NIOSH Manual of Analytical Methods (NMAM) 5th Edition

BACKUP DATA REPORT
NIOSH Method No. 6011

Title: Bromine and Chlorine

Analytes: Bromine and Chlorine

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Date: July 14, 2022

Note on NIOSH 6011, Issue 3

In this updated version of NIOSH 6011, Issue 3, the Chlorine and Bromine methods, found separately in the NMAM 4th edition, were combined. The original data used to develop and evaluate the method may be found in this report and additionally published in Applied Occupational and Environmental Hygiene [1].

Introduction

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. One such sorbent is silver. Halogen gases (X_2) react with metallic silver (Ag) to form silver halides (AgX) according to Equation 1 [2].

(1) $2Ag + X_2 = 2AgX$

Silver halides are soluble in ammonium hydroxide (NH_4OH), sodium thiosulfate ($Na_2S_2O_3$), and potassium cyanide (KCN), forming silver complexes [3] and releasing the halogen to be measured as the halide ion (X^-) (Equations 2-4).

(2) $AgX + 2NH_4OH = Ag(NH_3)_2^+ + X^- + 2H_2O$
(3) $AgX + 2Na_2S_2O_3 = 4Na^+ + Ag(S_2O_3)_2^{3-} + X^-$
(4) $AgX + 2KCN = 2K^+ + Ag(CN)_2^- + X^-$

All the silver halides are photosensitive. Although in pure form, they are almost unaffected by light, many other substances act as sensitizers [4]. 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 [5]. The use of silver films, silver wool, and silver membranes for the adsorption of mercury vapor has been reported in literature [6,7]. Silver membrane filters have been used in industrial hygiene for the analysis of silica [8]. 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 ion chromatography (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 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. [9] and the NIOSH statistical protocol [10]. 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.

Reagents
All chemicals were reagent grade. Deionized water was used throughout for 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, IL).

Development of preliminary analytical procedure

Determination of Silver Complexing Solution

As shown in equations 1-4 above, 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, were 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.

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 (~2 mM) was sufficiently dilute to avoid overloading the analytical column. Ruggedization experiments showed that a minimum of 10 min was required for complete desorption of the sample, although the silver filters may remain in the 6 mM desorbing solution for up to 24 h. 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.

Occasional swirling of the samples during desorption was adequate; no other means of agitation was necessary.

Analytical technique

Analyses were performed on a Dionex 4000i Ion Chromatograph with conductivity detector and AutoRegen accessory (Dionex Corp., Sunnyvale, CA), a WISP 710B autosampler (Waters Div. of Millipore, Milford, MA), and interfaced with a Hewlett-Packard 3357 Laboratory Data System (Hewlett- Packard, Avondale, PA).

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_2CO_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_2CO_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. Figure 1 illustrates the separation of chloride and oxychloride peaks that may be achieved when using the above-mentioned eluent, and Figure 2 illustrates the separation of bromide and oxybromide species. The sulfate peak is the result of partial decomposition of the thiosulfate matrix.

