CHLORINE IN WORKPLACE ATMOSPHERES

Method Number:	ID-101
Matrix:	Air
OSHA Permissible Exposure Limits: Final Rule Limits	1 ppm Chlorine (Short-Term Exposure Limit) 0.5 ppm Chlorine (Time Weighted Average)
Transitional Limit	1 ppm Chlorine (Ceiling)
Collection Device:	A calibrated personal sampling pump is used to draw a known volume of air through a midget fritted glass bubbler containing a 0.1% sulfamic acid solution.
Recommended Sampling Rate:	1 L/min
Recommended Air Volumes Short-Term Exposure Limit: Time Weighted Average:	 15 L 240 L
Analytical Procedure:	An aliquot of the sulfamic acid solution is added to a buffered potassium iodide solution. Any chlorine contained in the first solution oxidizes the potassium iodide to iodine which is then measured with a residual chlorine ion specific electrode.
Detection Limit: Qualitative	 0.014 ppm (15-L air sample)
Quantitative	0.14 ppm (15-L air sample)
Precision and Accuracy: Validation Level:	 0.56 to 2 ppm (15-L air sample)
CV_T	0.03
Bias	-0.006
Overall Error	±6.6%
Classification:	Validated Method
Chemists:	Steven Edwards, James Ku
Date (Date Revised):	1982 (May, 1991)

Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

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1. Introduction

This method describes the collection and analysis of airborne chlorine in the workplace. It is applicable for both short-term (STEL) and time weighted average (TWA) exposure evaluations.

1.1 History

Chlorine was previously determined using o-tolidine (8.1). The previous OSHA sampling method for chlorine was to capture it in a dilute o-tolidine/hydrochloric acid solution and then analyze the sample using a calorimetric procedure. This method was used as a field test to immediately determine atmospheric chlorine concentrations. Due to problems associated with interferences, instability, and hazards associated with the collecting media, this method is no longer used by OSHA. Another method which utilized the ability of chlorine to bleach an acidic methyl-orange solution had been reported (8.2); however, without any modifications the method was too sensitive for concentrations pertinent to industrial hygiene applications. Sample instability and significant interferences were also noted.

A method was developed by OSHA during the early 1980s which collected chlorine in a sulfamic acid solution and samples were analyzed using an ion specific electrode technique. The sulfamic acid collection and residual chlorine ion specific electrode (RCE) analysis has been evaluated (8.3) and has shown an acceptable level of precision and accuracy for the determination of chlorine in workplace atmospheres. Another evaluation by an independent laboratory has also been conducted (8.4).

1.2 Principle

The sampling method is based on a previous report of chlorine collection in sulfamic acid solutions (8.5). The analytical method is based on iodometric measurements of chlorine using a RCE. An iodide and a buffer reagent are added to the sulfamic acid-chlorine sample and the iodide reacts completely with the chlorine to form iodine:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

The iodine concentration formed after the reaction is indirectly measured by the RCE and is equal to the chlorine concentration before reaction. This reaction takes place in an acetic acid/sodium acetate buffer. This buffer provides the optimal pH range for the reaction (8.6).

1.3 Advantages and Disadvantages

1.3.1 This method has adequate sensitivity for measuring workplace concentrations of chlorine contained in the atmosphere.

1.3.2 No sample elution or desorption is required because the sample is collected in a liquid medium.

1.3.3 Collected samples are stable for at least 30 days before analysis.

1.3.4 The analytical equipment is inexpensive.

1.3.5 One disadvantage of this method is the use of a liquid in midget fritted glass bubblers (MFGB) to collect samples. Spillage or breakage can occur if precautions are not taken.

1.4 Properties (8.2, 8.7)

Chlorine (CAS No. 7782-50-5) is a greenish-yellow gas with an irritating odor. Some physical properties of chlorine are:

Atomic Number	17
Atomic Symbol	Cl
Molecular Weight (Cl_2)	70.91
Boiling Point	-33.6 °C
Density	13.546 g/mL (20 °C)
Vapor Pressure	670.8 kPa (6.62 atm) at 20 °C
Color (gas)	yellow-green
Flammability	nonflammable
Solubility (H_2O)	2.26 L of chlorine will dissolve in 1 L of H_2O at 20 °C

Chlorine reacts readily with metals, and by substitution or addition with a wide variety of organic compounds.

