Chlorine Dioxide

Method Number:	ID-202
Matrix:	Air
OSHA Permissible Exposure Limits	
Final Rule Limits:	0.1 ppm Time Weighted Average (TWA) 0.3 ppm Short-Term Exposure Limit (STEL)
Transitional Limit:	0.1 ppm TWA
Collection Device:	An air sample is collected using a calibrated sampling pump and a midget fritted glass bubbler. The bubbler contains a collection solution of 0.02% potassium iodide (KI) in a sodium carbonate/sodium bicarbonate buffer.
Recommended Sampling Rate	0.5 Liter per minute (L/min)
Recommended Air Volume	
TWA:	120 L (0.5 L/min for 240 min)
STEL:	7.5 L (0.5 L/min for 15 min)
Analytical Procedure:	In the weakly basic solution, chlorine dioxide reacts with KI to form chlorite (ClO_2^-) which is then determined by an ion chromatograph equipped with a conductivity detector and gradient pump.
Detection Limit	
Qualitative:	0.001 ppm (120-L air sample) 0.018 ppm (7.5-L air sample)
Quantitative:	0.004 ppm (120-L air sample) 0.059 ppm (7.5-L air sample)
Precision and Accuracy	
Validation Range:	0.058 to 0.202 ppm
CV_T:	0.076
Bias*:	+0.05
Overall Error*:	±20%
Method Classification:	Validated Method
Chemist:	James C. Ku
Date (Date Revised):	June, 1990 (Feb., 1991)

* As compared to the NIOSH chlorine dioxide method (chlorophenol red)

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1. Introduction

This method describes the sample collection and analysis of airborne chlorine dioxide (ClO_2). Samples are taken in the breathing zone of workplace personnel, and analysis is performed by ion chromatography (IC).

1.1. History

The previous method used to determine ClO_2 in the workplace involved collecting samples in 0.01 N sodium hydroxide (8.1). Because this method was also used to collect chlorine (Cl_2) and could not discriminate between the two species, a better method was needed. The scientific literature contains few articles addressing Cl_2 and ClO_2 analysis. A method proposed by NIOSH was a spectrophotometric technique based on the decolorization of chlorophenol red (CPR) by ClO_2 (8.2). Another method was proposed by the Workers' Compensation Board of British Columbia as the N,N-Dimethyl-p-phenylendiaminesulfate (NNDP) method (8.3), This method was later evaluated and modified by the National Council of the Paper Industry for Air and Stream Improvement (NCASI) (8.4). The basic technique of this method involves the reaction of Cl_2 and ClO_2 in neutral and acidic solution with iodide to form iodine, and then color comparison using a spectrophotometric technique. Chlorine and chlorine dioxide may be differentiated from one another on the basis of their reactivity toward iodine at neutral and acid pH.

After reviewing and checking the CPR method, it was found that:

1. Chlorine produces a significant positive interference;
2. The stock solution used for ClO_2 analysis is very difficult to prepare and extremely unstable.

A comparison of the CPR and NNDP method indicated a disagreement in results below 0.3 ppm ClO_2; NIOSH speculated this was due to shortcomings in the iodometric method (8.2).

For the volumetric NNDP method, the analysis is a time-consuming process, which uses an unstable reagent (NNDP) for color development (8.4). The method described herein uses a common analytical technique and is not susceptible to an interference from Cl_2. During the evaluation of this method (1988), a paper was published in the literature which describes a similar sampling and analytical approach (8.5); however, the collection solution the authors suggest using is buffered to a neutral instead of a weakly basic pH.

1.2. Principle

Chlorine dioxide is collected in a midget fritted glass bubbler (MFGB), containing 0.02% potassium iodide (KI) in a sodium carbonate/sodium bicarbonate (Na_2CO_3/$NaHCO_3$) buffer solution. Chlorine dioxide as well as chlorine are trapped and converted to chlorite (ClO_2^-) and chloride (Cl^-), respectively, in neutral or a weak basic solution according to the following chemical reactions:

$$ClO_2 + I^- \longrightarrow \tfrac{1}{2} I_2 + ClO_2^-$$

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

The collected ClO_2 (as ClO_2^-) is analyzed by IC using a conductivity detector. A gradient pump is used to facilitate the elution of the iodide ion present in the sampling solution. The amount of Cl_2 collected can be estimated as Cl^-; however, the evaluation of this method did not include a full validation of the sampling and analysis of Cl_2. Therefore, results for Cl_2 are only used as a screening tool. For further information regarding sampling and analysis of Cl_2, see OSHA method no. ID-101.

1.3. Advantages and Disadvantages

1.3.1. This method has adequate sensitivity for determining compliance with the OSHA Short-Term Exposure Limit (STEL) and time weighted average (TWA) permissible exposure limit (PEL) for workplace exposures to ClO_2.

1.3.2. The method is simple, rapid, and easily automated.

1.3.3. The analysis is specific for ClO_2 (determined as chlorite ion, ClO_2^-), in the presence of Cl_2.

1.3.4. This method requires the use of a gradient pump during analysis in order to allow the iodide contained in the collection solution to elute and still have a reasonably short analysis time.