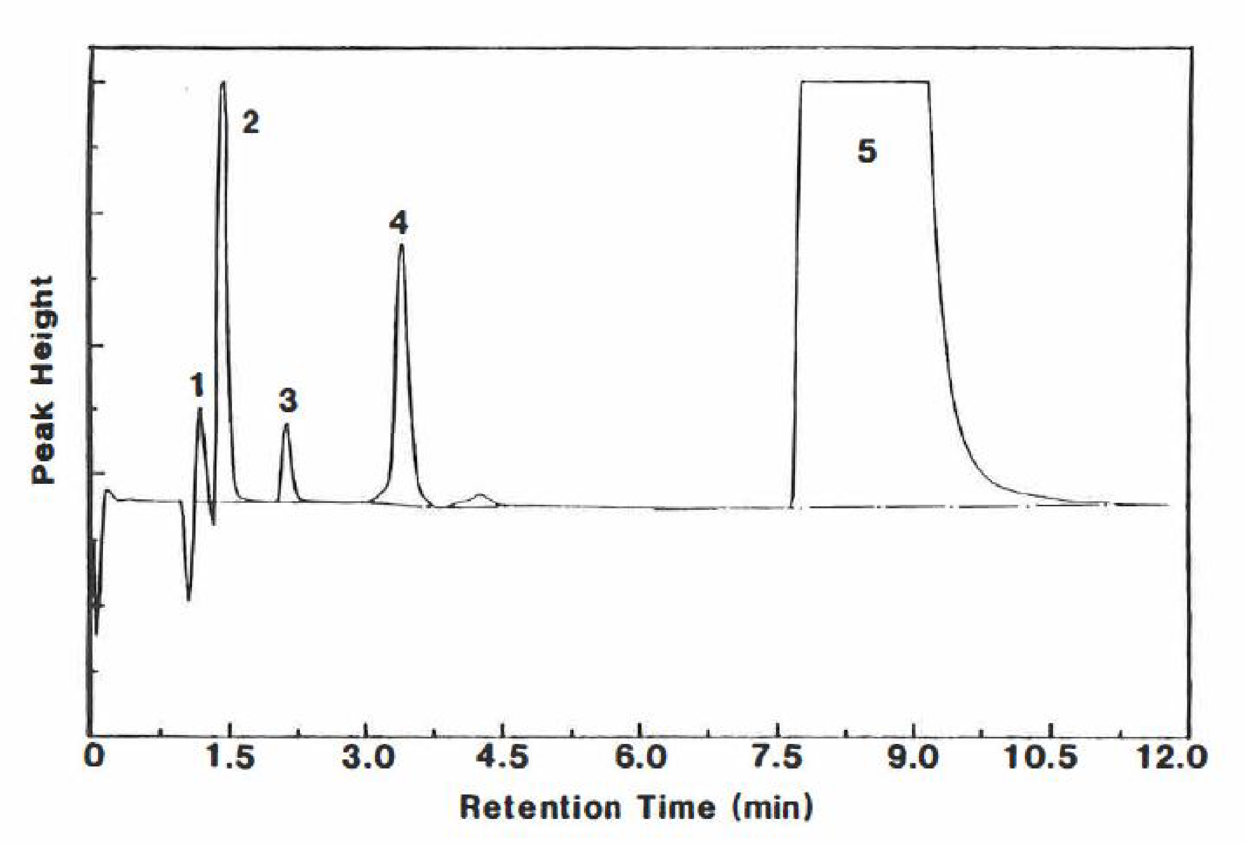

Figure 1. IC separation of chloride (2), chlorite (1), chlorate (3), sulfate (4), and thiosulfate (5).

