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A solid sorbent sampling and analytical method for chlorine (Cl_2) and bromine (Br_2) in air, based on the reaction of halogen gases with silver to form silver halides, has been developed. The sampler uses an opaque, 25-mm cassette containing a Zefluor™ or polyester prefilter and a cleaned silver membrane filter. The silver halides are complexed with thiosulfate, releasing the halide ion, which is determined by ion chromotography. The method was laboratory evaluated using generated test atmospheres (room temperature, 20% and 80% relative humidities, and concentration levels of 0.1 to 2 times the Permissible Exposure Limit [PEL] set by the U.S. Occupational Safety and Health Administration [OSHA]), and field evaluated at a chlorine-containing industrial environment. Precision of the method was 7.2 percent, and the bias was insignificant (-1.3%). High humidity (~80%) dramatically increased the capacity of the silver filter for Cl_2 and Br_2. Hydrogen chloride is a minor positive interference; however, hydrogen bromide presents a more significant interference. The method has the sensitivity to monitor Cl_2 at the current OSHA time-weighted average (TWA) PEL of 0.5 ppm and short-term exposure limit (STEL) of 1 ppm, as well as the TWA for Br_2 of 0.1 ppm and the STEL of 0.3 ppm. Cassinelli, M.E.: Development of a Solid Sorbent Monitoring Method for Chlorine and Bromine in Air with Determination by Ion Chromatography. Appl. Occup. Environ. Hyg. 6:215–226; 1991.

Introduction

A solid sorbent sampling and analytical method that is specific for halogen gases has long been sought by the industrial hygiene community. Over 166,000 workers are potentially exposed to chlorine (Cl_2), and approximately 18,000 are potentially exposed to bromine (Br_2) in numerous industrial processes.[1] Chlorine is used for bleaching (particularly in the pulp and paper industry); disinfecting; detinning and dezincing iron; chlorinating hydrocarbons; manufacturing synthetic rubber, plastics, pesticides, and refrigerants; and treating water and sewage.[2,3] Bromine is used for gold extraction, bleaching, disinfecting, and shrink-proofing wool; in the manufacture of pharmaceuticals, dyes, anti-knock gasoline, pesticides, and flame retardants; and in photography.[2-4]

Cl_2 and Br_2 are severe irritants to the eyes, skin, and mucous membranes.[2] Short-term exposure to high concentrations may result in breathing difficulties (often with delayed onset), pneumonia, headache, dizziness, abdominal pain, pulmonary edema, and even death.[3] Skin contact with liquid forms causes severe burns.[4] Long-term exposures to low concentrations may result in tooth corrosion, skin irritation, and with Br_2, a measles-like rash.[2]

Owing to the toxic effects of workplace exposure to chemical pollutants, the U.S. Occupational Safety and Health Administration (OSHA) has regulated the concentration levels of toxic substances to which a worker may be exposed. The OSHA permissible exposure limit (PEL) for Cl_2 is a time-weighted average (TWA) (8-hour day, 40-hour workweek) of 0.5 ppm (1.5 mg/m³) and a short-term exposure limit (STEL) (15-minute TWA) of 1 ppm (3 mg/m³).[5] The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is a ceiling level of 0.5 ppm (1.5 mg/m³).[6] The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) is a TWA of 0.5 ppm (1.5 mg/m³) with a STEL of 1.0 ppm (2.9 mg/m³).[7] The OSHA PEL, the NIOSH REL, and the ACGIH TLV for Br_2 are identical at a TWA of 0.1 ppm (0.7 mg/m³) and a STEL of 0.3 ppm (2 mg/m³).[5-7]

Present monitoring methods for halogen gases are generally nonspecific, and most use liquid-containing bubblers for sample collection. The NIOSH Method P&CAM 209 for Free Chlorine in Air[8] is a spectrophotometric method based on the bleaching by Cl_2 of a methyl orange solution contained in a bubbler. Other halogen gases interfere as do oxyhalides, sulfur dioxide, nitrogen dioxide, and ozone. The OSHA method for Cl_2[9] with collection by a sulfamic acid solution in a bubbler and analysis by
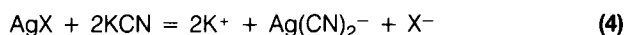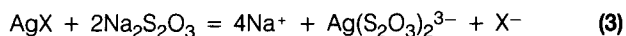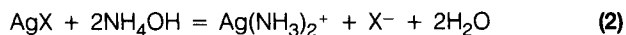

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ion-specific electrode (ISE) also has numerous interferences from strong oxidizing agents. A recently published bubbler method for Cl_2 and chlorine dioxide (ClO_2) uses a buffered potassium iodide solution for sampling with analysis by ion chromatography (IC).[10] Another method for Cl_2, which uses an o-tolidine-impregnated filter and X-ray analysis, lacks the sensitivity needed for personal monitoring.[11] NIOSH has no method for Br_2, although it may be determined by P&CAM 209.[8] Other methods for Br_2 use bubbler collection, i.e., OSHA Method ID-108 for Br_2,[12] which uses a carbonate/bicarbonate absorbing solution with IC analysis, and a phenol red method[13] with spectrophotometric analysis. Other analytical techniques for halides in solution have been reported in the literature, e.g., IC with post-column reaction,[14] gas chromatography,[15] flow injection analysis,[16] and IC separation with potentiometric detection;[17] however, no means of sampling from air were provided.

The goal of this research was to develop a reliable sampling and analytical method that uses a solid sorbent to collect halogen gases and is free from most interferences cited in other methods. One such sorbent is silver. Halogen gases (X_2) react with metallic silver (Ag) to form silver halides (AgX) according to Equation 1.[18]

$$2Ag + X_2 = 2AgX \tag{1}$$

Silver halides are soluble in ammonium hydroxide (NH_4OH), sodium thiosulfate ($Na_2S_2O_3$), and potassium cyanide (KCN), forming silver complexes[19] and releasing the halogen to be measured as the halide ion (X^-).

$$AgX + 2NH_4OH = Ag(NH_3)_2^+ + X^- + 2H_2O \tag{2}$$

$$AgX + 2Na_2S_2O_3 = 4Na^+ + Ag(S_2O_3)_2^{3-} + X^- \tag{3}$$

$$AgX + 2KCN = 2K^+ + Ag(CN)_2^- + X^- \tag{4}$$

All the silver halides are photosensitive. Although in pure form, they are almost unaffected by light, many other substances act as sensitizers.[20] Because of photolysis, the samples must be protected from light during sampling, storage, and desorption. This is easily done by using opaque samplers and vials and by transferring the samples in relative darkness.

The use of metallic silver is a unique approach to sampling for halogen gases in workplace air. Silvered zeolite has been used for scavenging radioactive iodine from radioactive noble gases.[21] The use of silver films, silver wool, and silver membranes for the adsorption of mercury vapor has been reported in the literature.[22,23] Silver membrane filters have been used in industrial hygiene for sampling coal tar pitch volatiles[8] and in the analysis of silica.[24] However, their use as a reactive sorbent for monitoring gases and vapors has not been reported. The reaction of halogen gases with silver offers a selective means of collecting Cl_2 and Br_2. Although silver may react with compounds that are interferences in other methods, most will produce anions that will be separated in the analysis. Coupled with IC analysis, the method offers convenience and specificity not found in most of the present monitoring methods.