1.3.5. A disadvantage is the need to prepare standards from a ClO_2^- stock solution. This solution, prepared from technical-grade sodium chlorite (about 80% purity), is unstable and must be standardized monthly.

1.3.6. Another disadvantage is the sampling device. Use of impinger collection techniques may impose inconveniences. Spillage can occur during sampling, handling, and transportation to the laboratory.

1.4. Physical Properties (8.6, 8.7)

Chlorine dioxide (CAS No. 10049-04-4):

Chemical formula	ClO_2
Molecular weight	67.5
Specific gravity	1.642 at 0 °C (liquid)
Melting point	-59.5 °C
Boiling point	10 °C
Vapor pressure	96 KPa (720 mmHg) at 20 °C
Vapor density	3.09 g/L
Synonym	chlorine peroxide
Other characteristics	Highly toxic, strong oxidizing agent, soluble and decomposes in water, dissolves in alkalis forming a mixture of chlorite and chlorate. Explodes when exposed to light, heated, or by reaction with organic materials.

1.5. Some sources for potential ClO_2 exposures are (8.6):

- Bleaching wood pulp, fats, oils, and flour production
- Removing tastes and odors from water supplies
- Biocide
- Disinfectant
- Odor control
- Flour maturing operations
- Additive in swimming pools

1.6. Toxicology

Note: Information listed within this section is a synopsis of current knowledge of the physiological effects of ClO_2 and is not intended to be used as the basis for OSHA policy.

Data from human exposures indicate that marked irritation occurs on inhalation of 5 ppm (no length of exposure specified), and that one death occurred at 19 ppm. Repeated exposures in humans have been linked to bronchitis and pronounced emphysema. Clinical studies revealed that the majority of workers who had been exposed for five years to average concentrations of ClO_2 below 0.1 ppm, combined with about 1 ppm Cl_2, experienced eye and respiratory irritation and slight bronchitis. Some gastrointestinal irritation was also observed in three workers (8.8).

2. Range, Detection Limit, and Sensitivity (8.9)

2.1. This method was validated over the concentration range of 0.058 to 0.202 ppm. An air volume of 120 L and a flow rate of 0.5 L/min were used. Samples were taken for 240 min.

2.2. The qualitative detection limit was 0.025 μg/mL or 0.375 μg (as ClO_2^-) when using a 15-mL solution volume. This corresponds to 0.001 ppm ClO_2 for a 120-L air volume.

2.3. The quantitative detection limit was 0.082 μg/mL or 1.23 μg (as ClO_2^-) when using a 15-mL solution volume. This corresponds to 0.004 ppm ClO_2 for a 120-L air volume. A 50-μL sample injection loop and a detector setting of 1 microsiemen (μS) were used for both detection limit determinations.

2.4. The sensitivity of the analytical method was calculated from the slope of a linear working range curve (0.5 to 10 μg/mL chlorite). The sensitivity for this curve was 4.07×10^6 area units per 1 μg/mL when using the instrumentation mentioned in Section 6.2.

3. Method Performance (8.9)

3.1. This method was compared to the NIOSH chlorophenol method for ClO_2 (8.2). All results were obtained using the NIOSH reference method results as known values. Bias and overall error values are reported below as compared to the NIOSH method.

3.2. The pooled coefficient of variation (CV_T), for samples taken at about 0.5, 1, and 2 times the TWA PEL (0.05 to 0.2 ppm) was 0.076. The method exhibited slight positive bias (+0.05) for this concentration range. The overall error was within acceptable limits ($\leq$ ±25%) at ±20%.

3.3. The CV_2 (pooled) for samples taken in the range of 0.028 to 0.33 ppm (about 0.3 to 3 times the TWA PEL) was 0.072. The method exhibited a slight positive bias (+0.033) and overall error was acceptable at ±18% for this broader concentration range.

3.4. The collection efficiency at 0.2 ppm ClO_2 was 100%. Samples were collected at a generated concentration of 0.202 ppm ClO_2 for 240 min.

3.5. A breakthrough test was performed at a concentration of 0.33 ppm ClO_2. No breakthrough was found for a sampling time of 240 min at an average sample flow rate of 0.5 L/min. Under the same conditions, for a concentration of 0.67 ppm, the average breakthrough of ClO_2 into a second impinger was 9.1%. At a flow rate of 1 L/min, about 10% breakthrough occurred after 90 min at a concentration of approximately 0.35 ppm ClO_2.

3.6. Samples can be stored at normal (20 to 25 °C) laboratory conditions for at least 96 days. Results of samples analyzed after 96 days were still within ±10% of the mean of samples analyzed after one day of storage. Samples were stored unprotected from light on a laboratory bench.

4. Interferences

4.1. Any compound having the same retention time as chlorite, when using the operating conditions described, is an interference.