1.5 Uses

Chlorine is used primarily as a bleaching agent or for chlorination of various organic compounds. Some industrial operations which have the potential for chlorine exposures are (8.2):

Aerosol propellant makers	Iron detinners
Alkali salt makers	Iron dezinkers
Aluminum purifiers	Laundry workers
Benzene hexachloride makers	Methyl chloride makers
Bleachers	Paper bleachers
Bleaching powder makers	Petroleum refinery workers
Bromine makers	Phosgene makers
Broommakers	Photographic workers
Carpetmakers	Pulp bleachers
Chemical synthesizers	Rayon makers
Calcium chloride makers	Refrigerant makers
Chlorinated solvent makers	Rubber makers
Chlorinated hydrocarbon makers	Sewage treaters
Chlorine workers	Silver extractors
Colormakers	Sodium hydroxide makers
Disinfectant makers	Submarine workers
Dyemakers	Sugar refiners
Ethylene glycol makers	Sulfur chloride makers
Ethylene oxide makers	Swimming pool maintenance workers
Flour bleachers	Tetraethyl lead makers
Fluorocarbon makers	Textile bleachers
Gasoline additive workers	Tin recovery workers
Gold extractors	Vinyl chloride makers
Inkmakers	Vinylidene chloride makers
Insecticide makers	Water treaters
Iodine makers	Zinc chloride makers

2. Working Range and Detection Limits

2.1 Using the iodide reagent as directed in the analytical procedure for chlorine, a linear response up to 20 µg/mL chlorine can be produced when the electrode potential versus log (Cl_2) concentration is plotted (8.6). To bring large concentrations (>20 µg/mL) into the linear working range, these samples can be diluted with 0.l% sulfamic acid solution before any aliquots are reacted with the iodide/buffer reagents.

2.2 Qualitative and quantitative detection limits of 0.01 and 0.1pg/mL, were estimated during validation studies and calculates to 0.25 and 2.5 µg per sample, respectively.

3. Method Performance (8.3)

Validation studies conducted over the concentration range of 0.56 to 2 ppm (15-L air volume) gave an overall pooled coefficient of variation of 0.03, a bias of -0.006, and an overall error of ±6.6%. Overall error was calculated using the equation:

$$OE_i = \pm [|\text{mean bias}_i| + 2CV_i] \times 100\%$$

where i is the respective sample pool being examined.

4. Interferences

Strong oxidizing agents including iodate, bromine, cupric ion, and manganese dioxide have been reported to interfere during analysis (8.6). These agents may react with the KI and produce a positive interference.

It has also been reported that silver and mercuric ion concentrations above 10 to 20 µg/mL in the sampled solution will also interfere with the analysis (8.6) by poisoning the RCE. However, concentrations of this magnitude may be unlikely when sampling for chlorine in the workplace.

Reduced sulfur-containing compounds (i.e. methyl mercaptan, dimethyl sulfide, dimethyl disulfide) and sulfur dioxide have been reported as negative interferences (8.4). These compounds apparently inhibit the recovery of chlorine from the sulfamic acid solution.

Particulate (i.e., hypochlorites, trichloroisocyanuric acid) which may break down to free chlorine in the sulfamic acid solution are a positive interference. Particulate may be excluded from the sulfamic acid solution by using a Teflon prefilter during sampling.

5. Sampling

5.1 Equipment

Note: If the workplace air being sampled is suspected of containing particulate (i.e. sodium hypochlorite, trichloroisocyanuric acid) which may liberate free chlorine in the collection solution, a prefilter as mentioned in Section 5.1.7 should be used.

5.1.1 Collection solution, 0.1% sulfamic acid: Dissolve 1.0 g sulfamic acid in deionized water and dilute to the mark in a 1-L volumetric flask.

5.1.2 Personal sampling pumps capable of sampling within ±5% of the recommended flow rate of 1 L/min are used.

5.1.3 Midget fritted glass bubblers (MFGBs) (25-mL, part no. 7532, Ace Glass Co., Vineland, NJ).

5.1.4 Shipping vials: Scintillation vials, 20-mL, part no. 74515 or 58515, (Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon cap liners. Tin or other metal cap liners should not be used.

