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

Research Report for Chlorine

to

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
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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 in work-place air. To take advantage of the relatively high inherent reactivity of chlorine, candidate reactive solids were screened for their potential utility as sampling media. Several reactive solid sorbents exhibited capacities for chlorine vapor that would be adequate for the determination of 8-h time-weighted-average (TWA) concentrations of chlorine in air near the Occupational Safety and Health Administration's (OSHA's) permissible exposure limit (PEL) of 1 ppm. These sorbents were as follows:

- diphenylamine on Fluoropak 80
- N-vinylcarbazole on Fluoropak 80
- m-aminophenol on Fluoropak 80
- sodium sulfamate and sodium hydroxide on silica gel

Although capacities were acceptable, our attempts to quantify the products resulting from the reaction of chlorine with these substrates were not entirely successful. Consequently, methods based on none of the sorbents studied were deemed worthy of validation. Recommendations have been given for future work that may lead to the successful development of a method for chlorine.

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CONTENTS

FIGURES

TABLES

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

Research Report for Chlorine

I. INTRODUCTION

This report describes our attempt to develop and validate a method for the sampling and analysis of chlorine in air at concentrations in the vicinity of the permissible exposure limit (PEL), 1.0 ppm (v/v) (1). 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 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, 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 vapor to form a unique product that was more stable and more amenable to determination than chlorine 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 and other substances that fell within the scope of this contract. This search consisted of, in part, a systematic perusal of the indexes 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 Services 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.

Much of the contract experimental work with chlorine entailed the preparation, evaluation, and calibration of chlorine test atmospheres and the screening and evaluation of candidate reactive sampling media. 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 TEST ATMOSPHERES

A. Construction and Operation of a Test-Atmosphere Generator

To generate test atmospheres of chlorine gas in air, we assembled a dynamic flow system with a standardized mixture of 100 ppm (v/v) chlorine vapor in nitrogen (Matheson, Inc., Morrow, GA) as the source of chlorine. The chlorine/nitrogen gaseous mixture was introduced into filtered air at controlled rates to produce steady-state chlorine vapor concentrations in the range of 0.05 to 2 ppm. The vapor-generation system was constructed as depicted schematically in Figure 1. All components that were exposed to chlorine vapor consisted of glass, Teflon, or other suitably inert materials. The entire system was shielded from light and was operated beneath a laboratory fume hood. The main components of the system were as follows:

- a primary generation source for chlorine vapor (as discussed above),
- a dilution and mixing chamber for mixing the analyte 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 chlorine 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 50 or greater as required. Humidity levels were determined at one of several output ports of the sampling chamber by sampling a known volume of the output air through a tared bed of desiccant (i.e., magnesium perchlorate or calcium sulfate) and weighing the collected water.

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 samping devices. An additional opening was employed for venting the excess effluent through a charcoal trap and into a laboratory fume hood.

The chlorine 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 in air at concentrations down to approximately $\sim$.005 ppm. The monitor's principle of operation is based on the

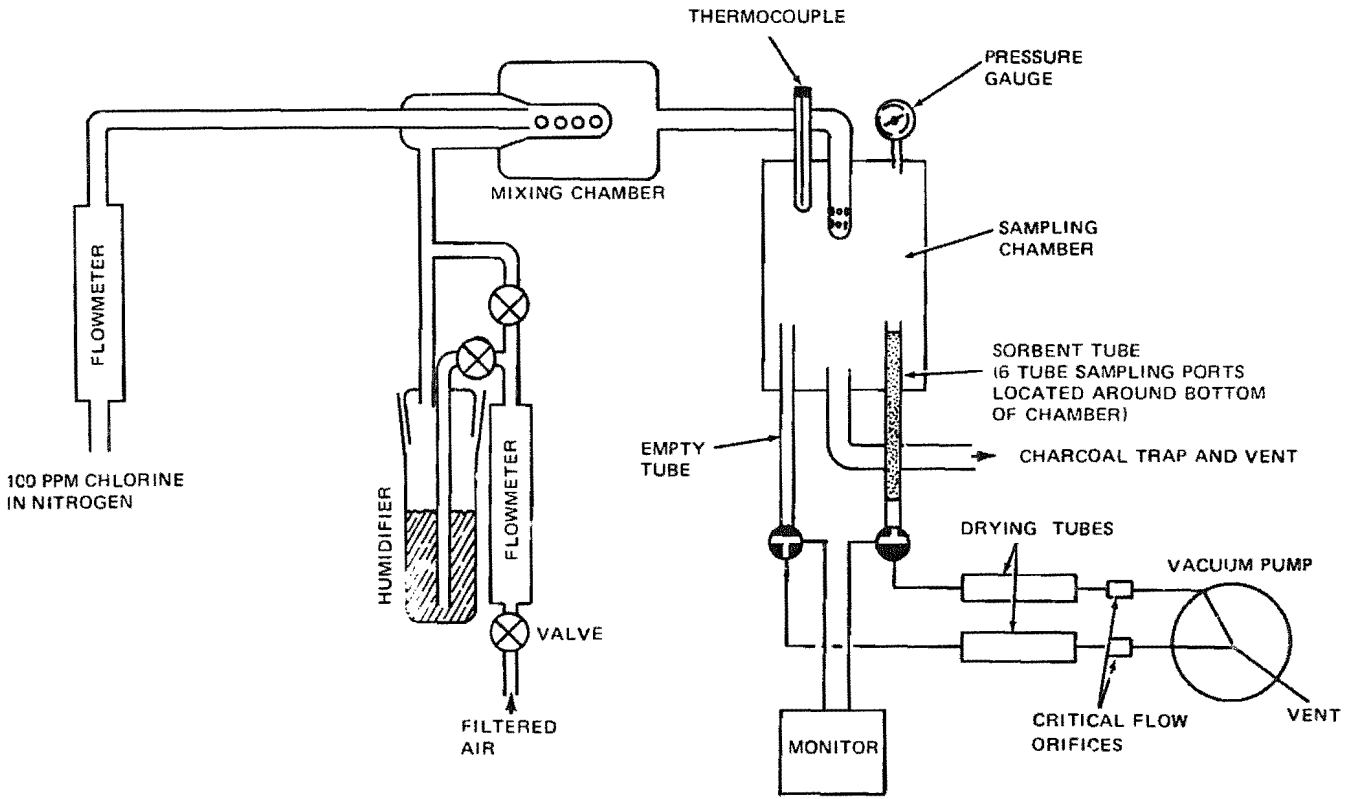

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Figure 1. Schematic of test-atmosphere generator and sampling system.

oxidation of iodine 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 in the parts-per-million and sub-parts-per-million range. The chlorine vapor concentration was adjusted to the desired level by altering the feed rate of chlorine 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

1. Chlorine-specific method

To calibrate the continuous monitor, a reference analytical method for chlorine 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, it was desired that the method be capable of being standardized with reagents other than the analytes themselves. Other factors that were considered included costs, analysis time, simplicity of execution, and linear dynamic range.

The analytical method that was chosen as the reference method for chlorine was the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method (2,3). Although DPD is also sensitive to chlorine dioxide (2,3), differentiation between chlorine and chlorine dioxide can be obtained by the use of malonic acid or glycine to tie up the chlorine or by the use of the more specific chlorophenol red method for chlorine dioxide (2-4). The principal advantage of the DPD method is that the DPD reagent may be standardized with potassium permanganate.

For use in the preparation of the reagent and standard solutions required by the DPD method, we prepared chlorine-demand-free water as follows. Approximately 4 L of 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 (w/v) chlorine solution. A 450-W high-pressure mercury vapor lamp was then placed in a large Pyrex tube, and the tube was 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/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 of the flask to direct sunlight, were evaluated without success.