4.2. Interferences may be minimized by changing the eluent concentration and/or pump flow rate, or by using concentration gradient techniques.

4.3. Contaminant anions normally found in the workplace, such as nitrate (NO_3^-), sulfate (SO_4^{2-}), and phosphate (HPO_4^{2-}), do not interfere. However, very large amounts (> 100 µg/mL) of Cl^{--} may interfere with the determination of ClO_2. The possibility of collecting this quantity of Cl^- in the workplace is minimal.

4.4. Particulate chloride contamination will present a positive interference for the screening determination of Cl_2. Care must be exercised to not contaminate the collection solutions with chloride salts if screening for Cl_2 is desired.

4.5. When other compounds are known or suspected to be present in the air, such information should be transmitted with the sample.

4.6. Altering the pH of the collection solution to more acidic conditions will alter the reaction of ClO_2 to ClO_2. If strongly acidic gases are present in the sampled atmosphere and convert the buffer to an acidic solution, the reaction will not proceed in the fashion mentioned in Section 1.2. The following reaction would most likely occur:

$$ClO_2^- + 4H^+ + 4\,I^- \longrightarrow 2I_2 + 2H_2O + Cl^-$$

The collection solution should have adequate buffering capacity for most industrial hygiene monitoring situations; however, sampling times should be decreased to maintain slightly basic conditions if sampling in the presence of large concentrations of acid gases (i.e. sulfur dioxide). The pH of the solution can also be measured with pH paper after sampling to determine if the collection solution has become acidic. If acidic, discard the sample and resample using shorter sampling times.

5. Sampling

5.1. Equipment and Reagents

5.1.1. Calibrated personal sampling pumps capable of sampling within ±5% of the recommended flow rate of 0.5 L/min.

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

5.1.3. Shipping vials: Glass scintillation vials, 20-mL, with Teflon-lined caps.

5.1.4. A stopwatch and bubble tube or meter - for pump calibration. Place a calibration MFGB containing 10 to 15 mL of collection solution in-line during flow rate calibration of each pump.

5.1.5. Various lengths of polyvinyl chloride (PVC) tubing are used to connect the MFGBs to pumps.

5.1.6. Buffer solution (1.5 mM Na_2CO_3/1.5 mM $NaHCO_3$):

Dissolve 0.636 g Na_2CO_3 and 0.504 g $NaHCO_3$ in 4.0 L of deionized water.

5.1.7. Collection solution:

Dissolve 0.2 g KI in 1.0 L of buffer solution.

5.2. Sampling Procedure

5.2.1. Place 15 mL of collection solution in a MFGB, and then connect the bubbler to a calibrated sampling pump using PVC tubing. Position the MFGB in the breathing zone of the employee.

5.2.2. For STEL determinations, collect the sample at a flow rate of 0.5 L/min and a sampling time of at least 15 min. For TWA samples, an air volume of 120-L is recommended at 0.5 L/min. Take enough samples to cover the work shift being monitored.

5.2.3. After sampling, transfer the bubbler solution into a 20-mL glass scintillation vial. Rinse the bubbler with 2 to 3 mL of unused collection solution and transfer the rinsings into the sample vial. Place the Teflon-lined cap tightly on the vial and seal the cap with vinyl or waterproof tape to prevent leakage during shipment.

6. Analysis

6.1. Precautions

6.1.1. Refer to instrument and standard operating procedures (SOP) for proper operation (8.10, 8.11).

6.1.2. Observe laboratory safety regulations and practices.

6.1.3. Sulfuric acid (H_2SO_4) can cause severe burns. Wear protective gloves, lab coat, and eyewear when using concentrated H_2SO_4.

6.2. Equipment

6.2.1. Ion chromatograph (Model 4000i or 4500i with a concentration-gradient pump, Dionex, Sunnyvale, CA) equipped with a conductivity detector.

6.2.2. Automatic sampler (Model AS-1, Dionex) and sample vials (0.5 mL).

6.2.3. Laboratory automation system: Ion chromatograph interfaced to a data reduction system.

6.2.4. Anion separator column with precolumn (Model HPIC-AS4A and AS4G, Dionex).

6.2.5. Anion suppressor (Model AMMS-1 micro-membrane suppressor, Dionex).

6.2.6. Disposable syringes (1 mL) and filters.

(Note: Some syringe pre-filters are not cation- or anion-free. Tests should be done with blank solutions first to determine suitability for the analyte being determined).

6.2.7. Miscellaneous volumetric glassware: Micropipettes, burette, volumetric flasks, graduated cylinders, and beakers.

6.2.8. Analytical balance (0.01 mg).

6.3. Reagents - All chemicals should be at least reagent grade (Note: Sodium chlorite may only be commercially available as technical grade)

- Sodium bicarbonate ($NaHCO_3$)
- Sodium carbonate (Na_2CO_3)
- Potassium iodide (KI)
- Sodium chloride (NaCl)
- Sulfuric acid

6.3.1. Eluent 1: Deionized water (DI H_2O) with a specific conductance of less than 10 μS.

6.3.2. Eluent 2 (10 mM Na_2CO_3):

Dissolve 2.12 g Na_2CO_3 in 2.0 L of DI H_2O.