The approach taken in this study was to develop a preliminary analytical procedure and then to evaluate commercially available silver sorbents (e.g., silver zeolite and silver membrane filters) for capacity, recovery, and compatibility with the analytical technique. The sorbent of choice was then evaluated for Cl_2 and Br_2 by monitoring known quantities of the halogen gases in air, following the guidelines for laboratory evaluation stated in the "Development and Evaluation of Methods" section of the *NIOSH Manual of Analytical Methods*, 3rd ed.,[24] and the NIOSH statistical protocol.[25] Finally, the chosen sampling and analytical method was field tested in a chlorine-containing industrial environment by collecting pairs of air samples using the test method and a previously published method.

Experimental Section

Test Atmosphere Generator

The halogen gas generator was a dynamic flow system shown schematically in Figure 1. All components exposed to the test atmosphere were constructed of Teflon® or glass. The dilution air and the test gas, which were regulated by mass flow controllers (Tylan Corp., Torrence, California), passed through two mixing chambers to ensure homogeneity. The test gas mixture then passed through an 11-port sampling manifold at flow rates of roughly 10–15 L/min, depending on the volume of dilution air required to produce a given concentration. Sampling rates
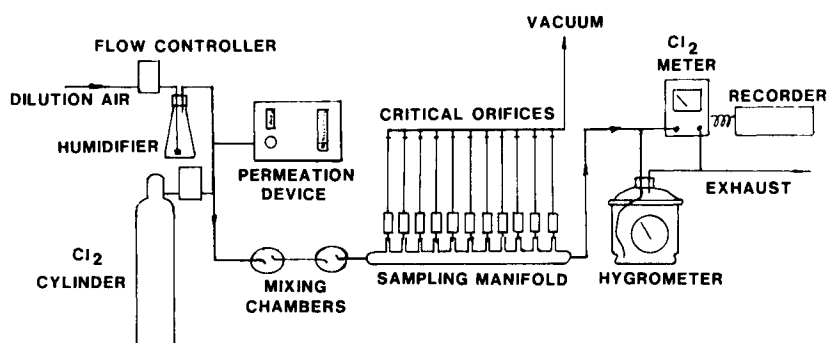

FIGURE 1. Halogen gas generation system.

were controlled by critical orifices at nominal rates of 0.3 and 1 L/min. The effluent from the manifold was continuously monitored for relative humidity (RH) with a Mason-type wet bulb/dry bulb hygrometer and for concentration with a chlorine meter (Model 1340, Interscan Corp., Chatsworth, California) interfaced with a strip chart recorder (Model 056, Hitachi, Ltd., Tokyo, Japan). The Cl_2 meter responded to Br_2 at approximately one-tenth of the response to Cl_2. The source of Cl_2 was a compressed gas cylinder (Scott Specialty Gases, Troy, Michigan) containing a mixture of 49 ppm Cl_2 in nitrogen. The Br_2 source was a permeation tube (VICI Metronics, Santa Clara, California) maintained at 30°C in a Dynacalibrator Model 340 permeation tube oven (VICI Metronics). Except for the electronic components and the compressed gas cylinder, the generator was placed in a fume hood for reasons of safety.

Instrumentation

Analyses were performed on a Dionex 4000i Ion Chromatograph with conductivity detector and AutoRegen accessory (Dionex Corp., Sunnyvale, California), a WISP 710B autosampler (Waters Division of Millipore, Milford, Massachusetts), and interfaced with a Hewlett–Packard 3357 Laboratory Data System (Hewlett–Packard, Avondale, Pennsylvania).

Reagents

All chemicals were reagent grade. Deionized water was used throughout from the preparation of solutions, eluents, and regenerants. Chloride and bromide working standards were prepared from NBS-traceable, 1000 µg/ml solutions (Alltech Assoc., Inc., Deerfield, Illinois).

Independent Methods

The test atmosphere concentration, as calculated from the analyte gas input and dilution flows, was used as the reference concentration throughout the laboratory evaluation. A modification of OSHA Method ID-108,[12] which uses a midget bubbler containing a carbonate/bicarbonate buffer solution, was used in the laboratory as an additional independent determination of concentration. The continuous monitor was used chiefly as a tracking mechanism to verify constant concentration. For the Cl_2 field study, the independent method was OSHA Method ID-101,[9] which uses a midget bubbler containing a 0.1 percent sulfamic acid solution.

Test Samplers

Silvered zeolite (Hi-Q Environmental Products Co., La Jolla, California) tubes were prepared and tested. Weights of 150 and 300 mg of the sorbent were packed into 4-mm i.d. glass tubes and held in place with glass wool plugs. The tubes were opaqued by wrapping with tape. The silver filter test sampler was a 25-mm, carbon-filled (opaque), polypropylene cassette with a 50-mm (2-in.) extension (Nuclepore Corp., Pleasanton, California) containing a thiosulfate-cleaned, 0.45-µm pore size, 25-mm silver membrane filter, (Nuclepore or Poretics Corp., Livermore, Cal-
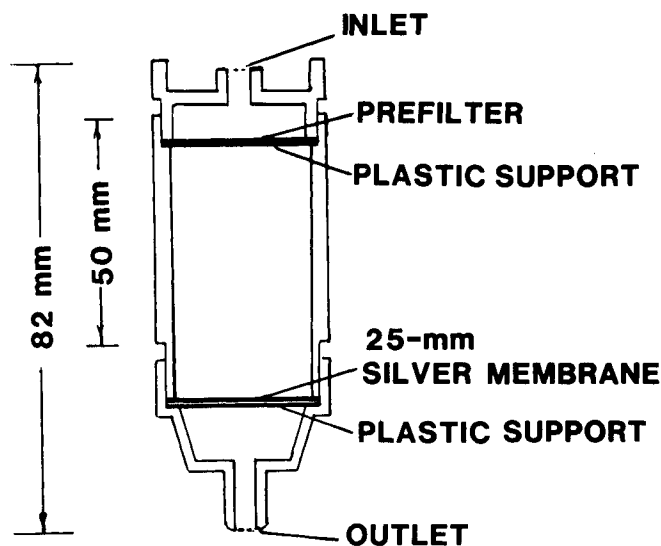

FIGURE 2. Silver filter sampler.

ifornia); a prefilter (described later); and porous plastic support pads (Nuclepore Corp.) (Figure 2).

Ten filter types (eight materials) were tested for use as prefilters for retention of Cl_2 at both high and low RH: Teflon (Teflo, 0.2-µm, Gelman; Zefluor®, 0.5-µm, Gelman); polyvinylchloride (PVC, 5-µm, Nuclepore; VM-1, 5-µm, Gelman); polycarbonate (0.4-µm, Poretics); mixed cellulose ester (MCE) (Type AA, 0.8-µm, Millipore); polyester (0.4-µm, Nuclepore); nylon (Nylaflo®, 0.45-µm, Gelman); polypropylene (0.2-µm, Gelman); and glass fiber (Type A/E, Gelman).

