corresponds to the sampling of air containing 0.05 ppm of analyte (0.5 PEL) at 0.25 L/min for 120 min.

To ascertain whether the sampling of air through the impinger media affected the experimental results, the previous experiment was repeated except that room air was sampled (at 0.22 L/min) immediately following the addition of aqueous chlorine dioxide to each impinger solution. Moreover, the spectrophotometric version of the iodometric analysis was employed in certain instances to supplement the dual-pH iodometric data. The results are given in Table 20.

It can be seen in Table 20 that the dual-pH iodometric method was again positively biased at low chlorine dioxide spike levels and negatively biased at the higher spike levels. These data generally resemble those of the previous experiment (Table 19), and thus it was concluded that the sampled air exerted no measurable effect on the results of the experiment.

To confirm that the dilution of air from the test-atmosphere generator exerted no significant effect upon the CPR results, each of several CPR sampling solutions was spiked with 8.4 μg of chlorine dioxide and then used to sample the dry (<10% RH), analyte-free generator dilution air for 120 min. The absorbances of the solutions, and of another spiked solution that had not sampled any air, were then measured in the usual manner. These absorbances are tabulated in Table 21. It can be seen that the dilution air produced only minor changes in the solution absorbances; these changes were probably due to evaporative losses of solvent.

To evaluate the iodometric method response to the generator dilution air, unspiked iodometric impingers, both with and without the pH 7 phosphate buffer, were used to sample from the dry, analyte-free generator dilution airstream at about 0.22 L/min for 120 min and were then titrated according to the dual-pH method. Table 22 contains the results of this experiment. The unbuffered impingers produced a significant "blank" response in the second titration, possibly due to air oxidation of the potassium iodide. However, this blank response was insufficient to account for the relatively large bias observed in previous experiments.

To illustrate graphically the systematic bias between the iodometric method and the CPR method, the data accumulated during the accuracy and precision studies were plotted as shown in Figure 7. Each CPR value of chlorine dioxide concentration was plotted against the corresponding iodometric value of chlorine dioxide concentration. The solid line in the figure is the linear regression curve computed from those data points that represent nonzero CPR values. (The dashed line is merely a diagonal with a slope of 1 and a y-intercept of 0.) Although they are included in the figure, the data points with CPR values of zero were not included in the regression analysis because zero CPR values might have occurred in conjunction with any iodometric values of less than about 0.1 ppm.

Table 20. Results of Chlorine Dioxide Spiking Experiments in Which Room Air was Sampled Through Spiked Sampling Media

Amt of chlorine dioxide spiked, µg	Sampling interval, min	Amt of chlorine dioxide found, µg		
		CPR	Dual-pH iodometry	Spectrophotometric iodometry
0	120	0	0	0
0	60	ND[a]	0	ND
4.0	120	3.2	5.2	3.5
4.3	60	ND	5.4	ND
8.0	120	7.4	7.0	6.7
8.6	60	ND	8.7	ND
16.0	120	16.1	14.3	13.5
17.2	60	ND	14.1	ND

[a] ND = not determined.

Table 21. Results of an Experiment in Which CPR Impingers were Spiked with Chlorine Dioxide and Allowed to Sample the Dilution Air from the Test-Atmosphere Generator

Sample No.	Sampling rate, L/min	Absorbance at 570 nm
Spiked "blank"	0	0.510
1	0.20	0.518
2	0.23	0.518
3	0.18	0.520
4	0.50	0.535
5	0.45	0.528
6	0.47	0.533

Table 22. Results of an Evaluation of the Blank Response of the Iodometric Method to Generator Dilution Air

Sample No.	Buffer	Blank response (as ClO_2), ppm
1	no	0.02
2	no	0.02
3	no	0.01
4	no	0.01
5	yes	<0.01
6	yes	<0.01
7	yes	<0.01
8	yes	<0.01