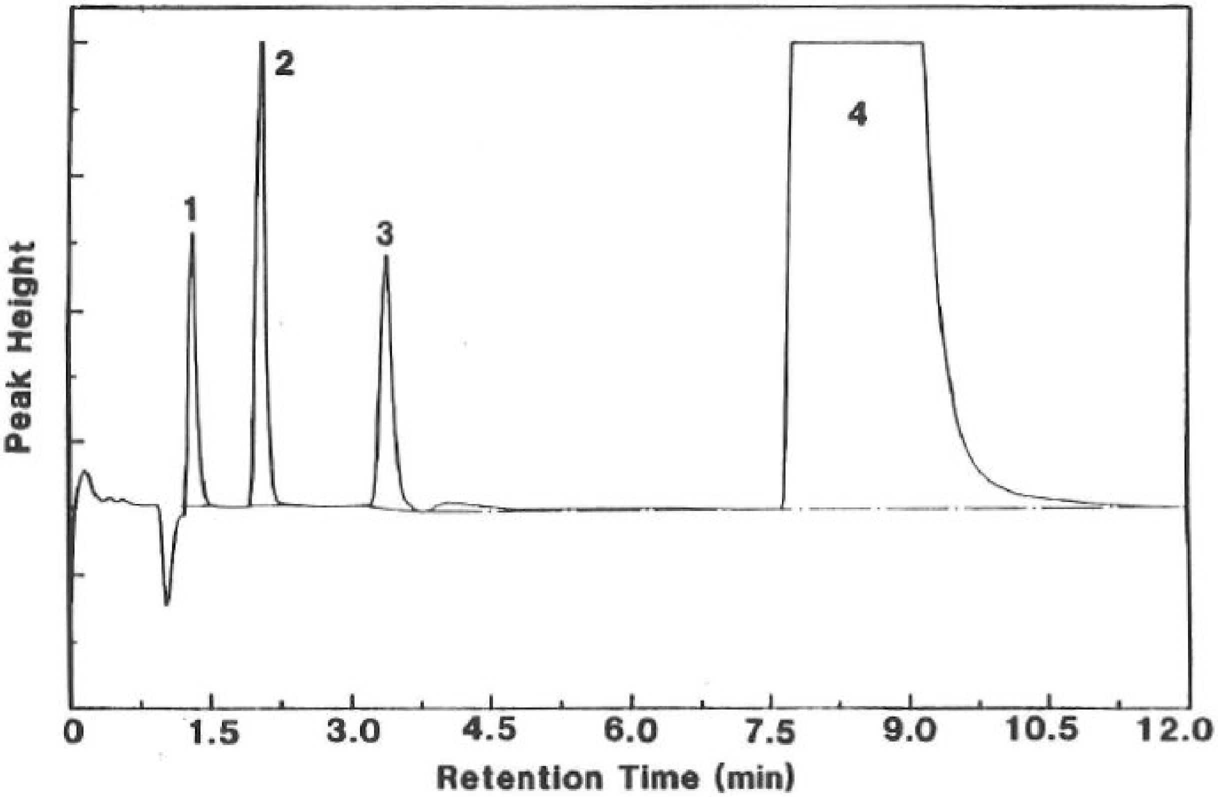

Figure 2. IC separation of bromate (1), bromide (2), sulfate (3) and thiosulfate (4).

Silver Sorbent Selection

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.

Silvered zeolite (Hi-Q Environmental Products Co., La Jolla, CA) tubes were prepared and tested. Weights of 150 and 300 mg of the sorbent were packed into 4-mm ID glass tubes and held in place with glass wool plugs. The tubes were opaqued by wrapping with tape. 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. Therefore, silvered zeolites tubes were excluded from further evaluation.

The silver filter sampler tested was a 25-mm, carbon-filled (opaque) polypropylene cassette with a 50-mm (2-inch) extension (Nuclepore Corp., Pleasanton, CA) containing a thiosulfate cleaned, 25-mm silver membrane filter, 0.45-µm pore size (Nuclepore or Poretics Corp., Livermore, CA), a prefilter (described later), and porous plastic support pads (Nuclepore Corp.) (Figure 3).

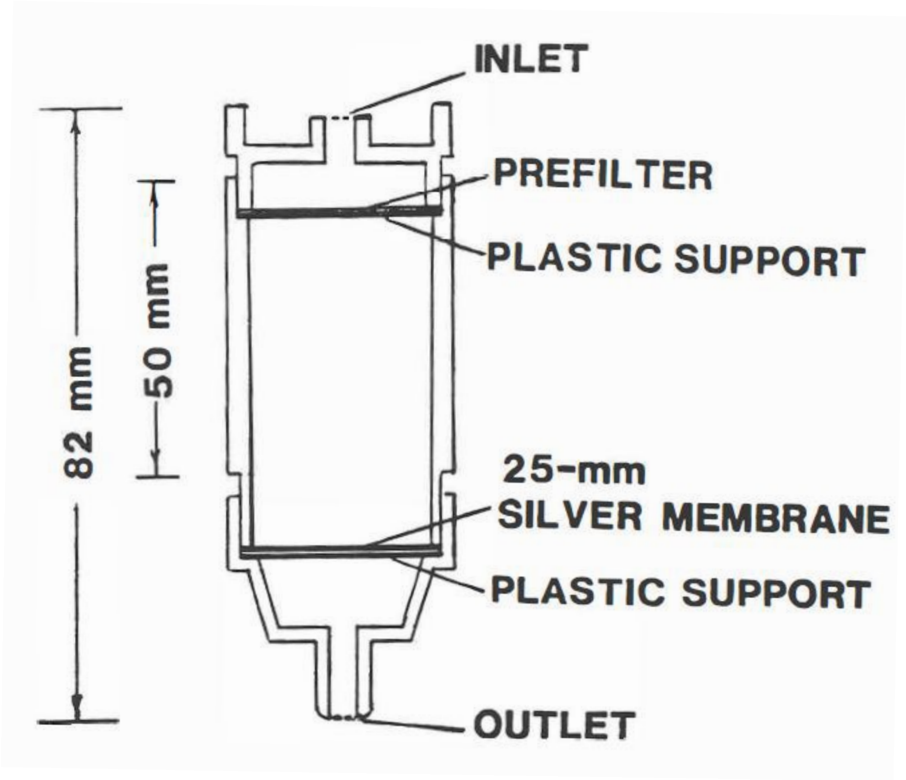

Figure 3. Silver filter sampler

Chromatograms of silver filters showed a large interfering Cl^- peak, which required removal by cleaning. The cleaning procedure was optimized with respect to the concentration of the complexing agent and desorption time. The final cleaning procedure used 6 mM $Na_2S_2O_3$ as a complexing agent to remove the Cl^-. The filters were desorbed for a minimum of 10 minutes with occasional swirling. The filters were rinsed thoroughly with deionized water and allowed to dry before use.