Procedures

Halogen samples were collected at flow rates of 0.3 L/min for TWA exposures and 1 L/min for STEL exposures. The desorption procedure was conducted under dim or red light because silver halides are photosensitive. For each sample, the silver sorbent was transferred to an amber or opaque, wide-mouth, desorption vial (30 ml). A 3-ml aliquot of $6\,mM$ $Na_2S_2O_3$ was added. The vial was capped and allowed to stand, with occasional swirling, for a minimum of 10 minutes. Once desorbed, the samples are no longer photosensitive. The sample volume was then brought to 10 ml by the addition of 7 ml of deionized water (more concentrated samples may require further dilution). The sample was then poured into an autosampler vial or a 10-ml plastic syringe for manual injection into the IC. The IC analytical conditions are listed in Table I.

TABLE I. Ion Chromatographic Conditions

Columns:	Dionex AS4A, AG4A, MFC-1
Suppressor:	AMMS Anion Micromembrane
Detector:	Conductivity
Sensitivity:	10 µS full scale
Eluent:	0.25 mM NaHCO$_3$/4 mM Na$_2$CO$_3$/0.78 mM p-Cyanophenol at 2 ml/min
Injection Volume:	50 µL

In the preliminary experiments, the source of Cl_2 was a permeation tube. Sorbent tubes with silvered zeolite and cassettes with silver filters sampled Cl_2 directly from the output of the permeation tube oven. Breakthrough was determined by passing the effluent from the sampler through the Interscan Cl_2 Meter. In later experiments, generated halogen atmospheres were sampled with silver filters, which had either a Draeger Short-Term Detector Tube (Chlorine 0.2/a, 0.2–3 ppm) or a second silver filter as a back-up sampler. Br_2 reacts with the chlorine detector tubes with about the same sensitivity as Cl_2. Breakthrough was indicated by the Draeger tubes and quantitated with the silver filter back-up samplers.

In order to collect any potentially interfering particulate matter, a prefilter was needed that would allow Cl_2 and Br_2 to pass through freely. Filters were tested for use as prefilters by placing the filter in the front stage of a three-piece cassette and a silver filter in the last stage (Figure 2). An atmosphere of Cl_2 (~2 mg/m^3) was sampled at 1 L/min for 15 minutes. After sampling, the prefilters were desorbed in deionized water and analyzed by IC for any adsorbed Cl_2. The silver filters were analyzed for Cl_2 according to the above analytical procedure, and the results compared with those of samplers without a prefilter. Prefilters found acceptable for Cl_2 were also tested for Br_2 by sampling an atmosphere of ~6 mg/m^3 at 0.3 L/min for 30 minutes.

A storage stability study was done to determine the maximum length of time between collection and analysis during which a sample may be stored without deterioration. Generated Cl_2 samples were stored at both room and refrigerated temperatures. Br_2 samples were stored at room temperature only. Groups of samples were analyzed on the day following generation (day 1), and then weekly for at least 4 weeks. Samples for the storage stability study were generated in five sets of six to seven samplers each, and stored in the opaque cassettes. Samples analyzed for each storage time period were randomly drawn from the pooled sets. Cl_2 samples were collected at 1 L/min for 15 minutes. Br_2 samples were collected at 0.3 L/min for 30 minutes.

Verification of Cl_2 and Br_2 Sources

The emission rates of permeation tubes maintained at 30°C were verified by determining their weight loss over time. The Interscan Cl_2 Meter, which was used to verify the Cl_2 source, was calibrated by means of Cl_2 permeation tube with an output of 19.43 µg/min in a carrier gas flow of 0.299 L/min. Dilutions of the Cl_2 output corresponding to 0.1–10 ppm at low RH were used to calibrate the Cl_2 Meter (meter scale is in ppm). Meter readings at other dilutions then were checked against the calculated values. The concentration of the Cl_2 mixture in the compressed gas cylinder was verified by setting the mass flow controllers for the cylinder gas and dilution air to produce a meter reading of 1 ppm. From the gas volumes corresponding to the mass flow controller settings, the concentration of the cylinder gas was calculated at 49.8 ± 1.0 ppm (147 ± 3 mg/m^3) (n = 4). The supplier reported 49 ppm

(145 mg/m^3). The source of Br_2 was a permeation tube with an emission rate of 6.06 µg/min at 30°C in a carrier flow of 0.299 L/min. The resulting output (20.3 mg/m^3) entered the mixing chamber where it was diluted with air to concentrations of 0.07–1.4 mg/m^3.

Results and Discussions

Complexing Agents

Silver halides are solubilized by complexing the Ag^+ with NH_4OH, KCN, or $Na_2S_2O_3$. Each of these matrices, in a concentration sufficient to ensure complete dissolution of the silver halide (6 mM) but dilute enough to avoid overloading the chromatographic column, was tested for compatibility with IC. The hydroxide ion (OH^-) matrix produced a broad negative peak that interfered with the quantitation of Cl^-. The cyanide ion (CN^-) caused no interference because the hydrocyanic acid (HCN), which is produced in the suppressor, is weakly dissociated. However, the bicarbonate added to stabilize the KCN solution was in sufficient concentration to affect the quantitation of Cl^-. The $Na_2S_2O_3$ matrix was the most compatible with IC. Although the thiosulfate ion ($S_2O_3^{2-}$) had a retention time of approximately 20 min when a standard eluent was used, no interfering peaks were produced. An eluent was then developed for use with the thiosulfate matrix.

Measurement

Ion chromatography was chosen as the analytical technique for its ability to separate the ions of interest from those that constitute interferences in other techniques. Several buffer combinations were tested as eluents with the purpose of achieving good resolution of the early-eluting peaks, the peaks of interest, while shortening the retention time of the late-eluting peaks. The eluent developed for use with the thiosulfate matrix was a buffer composed of 0.25 mM NaHCO$_3$/4 mM Na$_2$CO$_3$/0.78 mM p-cyanophenol. The weak concentration of NaHCO$_3$ allows the separation of the peaks of interest (Cl^-, ClO_2^-, BrO_2^-, Br^-), while the higher concentration of Na$_2$CO$_3$ shortens the retention time of the late-eluting $S_2O_3^{2-}$. The presence of the p-cyanophenol helps reduce peak tailing, which is ascribed mainly to adsorption processes rather than ion exchange. Large molecules such as p-cyanophenol have a pushing effect on adsorbed ions.[26] Figure 3 illustrates the separation of chloride and oxychloride peaks that may be achieved when using the above mentioned eluent, and Figure 4 illustrates the separation of bromide and oxybromide species. The sulfate peak is the result of partial decomposition of the thiosulfate matrix.