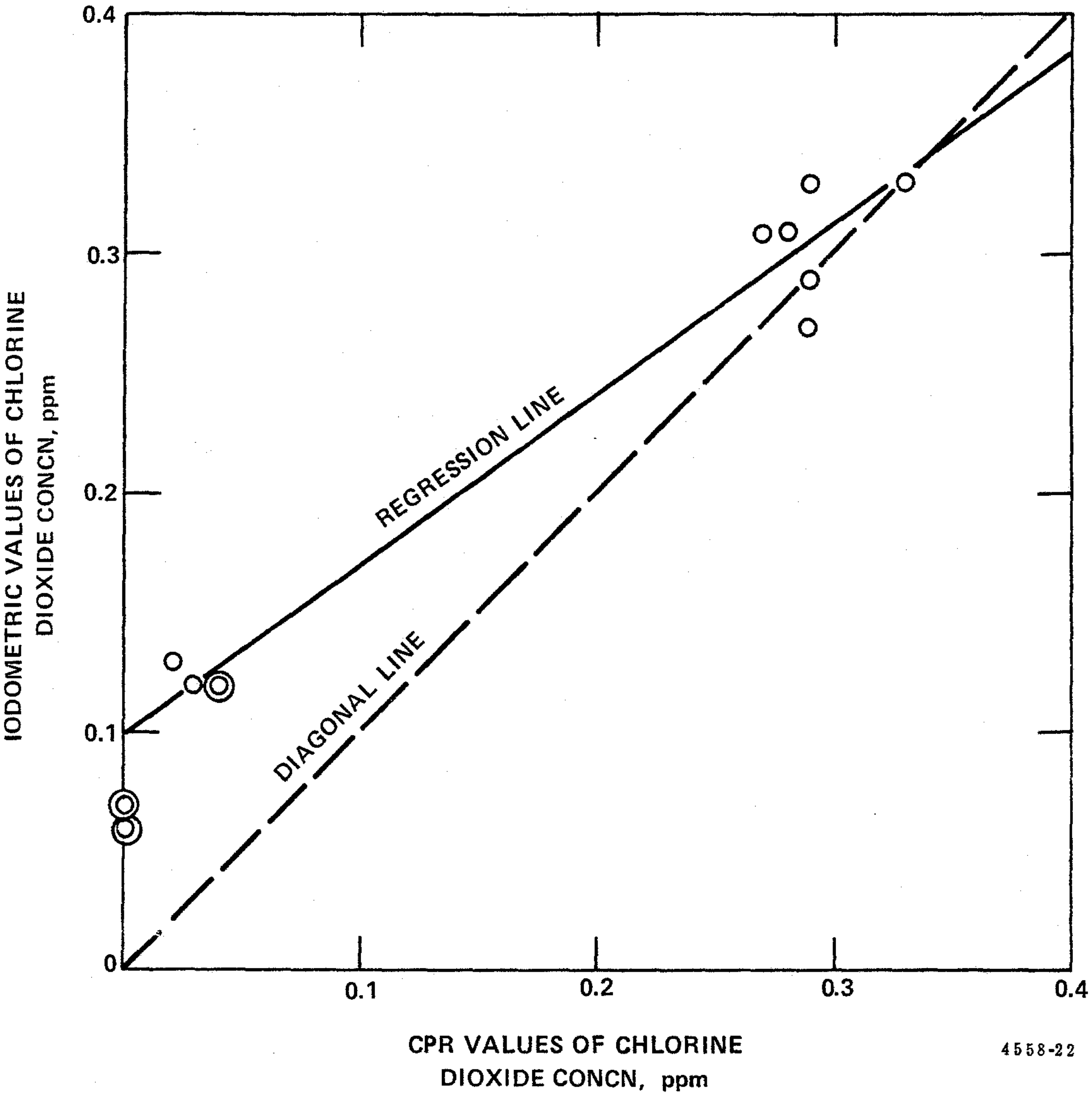

Figure 7. Plot of iodometric values of chlorine dioxide concentration versus the corresponding CPR values of chlorine dioxide concentration (Concentric circles indicate two coincident data points.)

Because only two clusters of data points were employed in the computation of the regression curve, it cannot be known with confidence that the functional relationship between the CPR data and the iodometric data was indeed linear. However, the individual data points demonstrate clearly that a bias existed at low concentration levels. The regression curve featured a slope of 0.705, a y-intercept of 0.101, and a correlation coefficient (r) of 0.9821. It is not known whether the bias was reversed or was nonexistent at analyte concentrations above 0.3 ppm.