To carry out the DPD method, colorimetric standards were prepared by reacting appropriate quantities of potassium permanganate with excess amounts of DPD. Amounts of a 4×10^{-5} M potassium permanganate solution ranging from 0.25 to 2.0 mL were combined with 0.5 mL of a pH 6.2 phosphate buffer solution (24 g of anhydrous sodium hydrogen phosphate, 0.8 g of disodium ethylenediaminetetraacetic acid (EDTA), and 20 mg of mercuric chloride dissolved in 1 L of water), 0.5 mL of DPD solution (1 g of DPD oxalate, 2 mL of concentrated sulfuric acid, and 0.2 g of disodium EDTA in 1 L of water), and enough chlorine-demand-free water to produce a total volume of 11 mL for each standard. The absorbance of each standard was measured at 515 nm; 1 mL of the potassium permanganate solution is equivalent to 7.1 μg of chlorine. To minimize the experimental error, new calibration curves were prepared each day. These calibration curves exhibited satisfactory linearity and precision throughout the chlorine concentration range of interest here A typical calibration curve is shown in Figure 2.

To determine the concentration of chlorine in the generator effluent, samples of the effluent were pumped through impingers containing DPD (0.5 mL of DPD solution, 0.5 mL of phosphate buffer, and 10 mL of water) at a rate of ≈0.5 L/min for ≈5 min. The absorbance of the impinger medium was then measured at 515 nm and related to the chlorine concentration with the calibration data. With the use of a back-up impinger also containing DPD, slippage of chlorine through the primary impinger was found to be less than 1%.

Throughout this work, the generator was tested for chlorine with the halogen detector tube marketed by Mine Safety Appliances, Inc. (MSA, Pittsburgh, PA). Values of chlorine concentrations determined in this manner were found to be invariably higher than the corresponding 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 chlorine.

2. Total-oxidant method

For total-oxidant analyses of chlorine-containing atmospheres, we used the traditional iodometric titration method. In this procedure, an impinger was charged with 15 mL of a 2% aqueous solution of potassium iodide at approximately neutral pH. The impinger was allowed to sample from the generator at 1.2 L/min for 30 min. The contents of the impinger were then titrated with standard (0.01 or 0.001 N) sodium thiosulfate solution and with the use of Thyodene indicator, a proprietary starch indicator manufactured by Magnus Chemical Company and marketed by Fisher Scientific Company (Fair Lawn, NJ). 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.)

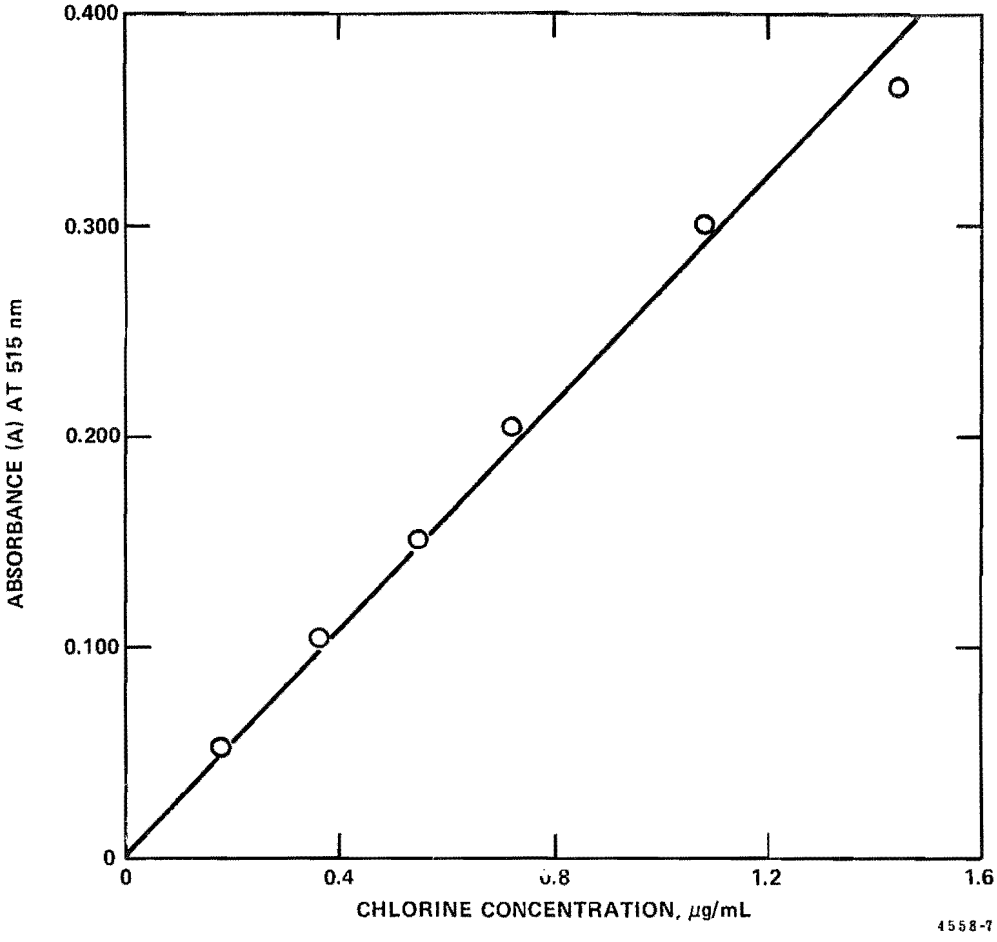

Figure 2. Typical calibration curve for the colorimetric method for chlorine based on N,N-diethyl-p-phenylenediamine (DPD).

C. Calibration of the Continuous Monitor for Chlorine

In a comparison of the DPD chlorine concentrations to the corresponding chlorine response values of the monitor, the two sets of values were found to be linearly related. A least-squares analysis of DPD results (y) versus monitor readings (x) yielded a slope of 1.12, an intercept of -0.002 ppm, and a correlation coefficient (r) of 0.9977. Measurements were taken in duplicate at each test concentration, and over a period of several days, the range from 0.05 to 2.14 ppm chlorine was covered. The average of each duplicate pair was plotted for use in the generator characterization studies; this plot is shown in Figure 3.

D. Characterization of Chlorine Test Atmospheres

The effluent from the chlorine test-atmosphere generator was characterized under various conditions of temperature, humidity, and elapsed time of operation while the chlorine concentration in the generator effluent was maintained in the general vicinity of 1 ppm. Both low and high values were chosen for each of the variables, and experiments were conducted under conditions representing different combinations of these high and low values. In each experiment, the generator effluent was analyzed by the DPD reference method, the iodometric titration method, and the calibration continuous monitor. The iodometric method and the monitor respond to a broad spectrum of oxidizing substances and may therefore be classed as "total-oxidant" methods. The DPD method, on the other hand, is somewhat more specific, and when used in conjunction with the two total-oxidant methods (including the monitor), it offers the possibility of ascertaining the presence of certain oxidants other than chlorine in the test atmosphere.

The results of the chlorine generator characterization experiments are summarized in Table 1. On the average, the iodometric values of total oxidant concentration (as chlorine) were only slightly higher than the chlorine concentrations obtained with the DPD method, and the DPD values were, on the average, slightly higher than the monitor readings of total oxidant concentration. The data indicate that oxidants other than chlorine were not present in the test atmospheres in significant amounts and, therefore, that the effects of temperature, humidity, and elapsed time upon the oxidant content were insignificant.