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 min and 1 h. No loss of sample was found for the filters exposed for 15 min; however, samples exposed to light for 1 h showed a loss of ~11%. To avoid any losses due to photodecomposition, desorption under dim or red light is recommended.

Pre-filter

To collect any potentially interfering particulate matter, a prefilter was needed that would allow Cl_2 and Br_2 to pass through freely. Ten filter types (eight materials) were tested for use as prefilters for retention of Cl_2 at both high and low RH: Teflon (Teflon, 0.2-µm, Gelman and Zefluor, 0.5-µm, Gelman); polyester (0.4-µm, Nuclepore); polypropylene (0.2-µm, Gelman); mixed cellulose ester (MCE) (Type AA, 0.8-µm, Millipore); polycarbonate (0.4-µm, Poretics); polyvinylchloride (PVC, 5-µm, Nuclepore and VM-1, 5-µm, Gelman); nylon (Nylaflo, 0.45-µm, Gelman); and glass fiber (Type A/E, Gelman). Filters were tested for use as prefilters by placing the filter in the front stage of a 3-piece cassette and a silver filter in the last stage (Figure 3). An atmosphere of Cl_2 (~2 mg/m^3) was sampled at 1 L/min for 15 min. 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 analytical procedure, and the results compared with those of samplers without a prefilter (Table 1). 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 min.

Table 1. Summary of prefilter study

Prefilter	RH[a]	Cl_2 on prefilter (%)	Total Cl_2 found[b] (%)	Acceptance Criteria: 2% or less on prefilter[c]	Acceptance Criteria: recovery of 100 ± 5%[c]
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
Teflon	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/m^3

[c] P = pass; F = fail

[d] Prefilter not evaluated at low humidity

Silver filter evaluation

Test atmosphere generator

All tests on the silver filters were done using active generation. The halogen gas generator was a dynamic flow system shown schematically in Figure 4. All components exposed to the test atmosphere were constructed of Teflon or glass.