I. Evaluation of Another Reference Analytical Method for Chlorine Dioxide

At this point, it appeared that no further progress could be made in resolving the bias problem unless a determination could be rendered as to which of the two methods—the CPR method or the dual-pH iodometric method—was more accurately reflecting the "true" chlorine dioxide concentration. It seemed that the only way to render this determination with sufficient confidence in the outcome was to bring a third analytical method to bear upon the problem. Ideally, this third method should also possess the qualities and characteristics of a good reference analytical method: It should be highly accurate, precise, sensitive, and specific for the species of interest. Based on what we had read in the literature, we believed that the colorimetric method employing Acid Chrome Violet K (ACVK) (7) offered a means by which to establish the source of the bias problem. The ACVK method involved the reaction of chlorine dioxide with excess ACVK and the subsequent determination of the residual ACVK by measurement of its absorbance at 550 nm. In principle, therefore, the ACVK method closely resembled the CPR method.

Stock ACVK solution was prepared by the following procedure: Approximately 175 mg of ACVK and 20 mg of sodium metaphosphate were mixed in 500 mL of oxidant-demand-free water. Approximately 48.5 g of ammonium chloride and 5.3 mL of concentrated ammonium hydroxide were then added to the mixture, and the mixture was diluted to 1 L with oxidant-demand-free water. The resulting suspension of ACVK was allowed to stabilize for 24 to 48 h, after which it was filtered through a 0.45-µm membrane filter. Prepared in this manner and stored in an amber bottle, the stock ACVK solution was reported to be stable for about 1 month.

The ACVK method was standardized with chlorine dioxide standard prepared from sodium chlorite and acetic anhydride as specified previously in connection with the CPR method. To do so, 1 to 5 mL of a 12.1-µg/mL stock solution of chlorine dioxide was mixed with 5 mL of stock ACVK solution and then diluted to 50 mL with oxidant-demand-free water. The absorbance at 550 nm was then measured. Reagent blanks containing no chlorine dioxide were also prepared and analyzed along with the standards.

In our application of the calibration procedure, we found that the sensitivity and precision of the ACVK method were much poorer than desired for meaningful use of the method for comparison with the CPR and iodometric methods. For instance, the working analyte concentration range of the method, 0.25 to about 1.25 μg/mL, corresponded to a range of absorbance measurements from 0.01 to 0.05. Consequently, small errors in the measurement of absorbances contributed to large errors in concentration determinations. These errors were demonstrated in the variability observed in the determination of calibration curves. The linear regression analysis of a typical calibration curve of absorbance (y) plotted as a function of chlorine dioxide standard concentration (x) in micrograms per milliliter yielded the following equation:

$$y = (-0.018 \pm 0.014)x + (0.245 \pm 0.010) \qquad (9)$$

where the uncertainties in the slope and intercept correspond to a 95% confidence interval. The large uncertainty in the slope of the curve rendered determinations of sample unknowns highly suspect. Some other experimentally determined curves exhibited less variability in both the slope and intercept; however, we could not obtain these more precise curves consistently.

An investigation of various potential sources of error in the ACVK method, including the pH of the reaction medium and the stability of the ACVK suspension, did not help to lower variability or to increase sensitivity. Consequently, the work with ACVK was stopped. Furthermore, additional work toward the validation of the CPR determination of chlorine dioxide was suspended.

V. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

During this contract, we screened 27 solid substances for their ability to react with chlorine dioxide vapor in a gas-solid reaction, and among these substances, only o-aminophenol and a silver metal membrane displayed a significant degree of reactivity. The silver membrane probably formed silver chloride, however, which is also produced upon exposure to chlorine, and therefore an analytical method based on this reaction might not have been sufficiently specific. The reaction involving o-aminophenol was also rejected because no nonionic reaction products were discovered in the HPLC analysis of chlorine dioxide-exposed o-aminophenol. Nevertheless, o-aminophenol may be worthy of continued investigation, with emphasis being accorded to a search for an ionic reaction product, i.e., a salt or possibly a stable complex.