5.1.5 A stopwatch and bubble tube or meter are used to calibrate pumps.

5.1.6 Various lengths of PVC tubing are used to connect bubblers to the pumps.

5.1.7 If any particulate may present an interference, a prefilter is attached to each bubbler such that sampled air enters the prefilter first. The prefilter should consist of:

a) Carbon-filled polypropylene cassette, 25-mm diameter, (part no. 300075, Nucleopore Corp., Pleasanton, CA).

b) Filter for particulate collection, PTFE, 0.45 µm pore size, 25-mm diameter (part no. 130620, Nucleopore).

c) Porous plastic support pad, (part no. 220600, Nucleopore).

Assemble the prefilter such that sampled air enters the PTFE filter first and the plastic support pad faces the MFGB.

5.2 Sampling Procedure

5.2.1 Calibrate the sampling pump with a MFGB containing about 10 mL of 0.1% sulfamic acid solution in-line. Also calibrate with a prefilter if necessary.

5.2.2 Place 10 to 15 mL of 0.1% sulfamic acid solution in an MFGB. Connect the MFGB (and prefilter if necessary) to a calibrated sampling pump. If a prefilter is necessary, use a minimum amount of tubing to connect the MFGB and prefilter together. Place the sampling device in the breathing zone of the employee.

5.2.3 Sample at a flow rate of 1 L/min. For STEL determinations, a minimum sampling time of 15 min is recommended.

5.2.4 For measurements of TWA exposures, sample up to 240 min. Take enough samples to cover the shift worked.

5.2.5 Transfer the collection solution into a 20-mL glass scintillation vial. Rinse the bubbler with 2 to 3 mL of fresh sulfamic acid solution and transfer the rinsings into the sample vial. Place the Teflon-lined cap tightly on each vial and seal with vinyl or waterproof tape around

the caps to prevent leakage during shipment. Attach an OSHA 21 seal lengthwise around each vial.

5.2.6 Prepare a blank solution by taking 10 to 15 mL of the sulfamic acid solution not used for collection and transfer to a 20-mL glass vial. Seal the vial as mentioned in Section 5.2.5.

5.2.7 If a prefilter was used, the filter can be submitted for analysis of available chlorine. Immediately after sampling, remove each filter from it's cassette and place in individual vials containing about 5 mL of fresh 0.1% sulfamic acid solution. Also prepare a blank filter/sulfamic acid solution and then seal all vials as mentioned in Section 5.2.5.

5.2.8 Request chlorine analysis on the OSHA 91A form. If prefilters are submitted, request the filters are analyzed for total available chlorine using OSHA stopgap method ID-101-SG.

5.2.9 Ship the samples to the laboratory using appropriate packing materials to prevent breakage.

6. Analysis

6.1 Safety Precautions

6.1.1 Care must be exercised when handling glacial acetic acid. Gloves and face protection should be used. The area where the acid is diluted should be well ventilated (NOTE: Do not vent acetic acid into hoods designated for perchloric acid use). Inhalation of acetic acid vapors should be avoided. The glacial acetic acid should be added to the aqueous solution, thus avoiding any splattering which can occur when water is added to a concentrated acid. If any acid contacts the eyes, skin, or clothes, flush the area immediately with copious amounts of cold water and then seek medical attention.

6.1.2 Care should be exercised when using laboratory glassware. Chipped pipettes, volumetric flasks, beakers, or any glassware with sharp edges exposed should not be used.

6.1.3 Pipetting is always done using a pipetting bulb, never by mouth.

6.2 Equipment

6.2.1 Residual chlorine electrode (Model 97-70, Orion Research Inc., Cambridge, MA).

6.2.2 Millivolt meter, capable of relative mV or concentration readings (Model EA 940 Expandable Ionanalyzer, Orion Research Inc.).

6.2.3 Laboratory glassware including Class A volumetric flasks, pipettes, beakers, graduated cylinders, etc.

6.2.4 Beakers, disposable plastic.

6.2.5 Analytical balance (0.01 mg).

6.3 Reagents - All reagents used should be reagent grade or better.

6.3-1 Deionized water (DI H_20).