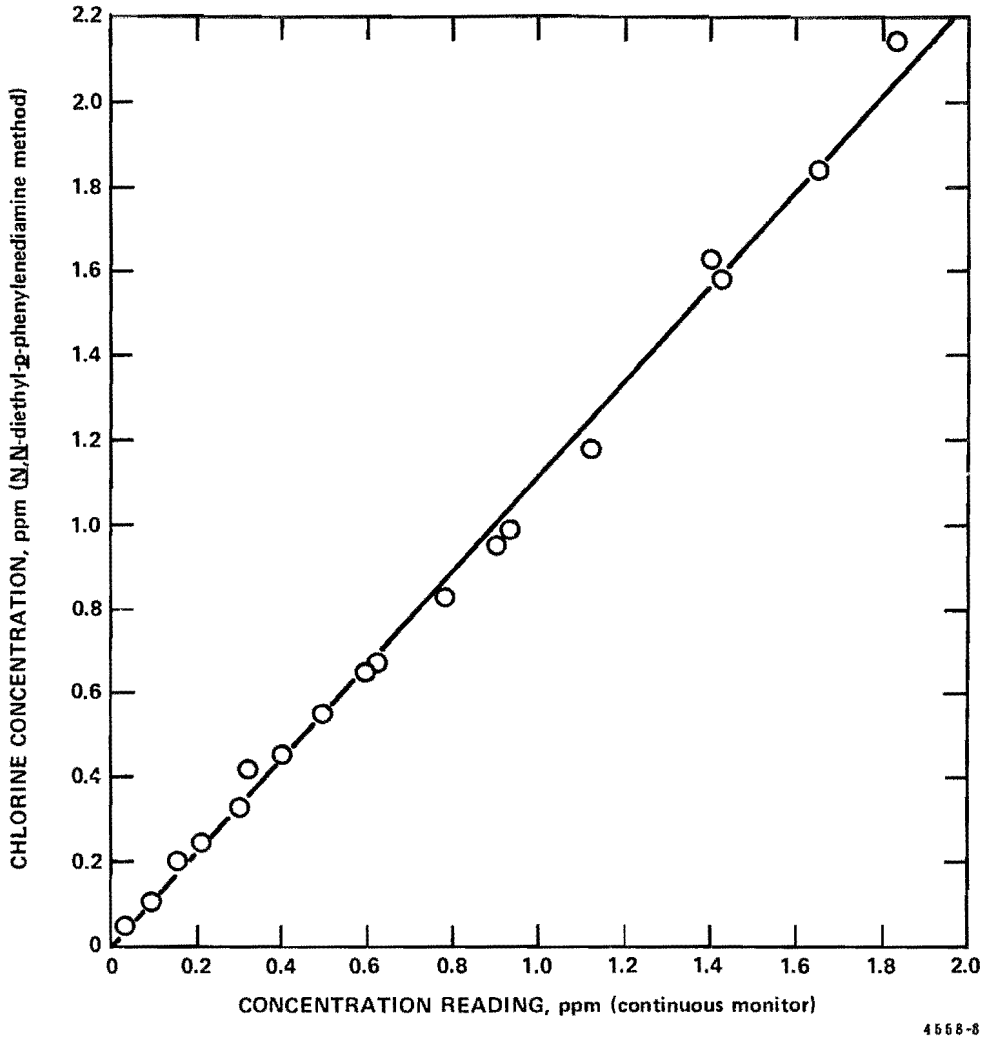

Figure 3. Plot of chlorine concentration as determined by the N,N-diethyl-p-phenylenediamine method versus the corresponding concentration readings given by the continuous monitor.

TABLE 1. INFLUENCE OF TEMPERATURE, HUMIDITY, AND TIME ON THE OXIDANT CONTENT OF CHLORINE TEST ATMOSPHERES

Test No.	Generator temp, °C	RH,[a] %	Chlorine or total oxidant concn (as Cl_2), ppm			$\frac{DPD - IODO}{DPD} \times 100$, %	$\frac{DPD - MON}{DPD} \times 100$, %
			DPD[b]	IODO[c]	MON[d]		
1	28	5	1.00	1.06	0.99	-6	1
2	28	5	1.08	1.15	1.09	-6	-1
3	41	5	0.95	1.04	0.97	-10	-2
4	45	5	1.13	1.20	1.10	-6	3
5	27	85	1.84	1.85	1.65	-1	10
6	27	85	1.49	1.46	1.32	2	11
7	28	5	0.99	1.08	0.96	-9	3
8	28	5	0.89	0.98	0.85	-10	5
9	27	85	1.02	0.97	0.94	5	8
10	27	85	0.87	0.85	0.81	2	7
11[e]	27	5	1.01	1.11	1.00	-10	1
12[e]	27	5	1.05	1.08	1.00	-3	5
						Avg -4	Avg 4

[a]RH = relative humidity.

[b]These values are chlorine vapor concentrations determinated by the DPD colorimetric method.

[c]These values are total oxidant concentrations (as Cl_2) determined by the iodometric titration method.

[d]These values are total oxidant concentrations (as Cl_2) determined by the calibrated continuous monitor.

[e]Test Nos. 11 and 12 were performed only after having operated the chlorine vapor generator continuously for more than 4 h.

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 (2,3,5-15), 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 (i.e., chlorine, chlorine dioxide, and bromine), all candidates were tested with all three analytes, including chlorine. The available literature describing the reactivity of chlorine 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. 2-031; 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 nonporous in nature. The supports that were chosen were 60/80-mesh solid glass 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.

TABLE 2. INITIAL LIST OF CANDIDATE REACTIVE SUBSTRATES SELECTED FOR EVALUATION AS SAMPLING MEDIA FOR CHLORINE

	Reference No.
Br^-/fluorescein	5
Triethylamine	6
Diphenylamine	7
Vanillin	8
o-Dianisidine	9
N-Vinylcarbazole	10
Br^-/phenol	11
Phenol red	12
Chlorophenol red	13
Bromocresol purple	12,13
N,N-Diethyl-p-phenylenediamine	2,3
Br^-/CN^-	14
Glycine	2
Malonic acid	2
Sulfamic acid	15
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.

The candidate support materials were tested for their inertness toward chlorine. 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 1.5 to 1.8 ppm (v/v) of chlorine from the test-atmosphere generator at a rate of about 0.2 L/min until breakthrough of chlorine 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. Hence, even though the MSA tube might have not been suitable for definitive measurements of breakthrough volume, it was used with apparent success in these preliminary studies where indications of only the approximately relative capacities of the candidate support materials were required. The criterion for breakthrough was the formation of a 1-mm blue stain in the MSA tube; the manufacturer's literature states that this occurs when 50 mL of air containing 1 ppm chlorine has been sampled.

Breakthrough was observed from silica gel, Fluoropak 80, and nonporous glass beads after only 200 mL (or less) of air containing chlorine vapor had been sampled; hence, each of these materials was considered to be suitably inert. Porasil A (porous glass beads) and charcoal exhibited more affinity for chlorine, with breakthrough volumes of 1.1 and 11.4 L, respectively. Consequently, these materials were not used as supports for candidate substrates. The pressure drop across the silica gel and the nonporous supports during the challenge tests was about 2.5 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 appropriate support materials by mixing 1.9 g of each suitable 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 vapor and assigned an approximate breakthrough volume.

B. Testing of Candidate Substrates for the Collection and Determination of Chlorine

The breadboard sampling devices, prepared as described above, were attached to the chlorine test-atmosphere generator, and the generator effluent was pumped through the devices until breakthrough of chlorine 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 blue stain within the MSA tube. During the test interval, the chlorine 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 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.