In general, the gas-solid reactivity of chlorine dioxide proved to be of substantially lesser magnitude than was expected from the available literature reports, which were concerned primarily with solution-phase reactivity. Apparently, organic reactions involving chlorine dioxide require the presence of a liquid solvent to enable the formation of the necessary reaction intermediates or activated complexes, and the gas-solid reactivity of chlorine dioxide thus appears to be confined largely to the formation of simple ionic salts or complexes. Consequently, we suggest that any future attempt to find a reactive solid substance for chlorine dioxide be directed toward materials that are capable of salt or complex formation. We further suggest that plans be adopted for the screening of a rather large number of candidate substrates.

Although the CPR method was not validated, we propose that the method may in fact be suitable for use tentatively in the absence of proof that the reference method against which the CPR method was compared is reliable. Consequently, we have written a CPR method summary, which appears in Appendix A.

The CPR impinger method for chlorine dioxide may yet offer the most promising short-term approach to the development of a method for chlorine dioxide. The precision, sampling capacity, storability, specificity (in conjunction with a means for removing concomitant chlorine vapor), sensitivity, and analyte slippage rates associated with this method appeared to be entirely satisfactory for validation. Our early experiments with the CPR method yielded quite promising results, and only in later attempts to establish the accuracy of the method was a significant problem encountered in the form of a systematic bias between the CPR method and the dual-pH iodometric method. We could not ascertain which of these two methods was actually biased with respect to the "true" chlorine dioxide concentration, despite our efforts to bring other analytical methods, such as the DPD and ACVK methods, to bear upon the problem. Even though we had no success with these extra reference methods, other researchers obviously have used them effectively, and it should be possible to resolve the bias question with the use of such methods.

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APPENDIX A

SAMPLING AND ANALYTICAL METHOD FOR CHLORINE DIOXIDE

CHLORINE DIOXIDE

Measurements Research Branch
Analytical Method

Analyte: Chlorine dioxide	Method No.: P&CAM
Matrix: Air	Range: 0.05 to 0.3 ppm of chlorine dioxide in 15 mL of absorbing solution
Procedure: Impinger collection, spectrophotometric determination of unreacted chlorophenol red	Precision: ≤ 0.05 (analytical)
Date Issued:	Classification: E (proposed)
Date Revised:	

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1. Synopsis

1.1 A known volume of air is drawn through 15 mL of a impinger solution containing chlorophenol red (CPR). Chlorine dioxide is absorbed by reaction with the CPR to form a colorless product. Thus, chlorine dioxide decolorizes the solution as the compound is absorbed.

1.2 The impinger is preceded by a 150-mg bed of silica gel impregnated with sodium sulfamate and sodium hydroxide to remove chlorine gas from the sample air. Chlorine gas is an interferent in the determination of chlorine dioxide.

1.3 The impinger is connected in tandem with a back-up impinger, also containing CPR solution, to avoid the loss of chlorine dioxide by breakthrough from the first impinger.

1.4 The absorbance of each exposed impinger solution is measured at 570 nm to determine the concentration of unreacted CPR.

1.5 The measured absorbance is compared to the absorbances obtained with standard solutions of chlorine dioxide in CPR absorbing solution.

2. Working Range, Sensitivity, and Detection Limit

2.1 The working range of the overall sampling and analytical method is estimated to be about 4 to 20 μg of chlorine dioxide, corresponding to 0.05 to 0.3 ppm (by volume) of chlorine dioxide in 25- to 30-L air samples. The lower limit is defined by the detection limit (see Section 2.3). The calculated capacity of 15 mL of the CPR impinger solution for chlorine dioxide is about 29 μg, based on a reaction stoichiometry of 3 mol of chlorine dioxide for each mole of CPR (see Reference 11.1). The upper limit of the method range is restricted to about 20 μg to ensure that determinations are within the linear response range of the analytical method.

2.2 The sensitivity as defined by the slope of a typical calibration curve (generated as stipulated in Section 9) is -0.0164 absorbance units (at 750 nm) per microgram of chlorine dioxide in a single sample.