6.3.2 Sulfamic acid solution, 0.1%: Dissolve 1.0 g sulfamic acid (NH_2SO_3H) in DI H_20 and dilute to 1 L.

6.3.3 Potassium iodide (KI), 0.5 M: Dissolve 20.75 g KI in DI H_2O and dilute to 250 mL. The solution should be prepared daily.

6.3.4 Buffer reagent, 6.4 M acetic acid/1.8 M sodium acetate: Dissolve 37.1 g sodium acetate in 100 mL of DI H_2O. Add 92 mL of glacial acetic acid and dilute the solution to 250 mL using DI H_2O. This buffer is acidic, having a pH of about 4.7. Prepare monthly.

6.3.5 Stock Solution: Dissolve 0.500 g potassium iodate in DI H_2O and dilute to 500 mL in a volumetric flask. This solution is equivalent to 1,000 µg/mL chlorine. Prepare every 6 months.

6.4 Standard Preparation

6.4.1 Dilute the 1,000 µg/mL stock solution (prepared in Section 6.3.5.) with 0.1% sulfamic acid using dilutions to make 100-, 10-, and 5.0-µg/mL standard solutions.

6.4.2 Working standards are prepared by diluting aliquots of the 100-, 10-, and 5.0-µg/mL standard solutions to the analytical range of 0.2 to 20µg/mL. A dilution scheme is shown below (also see note in Section 6.5.3):

Working Standard (µg/mL)	Standard Solution Aliquot (mL)	Standard Solution Concn (µg/mL)	Final Volume (mL)
0.2	2.0	5.0	50
0.6	3.0	10	50
1.0	5.0	10	50
10.0	5.0	100	50
20.0	10.0	100	50

Prepare the working standards the same day the analysis is performed. Use the following procedure for preparation:

1) An aliquot of the indicated standard solution (either 100-, 10-, or 5.0-µg/mL) is placed into a 50-mL volumetric flask.

2) Add 0.5 mL buffer reagent to the volumetric flask.

3) Add 0.5 mL KI to the volumetric flask and swirl to mix the reagents; allow the solution to react for at least 2 min before proceeding.

4) Dilute theworking standard to volume (50 mL) with 0.1% sulfamic acid solution. Mix thoroughly by inverting the flask several times. Store in a dark environment until the analysis is performed.

6.5 Sample Preparation

Note: If prefilters are submitted for analysis, they should be analyzed for total available chlorine using OSHA stopgap method ID-101-SG.

6.5.1 Collected liquid samples are stable for at least 30 days. Special precautions are not necessary during storage. Analyze samples the same day they are prepared for analysis.

6.5.2 Measure and record each sample volume received.

6.5.3 Place an aliquot of each sample solution into a separate 50-mL volumetric flask. It is recommended to take the majority of the solution for those air samples having less than 60-L air volumes (i.e. STEL or ceiling samples).

If necessary, a duplicate analysis can be conducted using the remaining aliquot; however, sensitivity may be significantly decreased.

Note: A "dilution" effect has been noted in the literature (8.8) and may result in a net decrease of analyte formed after reaction with KI. This effect is apparently caused by differences in pH of the sample or standard. Standards and samples should be matrix matched using 0.1% sulfamic acid. The volume of the aliquot taken may also alter the pH (for further information see reference 8.8). A significant "dilution" effect was not noted when standards and samples were prepared and diluted with 0.l% sulfamic acid, and the aliquot volumes were kept below 15 mL (8.9).

6.5.4 React each aliquot with KI and prepare for analysis using the following steps:

1) Add 0.5 mL buffer reagent to the volumetric flask.

2) Add 0.5 mL KI to the volumetric flask and swirl to mix; allow the solution to react for at least 2 min before proceeding.

3) Dilute the sample to volume (50 mL) using 0.1% sulfamic acid solution. Mix thoroughly by inverting the flask several times. Store in a dark environment until the analysis is performed.

6.6 Analytical Procedure

6.6.1 Set up the millivolt meter according to the Standard Operating Procedure (8.10) or manufacturers' guidelines.

6.6.2 Place the electrode into a disposable plastic beaker containing 1.0-µg/mL standard solution. Allow the electrode to stabilize (approximately 3 min) and then record the mV reading. Remove the electrode from the standard solution, rinse with DI H_2O, and blot dry. Place the electrode into a 10-µg/mL solution and record the mV reading. The difference between the 1.0- and 10-µg/mL standard should be approximately 29 mV.