The limit of detection (LOD), the smallest amount of analyte that can be distinguished from background, was defined in this study as three times the standard error of the calibration graph divided by its slope. The limit of quantitation (LOQ) was defined as ten times the standard error of the calibration graph divided by its slope.[24] The LOD of Cl^- in the thiosulfate matrix was 0.06 µg/ml with a LOQ of 0.19 µg/ml. For Br^-, the LOD and LOQ were 0.16
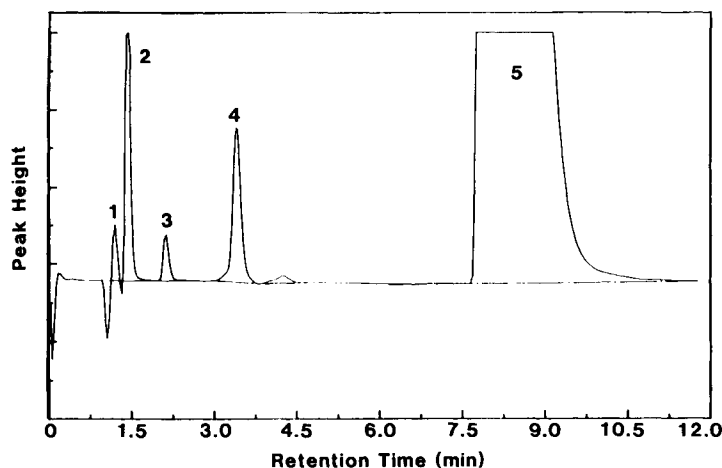
FIGURE 3. Ion chromatographic separation of chloride and oxychloride ions in thiosulfate matrix. KEY: 1 = ClO_2^-; 2 = Cl^-; 3 = ClO_3^-; 4 = SO_4^{2-}; 5 = $S_2O_3^{2-}$.

and 0.54 μg/ml, respectively. The linear range for Cl^- at the sensitivity setting used in this work (10 μS) was 0.05–5 μg/ml; for Br^-, it was 0.20–15 μg/ml. The LOD and LOQ may be reduced and linear range proportionally extended at the lower end by using a more sensitive instrumental setting, e.g., 3 μS or 1 μS full scale.

Column Maintenance

The silver thiosulfate anion, $Ag(S_2O_3)_2^{3-}$, produced in the desorption process (Equation 3) has a strong affinity for the stationary phase of the exchange resin and can only be eluted using very strong eluents.[26] The result is a reduction of ion exchange sites, degradation of peak resolution, and shortening of retention time. Although $Ag(S_2O_3)_2^{3-}$ is somewhat weakly complexed (log β_2 = 12.78)[27] and is likely to dissociate under the chromatographic conditions used,[28] the presence of excessive amounts of silver also produces a deleterious effect on column performance. Normal column cleaning procedures were ineffectual. The problem was partially solved by the addition of a metal-free precolumn (Dionex MFC-1),

which is designed to extract trace metals from the eluent stream. The most effective column reconditioning procedure was to pump through the columns at 2 ml/min: 30 ml of deionized water to rinse, 60 ml of 1 M HNO_3 to remove the contaminants, 30 ml of 0.1 M Na_2CO_3 to remove the NO_3^-, then eluent to equilibrate. Reconditioning is recommended after 100–150 analyses.

Desorption

To ensure complete dissolution of the silver halide sample, a twentyfold excess of complexing agent was necessary.[18] A 6-mM $Na_2S_2O_3$ solution was found sufficient to complex the silver and release the halide ion. When the sample was diluted to 10 ml, the resulting matrix ($\sim 2\ mM$) was sufficiently dilute to avoid overloading the analytical column. Ruggedization experiments showed that a minimum of 10 minutes was required for complete desorption of the sample, although the silver filters may remain in the 6-mM desorbing solution for up to 24 hours. Occasional swirling of the samples during desorption was adequate; no other means of agitation was necessary, e.g., ultrason-
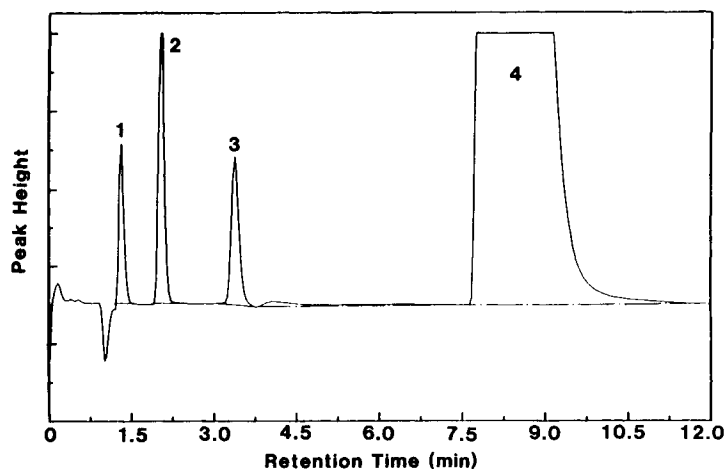
FIGURE 4. Ion chromatographic separation of bromate and bromide ions in thiosulfate matrix. KEY: 1 = BrO_3^-; 2 = Br^-; 3 = SO_4^{2-}; 4 = $S_2O_3^{2-}$.

ication. The need for the exclusion of light during transfer of the silver filters from the cassettes to the desorption vials was tested by exposing silver filter samples to laboratory fluorescent light for periods of 15 minutes and 1 hour. No loss of sample was found for the filters exposed for 15 minutes; however, samples exposed to light for 1 hour showed a loss of approximately 11 percent. To avoid any losses due to photodecomposition, desorption under dim or red light is recommended.

Evaluation of Sorbents

Silvered zeolite and silver membrane filters were evaluated for background and for the ability to collect Cl_2 and Br_2. Blank values were determined by carrying unexposed samplers through the analytical procedure. While silvered zeolite readily collected Cl_2, the sorbent contained a large amount of NO_3^- and had an extremely high background in the early portion of the chromatogram where Cl^- and Br^- elute. Cleaning the silvered zeolite with deionized water in a Soxhlet extractor reduced the background of water-extracted blanks. However, when blanks were extracted with a complexing agent, much higher levels of interfering substances were found. Several attempts were made to clean the sorbent with complexing agents, e.g., NH_4OH, KCN, $Na_2S_2O_3$, but each successive treatment produced more interferences. The cleaning treatment was more successful for silver filters. Chromatograms of silver filters showed a large interfering Cl^- peak, which was removed in one extraction. The cleaning procedure was optimized with respect to the concentration of the complexing agent and desorption time.