2.3 The detection limit, as defined by the quantity of chlorine dioxide in a single sample for which the uncertainty of analytical determination is ±10% in 95% of determinations, is estimated to be 4 μg. This quantity corresponds to the amount of chlorine dioxide that would be sampled in 29 L of air containing 0.05 ppm chlorine dioxide.

2.4 In tests designed to determine the collection efficiency of 15 mL of the CPR impinger solution for chlorine dioxide, slippage rates averaged 10% of the chlorine dioxide sampled at a rate of 0.2 L/min for 120 min from a test atmosphere maintained at about 25 °C and at a relative humidity of <10%. Subsequently, a back-up impinger was incorporated into the sampling train to avoid the loss of chlorine dioxide.

3. Interferences

3.1 Chlorine vapor produces a significant positive interference in the determinations of chlorine dioxide by the CPR method. Upon exposure to chlorine vapor, CPR solution turns from wine red to deep purple and then decolorizes. Unless chlorine is removed from the sample airstream, the eventual bleaching of the CPR solution by chlorine may be misinterpreted as bleaching by chlorine dioxide. Chlorine vapor at concentrations as high as 3 ppm in a 30-L air sample may be selectively removed from the sample airstream with a prefilter consisting of 150 mg of 20/40-mesh silica gel impregnated with 12% (w/w) sodium sulfamate and 6% (w/w) sodium hydroxide (see Reference 11.1).

3.2 The interference of other oxidants in the determination of chlorine dioxide by the CPR method was not assessed. According to published sources, the method is not susceptible to interference from many active chlorine compounds (see Reference 11.2).

4. Accuracy and Precision

4.1 Acceptable agreement between the CPR method and the reference method was obtained at a test concentration near 0.3 ppm; the iodometric reference method yielded a concentration of 0.31 ppm (RSD =7.6%), and the CPR method yielded 0.29 ppm (RSD = 7.0%). Significant discrepancies between the two methods were observed at chlorine dioxide concentrations below about 0.3 ppm (see Reference 11.1). The bias between the two methods at lower concentrations may have been the result of a fault in the iodometric method rather than the result of a deficiency in the CPR method.

4.2 The concentration of chlorine dioxide in stock solutions was determined by measuring the absorbance of the solutions at 360 nm. The standardization was based on a molar absorptivity of 1100 L/mol cm for chlorine dioxide at 360 nm (see Reference 11.2). The statistical analysis of typical calibration curves was used to estimate the precision of determinations. For six replicate determinations of 4 µg quantities of chlorine dioxide, an RSD of 5% was predicted; at 20 µg, an estimate of the RSD was about 1%.

4.3 Because the method involves the determination of unreacted CPR, storability of residual CPR in exposed impinger solutions is a measure, in part, of the reliability of the method when there is a delay between sampling and analysis. In one storage test in which six impinger solutions were exposed to roughly 15 µg of chlorine dioxide, the concentration averaged 0.25 ppm (RSD = 6.1%) both on the day of exposure and after storage in the dark at room temperature for 14 days.

5. Advantages and Disadvantages

5.1 The method is free from interference by chlorine when the sodium sulfamate/sodium hydroxide-coated silica gel is used as a prefilter.

5.2 The method is sensitive enough to allow determinations at the ceiling limit of 0.3 ppm within 15-min sampling periods and at 0.05 ppm. in 2-h sampling periods.

5.3 A disadvantage is that the method spans only a small range of quantities of chlorine dioxide (4 to 20 µg in a single sample).

5.4 The two midget impingers used in the sampler are connected with glass tubing.

6. Apparatus

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6.1 Personal sampling pump capable of accurate performance (±5%) at 0.05 to 0.3 L/min and calibrated with a representative sampling system.

6.2 Sampler. The sampler consists of two standard midget impingers connected in tandem with glass tubing. Teflon tubing was not evaluated, but we believe it would be an adequate substitute for glass. A 150-mg reactive sorbent bed to remove chlorine is placed in the inlet of the front impinger. The bed is held in place with two 4-mg plugs of silanized glass wool.