6.3.3. Eluent 3 (10 mM $NaHCO_3$):

Dissolve 1.68 g $NaHCO_3$ in 2.0 L of DI H_2O.

6.3.4. Buffer solution (1.5 mM Na_2CO_3/1.5 mM $NaHCO_3$):

Dissolve 0.636 g Na_2CO_3 and 0.504 g $NaHCO_3$ in 4.0 L of DI H_2O.

6.3.5. Collection solution:

Dissolve 0.2 g KI in 1.0 L of buffer solution.

6.3.6. Regeneration solution (0.02 N H_2SO_4):

Place 1.14 mL concentrated H_2SO_4 into a 2-L volumetric flask which contains about 500 mL DI H_2O. Dilute to volume with DI H_2O.

6.3.7. Chloride stock standard (1,000 µg/mL):

Dissolve 1.6479 g dried NaCl and dilute to the mark in a 1-L volumetric flask with DI H_2O.

6.3.8. Chloride standards (100, 10, and 1 µg/mL):

Perform serial dilutions of the 1,000 µg/mL chloride stock standard with collection solution. Prepare weekly. [Note: Prepare only if necessary. These standards are only used to screen Cl_2 (as Cl^-) concentrations.]

6.3.9. Chlorite stock standard (1,000 µg/mL):

Dissolve in a 1-L volumetric flask approximately 1.7 g sodium chlorite ($NaClO_2$) in 500 mL DI H_2O. Dilute to the mark with DI H_2O. Wrap the volumetric flask with aluminum foil and store in a refrigerator at about 4 °C. **This solution must be standardized monthly** as described in Section 6.4.1.

6.3.10. Chlorite standard (100 µg/mL). Dilute 10 mL of the 1,000 µg/mL chlorite stock standard to 100 mL with collection solution. Prepare monthly.

6.3.11. Chlorite standard (10 µg/mL). Dilute 10 mL of the 100 µg/mL chlorite stock standard to 100 mL with collection solution. Prepare weekly.

6.3.12. Chlorite standard (1 µg/mL). Dilute 10 mL of the 10 µg/mL chlorite stock standard to 100 mL with collection solution. Prepare weekly.

6.3.13. Reagents for standardizing the chlorite stock standard solution:

Note: If a 0.1 N (< ±0.5% variation) sodium thiosulfate solution traceable to a primary standard is unavailable, any laboratory-prepared sodium thiosulfate solutions must be standardized according to procedures listed in reference 8.12. Standardize any sodium thiosulfate solution has aged significantly.

1. Sodium thiosulfate solution ($Na_2S_2O_3$), 0.1 N, traceable to a primary standard (Cat. No. SS368-1, Fisher Scientific, Pittsburgh, PA). Any expiration date must be adhered to. This solution can be prepared and standardized according to procedures in reference 8.12.

2. Sulfuric acid (H_2SO_4), concentrated.

3. Sulfuric acid, dilute.

   Slowly and cautiously add 40 mL of concentrated H_2SO_4 to a 200-mL volumetric flask which contains 150 mL DI H_2O. Allow to cool, then dilute to volume with DI H_2O.

4. Potassium iodide (KI).

5. Starch indicator solution, (1% w/v): Gradually add about 5 mL of DI H_2O to 1 g soluble starch, with stirring, until a paste is formed. Add the paste to 100 mL of boiling DI H_2O. Allow to cool, then add 5 g KI and stir until the KI is dissolved. Prepare a fresh solution for each standardization. Alternatively, a commercial indicator can be used (Starch indicator, Cat. No. 8050, Ricca Chemical Co., Arlington, TX).

6.4. Standard Preparation

6.4.1. Standardization of chlorite stock solution. (Note: This procedure is adapted from those found in reference 8.12)

1. Add 10 mL of dilute H_2SO_4 into a 125-mL Phillips beaker which contains 20.0 mL of $NaClO_2$ stock solution (1,000 µg/mL, from Section 6.3.9).

2. Add 1 g of KI and 40 mL of DI H_2O.

3. Titrate with standardized 0.1 N $Na_2S_2O_3$ until a color change to a light straw color is achieved.

4. Add 2 mL of 1% starch indicator. A blue color should appear.

5. Titrate again with 0.1 N $Na_2S_2O_3$ until the blue color completely disappears.

6. For blank sample(s), repeat steps 1 through 5 except use 20.0 mL DI H_2O instead of 20.0 mL of the $NaClO_2$ stock solution.