1. Tests with substrates on silica gel

The results of capacity tests with substrates on silica gel are summarized in Table 3. Breakthrough volumes in excess of 23 L were not measured because the sampling of 23 L of air at 0.19 L/min required 2 h, and no further sampling was necessary to demonstrate that these materials were worthy of further evaluation. The results of these tests revealed several promising candidate substrates for continued evaluation, including diphenylamine, o-dianisidine, N,N-diethyl-p-phenylenediamine, N-vinylcarbazole, glycine, and the Br^-/phenol substrate.

As mentioned previously in Section III.A, we experienced difficulty in stripping these substrate coatings off the silica gel support for subsequent investigations of the reaction products. Consequently, we evaluated nonporous supports for the most promising substrates as described subsequently.

2. Tests with substrates on nonporous supports

The breakthrough volumes measured for substrates on nonporous supports are presented in Table 4.

A comparison of the data in Table 4 to the data in Table 3 suggests that most of the candidate substrates exhibited lower capacities on the nonporous supports than on silica gel. This phenomenon was probably due either to the greater surface exposure likely to have been provided by silica gel or else

TABLE 3. APPROXIMATE BREAKTHROUGH VOLUMES FOR CHLORINE IN SAMPLING TUBES CONTAINING SUBSTRATES COATED ONTO SILICA GEL

Substrate	Avg Cl_2 test concn, ppm	Approx breakthrough vol, L
Vanillin	1.75	0.53
Br^-/fluorescein	1.70	5.2
Triethylamine	1.65	11
Diphenylamine	1.40	>23
o-Dianisidine	1.55	>23
Phenol red	1.70	4.6
Chlorophenol red	1.60	0.29
N,N-Diethyl-p-phenylenediamine	1.60	13
N-Vinylcarbazole	1.60	>23
Glycine	1.65	19
Malonic acid	1.60	2.5
Sulfamic acid	1.65	1.1
Bromocresol purple	1.60	7.4
Br^-/phenol	1.80	>23
Br^-/CN^-	1.65	0.38
Silver metal membrane	1.70	2.2

TABLE 4. APPROXIMATE BREAKTHROUGH VOLUMES FOR CHLORINE IN SAMPLING TUBES CONTAINING CANDIDATE SUBSTRATES COATED ONTO NONPOROUS SUPPORTS

Substrate	Avg Cl_2 test concn, ppm	Approx breakthrough vol, L	
		Glass beads	Fluoropak 80
Diphenylamine	1.85	>23	>23
N-Vinylcarbazole	1.80	19	>23
Triethylamine	1.80	0.29	0.33
o-Dianisidine	1.80	0.29	1.2
Glycine	1.80	0.10	0.11
N,N-Diethyl-p-phenylenediamine	1.80	2.2	2.6
Br^-/phenol	1.80	0.09	0.11

to the substantial hydrophilicity of silica gel. Moreover, the data of Table 4 show that slightly higher capacities were obtained with the irregularly shaped granules of Fluoropak 80 than with the spherical glass beads; this also may have been a surface area phenomenon. In any event, our attempts to strip the coatings (including the reaction products) from these nonporous supports with appropriate solvents appeared on visual inspection to have been entirely successful, in marked contrast to our experience with the porous supports.

As can be seen in Table 4, diphenylamine and N-vinylcarbazole stood out as the most promising prospects for continuing consideration. We subsequently evaluated analytical methods that could be applied to the analyses of these solid coatings for their principal reaction products.

3. Further evaluation of diphenylamine

When the diphenylamine-coated supports were exposed to chlorine vapor during the previously described breakthrough tests, the sorbent materials changed from colorless to bright green. Therefore, plans were made to record the UV-visible absorption spectrum of the colored product in the hope that an absorption measurement ultimately could be related to the amount of chlorine sampled.

A sampling tube packed with the diphenylamine/Fluoropak 80 sampling medium (as described above) was allowed to sample test atmospheres containing 1.8 ppm of chlorine vapor at 0.5 mL/min for 30 min. The sorbent particles were then removed from the sampling tube and immersed in 4.0 mL of methanol in a test tube. The mixture was capped and agitated in an ultrasonic bath to achieve complete dissolution of the diphenylamine and the reaction product. After the particles of Fluoropak 80 had settled to the bottom of the extraction vessel, a portion of the particle-free liquid was pipetted into a spectrophotometer cuvette, and its absorbance was scanned from 300 to 800 nm. During this measurement, the reference cell of the spectrophotometer contained a solution prepared by extracting an unexposed diphenylamine sampling tube. This reference solution was used to minimize the contribution of the absorption maxima of diphenylamine to the net absorption spectrum of the sample extract.

However, the absorption spectrum measured in this manner appeared to contain no bands due to the colored reaction product. In a subsequent experiment, we noted that the green color in an exposed diphenylamine tube faded upon standing for a few hours, suggesting that the colored reaction product was decomposing spontaneously. Because of this evidence for the decomposition of the product species, no further evaluation was conducted of diphenylamine.

4. Further evaluation of N-vinylcarbazole

Methods were sought by which N-vinylcarbazole sorbent could be analyzed for the appropriate reaction products after exposure to chlorine.

Our early method-development efforts were centered on the use of the gas chromatograph equipped with a flame ionization detector. Three different analytical columns were evaluated in this work: 1) a 6-ft by 0.125-in.-OD, 0.0625-in.-ID Teflon column packed with 10% FFAP on 60/80-mesh Chromosorb W DMCS-AW; 2) a 7-ft by 0.125-in.-OD, 0.083-in.-ID nickel column packed with 3% OV-17 on 100/120-mesh Chromosorb W; and 3) a 6-ft by 0.125-in.-OD, 0.0625-in.-ID Teflon column packed with 3% OV-101 on 80/100-mesh Gas-Chrom Q. However, none of the experimental columns produced a satisfactory peak for N-vinylcarbazole when methanolic solutions of N-vinylcarbazole were injected under a variety of operating conditions, so we decided to investigate the use of high-pressure liquid chromatography (HPLC).

The reversed-phase HPLC method employed for all work with N-vinylcarbazole used a column marketed by Perkin-Elmer Corporation (Norwalk, CT) with the trade designation HC ODS-SIL-X (Part No. 089-0716). Elution was performed isocratically with 50% water and 50% acetonitrile at a flow rate of 1 mL/min; the solvents and column were maintained at 30 °C throughout. The chart speed was 0.5 cm/min. The detector, a variable-wavelength UV-visible absorption unit, was operated at 241 nm, the wavelength of maximum absorption for N-vinylcarbazole. When compared to a fluorescence detector that excited the effluent stream at 280 nm and collected the emitted fluorescence at wavelengths above 389 nm, the UV absorption detector was found to yield a superior signal-to-noise ratio. Satisfactory chromatographic efficiency and sensitivity for N-vinylcarbazole were obtained by this method, as can be seen in the HPLC chromatogram of unreacted N-vinylcarbazole shown in Figure 4.

An experimental sampling tube containing N-vinylcarbazole on Fluoropak 80 (prepared as described previously) was challenged with 1.74 ppm chlorine from the vapor generator; sampling of this vapor was conducted at 0.52 L/min for 30 min. The tube's contents were then extracted with methanol, and a 10-μL aliquot of the extract was injected into the HPLC. The resulting chromatogram, reproduced in Figure 5, disclosed the presence of several reaction products. After a subsequent injection of this extract, the three major products--with peaks at retention times (t_r) of 2.8, 5.4, and 10.6 min, respectively--were scanned in the UV by the detector and were thereby determined to possess absorption maxima near the absorption maximum for N-vinylcarbazole. These compounds were collected as fractions and submitted for analysis by mass spectrometry. As shown in Figure 5, the peak at t_r = 2.8 min was identified unambiguously as carbazole, and the peak at t_r = 10.6 min was believed to represent N-(2-chlorovinyl)carbazole. The peak at t_r = 7.8 min was due to unreacted N-vinylcarbazole.