Bulk quantities of the reactive sorbent bed are made as follows: Mix 3.2 g of 20/40-mesh silica gel (Catalog No. 226-10-01, SKC, Inc., Eighty Four, PA) with 20 mL of a methanolic solution containing 400 mg of sulfamic acid and 400 mg of sodium hydroxide. Place the mixture in a rotary evaporator maintained at 100 °C and apply vacuum until the sorbent appears dry (about 1 h).

6.3 A spectrophotometer capable of accurate absorbance measurements at 570 nm and at 360 nm.

6.4 Cuvettes, 1-cm—quartz for measurements at 360 nm and Pyrex or quartz for measurements at 570 nm.

6.5 Pipets, volumetric, convenient sizes for making dilutions.

6.6 Flasks, volumetric, convenient sizes for making dilutions.

7. Reagents

All reagents should be ACS reagent grade or better.

7.1 Chlorophenol Red (CPR), 97% (w/w).

7.2 Oxidant-Demand-Free Water. Although the following procedure more specifically produces chlorine-demand-free water, for practical purposes, the water is also chlorine dioxide-demand-free. To produce a reservoir of oxidant-demand-free water, chlorinate approximately 4 L of distilled-dionized water contained in a large foil-covered Erlenmeyer flask by the addition of a sufficient quantity of commercially available bleach to create a 2- to 3-ppm (µg/mL) chlorine solution. Then place a 450-W high-pressure mercury vapor lamp in a large Pyrex test tube and lower the tube into the chlorine solution. During the ensuing irradiation step, the heat evolved from the lamp will raise the temperature of the water to its boiling point; however, the rate of boiling will be too low to cause a significant loss of water. After 30 min of irradiation, test a sample of water for the absence of chlorine by treatment with an iodide/starch indicator mixture and then cap the Erlenmeyer flask with aluminum foil and set it aside for later use.

7.3 Borate/Boric Acid Buffer (pH 10). Mix 50 mL of 0.125 M sodium tetraborate (made with oxidant-demand-free water) with 100 mL of 0.5 M sodium hydroxide (made with oxidant-demand-free water) and then dilute to 100 mL with oxidant-demand-free water.

7.4 CPR Impinger Solution (9.46×10^{-6} M CPR). Mix 100 mL of 4.73×10^{-4} M CPR in oxidant-demand-free water with 100 mL of the borate/boric acid buffer and dilute to 2 L with oxidant-demand-free water. Dilute 400 mL of this 2.36×10^{-5} M solution to 1 L with oxidant-demand-free water. This solution is stable indefinitely.

7.5 Stock Chlorine Dioxide Solution (≃300 µg/mL). Combine 3.2 g of acetic anhydride with 1.0 g of sodium chlorite (80%, w/w) dissolved in 900 mL of oxidant-demand-free water. Dilute the resulting solution to 1 L with oxidant-demand-free water. Store the stock solution in a refrigerator in the absence of light and with minimum headspace above the liquid. Stored in this manner the stock solution is stable for at least 1 week. Standardize the stock solution each time it is used by measuring its absorbance at 360 nm in a 1-cm quartz spectrophotometric cell and by subsequently calculating the chlorine concentration from a molar absorbtivity of 1100 L/mol·cm.

8. Procedure

8.1 Cleaning of equipment. All glassware should be cleaned initially with dichromate cleaning solution followed by three tap-water and three distilled-water rinses. Then soak the glassware overnight in a 0.5% (w/w) solution of sodium hypochlorite prepared from commercially available bleach. Before use, rinse the glassware with oxidant-demand-free water.

8.2 Collection of Samples

8.2.1 Pipet exactly 15 mL of the CPR impinger solution into each of two impingers. The inlet of one impinger should contain the reactive sorbent bed as specified in Section 6.2.

8.2.2 Assemble a sampling train composed of the impinger with the sorbent bed connected with glass tubing in tandem with the back-up impinger. Connect the back-up impinger to the personal sampling pump with flexible tubing. Place a moisture trap, such as a bed of silica gel, in the sampling line between the back-up impinger and the pump.