7. Calculate µg/mL chlorite as follows:

$$ug/mL\ \mathrm{ClO_2^-} = \frac{(A-B)(C)(D)}{E}$$

where:

A = mL of the standardized $Na_2S_2O_3$ solution required to titrate the sample

B = mL of the standardized $Na_2S_2O_3$ solution required to titrate the blank

C = normality of the standardized $Na_2S_2O_3$ solution (meq/mL)

D = (16.875 mg/meq ClO_2^-)(1,000 µg/mg) = 16.875×10^3 µg/meq of ClO_2^-

E = mL of ClO_2^- used = 20 mL

6.4.2. Working standard preparation:

1. Prepare chlorite (or chloride, or a chlorite and chloride mixture) working standards in the ranges specified below:

Working std µg/mL	Standard Solution µg/mL	Aliquot mL
0.5	1	5
1	1	*
2	10	2
5	10	5
10	10	*
20	100	2

*Already prepared in Section 6.3.

2. Pipette appropriate aliquots of standard solutions (prepared in Section 6.3) into 10-mLvolumetric flasks and dilute to volume with collection solution.

6.4.3. Pipette a 0.5- to 0.6-mL portion of each standard solution into separate automatic sampler vials. Place a 0.5-mL filter cap into each vial. The large exposed filter portion of the cap should face the standard solution.

6.4.4. Prepare a reagent blank from the collection solution.

6.5. Sample Preparation

6.5.1. Carefully transfer sample solutions from the 20-mL glass scintillation vials into 25-mL graduated cylinders. Measure and record the sample solution volumes.

6.5.2. If the sample solutions contain particulate, remove the particles using a pre-filter and syringe. Fill the 0.5-mL automatic sampler vials with sample solutions and push a 0.5-mL filter cap into each vial.

6.5.3. Load the automatic sampler with labeled samples, standards and blanks.

6.6. Analytical Procedure

6.6.1. Set up the ion chromatograph in accordance with the SOP (8.10).

Typical operating conditions for a Dionex 4000i or 4500i with an automated sampler are listed below.

Gradient pump

Eluent 1:	DI H_2O
Eluent 2:	10.0 mM Na_2CO_3
Eluent 3:	10.0 mM $NaHCO_3$
Pump pressure:	approximately 900 psi
Flow rate:	2 mL/min

Time	Flow	Eluent			
min	mL/min	%1	%2	%3	Comments
0.0	2.0	70	0	30	Initial conditions
0.1	2.0	70	0	30	Inject sample
3.1	2.0	70	0	30	*
11.1	2.0	40	30	30	
14.0	2.0	40	30	30	**
19.1	2.0	70	0	30	

*Gradient change in eluent concentration from 3.1 to 11.1 min is performed to facilitate elution of iodide present in the collection solution.

** Gradient return in eluent concentration to initial analytical conditions.

Column & Sample Injection	
Column:	HPIC-AS4A
Column temperature:	ambient
Sample injection loop:	50 µL
Chromatogram	
Run time:	18 min
Peak retention time:	
ClO_2^-	approximately 2 min
Cl^-	approximately 3 min

6.6.2. Follow the SOP (8.10) for further analytical instructions.

7. Calculations

7.1. After the analysis is completed, the peak areas and heights can be retrieved using a variety of methods or programs. Obtain hard copies of chromatograms from a printer. A chromatogram of a mixed standard of 5 µg/mL ClO_2^- and 0.5 µg/mL Cl^- is shown in Figure 1.

7.2. Prepare a concentration-response curve by plotting the concentration of the standards in µg/mL versus peak areas or peak heights. Determine the concentration (µg/mL) of each sample by comparing the area or height to the curve. Blank correct all samples as shown:

$$ugC\text{ Analyte} = (S)(SV) - (BL)(BLV)$$

where:

µgC Analyte = Corrected amount (µg) in the sample solution

S = µg/mL sample (from curve)

SV = Sample solution volume, mL (from Section 6.5.1).

BL = µg/mL blank (from curve)

BLV = Blank solution volume, mL (from Section 6.5.1).

7.3. The concentration of ClO_2 and Cl_2 in each air sample is expressed in ppm.

$$ppm\ \mathrm{ClO_2} = \frac{ug\mathrm{C\ Analyte} \times \text{molar volume}}{\text{air volume} \times \text{molecular weight}}$$

$$ppm\ \mathrm{Cl_2}^* = \frac{ug\mathrm{C\ Analyte} \times \text{molar volume} \times \mathrm{GF}}{\text{air volume} \times \text{molecular weight}}$$

where

μgC Analyte = Corrected amount (µg) in the sample solution

molar volume = 24.45 (25 °C and 760 mmHg)

molecular weight for ClO_2 = 67.5

molecular weight for Cl_2 = 71.0

Gravimetric Factor (GF) = 2

* Note: Results for Cl_2 are used for screening purposes only.

7.4. Reporting Results

Report results to the industrial hygienist as ppm chlorine dioxide. Results determined for exposure to chorine may be used as information to the industrial hygienist. Additional sampling for chlorine may be recommended using OSHA method no. ID-101.

8. References

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8.5. **Bjorkholm, E., A. Hultman, and J. Rudling:** Determination of chlorine and chlorine dioxide in workplace air by impinger collection and ion-chromatographic analysis. *J Chromatogr. 457*: 409-414 (1988).