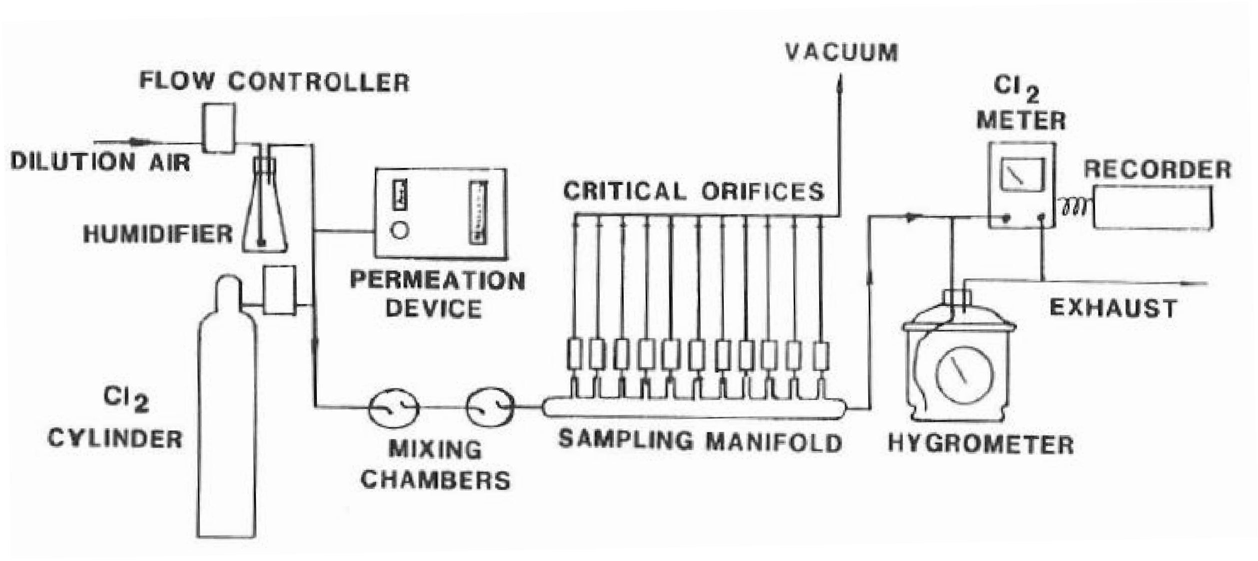

Figure 4. Halogen gas generation system

The source of Cl_2 was a compressed gas cylinder (Scott Specialty Gases, Troy, MI) containing a mixture of 49 ppm Cl_2 in nitrogen (in a few preliminary experiments the Cl_2 source was a permeation tube). The Br_2 source was a permeation tube (VICI Metronics, Santa Clara, CA) maintained at 30 °C in a Dynacalibrator Model 340 permeation tube oven (VICI Metronics, Santa Clara, CA). The permeation tube had an emission rate of 6.06 µg/min at 30 °C in a carrier flow of 0.299 L/min. The emission rates of Br_2 source permeation tubes were verified by determining their weight loss over time. The resulting output (20.3 mg/m^3) entered the mixing chamber where it was diluted with air to concentrations of 0.07 to 1.4 mg/m^3.

The dilution air and the test gas, which were regulated by mass flow controllers (Tylan Corp., Torrence, CA), passed through two mixing chambers to ensure homogeneity. The test gas mixture then passed through an eleven-port sampling manifold at flow rates of roughly 10 to 15 L/min, depending on the volume of dilution air required to produce a given concentration. Sampling rates were controlled by critical orifices at nominal rates of 0.3 and 1 L/min. Halogen samples were collected at flow rates of 0.3 L/min for TWA exposures and at 1 L/min for STEL exposures. 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, CA) interfaced with a strip chart recorder (Model 056, Hitachi, Ltd., Tokyo, Japan).

The Interscan Chlorine Meter was calibrated by means of a 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 to 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 Cl_2 meter responded to Br_2 at approximately one tenth of the response to Cl_2.

Except for the electronic components and the compressed gas cylinder, the generator was placed in a fume hood for reasons of safety.

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, [11] 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 [12], which uses a midget bubbler containing a 0.1% sulfamic acid solution.

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 (see silver sorbent selection). Silver filters were cleaned and then stored under three separate conditions: (1) assembled in the cassettes, where light is excluded; (2) separated by paper disks and returned to the manufacturer's package, where air and light are 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 (~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%. Filters stored in the plastic bag had a 94.1% recovery, but those stored in the cassettes had the poorest recovery at 88.1%. The reason for this was 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% confidence level, the recommended long-term storage mode for cleaned silver filters is to repack them between paper disks in the manufacturer’s container, because recovery from this mode of storage was essentially complete.

Desorption and sample analysis

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 min. 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 2.

Table 2. IC Conditions

Columns	Dionex AS4A, AG4A, MFC-1
Suppressor	AMMS Anion Micromembrane
Detector	Conductivity
Sensitivity	10 µS full scale
Eluent	0.25 m*M* $NaHCO_3$/4 m*M* Na_2CO_3/0.78 m*M* p-Cyanophenol at 2 mL/min
Injection Vol.	50 µL

Column Maintenance.

The silver thiosulfate anion, $Ag(S_2O_3)_2^{3-}$, produced in the desorption process has a strong affinity for the stationary phase of the exchange resin and can only be eluted using very strong eluents. 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) and is likely to dissociate under the chromatographic conditions used, 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 only 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 to 150 analyses.

Breakthrough and capacity of silver filters

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. 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 backup 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 backup samplers.