The chromatographic peak at t_r = 5.4 min could not be identified from its mass spectrum. The mass spectrum suggested that the molecular weight of this species should be that of N-vinylcarbazole plus 32 mass units. Because 32 is the molecular weight of methanol, which was employed in the extraction step, a reaction with the extraction solvent was suspected. When the experiment was repeated with ethanol as the extracting solvent, the chromatographic

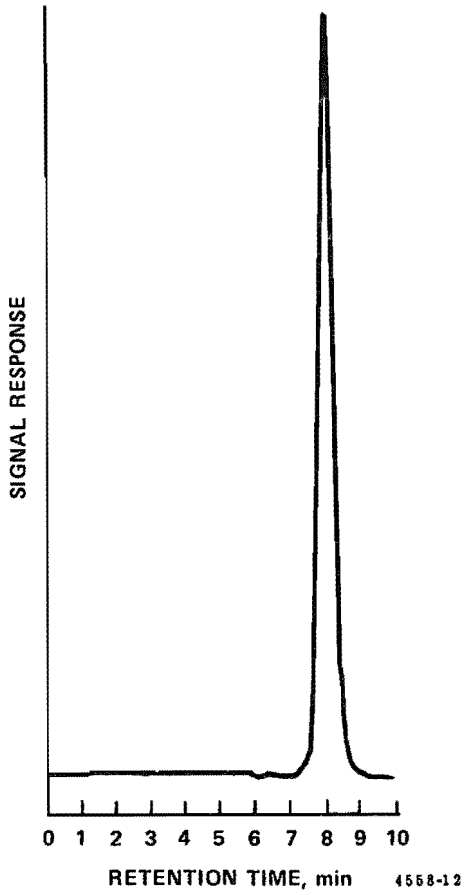

Figure 4. Chromatogram from HPLC analysis of N-vinylcarbazole.

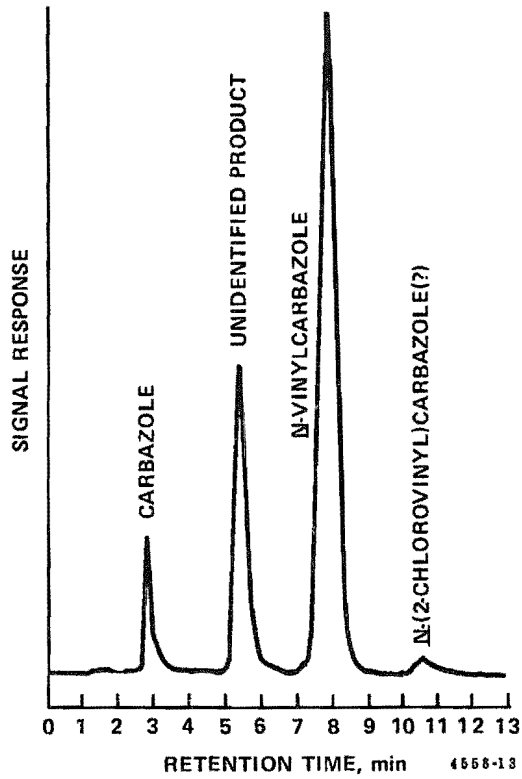

Figure 5. Chromatogram from HPLC analysis of N-vinylcarbazole after exposure to chlorine vapor.

peak at t_r = 5.4 min disappeared, and a new peak was observed whose retention time was very near that of N-vinylcarbazole. This new substance was confirmed by mass spectrometry to be the ethanolic analog of the substance that appeared originally at t_r = 5.4 min. However, neither substance could be assigned an identity.

The sampling experiment conducted at a chlorine challenge concentration of 1.74 ppm (and whose result is depicted in Figure 5) was repeated at chlorine challenge concentrations of 0.94 and 0.54 ppm to assess the extent of product formation as a function of the chlorine exposure level. A plot of peak area (y) of the largest product peak (at t_r = 5.4 min) versus the chlorine challenge concentration (x) was found to obey the linear relationship, $y = mx + b$, with a slope (m) of 1.06×10^6 area units/ppm, an intercept of 3.6×10^4 area units, and a correlation coefficient (r) of 0.9998. Thus, good linearity was obtained, which suggested that the area of this peak might be expected to reflect accurately the chlorine concentration to which the sampler was exposed.

An N-vinylcarbazole sampling tube was permitted to sample a standard atmosphere containing ≈3 ppm of chlorine dioxide from the test-atmosphere generator to ascertain whether this gas would be likely to cause the formation of the same reaction products or otherwise interfere with a determination of chlorine. Sampling was conducted at 0.52 L/min for 2 h, and the tube was then extracted with 4.0 mL of methanol as before. After injection of the extract into the HPLC, the consequent chromatogram displayed only a single peak, i.e., that due to N-vinylcarbazole itself. Hence, there appeared to be no reaction between chlorine dioxide and N-vinylcarbazole under the specified sampling conditions.

To determine the effects of water vapor upon the outcome of a sampling experiment, sampling was conducted from the chlorine test-atmosphere generator under conditions of high RH (>80%). Humidified chlorine vapor at 0.95 ppm was sampled through an N-vinylcarbazole sampling tube at 0.50 L/min for 30 min, and the tube's contents were extracted with 4.0 mL of methanol. The HPLC chromatogram obtained from this extract disclosed a severely diminished peak amplitude for the unidentified peak at t_r = 2.8 min. This experiment was repeated with the use of a prefilter containing ≈1.0 g of silica gel, ≈1.0 g of calcium sulfate (Drierite), or ≈0.5 g of magnesium perchlorate. The prefilter was attached to the inlet end of the sampling tube and was intended to remove the water vapor from the sampled airstream without removing the chlorine. Of the three desiccants tested, only magnesium perchlorate appeared to restore the original amplitude ratio for the two product peaks mentioned above, which implied that the magnesium perchlorate successfully removed most of the water vapor from the sample. However, the amplitudes of all the product peaks were lower than expected, suggesting that the magnesium perchlorate tube trapped a portion of the influent chlorine vapor.

To confirm these observations, the experiment was performed again at the chlorine concentration of 0.95 ppm with and without the use of a magnesium perchlorate prefilter and at both high and low RH (i.e., a total of four separate experiments). Duplicate samples were taken under each set of conditions. Figure 6 contains an HPLC chromatogram from each of these four experiments. (Refer to Figure 5 for identification of the product peaks.)