8.6. **Hawley, G.G.:** *The Condensed Chemical Dictionary*. 11th ed. New York: Van Nostrand Reinhold Co., 1987.

8.7. **Weast, R.C., ed.:** *CRC Handbook of Chemistry and Physics*. 59th ed. Boca Raton, FL: CRC Press, Inc., 1979.

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8.9. **Occupational Safety and Health Administration Technical Center:** *Chlorine Dioxide Backup Data Report (ID-202)*. Salt Lake City, UT. Revised 1991.

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8.11. **Occupational Safety and Health Administration Technical Center:** *Ion Chromatography Standard Operating Procedure*. Salt Lake City, UT. In progress (unpublished).

8.12. **American Society for Testing and Materials:** *Standard Recommended Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals* (Annual Book of ASTM Standards, Part 12, E-50). Philadelphia, PA: American Society for Testing and Materials, 1978.

Chromatogram of a Mixture of 5 µg/mL ClO_2^- and 0.5 µg/mL Cl^-

PEAK NUM	RET TIME	PEAK NAME	AREA	HEIGHT
2	0.95		1.028e+007	1179972
3	1.47		1.696e+005	18079
4	1.92		1.482e+005	19795
5	2.28	chlorite	2.222e+007	2174692
6	3.53	chloride	4.259e+006	343291
7	5.28		2.713e+007	428639
8	6.87		1.569e+007	1678083
9	11.10		6.284e+006	960400
10	14.78		3.672e+007	6410

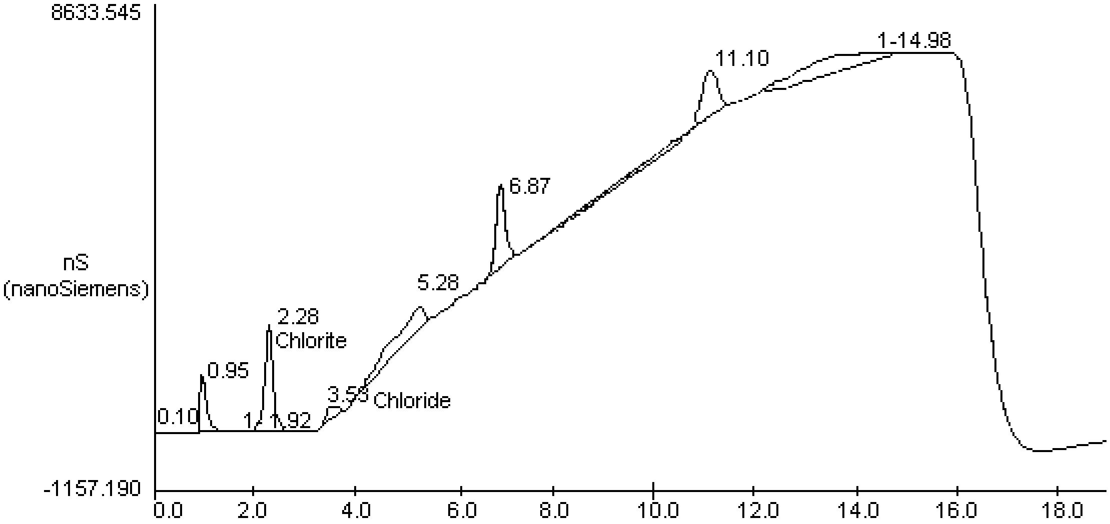

Figure 1

Backup Report

Introduction

The procedure for collection and analysis of air samples for chlorine dioxide (ClO_2) is described in OSHA Method No. ID-202 (9.1). Chlorine dioxide and chlorine (Cl_2) are both collected in a midget fritted glass bubbler (MFGB), containing 0.02% potassium iodide (KI) in a weak buffer. These two species are trapped and converted to chlorite (ClO_2^-) and chloride (Cl^-), respectively, based on the following chemical reactions:

$$ClO_2 + I^- \longrightarrow \frac{1}{2} I_2 + ClO_2^-$$

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

These reactions occur in neutral or weakly basic solutions. The collection solution used for this method contains 0.02% KI in 1.5 mM sodium carbonate and 1.5 mM sodium bicarbonate. The collected chlorine dioxide (as ClO_2^-) and chlorine (as Cl^-) are then analyzed by ion chromatography (IC).

This method has been validated for a 120-L, 240-min sample based on a flow rate of 0.5 L/min. The method validation was conducted near the OSHA time weighted average (TWA) permissible exposure limit (PEL) of 0.1 ppm and consisted of the following experiments and summaries:

1. An analysis of 18 samples (6 samples at each test level).
2. A sampling and analysis of 18 samples (6 samples at each test level, 50% RH) collected from dynamically generated test atmospheres. Additional samples at other test levels and humidities were also taken.
3. A determination of the sampling media collection efficiency at 0.2 ppm (2 times the TWA PEL).
4. A determination of breakthrough.
5. An evaluation of room temperature storage stability for 12 collected samples.
6. A determination of any significant effects on results when sampling at different humidities.
7. A determination of the qualitative and quantitative detection limits.
8. A determination of sampling efficiency of the collection solution when sampling a mixture of dynamically generated ClO_2 and Cl_2.
9. Summary.