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/m^3 (1.5 x OSHA PEL), at low RH 3 mg/m^3 (1 x 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 3). At high RH (~80%), however, a dramatic increase was seen. The breakthrough volume was reported to be 1150 L and the capacity reported to be 2681 µg. These values do not match each other for a reported challenge concentration of 4.5 mg/m^3. However, the breakthrough volume is clearly increased at the higher RH. 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 h of sampling. The maximum sample volume is calculated as: maximum volume = 0.667 x observed mass capacity ÷ PEL. This calculation was done using the capacity of the silver filter at low RH, as that was the more limiting condition. Thus, for Cl_2: Maximum Sampling Volume (L) = 0.667 x (198 µg) ÷ PEL (2.9 µg/L) = 46 L (rounded to 45 L); and for Br_2: Maximum Sampling Volume (L) = 0.667 x (355 µg) ÷ PEL (0.653 µg/L) = 363 L (rounded to 360 L). Therefore, the maximum sample volume is 45 L for Cl_2 and 360 L for Br_2.

The upper limit for the working range of air concentrations for a given sampling volume can be calculated be rearrangement of this same equation:

Upper limit of the working range (mg/m^3) = (0.667 x observed mass capacity)/sampling volume

For Cl_2: Upper limit of the working range for 45 L sampling volume = (0.667 x 198 µg)/45 L = 2.93 mg/m^3

For Br_2: Upper limit of the working range for 360 L sampling volume = (0.667 x 355 µg)/360 L = 0.658 mg/m^3

Table 3. Breakthrough volume and capacity of silver filters

	Bromine[a]		Chlorine[b]	
Humidity	High	Low	High	Low
Concentration (mg/m^3)	1.4	5.6	4.5	3
Concentration level (x 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

The data in Table 3 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 [13]. 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 [3], the resulting hypohalous acid may then oxidize the Ag, as illustrated by the following reactions for Cl_2.

$Cl_2 + H_2O = HOCl + HCl$ (5)
$2Ag + HOCl = Ag_2O + HCl$ (6)
$Ag_2O + 2HCl = 2AgCl + H_2O$ (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.

Storage Stability

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 ambient (25 °C) and refrigerated (5 °C) 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 min. Br_2 samples were collected at 0.3 L/min for 30 min.

Recoveries are expressed as percentage of the mean concentration for samples analyzed on day 1. Chlorine recoveries were 103 ± 4% for 30-day ambient storage (n=4), 101 ± 3% 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% (n=3). Bromine recovery after 30 days was 99.4 ± 5.5% (n=5) and after 60 days was 99.2 ± 10.1% (n=6). Therefore, samples are stable at ambient temperature for at least 30 days (Cl_2) or 60 days (Br_2) and probably longer.

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 to 98.2%. Likewise, bromine-containing particulates (bromides and bromates) do not interfere with Br_2, as shown by recoveries of 93.9 to 100.5%.

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 x 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% (Table 4).

Table 4. Effect of Hydrogen Sulfide on chlorine recovery

Sampling order		RH	n	Cl_2 Concentration (mg/m^3)	Cl_2[a] Recovery (%)
1st	2nd				
H_2S[b]	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] Based on Cl_2 concentration of 0.354 mg/m^3
[b] H_2S concentration = 14 mg/m^3

However, when H_2S was sampled after Cl_2, losses were from 36% at low RH to 61% 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.

$$2AgCl + H_2S = Ag_2S + 2HCl \qquad (8)$$

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 [14]. Accordingly, H_2S is a negative interference.

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 1). ClO_2 was generated by passing Cl_2 through a concentrated solution of sodium chlorite (4.42 mM $NaClO_2$) in a bubbler [15].

$Cl_2 + 2NaClO_2 = 2ClO_2 + 2NaCl$ (9)

Samples were collected on silver filters and reference bubblers for time periods of 15, 30, and 60 min at concentrations equivalent to 3 and 4.5 times the OSHA PEL for ClO_2. The bubblers contained 15 mL of a buffer solution (0.25 mM $NaHCO_3$/4 mM Na_2CO_3/0.78 mM p-cyanophenol). The silver filters contained no ClO_2; however, the backup bubblers that were used with the 30-min samples contained approximately 86% of the 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 were also tested as interferences. 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.