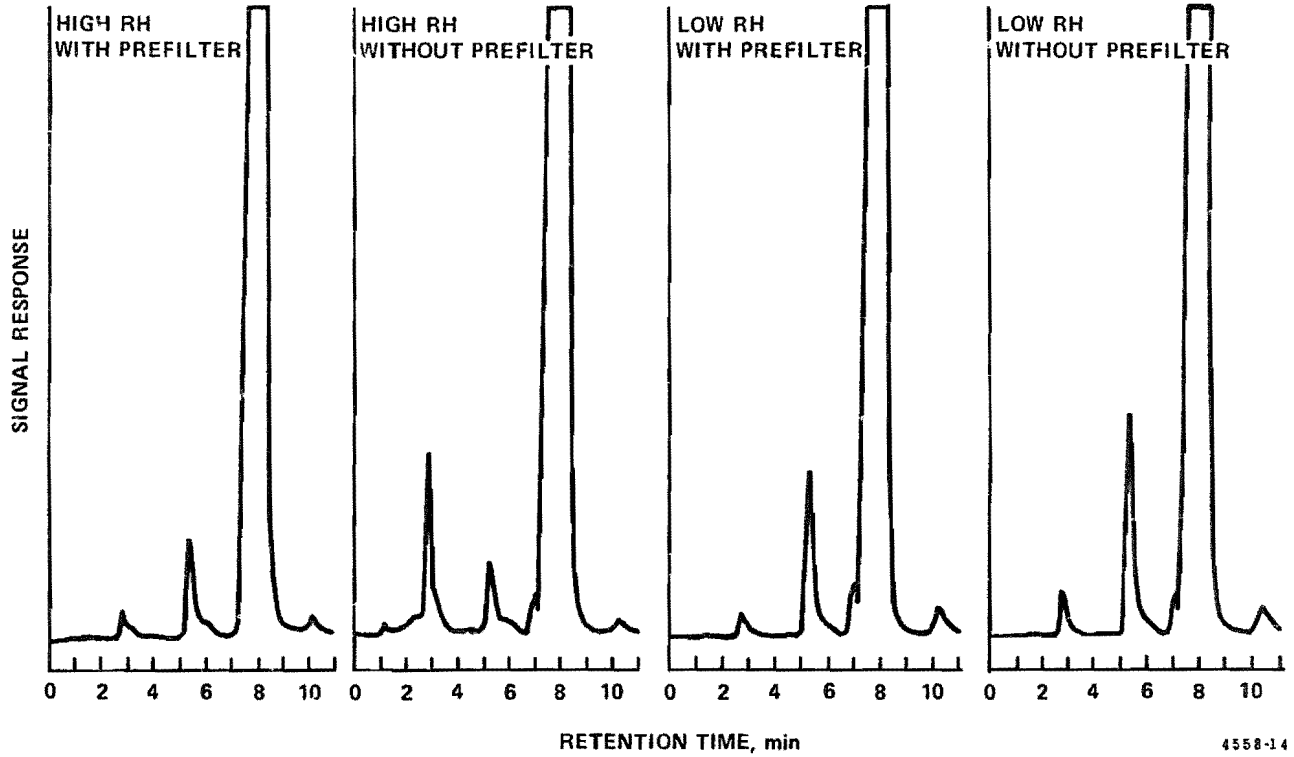

Figure 6. Chromatograms from HPLC analysis of N-vinylcarbazole after exposure to chlorine both with and without the use of a magnesium perchlorate prefilter and at both high and low relative humidity (RH).

These chromatograms essentially confirmed the results of the earlier experiment with the magnesium perchlorate prefilter. In addition, the apparent retention of chlorine in the prefilter was found to be worse at high RH than at low RH.

In view of this dependence of product formation upon the RH of the sample, we decided to abandon this approach.

C. Selection and Testing of Additional Substrates for the Collection and Determination of Chlorine

1. Description of new substrates and breakthrough test procedure

The results just described indicated that aromatic amines, of the compounds tested, are the most reactive toward chlorine. N-Vinylcarbazole, in addition to being an aromatic amine, contains an unconjugated double bond. These are, of course, merely empirical correlations that 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 5. This list includes several inorganic candidate substrates that were also evaluated

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.

2. Results of breakthrough tests with new substrates

Table 6 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. From the data, it is apparent that several substrates revealed a significant capacity for the trapping of chlorine vapor: m-aminophenol, sulfamic acid/sodium hydroxide, and potassium iodide/potassium hydroxide. Two of the three sorbents--m-aminophenol and sulfamic acid/sodium hydroxide--offered the potential for specificity in the determination of chlorine; these were investigated further as described below. The potassium iodide sorbent was not considered for additional tests because of the nonspecificity of the sorbent (i.e., many other oxidants are capable of oxidizing iodide ion).

3. Further evaluation of m-aminophenol

In an attempt to determine the reaction product between m-aminophenol and chlorine, the substrate was analyzed by HPLC for reaction products following the exposure of substrate to chlorine vapor. Tubes containing 100-mg portions

TABLE 5. 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 6. APPROXIMATE BREAKTHROUGH VOLUMES FOR CHLORINE IN SAMPLING TUBES CONTAINING ADDITIONAL CANDIDATE SAMPLING MEDIA

Candidate substrate	Avg Cl_2 test concn, ppm	Approx breakthrough vol, L	
		Fluoropak 80	Glass beads
Butadiene sulfone	1.75	0.11	0.36
Hydroquinone	1.69	0.09	0.17
2,6-Di-tert-butyl-4-methylphenol	1.69	0.11	0.11
Catechol	1.69	0.33	0.22
o-Aminophenol	1.67	1.98	0.67
m-Aminophenol	1.64	12.54	7.36
1-Adamantanamine	1.58	0.07	0.07
Maleimide	1.64	0.07	0.07
Sulfamic acid (10%)/ sodium hydroxide (10%)	0.98	7.7	--
Potassium iodide (10%)/ potassium hydroxide (10%)	0.98	11	--
Potassium hydroxide	1.55	0.07[a]	
Potassium hydroxide (10%)	1.37	0.40[a]	
Sulfamic acid (10%)/ sodium hydroxide (10%)	1.60	>24[a]	

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

of 5% m-aminophenol on Fluoropak 80 were exposed to about 1 ppm of chlorine vapor at about 0.25 L/min for periods ranging from 20 to 120 min. The contents of each tube thus exposed were extracted with 4.0 mL of methanol, and the extracts were analyzed by reversed-phase HPLC.

The HPLC analyses were conducted with the use of a C_{18} reversed-phase column marketed by Perkin-Elmer Corporation (Norwalk, CT) with the trade designation HC ODS-SIL-X, 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 above-mentioned extracts. The chromatographic elutions were carried out isocratically with 40% acetonitrile and 60% water. For all analyses, the solvent flow rate was 1 mL/min, and the detector, a UV absorption unit, was set at 280 nm.

The exposed m-aminophenol sorbent extracts yielded a single chromatographic peak at a short retention time (1.47 min), apparently due entirely to the unreacted substrate, with no evidence of a reaction product. However, the short retention time indicated that the m-aminophenol was essentially unretained by the column packing material, and if this had been true also of a related reaction product, then that reaction product might not have been chromatographically resolved from the m-aminophenol.

Analyses of exposed-sorbent extracts were then performed with a different solvent mixture to increase the retention of m-aminophenol on the HPLC column. All other HPLC operating conditions were the same as those reported for the previously described experiments. When introduced into the chromatograph, the m-aminophenol sorbent extract produced but a single peak, which was due to unreacted m-aminophenol and which was eluted at a retention time of 3.0 min. Thus, it seemed likely that the reaction products generated by these exposures were ionic salts or other species that are not amenable to separation and detection by HPLC. Although the investigation of alternative analytical methods may have been profitable, work with m-aminophenol was consequently discontinued to allow ample time for the evaluation of the sulfamic acid/sodium hydroxide sorbent.

4. Further evaluation of the sulfamic acid/sodium hydroxide sorbent

Emphasis was subsequently accorded to an evaluation of the sulfamic acid/sodium hydroxide system, henceforth called the sulfamate sorbent.