6.6.3 Analyze the standards and samples according to the SOP (8.10.). Take a fresh aliquot from the volumetric flasks and prepare as mentioned in Section 6.4 each time a standard is analyzed. Using a relative reading of 0 mV for the 1 µg/mL standard and equipment mentioned in Section 6.2, typical standard readings and differences in mV values are shown below:

Std, µg/mL	mV Reading
20.00	35.00
10.00	29.00
1.00	0.00
0.50	-11.00
0.20	-20.00

Note: For the 1 µg/mL standard, a relative mV setting of zero was used. Absolute readings may be different.

6.6.4 Always rinse the residual chlorine electrode with DI H_2O and blot dry with a clean dry tissue before placing it in the next solution to be analyzed.

6.6.5 Analyze a standard in the concentration range of the samples after every fourth or fifth sample and at the end of the analysis. If a sample reading indicates the concentration is greater than the largest standard, dilute the unreacted sample to bring the concentration within the analytical range:

1) take an aliquot from the remaining unreacted sample,

2) dilute with sulfamic acid, and

3) follow the procedure described in Section 6.5.4.

Do not dilute any reacted samples into the analytical range.

7. Calculations

7.1 Determine the roral µg/mL chlorine content of each sample and blank using a concentration-response regression curve if readings were measured in concentration units. If mV readings were taken, plot the log(concentration) versus the mV readings and determine µg/mL chlorine for each sample and blank.

7.2 The total µg chlorine for each sample or blank is calculated as:

$$\mu g\ \text{Chlorine} = \frac{\mu g/mL\ \text{Chlorine} \times \text{Sample Volume, mL} \times 50\ mL}{\text{Aliquot taken, mL}}$$

where:
µg/mL Chlorine = From curve (Section 7.1)

7.3 Each sample is blank-corrrected and the air concentration is calculated to determine chlorine exposure using the following equation:

$$\text{ppm Chlorine} = \frac{MV \times (\mu g\ \text{Sample} - \mu g\ \text{Blank})}{\text{Molecular Weight} \times \text{Air Volume, L}}$$

where:

MV (Molar Volume) = 24.45 (25 °C and 760 mmHg)
Molecular Weight (Cl_2) = 70.91

7.4 Reporting Results

Results are reported to the industrial hygienist as ppm chlorine.

8. References

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Chlorine

OSHA Method ID-101 Backup | Revised May 1991

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Introduction

The OSHA sampling and analytical method for chlorine is discussed in Reference 9.1. The principle of sampling is described in Reference 9.2. The analytical procedure is based on an iodometric technique, which uses a residual chlorine electrode (RCE) for detection (9.3). The validation of the chlorine method consisted of the following experimental studies:

1. Analysis of a total of eighteen samples (six samples at each of the three test levels) which were prepared by adding known amounts of standardized chlorine solution to 0.1% sulfamic acid collecting solution.

2. Analysis of a set of eighteen samples (six samples at each of the three test levels) collected from dynamically generated test atmospheres at approximately 0.5, 1, and 2 times the OSHA Permissible Exposure Limit (PEL) of 1 ppm.

3. Determination of the collection efficiency of the 0.1% sulfamic acid sampling solution.

4. Determination of potential breakthrough when sampling.

5. Determination of the storage stability over 30 days for collected samples.

6. Comparison with an independent method.

7. Assessment of the method.

The details with respect to each of these items are discussed in the following sections. All experiments were based on the ability of the method to collect and analyze a 15-L air sample for each concentration tested. The sample preparation and analytical technique used during the method evaluation follow that described in Reference 9.4. A revised method (9.1) is also available.

Note: The revised version of the method (9.1) differs in one major point from Reference 9.4: Preparation of samples and standards for analysis. It is now recommended to prepare samples and standards in 0.1% sulfamic acid solutions rather than the deionized water previously used (9.5).