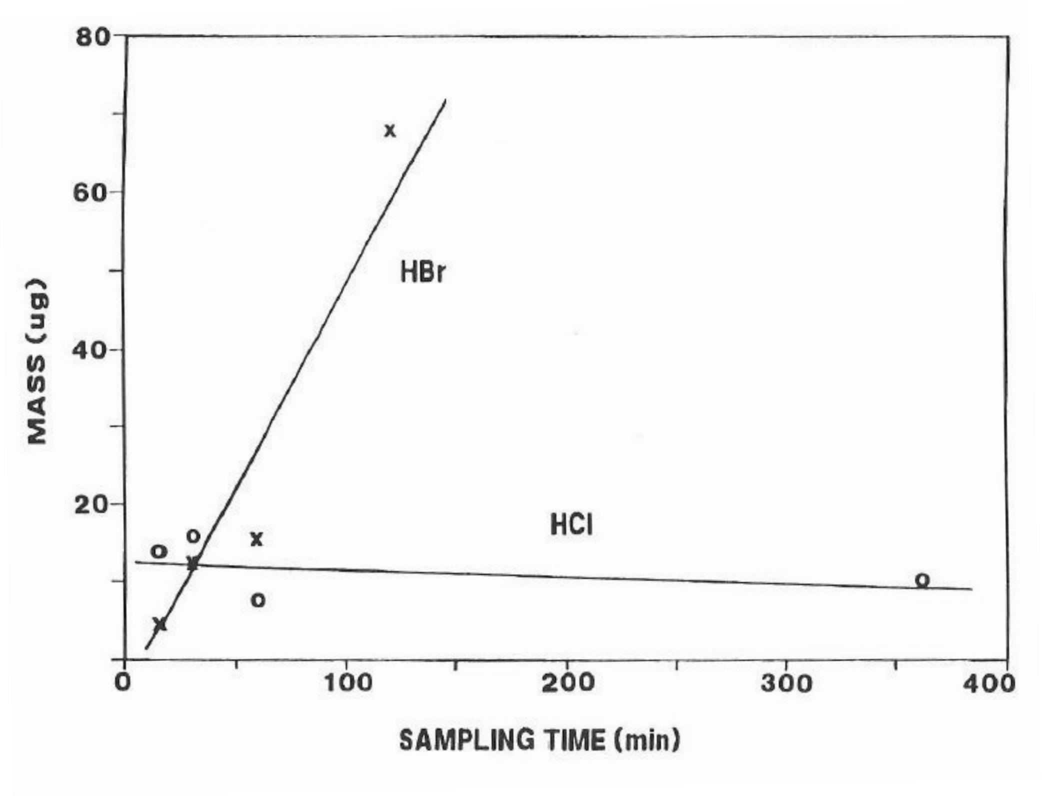

Figure 5. Effect of sampling time on mass of HBr and HCl collected by silver filters

Approximately 15 µg of HCl were collected by the filter within the first 15 min of sampling and this mass remained constant for up to 16 h. 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 using NIOSH Method 7907 [16].

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 [4]. 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 [3].

$Ag_2O + HX = AgX + AgOH$ (10)
$AgOH + HX = AgX + HOH$ (11)

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) (This method is no longer recommended for use but is referenced here as it was used in this method development) [17]. (Note: When silica gel tubes were used to sample atmospheres of Cl_2 and Br_2, they collected approximately 30% 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.) Recovery of HBr was 46% for filters aged 1 day, 68% for 14 days, and 89% for 30 days aging. These data suggest that oxidized silver was the basis for the reaction with hydrogen halides. 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% 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 (Eqs. 12 & 13), and then it reacts with AgX [3].

$AgX + HX = H^+ + (AgX_2)^-$ (12)
$(AgX_2)^- + HX = H^+ + (AgX_3)^{2-}$ (13)

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 [18]. 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.

Method validation

Accuracy and precision

Samples were generated at concentration levels of 0.1, 0.5, 1, and 2 x 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, sampled for 15 min at 1 L/min, was 98.6% (96.2% at high RH and 101% at low RH). The sampling and analytical precision, the pooled relative standard deviation (s_r), was 6.7% for both high and low RH data (Tables 5 & 6). The estimate of the total coefficient of variation (CV_T), including 5% pump error, was 7.5%.

Table 5. Method validation for chlorine at high humidity (~80%)

Concentration Level (x PEL)	n	Concentration taken[a] (mg/m^3)	Concentration found (mg/m^3)	s_r	Recovery (%)
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 = 96.2%; Precision (pooled s_r) = 0.067

[a]Concentration determined from generator source and dilution flows where sampling rate=1 L/min and sampling time=15 min.