As a first step, the sulfamate sorbent (with Fluoropak 80 as the support) that had previously been challenged with chlorine vapor during the measurement of breakthrough volume was analyzed for trapped chlorine (in the form of sodium N-chlorosulfamate) by iodometry. The sampled chlorine was believed to have reacted with sodium sulfamate according to the following reaction (16):

$$NH_2SO_3^-Na^+ + Cl_2 + NaOH \longrightarrow ClNHSO_3^-Na^+ + NaCl + H_2O \qquad (1)$$

Note that the most significant reaction product is essentially a chloramine, which may be expected to possess the ability to oxidize iodide ion to iodine in aqueous solution:

$$ClNHSO_3^-Na^+ + 2KI + H^+ \longrightarrow I_2 + NH_2SO_3^-Na^+ + KCl + K^+ \qquad (2)$$

Hence, the stoichiometric ratio between the chlorine that was trapped and the iodine that was generated should have been unity.

To perform the iodometric determination, the sorbent was extracted into a few milliliters of water, and the pH of the extract was adjusted to about 4 with acetic acid. To this solution was added 15 mL of 0.1% potassium iodide and a suitable excess of Thyodene (starch) indicator. The resulting blue solution was then titrated to a colorless endpoint with standardized 0.001 N sodium thiosulfate. After the endpoint had been reached, the pH of the solution was lowered to about 2, but no additional formation of the blue starch iodine complex was observed. This suggested that the reaction between the iodide and N-chlorosulfamate ions proceeded to completion at pH 4.

The titration of the extract indicated that the chlorine concentration in the generator had been 1.5 ppm, whereas the continuous monitor had indicated that it was approximately 1.0 ppm. The monitor was recalibrated against the DPD spectrophotometric reference method and found to be accurate. Despite the above discrepancy, however, it was concluded that the sulfamate sorbent warranted further investigation as a sampling medium for chlorine.

To evaluate the ionic content of an exposed sulfamate sorbent tube, a tube was exposed to 1.1 ppm of chlorine for 1 h at 0.23 L/min and extracted into 4.0 mL of water, and the extract was submitted for analysis by ion chromatography. For comparison, an extract of an unexposed sampling tube was also analyzed by ion chromatography. The ion chromatograms produced by these two samples were nearly identical; each chromatogram displayed an unresolved group of peaks. Therefore, no further ion chromatographic work was performed.

A sensitive procedure for the determination of oxidant species in solution is the spectrophotometric procedure based on the oxidation of iodide ion to iodine and the subsequent determination of the starch/iodine complex (17). Spectrophotometric standards can be prepared from solutions containing iodide ion by the addition of known amounts of iodate ion. In acidic solution, iodate reacts with iodide to form iodine by the following reaction:

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

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

To evaluate this procedure for use with the sulfamate sorbent, three tubes containing this sorbent were each allowed to sample 1.02 ppm chlorine for 1 h at 0.2 L/min. (In this and all subsequent experiments, silica gel was substituted for Fluoropak 80 as the support because silica gel was more easily wetted by water.) Each tube was then extracted ultrasonically for 30 min with 4.0 mL of distilled water, and 1.0 mL of each extract was taken for analysis. To each 1.0-mL aliquot were added (in order) 0.25 mL of a 1.7% (w/v) sulfamic acid solution, 0.1 mL of 2% (w/v) potassium iodide solution, 1.0 mL of distilled water, and 3 mL of a 0.5% (w/v) Thyodene solution. The addition of the sulfamic acid reduced the pH to approximately 2.5. The absorbances of the resulting solutions were determined at a wavelength of 345 nm.

The spectrophotometric standards were prepared in the same manner except that unexposed sorbent tubes were extracted instead of the chlorine-exposed sorbent tubes used in the above procedure. In addition, the 1.0-mL portion of distilled water was replaced with 0.1, 0.2, 0.4, 0.6, or 0.8 mL of a 25-μg/mL solution of potassium iodate, each made up to 1.0 mL with distilled water. A blank was prepared without the use of iodate, and its absorbance was subtracted from those of the standards and samples.

The three values of chlorine vapor concentration determined by this method were 0.78, 0.77, and 0.69 ppm. The values were, respectively, 77, 75, and 68% of the chlorine vapor concentration value given by the continuous monitor (1.02 ppm). Because it was suspected that the low results might be due to an incomplete extraction, each of the three sorbent samples was capped and allowed to stand overnight in the remaining 3 mL of the extracting water. On the following day, they were again immersed briefly in the ultrasonic bath, and another 1.0-mL portion was removed from each extract. When these aliquots were analyzed, the chlorine vapor concentration values were, respectively, 75, 91, and 90% of the extracted value (1.02 ppm). This result was considered to be rather ambiguous, and no conclusions were drawn, pending the generation of additional data.

In additional experiments with the sulfamate sorbent (prepared with silica gel as the support), sulfamate tubes were exposed to chlorine vapor in air at high RH (>80%) and low RH (<15%). The tubes were exposed at about 0.2 L/min for about 60 min. At the end of the sampling interval, the exposed tubes were extracted, and the extracts were analyzed by the colorimetric iodometric procedure.

In the first of these experiments, three sorbent tubes sampled from the generator at low RH, and three additional tubes sampled at high RH. The chlorine vapor concentration values determined from these tubes and the chlorine "recoveries" represented by these values are given in Table 7. The values of chlorine recovery were calculated by dividing each of the measured chlorine

TABLE 7. CHLORINE CONCENTRATIONS DETERMINED AT HIGH AND LOW RH WITH THE EXPERIMENTAL SULFAMATE SORBENT TUBES

Sorbent tube No.	RH, %	Cl_2 concn, ppm		Cl_2 recovery from sorbent tube, %
		Sorbent tube	Continuous monitor	
1	<15	1.19	1.00	119
2	<15	1.16	1.00	116
3	<15	0.93	1.00	93
				Avg 109
4	>80	1.34	1.02	132
5	>80	1.40	1.02	138
6	>80	1.25	1.02	122
				Avg 131

concentration values by the "true" chlorine concentration (as given by the continuous monitor) and multiplying the results by 100%. The data in Table 7 indicate that the sorbent tube results were positively biased with respect to the monitor values and that chlorine concentrations determined at high RH were even higher than those determined at low RH.

Because the sorbent tube-determined chlorine concentration values were high relative to the response of the monitor to chlorine, the experiment was repeated except that during the sampling intervals the test atmosphere was also analyzed by the chosen reference DPD analytical method for chlorine. The chlorine vapor concentrations determined with the sorbent tubes, with the continuous monitor, and with the DPD method are given in Table 8. These data suggest that the bias of the sorbent tube results (relative to the monitor readings) was due to a source of error other than that associated with the monitor response.

Also of serious concern in these experiments was the substantial discrepancy between the sorbent tube results observed at low RH and the corresponding results observed at high RH. Specifically, the average absolute discrepancy was 22% in the first experiment (Table 7) and 27% in the second experiment (Table 8). We hypothesized that this phenomenon might be partially or wholly eliminated if the water adsorption capacity of the silica gel support were satiated during the sorbent-coating step. Accordingly, sorbent material containing sulfamic acid and sodium hydroxide that had been deposited from an aqueous solution, rather than from a methanolic solution, was used in a third performance of this experiment. The DPD reference method was again used as a check on the monitor response. The results of this last experiment are shown in Table 9. Because the chlorine recoveries were much lower than those obtained in the previuos experiments, no additional conclusions were drawn from this experiment, and because of time constraints on the project, no further work with this or any other candidate sorbent for chlorine was carried out.