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1. Generation

A dynamic standard generator (Model 350, Analytical Instrument Development Inc., Avondale, PA) was used for generating test atmospheres of chlorine. The system is further described in Reference 9.6. Two chlorine permeation vials were used as the chlorine source. The permeation vials were maintained at a constant temperature of 30 ± 0.1°C. The chlorine concentration was determined from the weight loss of the permeation vial over a measured time period and was calculated according to the equation listed in Appendix A. After the chlorine was produced it was then diluted with tempered air so that a controlled concentration at 80% RH and 25°C was achieved. Flow rates for the generation system were measured with a soap bubble flow meter to accurately determine dilution and the final concentration of the gas.

Samples were taken from a glass-sampling manifold, which was attached to the generation system. The majority of samples were collected in sets of six at one of three concentrations, about 0.5, 1, or 2 ppm chlorine.

2. Analysis

Procedure: Samples containing 0.1% sulfamic acid were spiked with standardized chlorine solutions. This test determined the precision and accuracy of the analysis portion of the method.

Results: The results are shown in Table 1. Average analytical recovery was 96.7% and the coefficient of variation (CV1) was 0.03 for the three sets of spiked samples.

3. Sampling and Analysis

Procedure: Samples were collected in 0.1% sulfamic acid solutions at three different chlorine concentrations using the generation system described in Section 1. Midget fritted glass bubblers (MFGB) were used to disperse the air samples in the sulfamic acid solutions. This test determined the precision and accuracy of the sampling and analysis portion of the method.

Results: Sampling and analysis data are presented in Table 2. The NIOSH Statistical Protocol (9.7) developed for evaluation of methods under the Standards Completion Program (SCP) was used as a guide for the determination of precision and accuracy from this data. The precision for this method using these statistical procedures is:

$$CV1 = 0.03 \qquad CV2 = 0.03 \qquad CVT = 0.03$$

The average recovery for sampling and analysis over all levels was 99.4%. Any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. The Bartlett's test for homogeneity of variances and an outlier test (9.7) were applied to this data. The sampling and analysis data passed the Bartlett's test, indicating the CVs could be pooled for all sets of generated samples. One data point in the third set (2 × PEL, n=5) was rejected as an outlier.

4. Collection Efficiency

Procedure: The collection efficiency (CE) of MFGBs containing 0.1% sulfamic acid was assessed. A chlorine concentration of approximately 2 ppm was generated and samples were collected in series using the MFGBs. A flow rate of 1 L/min and a 15-min sampling period were used. The amount of chlorine collected in each of the two bubblers connected in series was measured.

Results: The results are shown in Table 3. The CE of the single bubbler was determined to be 1.00; therefore, a recovery correction or sampling train is not necessary.

5. Breakthrough

Procedure: Breakthrough is defined as the time the effluent concentration in a second bubbler (containing 0.1% sulfamic acid) connected in series reaches 5% of the concentration of the test gas mixture. A test for breakthrough was conducted at about 2 ppm and at a 1 L/min sample collection flow rate. A sample set consisting of two bubblers in series was used to collect samples for each time interval listed: 15, 30, 60, 120, 180, and 240 min.

Results: No breakthrough occurred at this flow rate, during these sampling times, or at the concentration tested. The results are given in Table 4.

6. Storage Stability

Procedure: A study was conducted to assess whether chlorine samples collected at the 1 ppm PEL could be successfully stored in the 0.1% sulfamic acid collection solution. After sample collection using MFGBs, samples were transferred into 20-mL vials, capped with Teflon-lined caps, and stored at ambient laboratory temperatures in a dark environment for 1, 5, 15, or 30 days before analysis.

Results: Samples analyzed after 30 days were found to be within 3% of those analyzed immediately. Thus, storage does not represent a source of bias that would need to be corrected in the method. Storage stability data are presented in Table 5.

7. Independent Method (Analytical)

An independent volumetric method (9.8) involving a thiosulfate titration was used to determine the concentration of chlorine used for spiking. Chlorine gas was generated at a theoretical concentration which would give a chlorine concentration of 21.70 µg/mL in a specified volume of sulfamic acid. This value was calculated using the equation given in Appendix A. The gas was collected in 0.1% sulfamic acid solution which was then used as a chlorine stock solution for spiked samples (Section 2). All other samples were taken using the generation system. Analyses of the stock solution were performed using the RCE and the thiosulfate titration methods. The following results were obtained:

Method	Chlorine (µg/mL)
Titration	20.45
RCE	20.92

The average value of 20.69 µg/ml from both methods was used as the stock solution concentration for the spiked samples mentioned in Section 2.