All theoretical (known) concentrations of generated test atmospheres were determined using the NIOSH chlorophenol red (CPR) method for ClO_2 (9.2). All sampling tests performed were conducted side-by-side with IC and CPR samples being taken and analyzed using the conditions recommended in their methods (9.1, 9.2). The CPR method was slightly modified for these experiments. The chlorite stock solution was prepared without the addition of acetic anhydride and the solution was standardized using a primary standard instead of molar absorbance as mentioned in the NIOSH method. The unknown potential effect on the IC determinations from having small amounts of acetic anhydride in the standards and not in the samples was one reason for its exclusion. The chlorite stock solution was standardized using the procedure advocated by the National Council of the Paper Industry for Air and Stream Improvement (NCASI) (9.3) and the acetic anhydride may also have presented an effect on this titration. This standardization was felt to be more accurate than the NIOSH approach.

All results were calculated from concentration-response curves and statistically examined for outliers. In addition, the analysis (Section 1) and sampling and analysis results (Section 2) were tested for homogeneity of variance. Possible outliers were determined using the Treatment of Outliers test (9.4). Homogeneity of variance was determined using the Bartlett's test (9.5). Statistical evaluation was conducted according to Inorganic Methods Evaluation Protocol (9.6). Overall error (9.6) was calculated using the equation:

$$\text{Overall error}_i = \pm(|\text{bias}_i| + 2CV_i) \times 100\% \text{ (95\% confidence level)}$$

Where i is the respective sample pool being examined.

1. Analysis

1.1. Preparation of Known ClO_2 Concentrations

Samples were prepared by adding known amounts of sodium chlorite ($NaClO_2$) solution into 25-mL volumetric flasks containing collection solution. Technical-grade $NaClO_2$ was used to prepare the stock solution and was standardized according to the procedure described in the method (9.1).

1.2. Analysis of Spiked Samples

Analysis was performed using an ion chromatograph equipped with a conductivity detector (9.1).

1.3. Determination of Analytical Method Recovery (AMR)

Recoveries were compared to the known amounts of chlorite spikes and are presented in Table 1. All results passed the Test for Outliers and the Bartlett's test. The AMR was 97.8% and the analytical precision (CV_1 pooled) was 0.024.

2. Sampling and Analysis

2.1. Preparation and Collection of Known Generated Samples

2.1.1. Dynamic generation system

A diagram of the generation system is shown in Figure 1. The system consists of five essential elements: A flow-temperature-humidity control system (Miller-Nelson Research Inc., Monterey, CA, Model HCS-301) which is used for air flow control and conditioning, a ClO_2 or ClO_2 + Cl_2 mixture vapor generating system, a mixing chamber, and sampling manifold. All generation system fittings and connections were Teflon. A glass mixing chamber was used.

2.1.2. Chlorine dioxide vapor generation system

Chlorine dioxide, a very unstable gas, is extraordinarily reactive and commercially unavailable. Special techniques are required to produce it. For this study, the technique selected involved the passage of a dilute stream of Cl_2 vapor through a concentrated aqueous solution of $NaClO_2$, (specifically, 10 g of $NaClO_2$ in 25 mL of deionized water) to produce ClO_2 by the reaction:

$$Cl_2 + 2NaClO_2 \longrightarrow 2ClO_2 + 2NaCl$$

The Cl_2 source was a cylinder containing 530 ppm Cl_2 in nitrogen (certified, Airco, Phoenix, AZ). This technique produced a chlorine-free stream of ClO_2 vapor. The components exposed to this analyte vapor were composed of glass, Teflon, or other suitably inert materials. The entire system was shielded from light and was operated within the confines of an exhaust hood.

All known (taken) concentrations of ClO_2 were determined by the chlorophenol red (CPR) reference method (9.2). The CPR samples were taken from the generation system side-by-side with all IC samples.

The generator was also designed to produce test atmospheres of Cl_2 in air as required during the Cl_2 + ClO_2 mixture study. A vapor-generation system intended to produce steady-state vapor concentrations of ClO_2 (and Cl_2) at the appropriate test levels was constructed as shown in Figure 2.

2.1.3. The ClO_2 (and Cl_2) and diluent air flow rates were adjusted using mass flow controllers. The total flow rate of the system was measured before and after each experiment using a dry test meter.

2.1.4. All samples were taken from the sampling manifold using constant flow pumps. Du Pont Model Alpha-l and -2 pumps were used at sample flow rates of 0.5 L/min for IC and 0.2 L/min for CPR samples, respectively.

2.2. Analysis of Generated Samples

As previously mentioned, side-by-side samples were taken for the IC and CPR methods. Samples taken using the KI/buffer were analyzed by IC (9.1). Analysis of the CPR samples was performed by colorimetry (9.2). Table 2 shows the sampling and analysis for 0.5, 1, and 2 times OSHA TWA PEL. Table 3 lists a broad range of concentrations of ClO_2 from about 0.3 to 3 times the OSHA TWA PEL. Table 4 shows the comparison of results between the IC and CPR samples taken side-by-side.