TABLE 8. CHLORINE CONCENTRATIONS DETERMINED AT HIGH AND LOW RH WITH THE EXPERIMENTAL SULFAMATE TUBES, WITH THE CONTINUOUS MONITOR, AND WITH THE DPD REFERENCE METHOD

Sorbent tube No.	RH, %	Cl_2 concn, ppm			Cl_2 recovery from sorbent tube,[a] %
		Sorbent tube	Continuous monitor	DPD method	
1	<15	0.75	0.95	0.92	81
2	<15	0.76	0.95	0.92	83
3	<15	0.75	0.95	0.92	82
				Avg	82
4	>80	0.99	0.87	0.88	113
5	>80	0.97	0.87	0.87	110
6	>80	0.92	0.87	0.88	105
				Avg	109

[a]These recovery values are based on the DPD values of chlorine concentration.

TABLE 9. CHLORINE CONCENTRATIONS DETERMINED AT HIGH AND LOW RH WITH SULFAMATE SORBENT MATERIAL PREPARED FROM AN AQUEOUS SOLUTION

Sorbent tube No.	RH, %	Cl_2 concn, ppm			Cl_2 recovery from sorbent tube,[a] %
		Sorbent tube	Continuous monitor	DPD method	
1	<15	0.65	0.93	0.95	68
2	<15	0.71	0.93	0.95	75
3	<15	0.66	0.93	0.95	69
					Avg 71
4	>80	0.67	0.82	0.80	84
5	>80	0.72	0.82	0.80	90
6	>80	0.71	0.82	0.80	89
					Avg 88

[a]These recovery values are based on the DPD values of chlorine concentration.

IV. SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

A. Summary of Results

During this work, we screened 27 solid sorbents for their ability to react specifically with chlorine vapor in a gas/solid reaction. Among these, diphenylamine, N-vinylcarbazole, m-aminophenol, sodium sulfamate in excess sodium hydroxide, and potassium iodide displayed a significant degree of reactivity; however, none of the substrates provided an entirely suitable collection medium.

The reaction of chlorine with diphenylamine produced a green color that faded within a few hours. Consequently, this reaction was deemed to be of little practical value in the development of a sampling medium for the determination of 8-h time-weighted-average (TWA) chlorine concentrations.

Upon exposure to chlorine in dry air, N-vinylcarbazole produced an unidentified product that reacted with the methanol extraction solvent to produce a compound that could be separated from other reactants and N-vinylcarbazole by HPLC. Furthermore, the area of the peak attributed to the compound was found to be proportional to the quantity of chlorine sampled into the N-vinylcarbazole sorbent tubes. Unfortunately, the reaction product was not observed when chlorine was sampled from humidified air. Attempts to remove water vapor with magnesium perchlorate upstream from the sorbent bed were partially successful in restoring the product, but the desiccant also sorbed some chlorine. The apparent retention of chlorine by magnesium perchlorate was found to be worse at high RH than at low RH.

The compound m-aminophenol demonstrated a great affinity for chlorine, but we were unable to identify the reaction product. The product could have been one of several types of compounds, including a chloramine, a charge-transfer complex, a chlorine addition product, or a "diazo" compound. Our attempts toward identification of the product were limited to HPLC. Perhaps other analytical techniques, such as iodometry, gas chromagraphy, ion chromatography, or paired-ion HPLC, would have given definitive results.

The sulfamate sorbent offered adequate capacity for chlorine and, because of its low affinity for chlorine dioxide, provided a means of detecting chlorine in the presence of chlorine dioxide. As with N-vinylcarbazole, the presence of water seemed to affect the determination of the chloramine produced by reaction of chlorine and sulfamate ion; however, the effect was less severe in magnitude with the sulfamate sorbent than was observed with the N-vinylcarbazole sorbent. Moreover, high RH increased chlorine recoveries (as with chloramine) with the sulfamate sorbent rather than decreasing recoveries as observed with N-vinylcarbazole.

The potassium iodide substrate was not investigated extensively because it was expected to offer little specificity for reaction with chlorine.

B. Recommendations for Future Work

We feel that additional work with the solid sorbents that demonstrated adequate affinity for chlorine may be warranted. The following suggestions are given in an order of performance that we believe to offer the best chance of success:

- First, we believe that additional investigations of the sulfamate sorbent may be fruitful if the effect of water can be made reproducible.

- Second, despite the deleterious effect of water upon the formation of the product, N-vinylcarbazole may be worthy of continued investigation, with emphasis being afforded to the search for a means of excluding water vapor from the sorbent without reducing the chlorine concentration in the sample air.

- Third, we believe that a variety of analytical techniques (see Section IV.A) could be evaluated in additional attempts to identify the product of the reaction of m-aminophenol with chlorine.

If suitable solid sorbents cannot be found, then the adaptation of liquid reactive systems to passive dosimetry may offer better potential than did the solid substrates investigated in this project in developing a suitable personal sampling and analytical method for chlorine. We believe that some of the reagent systems just discussed as well as others may show greater promise when used in solution as opposed to being used as a solid coating on a solid support. For exampe, the reaction of chlorine and sulfamic acid is quantitative in an aqueous bubbler solution. In fact, this reaction and the determination of the resulting chloramine is the basis for an air sampling and analyticel method developed by OSHA personnel (15). Rather than rely on a bubbler sampling method for chlorine, however, we believe that systems more useful and adaptable to industrial hygiene air sampling can be develeped by incorporating liquid reagent systems--such as sulfamic acid in water--into passive membrane permeation sampling devices or related passive samplers.

Two passive permeation samplers with liquid solutions as collection media for chlorine are presently available commercially. We intended to attempt the validation of one or both of the devices as part of our program, but could not because of time and budget constraints. Hardy et al. (5) developed one of the devices--a chlorine monitor with a liquid reagent containing bromide ion and fluorescein separated from the sample air by a permeable membrane. Chlorine diffuses through the membrane and into solution, where the compound oxidizes bromide ion to bromine, which in turn oxidizes fluorescein to tetrabromofluorescein. The tetrabromofluorescein is then determined spectrophotometrically. Moleculon Research Corporation (18) developed the other passive diffusional monitor for chlorine that we considered for evaluation. The collection and reaction medium of the monitor is a

proprietary liquid solution reagent held within a porous polymer film called Poroplastic. Chlorine gas diffuses through a microporous diffusion barrier and into the film, where the compound reacts in solution to yield a color change from almost colorless to violet. In a recent evaluation, this device was found to perform favorably in TWA monitoring of chlorine in standard test atmospheres (18).

Other devices developed recently that have demonstrated promise in the determination of chlorine in air and that may have application as personal dosimeters are electrochemical sensors. In the same study involving the evaluation of the Moleculon passive dosimeter described above, three electrochemical devices were also challenged with chlorine standard test atmospheres (18). Results were judged generally acceptable, and the relative strengths and weaknesses of the devices were discussed.

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16. ABSTRACT This report describes an unsuccessful attempt to develop a personal air sampling and analysis method for the determination of chlorine in work-place air. To take advantage of the relatively high inherent reactivity of chlorine, candidate reactive solids were screened for their potential utility as sampling media. Several reactive solid sorbents exhibited capacities for chlorine vapor that would be adequate for the determination of 8-h time-weighted-average (TWA) concentrations of chlorine in air near the Occupational Safety and Health Administration's (OSHA's) permissible exposure limit (PEL) of 1 ppm. These sorbents were as follows:

- diphenylamine on Fluoropak 80
- N-vinylcarbazole on Fluoropak 80
- m-aminophenol on Fluoropak 80
- sodium sulfamate and sodium hydroxide on silica gel

Although capacities were acceptable, our attempts to quantify the products resulting from the reaction of chlorine with these substrates were not entirely successful. Consequently, methods based on none of the sorbents studied were deemed worthy of validation. Recommendations have been given for future work that may lead to the successful development of a method for chlorine.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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