Breakthrough/Capacity

Breakthrough volume is defined as the volume at which the analyte concentration in the effluent compared to the concentration in the influent is significant (usually 5%). Capacity is defined as the mass of analyte collected by the sampler at the breakthrough volume. Breakthrough and capacity of the silver filter were investigated at both high and low RH. In these experiments, Cl_2 was sampled at a rate of 1 L/min. The concentration of Cl_2 at high RH was 4.5 mg/m³ (1.5 × OSHA PEL), at low RH, 3 mg/m³ (1 × OSHA PEL). At low RH (~20%), the breakthrough volume of the silver filter for Cl_2 was approximately 67 L resulting in a mean capacity of approximately 198 μg of Cl_2 (Table II). At high RH (~80%), however, a dramatic increase was seen. The breakthrough volume was approximately 1150 L with a capacity of 2681 μg of Cl_2. For Br_2 sampled at 0.3 L/min, a similar variation was seen. At low RH, the breakthrough volume was 70 L with a capacity of approximately 360 μg Br_2. The breakthrough experiment for Br_2 at high RH was terminated when no breakthrough had occurred after 24 hours of sampling. The recommended sample volume, based on the capacity of the silver filter at low RH, for routine sampling is 45 L for Cl_2 and 135 L for Br_2. The data in Table II illustrate the extraordinary effect that high humidity had on the capacity of the silver filter for both Cl_2 and Br_2. This increase may be the combined result of two

phenomena: long residence time in the filter and dissociation. Gas molecules have a remarkably long residence time in membrane filters with an estimated 10^{10} collisions with the walls before exiting the filter.[29] With an increase in the number of water molecules present, some of the halogen molecules will collide with the water and dissociate. Since disproportionation occurs very rapidly,[19] the resulting hypohalous acid may then oxidize the Ag, as illustrated by the following reactions for Cl_2.

$$Cl_2 + H_2O = HOCl + HCl \tag{5}$$

$$2Ag + HOCl = Ag_2O + HCl \tag{6}$$

$$Ag_2O + 2HCl = 2AgCl + H_2O \tag{7}$$
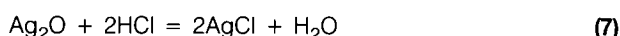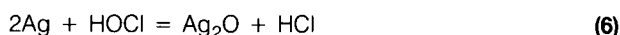
The kinetics of the above reactions are probably more favorable than the direct reaction with silver (the predominant mechanism at low RH), particularly since the HCl produced by disproportionation would react with any oxidized silver already present on the filter.

Prefilter Selection

In order to collect any potentially interfering particulate matter, a prefilter was needed that would allow Cl_2 and Br_2 to pass through freely. Ten commercially available filters were tested with Cl_2 atmospheres at 1.8 mg/m³ (Table III). The acceptance criteria chosen were 1) less than 2 percent of total halogen collected on the prefilter and 2) total recovery of halogen from the silver filter of 100 ± 5 percent. Based on these criteria, Gelman Zefluor and Nuclepore polyester filters were the only acceptable prefilters. In later tests with Br_2 atmospheres at 6.2 mg/m³, Zefluor and polyester filters were also found acceptable. Although the sampling time periods for the prefilter tests were approximately 30 minutes, the prefilters were used in the samplers for all the remaining experiments where recovery data averaged 97 percent for sampling periods of 15 minutes to 7 hours. Glass fiber and MCE filters, generally used as prefilters, failed particularly at high RH because the adsorbed water vapor collected Cl_2. Even non-hygroscopic materials, such as polycarbonate, Teflon, and PVC, can rapidly adsorb significant amounts of moisture.[30] The PVC filters tested showed widely varied results. Not only did the prefilters collect approximately 16 percent of

TABLE II. Breakthrough Volume and Capacity of Silver Filters

Humidity	Bromine[A]		Chlorine[B]	
	High	Low	High	Low
Concentration (mg/m³)	1.4	5.6	4.5	3
Concentration level (× OSHA PEL)	2	8	1.5	1
Number of tests	5	3	3	3
Breakthrough Volume (± s)(L)	> 430	70 ± 7	1150 ± 199	67 ± 22
Capacity (± s)(μg)	> 596	355 ± 76	2681 ± 14	198 ± 37

[A]Sampling rate ~0.3 L/min.
[B]Sampling rate ~1 L/min.

TABLE III. Summary of Prefilter Study

Prefilter	RH[A]	Cl_2 on Prefilter (%)	Total Cl_2 Found[B] (%)	Acceptance Criteria[C] 1	2
Zefluor	Low	0	99	P	P
	High	0	105	P	P
Polyester	Low	0	101	P	P
	High	0	96	P	P
Polypropylene	Low	2	88	P	F
	High	0	109	P	F
Teflo	Low	0.5	104	P	P
	High	0.2	113	P	F
MCE	Low	3	92	F	F
	High	1.7	136	F	F
Polycarbonate	Low	2.2	65	F	F
	High	1.2	87	P	F
Gelman VM-1	Low	12	98	F	P
	High	7	147	F	F
Nuclepore PVC	Low	10	20	F	F
	High	16	34	F	F
Nylaflo[D]	High	16	114	F	F
Glass Fiber[D]	High	27	115	F	F

[A]Relative humidity.
[B]Based on Cl_2 atmosphere of 1.8 mg/m³.
[C]Acceptance criteria: 1 = 2% or less on prefilter; 2 = Recovery of 100 ± 5%; P = pass; F = fail.
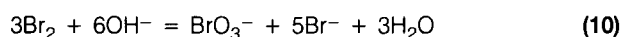[D]Prefilter not evaluated at low humidity.

the Cl_2, but the total Cl_2 found for the Gelman VM-1 was 147 percent and only 34 percent for the Nuclepore PVC filter.

Independent Methods

Although the reference concentration of the test atmospheres was determined from the analyte source and dilution air flows, an adaptation of OSHA Method ID-108 was used in this study as an independent comparison method. Method ID-108 is an ion chromatographic method in which Br_2 is collected in a bubbler containing a carbonate/bicarbonate buffer solution (pH > 8), 3 mM $NaHCO_3$/2.4 mM Na_2CO_3, the eluent used in the IC analysis. The adaptation was the use of the eluent developed for the halogens work, 0.25 mM $NaHCO_3$/4 mM Na_2CO_3/0.78 mM p-cyanophenol (pH = 10), as the absorbing medium. In basic solution, Br_2 disproportionates to hypobromite (BrO^-) and Br^-. The disproportionation of BrO^- to Br^- and bromate (BrO_3^-) is moderately fast even at room temperature.[19]

$$Br_2 + 2OH^- = Br^- + BrO^- + H_2O \qquad (8)$$

$$3BrO^- = 2Br^- + BrO_3^- \qquad (9)$$
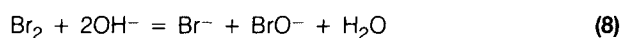
The combined equation is

$$3Br_2 + 6OH^- = BrO_3^- + 5Br^- + 3H_2O \qquad (10)$$

Since the stoichiometric mass ratio of $3Br_2$ to $5Br^-$ is 1.2, the concentration of Br^- is measured directly by IC and multiplied by 1.2 to obtain the Br_2 concentration.[12]

The method for Br_2 was also applied to Cl_2. In solution, Cl_2 disproportionates to hypochlorite (OCl^-) and Cl^- ac-

cording to Equation 5.[27] Both ions have the same retention time,[31] and it was determined experimentally that they have comparable peak heights per unit mass of chlorine. Therefore, the peaks may be calibrated using only Cl^- standards. This adaptation of Method ID-108 to Cl_2 monitoring was the independent method used for the Cl_2 work. Recoveries were comparable to those found when the method was applied to Br_2 sampling.