Table 6. Method validation for chlorine at low humidity (~20%)

Concentration Level (x PEL)	n	Concentration taken[a] (mg/m^3)	Concentration found (mg/m^3)	s_r	Recovery (%)
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 = 101%; Precision (pooled s_r) = 0.067

[a]Concentration determined from generator source and dilution flows where sampling rate=1 L/min and sampling time=15 min.

The mean recovery for Br_2, sampled for 4 hr at 0.3 L/min, was 98.8% (96.1% and 102% for high and low RH, respectively). The sampling and analytical precision was slightly better for low RH at 3.2% over 5.8% at high RH (Tables 7 & 8), and the CV_T estimate was 6.9%.

Table 7. Method validation for bromine at high humidity (~80%)

Concentration Level (x PEL)	n	Concentration taken[a] (mg/m^3)	Concentration found (mg/m^3)	s_r	Recovery (%)
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 = 96.1%; Precision (pooled s_r) = 0.058

[a]Concentration determined from generator source and dilution flows where sampling rate=0.3 L/min and sampling time=4 hr.

Table 8. Method validation for bromine at low humidity (~20%)

Concentration Level (x PEL)	n	Concentration taken[a] (mg/m^3)	Concentration found (mg/m^3)	s_r	Recovery (%)
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 = 102%; Precision (pooled s_r) = 0.032

[a] Concentration determined from generator source and dilution flows where sampling rate=0.3 L/min and sampling time=4 hr.

All data were within the accuracy criterion of ±25% at the 95% confidence level and coefficient of variation (precision) recommended for a valid NIOSH method [10]. Bartlett's test for homogeneity was applied to the data before pooling. The mean recovery for the overall method (Cl_2 and Br_2) was 98.7% (-1.3% bias) with a sampling and analytical precision of 5.2%, and a total coefficient of variation estimate (CV_T) of 7.2%.

Instrument LOD/LOQ and linear range

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 [9]. The LOD of Cl^- in the thiosulfate matrix was 0.06 µg/mL with a limit of quantitation (LOQ) of 0.19 µg/mL. For Br^-, the LOD and LOQ were 0.16 and 0.54 µg/mL, respectively. The linear range for Cl^- at the sensitivity setting used in this work (10 µS) was 0.05 to 5 µg/mL, and for Br^-, 0.20 to 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. Similarly, the linear range can be extended at the upper end by using a less sensitive instrumental setting or by diluting the sample.

The lower limit for the working range of air concentrations for a given sampling volume can be calculated based on the limit of quantitation (LOQ) of the analytical method and the liquid sample volume. The lower limit for the working range of air concentrations (mg/m^3) for a given sampling volume = LOQ (µg/mL) x liquid sample volume (mL) ÷ air sample volume (L):

For Cl_2: Lower limit of the working range for 45 L sampling volume = 0.19 µg/mL x 10 mL ÷ 45 L = 0.04 mg/m^3.

For Br_2: Lower limit of the working range for 360 L sampling volume = 0.54 µg/mL x 10 mL ÷ 360 L = 0.015 mg/m^3.

Cl_2 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) [12] were collected at rates of 0.5 and 1.0 L/min, respectively. The results are presented in Table 9.

Table 9. Chlorine field study results using paired silver filters and bubbler[a] samples

Pair number	Sampler numbers	Air volume (L)	Mass Cl_2 (µg)	Concentration (mg/m^3)	Difference[b] (mg/m^3)
1	Filter – 1	189	134	0.71	0.10
1	Bubbler – 1	377	230	0.61	
2	Filter – 3	211	122	0.578	0.12
2	Bubbler – 4	305	140	0.459	
3	Filter – 13	167	368	2.20	-0.02
3	Bubbler – 11	239	530	2.22	
4	Filter – 11	157	257	1.64	-0.10
4	Bubbler – 13	270	470	1.74	
5	Filter – 10	152	41.4	0.272	0.14
5	Bubbler – 12	313	43.0	0.137	
6	Filter – 4	218	460	2.11[c]	
6	Bubbler – 2	361	1700	4.71	
7[d]	Filter – 2	185	11.5	0.062	
7[d]	Bubbler – 3	342	4.8	0.014	
8[d]	Filter – 12	158	ND[e]	ND[e]	
8[d]	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

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 to 5 was 0.048 mg/m^3. When a paired t-test for determining differences in paired observations [19] was applied to these data, the results showed that the difference between the two monitoring methods was not statistically significant at the 95% 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.

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