8. Conclusions

This sampling and analytical method has been shown to be precise and accurate at exposures near the OSHA PEL of 1 ppm when using 15-L air volumes. Breakthrough or storage stability do not pose significant problems under the conditions tested.

The development and evaluation of this method took place when the OSHA PEL for chlorine was a Ceiling value (15-min samples were taken). Although long-term samples were only taken during breakthrough studies, the data appears to indicate the method is capable of taking samples for chlorine TWA assessments. Two 4-h samples are recommended for TWA determinations of chlorine. When considering the amount of chlorine collected (as mass), any samples taken near the TWA PEL of 0.5 ppm will have slightly larger mass concentrations of chlorine than those tested for this evaluation. In addition, during the evaluation, no breakthrough was noted after 240 minutes of sampling and collection efficiency was excellent after 15 minutes of sampling. Both of these experiments were conducted at approximately 4 times the TWA PEL of 0.5 ppm.

9. References

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Table 1
Analysis - Chlorine

0.5 × PEL*			1 × PEL*			2 × PEL*		
µg Taken	µg Found	AMR	µg Taken	µg Found	AMR	µg Taken	µg Found	AMR
20.7	18.3	0.88	62.1	54.0	0.87	103.5	108.8	1.05
20.7	17.8	0.86	62.1	57.0	0.92	103.5	107.8	1.04
20.7	17.5	0.84	62.1	60.1	0.97	103.5	111.8	1.08
20.7	18.0	0.87	62.1	60.4	0.97	103.5	114.3	1.10
20.7	18.1	0.87	62.1	59.9	0.96	103.5	114.5	1.11
20.7	18.1	0.87	62.1	62.4	1.00	103.5	111.3	1.07
N		6			6			6
Mean		0.87			0.95			1.08
Std Dev		0.01			0.05			0.03
CV1		0.02			0.05			0.02

* PEL of 1 ppm chlorine (for a calculated 15-L air volume)

AMR = Analytical Method Recovery (Found/Taken)

CV1 Pooled = 0.03

Average AMR = 0.967

Table 2
Sampling and Analysis - Chlorine

Test Level	- - - - - - - - - - Found - - - - - - - - - -				Taken	
	µg	Liters	mg/m3	ppm	ppm	% Recovery
0.5 × PEL *						
1	27.9	15.6	1.79	0.62	0.56	110.7
2	27.5	15.2	1.81	0.62	0.56	110.7
3	26.1	14.5	1.80	0.62	0.56	110.7
4	25.4	14.8	1.72	0.59	0.56	105.4
5	23.7	15.0	1.58	0.54	0.56	96.4
6	24.9	14.9	1.67	0.58	0.56	103.4
			N	6		
			Mean	0.60		106.2
			Std Dev	0.03		
			CV2	0.054		
1 × PEL *						
1	72.1	19.2	3.76	1.29	1.25	103.2
2	68.5	19.0	3.61	1.24	1.28	96.9
3	68.5	18.9	3.62	1.25	1.29	96.9
4	68.0	18.9	3.60	1.24	1.27	97.6
5	66.3	18.8	3.53	1.21	1.27	95.3
6	64.8	18.5	3.50	1.21	1.27	95.3
			N	6		
			Mean	1.24		97.5
			Std Dev	0.03		
			CV2	0.024		
2 × PEL *						
1	79.2	14.7	5.39	1.86	1.99	93.5
2	79.2	14.5	5.46	1.88	1.98	94.9
3	80.8	14.9	5.42	1.87	1.98	94.4
4	82.4	15.0	5.49	1.89	1.98	95.5
5	81.4	15.0	5.43	1.87	1.98	94.4
			N	5		
			Mean	1.87		94.5
			Std Dev	0.01		
			CV2	0.006		

* PEL of 1 ppm chlorine (15-L air volume)