A 30 to 40 percent bias was found, however, between the independent method bubblers and the test method (silver filter), although the test method agreed favorably with the actual test atmosphere concentration. After investigating the effect of flow rate on sample collection and the completeness of disproportionation in an endeavor to explain the discrepancy, a remaining probable cause was the presence of p-cyanophenol in the absorbing solution, the halogens eluent. The pH of the standard eluent (pH = 8.9), as used in the OSHA method, and of the halogens eluent (pH = 10), developed in this work, was greater than that required for disproportionation.[19] The chief difference was the presence of p-cyanophenol in the halogens eluent.

To investigate the effect of this variable, an experiment was designed to test the efficiency of silver filters and three buffer solutions for sampling Br_2: 1) a standard eluent (1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3), 2) halogens eluent (0.25 mM $NaHCO_3$/4 mM Na_2CO_3/0.78 mM p-cyanophenol), and 3) halogens eluent plus an excess of p-cyanophenol (4.7 mM). A Br_2 test atmosphere was sampled with silver filters and with bubblers containing each of the three eluents,

TABLE IV. Efficiency of Eluent Buffers and Silver Filters for Sampling Br_2

Sampler	n	Mean Concentration (mg/m³)	S_r	Recovery[A] (%)
Halogens eluent	3	0.282	0.046	52.3
Halogens eluent + 4.7 mM p-cp[B]	3	0.325	0.096	60.3
Standard eluent	9	0.489	0.045	90.7
Silver filter	8	0.530	0.023	98.4

[A]Recovery based on calculated Br_2 concentration of 0.539 mg/m³.
[B]p-cyanophenol.

and the results compared (Table IV). The recovery of Br_2 from the standard eluent at 90.7 percent, based on the actual atmospheric concentration of 0.539 mg/m³, is in keeping with the 93.9 percent recovery reported in the backup data for OSHA Method ID-108.[12] The results of the standard eluent and the silver filter were statistically greater at the 5 percent significance level than the halogens eluent alone or that with excess p-cyanophenol. The negative bias of these absorbing solutions was comparable to the discrepancy previously observed. Therefore, the presence of p-cyanophenol in the collection medium affects the conversion of Br_2 to Br^-, and presumably Cl_2 to Cl^-. The probable mechanism is the halogenation of the phenol ring.

Interferences

Known positive interferences, substances that decompose releasing Cl_2, e.g., chloramine-T, were not investigated.

Particulate Interferences

The possible interference of particulate halides or oxyhalides was determined by spiking approximately 100 μg of the appropriate salt in solution onto a prefilter, drying overnight, then sampling a halogen atmosphere. Testing was done with both Zefluor and polyester prefilters. The data show that chlorine-containing particulates (chlorides, chlorites, chlorates, and perchlorates) are not an interference in the collection of Cl_2, as shown by recoveries of 94.2–98.2 percent. Likewise, bromine-containing particulates (bromides and bromates) do not interfere with Br_2, as shown by recoveries of 93.9–100.5 percent.

Hydrogen Sulfide

The interference of hydrogen sulfide (H_2S) was determined by sampling a generated atmosphere. The source of H_2S was a permeation tube with an output of 4.2 μg/min in a carrier stream of 0.299 L/min. Because the resulting concentration was 14 mg/m^3 (1 × OSHA PEL), H_2S samples were collected directly from the output of the permeation tube oven either before or after sampling an atmosphere of Cl_2. The results show that H_2S sampled before Cl_2 diminished the collection of Cl_2 by 11 percent (Table V). However, when H_2S was sampled after Cl_2, losses were from 36 percent at low RH to 61 percent at high RH. These data suggest that the sulfide ion (S^{2-}) displaces Cl^- from AgCl and that the process is facilitated by the presence of water.

$$2AgCl + H_2S = Ag_2S + 2HCl \tag{11}$$

This hypothesis is supported by the fact that the solubility product constants for AgCl and AgBr are on the order of 10^{-10} and 10^{-13}, respectively, as compared with 10^{-49} for Ag_2S.[32] Accordingly, H_2S is a negative interference.

Chlorine Dioxide

Chlorine dioxide (ClO_2) is used with Cl_2 as a bleaching agent in the pulp and paper industry. The ability of the silver filter to react with ClO_2 to form silver chlorite ($AgClO_2$) was investigated, although it has been shown that the chlorite ion (ClO_2^-) can be separated from Cl^- in the analysis (Figure 3). ClO_2 was generated by passing Cl_2 through a concentrated solution of sodium chlorite (4.42 mM NaClO$_2$) in a bubbler.[33]

$$Cl_2 + 2NaClO_2 = 2ClO_2 + 2NaCl \tag{12}$$
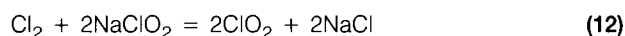
Samples were collected on silver filters and reference bubblers for time periods of 15, 30, and 60 minutes at concentrations equivalent to 3 and 4.5 times the OSHA PEL for ClO_2. The bubblers contained 15 ml of a buffer solution (halogens eluent). The silver filters contained no ClO_2; however, the backup bubblers that were used with the 30-minute samples contained approximately 86 percent of the

TABLE V. Effect of Hydrogen Sulfide on Chlorine Recovery

Sampling Order		RH^A	n	Cl_2 Concentration (mg/m^3)	Cl_2^B Recovery (%)
1st	2nd				
H_2S^C	Cl_2	Low	3	0.315 ± 0.006	89
Cl_2	H_2S	Low	3	0.225 ± 0.104	64
Cl_2	H_2S	High	2	0.136 ± 0.007	39

^{A}Relative humidity.
^{B}Based on Cl_2 concentration of 0.354 mg/m^3.
^{C}H_2S concentration = 14 mg/m^3.

ClO_2 in the generated atmosphere (86% recovery is within the bias found for bubblers in this study). Therefore, ClO_2 is not an interference in the test method for Cl_2.

Hydrogen Chloride and Hydrogen Bromide

Theoretically, the hydrogen halides (HX) will not react with metallic silver because they are not oxidizing gases. Nonetheless, HCl and HBr were collected by the silver filter. The plot in Figure 5 shows that the interference from HCl is minor, but HBr poses a more significant interference problem. Approximately 15 μg of HCl were collected by the filter within the first 15 minutes of sampling, and this mass remained constant for up to 16 hours. The uptake of HBr, however, increased with time at a rate of approximately 0.4 μg/min. While collection was incomplete for HBr, the increase in uptake presents a positive interference that is not readily correctable. The presence of HCl or HBr in an atmosphere may be determined by sampling with silica gel tubes (NIOSH Method 7903, Inorganic Acids);[24] however, when silica gel tubes were used to sample atmospheres of Cl_2 and Br_2, they collected approximately 30 percent of the free halogen in the atmosphere. Thus, a correction for the presence of hydrogen halides in an atmosphere containing a halogen gas is not a simple subtraction.