8.2.3 Mount the impingers so that the inlet will sample air from the breathing zone of the individual being monitored.

8.2.4 When determining time-weighted-average concentrations, sample the air at 0.2 L/min for 120 min (2 h) or at 0.05 L/min for 480 min (4 h). When determining ceiling levels, sample at 0.3 L/min for 15 min. The air sample volume should not exceed 25 to 30 L. Measure and report the flow rate and time or volume sampled.

8.2.5 Record the temperature and pressure of the air being sampled.

8.2.6 Immediately after sampling, remove the impinger stems from the impingers, cap the impingers with ground-glass stoppers, and pack the impingers for shipment. Exclude light from the impingers during storage. Samples may be stored for at least 14 days prior to analysis.

8.2.7 To obtain a blank sample, process one unused impinger in the sample manner as the exposed impingers but do not sample air through this impinger. Submit at least one blank impinger to analysis for every 10 exposed impingers.

8.3 Analysis of Samples

8.3.1 Measure the volume of the absorbing reagent in the impinger. If the volume is <15 mL, add oxidant-demand-free water to bring the volume up to 15 mL.

8.3.2 Transfer a portion of the sample or blank to a cuvette and determine the absorbance at 570 nm. A cuvette containing distilled water is used as the reference.

9. Calibration and Standards

9.1 Prepare chlorine dioxide standards, fresh when needed, as follows:

9.1.1 Dilute 1 mL of the Stock Chlorine Dioxide Solution (≈300 μg/mL) to 25 mL with oxidant-demand-free water, chilled to about 5 °C, to yield a solution with a chlorine dioxide concentration of about 12 μg/mL.

9.1.2 Combine each of 0-, 1-, 2-, 3-, 4-, and 5-mL aliquots of the 12-μg/mL solution with 20 mL with oxidant-demand-free water. This procedure will produce standards corresponding to concentrations of about 0, 3.6, 7.2, 10.8, 14.4 and 18.0 μg of chlorine dioxide per 15 mL of solution.

9.2 Determine the absorbance of each chlorine dioxide standard at 570 nm with a 1-cm Pyrex or quartz cuvette.

9.3 Plot the absorbance of the standard solutions against the corresponding quantity of chlorine dioxide in 15 mL of each standard.

10. Calculations

10.1 Upon determining the absorbance of a sample solution, use the standard calibration curve to find the quantity of chlorine dioxide (in micrograms) in the 15-mL sample solution volume.

10.2 Correct the quantity found for the blank.

10.3 Add the net quantities of chlorine dioxide found in corresponding front and back-up impingers to determine the total net quantity of chlorine dioxide found in a single air sample.

10.4 Calculate the air sample volume (corrected to 25 °C and 760 torr as follows:

$$V_R = F_S \times \left(\frac{298}{T_S + 273}\right) \times \left(\frac{P_S}{760}\right) \times t_s$$

where

V_R = corrected air sampling volume, L

F_S = air sampling rate at sampling conditions, L/min

T_S = temperature at sampling conditions, °C

P_S = barometric pressure at sampling conditions, torr

t_s = sampling time, min

10.5 Calculate the chlorine dioxide concentration (in milligrams-per-cubic meter) as:

$$\text{mg/m}^3\ \text{ClO}_2 = \left(\frac{\mu\text{g ClO}_2\ \text{(total net)}}{V_R}\right) \times \left(\frac{1\ \text{mg}}{1000\ \mu\text{g}}\right) \times \left(\frac{1000\ \text{L}}{1\ \text{m}^3}\right)$$

10.6 Convert the concentration in milligrams per cubic meter to the corresponding value in parts-per-million (v/v) at standard conditions as follows:

$$\text{ppm ClO}_2 = \text{mg/m}^3 \times \left(\frac{24.45}{67.46}\right)$$

where

24.45 = molar volume (L/mol) at 25 °C and 760 torr

67.46 = molecular weight of chlorine dioxide, daltons

11. References

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APPENDIX B

SAMPLING DATA SHEET
FOR
CHLORINE DIOXIDE

NIOSH SAMPLING DATA SHEET NO. _____ CLASS E

Substance: Chlorine Dioxide

Standard: 0.1 ppm (0.3 mg/m^3), OSHA Permissible Limit (PEL)
(see Reference 2)

Sampling Equipment

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1. Personal sampling pump capable of accurate performance (±5%) at 0.05 to 0.3 L/min and calibrated with a representative sampling system in the sampling line.