CV1 Pooled = 0.03

Average Recovery = 99.4%

CV2 Pooled = 0.03, CVT Pooled = 0.03

Table 3
Collection Efficiency - Chlorine

Sample Number	- - - - - - - - µg found - - - - - - - - First Bubbler	Second Bubbler	Collection Efficiency
1	79.2	ND*	1.00
2	79.2	ND	1.00
3	81.2	ND	1.00
4	83.3	ND	1.00
5	82.0	ND	1.00
6	74.6	ND	1.00

* Based upon a detection limit of 0.01 µg/mL

Table 4
Breakthrough - Chlorine

Time (min)	- - - - - - - - µg found - - - - - - - - First Bubbler	Second Bubbler	% Breakthrough
15	78.10	ND*	0
30	157.48	ND	0
60	325.42	ND	0
120	642.39	ND	0
180	909.29	ND	0
240	1,025.24	ND	0

*Based upon a detection limit of 0.01 µg/mL
Bubblers were connected in series and the flow rate was about 1 L/min

Table 5
Stability Test - Chlorine

	- - - - - - - - - - - - Found - - - - - - - - - - - -				Taken	
Sample	µg	Liters	mg/m3	ppm	ppm	% Recovery
1 Day						
1	72.1	19.2	3.76	1.29	1.25	103.2
2	68.5	19.0	3.61	1.24	1.28	96.9
3	68.5	18.9	3.62	1.25	1.29	96.9
4	68.0	18.9	3.60	1.24	1.27	97.6
5	66.3	18.8	3.53	1.21	1.27	95.3
6	64.8	18.5	3.50	1.21	1.27	95.3
			N	6		
			Mean	1.24		97.5
			Std Dev	0.03		
			CV2	0.024		
5 Days						
1	69.8	18.8	3.71	1.28	1.27	100.8
2	72.4	18.5	3.91	1.35	1.27	106.3
3	70.8	19.0	3.73	1.28	1.27	100.8
4	72.9	18.5	3.94	1.36	1.27	107.1
5	76.0	18.7	4.06	1.40	1.27	110.2
6	73.4	18.8	3.90	1.34	1.27	105.5
			N	6		
			Mean	1.34		105.1
			Std Dev	0.05		
			CV2	0.035		
15 Days						
1	61.5	19.0	3.24	1.11	1.27	87.4
2	66.3	18.3	3.62	1.25	1.27	98.4
3	67.7	18.2	3.72	1.28	1.27	100.8
4	60.1	18.2	3.30	1.14	1.27	89.8
5	63.4	17.9	3.54	1.22	1.27	96.1
6	65.4	18.2	3.59	1.24	1.27	97.6
			N	6		
			Mean	1.21		95.0
			Std Dev	0.07		
			CV2	0.055		
30 Days						
1	62.3	18.1	3.44	1.19	1.27	93.7
2	65.0	18.3	3.55	1.22	1.27	96.1
3	62.9	18.4	3.42	1.18	1.27	92.9
4	62.9	18.3	3.44	1.18	1.27	92.9
5	62.5	18.1	3.45	1.19	1.27	93.7
6	65.5	18.2	3.60	1.24	1.27	97.6
			N	6		
			Mean	1.20		94.5

	Std Dev	0.02
	CV2	0.020

Appendix A

Calculation of Generated Concentrations from Permeation Tubes (9.6)

The calculation of chlorine concentration in the generation system was obtained using the following equation:

$$C = \frac{(R \times k)}{f}$$

Where:

C = Concentration in ppm (vol/vol)
R = Permeation or diffusion rate (ng/min)
f = Total gas flow rate (mL/min)
k = Constant (nL/ng)

The permeation or diffusion rate (R) for commercial permeation or diffusion tubes is usually given by the manufacturer or can be determined by weight loss over an extended period. The constant (k) is the reciprocal density and is calculated as follows:

$$k = \frac{(22.4) \times (T + 273) \times (760)}{MW \times 273 \times P}$$

Where

22.4 = molar gas volume at 760 mmHg and 0°C

MW = molecular weight of material used in permeation or diffusion device

T = Temperature (°C)

P = Pressure (mmHg)

Note: T and P are the temperature and pressure at which f is measured and not necessarily the temperature and pressure at which the chamber oven is operating.