If HCl or HBr were physically adsorbed on the surface of the filter, it could be removed with water. A water wash of the filter produced no Cl^- or Br^- in the resulting solution. A review of the literature revealed that oxygen is chemisorbed on metallic silver forming a definite stoichiometric compound.[20] Therefore, it was postulated that HX had reacted with oxidized silver (presumably Ag_2O) on the surface of the filter to produce silver halide (AgX) according to the following reactions.[19]

$$Ag_2O + HX = AgX + AgOH \tag{13}$$

$$AgOH + HX = AgX + HOH \tag{14}$$
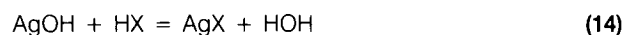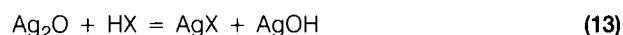
If the hypothesis holds, the degree of filter oxidation would be the determining factor in the interference from HCl and HBr. Thiosulfate-cleaned silver filters, which were oxidized by aging for periods of 1, 14, and 30 days, were used to sample an atmosphere of HBr. Recoveries were determined based on silica gel tube data (NIOSH Method 7903).[24] Recovery of HBr was 46 percent for filters aged 1 day, 68 percent for 14 days, and 89 percent for 30 days
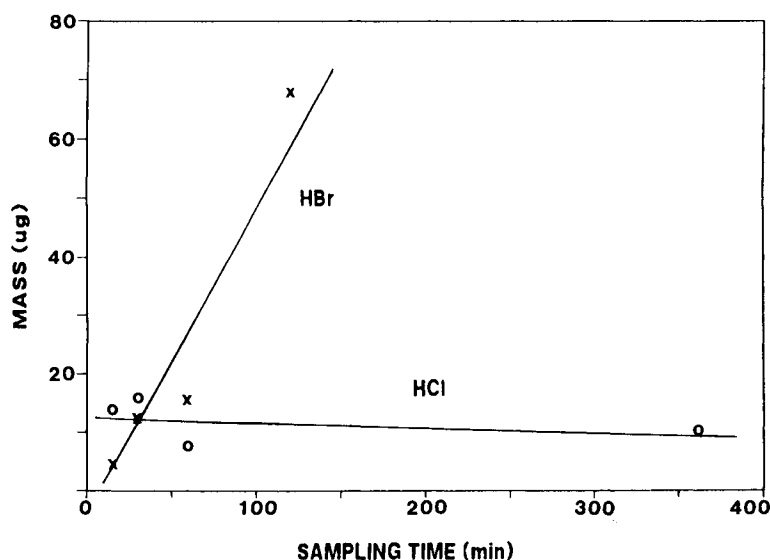
FIGURE 5. Effect of sampling time on mass of HBr and HCl collected by silver filters.

aging. These data suggest that oxidized silver was the basis for the reaction with hydrogen halides. In an attempt to remove the oxidized silver, the silver filters were treated with aqueous HBr or HCl. Overnight soaking in acid did not effectively remove the oxidized silver, since filters so treated collected 36 percent of the HBr atmosphere. Hence, it was assumed that Ag_2O was being formed continuously during sampling. The uptake of HX, particularly the continued uptake of HBr with time, may be explained partially by the ability of hydrogen halides to form complexes. HX reacts initially with Ag_2O to form AgX (Equations 13 and 14), and then it reacts with AgX.[19]

$$AgX + HX = H^+ + (AgX_2)^- \qquad (15)$$

$$(AgX_2)^- + HX = H^+ + (AgX_3)^{2-} \qquad (16)$$
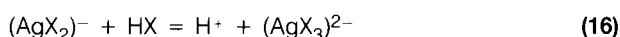
When the ligand is Cl^-, the reaction will proceed to the complex $(AgCl_3)^{2-}$, and when the ligand is Br^-, $(AgBr_4)^{3-}$ will be formed.[27] The limited uptake of HCl versus the continuing uptake of HBr may be due, in part, to kinetics, or it may be a function of the greater stability of Br^- complexes ($\log \beta_4 = 9.5$) over Cl^- complexes ($\log \beta_3 = 6.0$). Although we have no confirming experimental evidence, the formation of silver halide complexes seems a reasonable explanation for the positive interference from HBr, and possibly HCl. Therefore, there appears to be no simple correction for these positively interfering compounds.

Storage Stability

The stability of Cl_2 samples stored in opaque cassettes was determined for both ambient (25°C) and refrigerated (5°C) storage. Recoveries are expressed as percentage of the mean concentration for samples analyzed on day 1. Chlorine recoveries were 103 ± 4 percent for 30-day ambient storage (n = 4), 101 ± 3 percent for 64-day refrigerated storage (n = 4), and for samples refrigerated for 30 days and then stored at ambient for an additional 34

days, 103 ± 3 percent (n = 3). The stability of Br_2 samples stored in the cassettes was determined for ambient storage only. Bromine recovery after 30 days was 99.4 ± 5.5 percent (n = 5), and after 60 days, it was 99.2 ± 10.1 percent (n = 6). Therefore, samples are stable at ambient temperature for at least 30 days (Cl_2) or 60 days (Br_2) and probably longer.

Shelf-Life of Cleaned Silver Filters

The shelf-life, i.e., storage time before deterioration, was examined for cleaned silver filters. As received from the manufacturer, silver filters have a high AgCl background that is removed by treatment with a $Na_2S_2O_3$ solution (the desorption procedure). Silver filters were cleaned and then stored under three separate conditions: 1) assembled in the cassettes, where light was excluded; 2) separated by paper disks and returned to the manufacturer's package, where air and light were excluded; and 3) placed in a plastic bag, exposed to light but not to air. Each month three filters from each group were observed and analyzed. Over a period of 8 months, there were no changes in the appearance of the filters or in the analyzed blank values. At the end of this time, the filters were used to sample a Cl_2 atmosphere (approximately 0.35 mg/m^3, low RH at 1 L/min). The filters stored in the manufacturer's package gave the best recovery at 101 percent. Filters stored in the plastic bag had a 94.1 percent recovery, but those stored in the cassettes had the poorest recovery at 88.1 percent. The reason for this is unclear. There may be sufficient leakage around the cassette plugs to allow airborne contaminants to enter and react with the filter, or the cassettes may off-gas during the long storage period. Thus, the stability of cleaned silver filters appears to be more affected by exposure to air than to light. Although the differences in recovery for the three storage conditions are not statistically significant at the 95 percent confidence level, the recommended long-term storage mode for cleaned silver

TABLE VI. Verification of Final Method for Chlorine

Concentration Level (× PEL)	n	Concentration Taken* (mg/m³)	Concentration Found (mg/m³)	s_r	Recovery (%)
Verification at High Relative Humidity (~80%)					
0.1	6	0.473	0.478	0.103	101
0.5	5	1.45	1.37	0.041	94.5
1	6	2.78	2.58	0.066	92.7
2	6	6.77	6.53	0.030	96.4
Mean recovery at high RH					96.2
Precision (pooled $\bar{s}_r$)				0.067	
Verification at Low Relative Humidity (~20%)					
0.1	6	0.354	0.347	0.086	98.0
0.5	6	1.45	1.55	0.094	107
1	6	2.78	2.70	0.024	97.1
2	6	6.12	6.24	0.031	102
Mean recovery at low RH					101
Precision (pooled $\bar{s}_r$)				0.067	
Total mean recovery					98.6%
Total coefficient of variation (CV_T)					7.5%

*Concentration determined from generator source and dilution flows. Sampling rate = 1 L/min; sampling time = 15 min.

filters is to repack them between paper disks in the manufacturer's container because recovery from this mode of storage was essentially complete.