2. Sampler. The sampler consists of two standard midget impingers connected in tandem with glass tubing. Teflon tubing was not evaluated, but we believe it would be an adequate substitute for glass. A 150-mg reactive sorbent bed to remove chlorine is placed in the inlet of the front impinger. The bed is held in place with two 4-mg plugs of silanized glass wool.

   Bulk quantities of the reactive sorbent bed are made as follows: Mix 3.2 g of 20/40-mesh silica gel (Catalog No. 226-10-01, SKC, INC., Eighty Four, PA) with 20 mL of a methanolic solution containing 400 mg of sulfamic acid and 400 mg of sodium hydroxide. Place the mixture in a rotary evaporator maintained at 100 °C and apply vacuum until the sorbent appears dry (about 1 h).

Sample Size

The volume of air sampled should not exceed 25 to 30 L.

Sampling Procedure

1. Pipet exactly 15 mL of the CPR impinger solution into each of two impingers. The inlet of one impinger should contain the reactive sorbent bed as specified in Section 6.2.

2. Assemble a sampling train composed of the impinger with the sorbent bed connected with glass tubing in tandem with the back-up impinger. Connect the back-up impinger to the personal sampling pump with flexible tubing. Place a moisture trap, such as a bed of silica gel, in the sampling line between the back-up impinger and the pump.

3. Mount the impingers so that the inlet will sample air from the breathing zone of the individual being monitored. Although only standard midget impingers were investigated, any type of impinger system which allow easier mounting could be used.

4. When determining time-weighted average concentrations, sample the air at 0.2 L/min for 120 min (2 h) or at 0.05 L/min for 480 min (8 h). When determining ceiling levels, sample at 0.3 L/min for 15 min. Measure and report the flow rate and time or volume sampled.

5. Record the temperature and pressure of the air being sampled. If atmosphere pressure data is not available, record elevation.

6. Immediately after sampling, remove the impinger stems from the impingers. cap the impingers with ground-glass stoppers, and pack the impingers for shipment. Exclude light from the impingers during storage. Samples may be stored for at least 14 days prior to analysis.

7. To obtain a blank sample, process one unused impinger in the same manner as the exposed impingers but do not sample air through this impinger. Submit at least one blank impinger to analysis for every 10 exposed impingers.

Special Considerations

1. Information regarding the identities of all substances that are known or suspected to be present in the air that is samples should be transmitted to the analyst along with the exposed samplers.

2. The pumps should not be operated more than 8 h continuously without recharging the battery.

3. A fresh reactive sorbent prefilter must be used during the collection of every sample to avoid interference by chlorine.

Bulk Samples

Do not transport bulk quantities of chlorine dioxide to the laboratory; chlorine dioxide is explosive. Frozen chlorine dioxide hydrate may be shipped according to U.S. Department of Transportation Rules and Regulations (see Reference 3).

Shipping Instructions

Stoppered impingers should be packed tightly and padded before they are shipped to minimize breakage during shipping. Never transport, mail, or ship the bulk samples in the same container as the samplers. See U.S. Department of Transportation Regulations in Reference 3 for shipment instructions for an alkaline liquid. When the samplers are received by the laboratory, they should be stored in the dark and analyzed within 14 days.

References

1. Chlorine Dioxide. NIOSH Method No. P&CAM.

2. Occupational Safety and Health Administration. General industry standards. OSHA safety and health standards reprinted from 29 CFR 1910. U.S. Department of Labor, OSHA; 1976: 540.

3. U. S. Department of Transportation. Identification numbers, hazardous wastes, hazardous substances, international descriptions, improved descriptions, forbidden materials, and organic peroxides. Fed. Reg. 45 (101): 34560-34705; 1980 May 22.