Verification of the Final Method

Verification samples were generated at concentration levels of 0.1, 0.5, 1, and 2 × PEL (6/level) and at both high and low humidity. The test atmosphere concentration was determined from the analyte gas source and dilution flows. The mean recovery of Cl_2 was 98.6 percent (96.2% at high RH and 101% at low RH) when sampled for 15 minutes at 1 L/min. The sampling and analytical precision, the pooled relative standard deviation ($\bar{s}_r$), was 6.7 percent for both high and low RH data (Table VI). The estimate of the total

coefficient of variation (CV_T), including 5 percent pump error, was 7.5 percent. The mean recovery for Br_2, sampled for 4 hours at 0.3 L/min, was 98.8 percent (96.1% and 102% for high and low RH, respectively). The sampling and analytical precision was slightly better for low RH at 3.2 percent over 5.8 percent at high RH (Table VII); the CV_T estimate was 6.9 percent. All data were within the accuracy criterion of ± 25 percent at the 95 percent confidence level and coefficient of variation (precision) recommended for a valid NIOSH method.[25] Bartlett's test for homogeniety was applied to the data before pooling. The mean recovery for the overall method (Cl_2 and Br_2) was 98.7 percent (−1.3% bias) with a sampling and analytical precision of 5.2 percent and a total coefficient of variation

TABLE VII. Verification of Final Method for Bromine

Concentration Level (× PEL)	n	Concentration Taken* (mg/m³)	Concentration Found (mg/m³)	s_r	Recovery (%)
Verification at High Relative Humidity (~80%)					
0.1	6	0.069	0.067	0.097	97.1
0.5	5	0.346	0.336	0.044	97.1
1	6	0.639	0.582	0.027	91.1
2	6	1.21	1.20	0.035	99.2
Mean recovery at high RH					96.1
Precision (pooled $\bar{s}_r$)				0.058	
Verification at Low Relative Humidity (~20%)					
0.1	6	0.076	0.077	0.039	101
0.5	6	0.351	0.358	0.033	102
1	6	0.696	0.673	0.026	96.7
2	6	1.42	1.50	0.028	106
Mean recovery at low RH					102
Precision (pooled $\bar{s}_r$)				0.032	
Total mean recovery					98.8%
Total coefficient of variation (CV_T)					6.9%

*Concentration determined from generator source and dilution flows. Sampling rate = 0.3 L/min; sampling time = 4 hr.

estimate (CV_T) of 7.2 percent.

When the comparison data in Table IV are considered, there is a statistically significant difference at the 95 percent confidence level between the silver filter method for Br_2 and the standard eluent data. Only the silver filter method gave results that were statistically indistinguishable from the actual concentration in the generator.

Chlorine Field Study

Field samples for Cl_2 were collected at a plant that produces trichloroisocyanuric acid. The compound is prepared by treating cyanuric acid with Cl_2. Paired silver filter samples and sulfamic acid bubblers (OSHA Method ID-101)[9] were collected at rates of 0.5 and 1.0 L/min, respectively. The results are presented in Table VIII. Pairs 1 through 6 were area samples collected at the production site. Pairs 7 and 8 were collected in the plant but away from the chlorination operation to ascertain background levels of Cl_2. In pair 6, possible breakthrough of the silver filter occurred, as evidenced by the large mass of Cl_2 found in the bubbler. The mean difference for pairs 1 through 5 was 0.048 mg/m^3. When a paired t-test for determining differences in paired observations[34] was applied to these data, the results showed that the difference between the two monitoring methods was not statistically significant at the 95 percent confidence level. However, since the number of samples taken at this field site was limited, more field studies must be done to verify the soundness of the significance statement.

Conclusions

The results of this study show that silver membrane filters are practical solid sorbents for sampling Cl_2 and Br_2 when used in opaque cassettes. Although high relative humidity markedly increases the capacity of the silver membrane, at low humidity it has the capacity to sample for 4 hours at the TWA of Cl_2 and 2 × TWA of Br_2. The method has the sensitivity to monitor Cl_2 at the current OSHA PEL (TWA of 0.5 ppm and STEL of 1 ppm) and to monitor Br_2 at the OSHA PEL (TWA of 0.1 ppm and STEL of 0.3 ppm). The silver filter sampler developed in this study has the potential for use in monitoring other toxic gases and vapors (e.g., iodine, fluorine, hydrogen sulfide).

Recommendations

The silver filter method for sampling Cl_2 and Br_2 is especially suited to environments where liquid-containing samplers may not be used, e.g., chlorine production sites. The industrial hygienist is encouraged to take relative humidity measurements early in the sampling period in order to prevent possible breakthrough of the silver membrane filter because of the lower capacity of the silver membrane for sampling Cl_2 and Br_2 at low humidity. The opaque cassette protects the photosensitive reaction products produced in the sampling procedure from light. It is recommended that the samples remain in the cassettes until analysis.

TABLE VIII. Chlorine Field Study Using Paired Silver Filter and Bubbler[A] Samples

Pair No.	Sampler No.	Air Volume (L)	Mass Cl_2 (μg)	Concentration (mg/m³)	Difference[B] (mg/m³)
1	Filter-1	189	134	0.71	0.10
	Bubbler-1	377	230	0.61	
2	Filter-3	211	122	0.578	0.12
	Bubbler-4	305	140	0.459	
3	Filter-13	167	368	2.20	−0.02
	Bubbler-11	239	530	2.22	
4	Filter-11	157	257	1.64	−0.10
	Bubbler-13	270	470	1.74	
5	Filter-10	152	41.4	0.272	0.14
	Bubbler-12	313	43.0	0.137	
6	Filter-4	218	460	2.11[C]	
	Bubbler-2	361	1700	4.71	
7[D]	Filter-2	185	11.5	0.062	
	Bubbler-3	342	4.8	0.014	
8[D]	Filter-12	158	ND[E]	ND[E]	
	Bubbler-14	293	1.6	0.006	

[A]OSHA Method ID-101.
[B]Differences not statistically significant at 95% confidence level.
[C]Probable breakthrough of silver filter.
[D]Background levels in plant.
[E]None detected, detection limit = 0.6 μg/sample.

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