The data considered to determine precision and accuracy (Table 2) are for 0.5 to 2 times the PEL only [as stated in NIOSH and OSHA Inorganic Methods statistical protocols (9.5, 9.6)]. The generated sample (Sampling and Analysis - Table 2) results passed the Bartlett's test. Data not passing the Test for Outliers were omitted from final calculations. For 0.5, 1, and 2 times OSHA TWA PEL (Table 2), the pooled coefficients of variation are:

$$CV_1 \text{ (pooled)} = 0.024;\ CV_2 \text{ (pooled)} = 0.075;\ CV_T \text{ (pooled)} = 0.076$$

The average recovery of generated samples was 105%. The bias for the overall method was +0.05, and the OE was ±20%.

For all levels tested (0.3 to 3 times the PEL), as shown in Table 3, the pooled CV was 0.072. The bias was +0.033 and the OE was ±18%. All levels tested, presented also in Table 4, gave pooled CVs of 0.035 and 0.072 for CPR and IC samples, respectively.

3. Collection Efficiency and Breakthrough

3.1. Collection Efficiency

Procedure: Six samples, each arranged in a sampling train, were collected at a concentration of 2 times the OSHA PEL for 240 min at 0.5 L/min (50% RH and 25 °C). Each sampling train consisted of two MFGBs connected in series and a sampling pump. The amount of ClO_2 vapor collected in each of the two MFGBs was determined for each sampling train. The collection efficiency was calculated by dividing the amount collected in the first MFGB by the total amount of ClO_2 collected in the first and second MFGBs.

Results: The results in Table 5a show a collection efficiency of 100%.

3.2. Breakthrough (> 5% loss of analyte through the sampling media)

Procedure: The same procedure as the collection efficiency experiment was used with one exception: The concentration was varied to include two tests conducted at 0.33 and 0.67 ppm ClO_2. A preliminary test was also performed at 1 L/min and about 0.35 ppm (90-min sampling time). The amount of breakthrough was calculated by dividing the amount collected in the second MFGB by the total amount of ClO_2 collected in the first and second MFGBs.

Results: For a concentration of 0.33 ppm ClO_2, no breakthrough was found after 240 min. For a concentration of 0.67 ppm, the average breakthrough of ClO_2 into a second impinger was 9.1%. Results are shown in Table 5b. The preliminary test indicated about 10% breakthrough was noted at a flow rate of 1 L/min (90-min sampling time, about 0.35 ppm ClO_2).

4. Storage Stability

Procedure: A study was conducted to assess the stability of ClO_2 in the collecting solution. An evaluation was performed of the room temperature storage stability of 12 samples taken near the OSHA TWA PEL of 0.1 ppm. The first test (6 samples) was conducted at 0.07 ppm. When noting an increase in concentration in these samples after 15 days of storage, a second test was performed (6 samples at 0.13 ppm). All samples were stored under normal laboratory conditions (20 to 25 °C) on a lab bench and were not protected from light. An aliquot from each of the samples was analyzed after various periods of storage.

Results: For the storage stability study conducted at 0.07 ppm ClO_2, a 11% increase in recoveries occurred after 15 days of storage and then stayed constant through the 102 day study. The mean of samples analyzed after 102 days was within 15% of the mean of samples analyzed the first day.

Results of the room temperature stability study of samples taken at 0.13 ppm (Table 6) show that samples can be stored at ambient (20 to 25 °C) laboratory conditions. A positive bias was not evident during this 96 day study. The mean of samples analyzed after 96 days was still within ±10% of the mean of samples analyzed after 1 day of storage.

5. Humidity Study

Procedure: A study was conducted to test the effect of different humidities during sample collection. Generation system samples were taken using the procedure described in Section 2. Test atmospheres were generated at 25 °C and at the OSHA PEL. Relative humidities of 26, 50, and 80% were used.

Results: Results are listed in Table 7. An F test was used to determine if any significant effect occurred when sampling at different humidities. As shown, a significant difference is not noted when using the F test. This indicates no significant change in results occurred in the humidity ranges tested.

6. Mixture Study

Procedure: In order to determine if the presence of Cl_2 can affect the analysis of ClO_2, a mixture of Cl_2 and ClO_2 at 25 °C and 50% RH was generated, and 12 samples were taken using this and the CPR method (6 side-by-side samples for each method). The system used to generate the mixture is described in Section 2 and illustrated in Figure 2.

Results: The known (taken) concentrations of Cl_2 and ClO_2 were measured individually prior to the experiment using the IC and CPR methods, respectively. The IC method results for both Cl_2 and ClO_2 after mixing the two gases are shown in Table 8 (Note: A correction was applied to the **results of the CPR method** due to the positive interference from Cl_2 on the ClO_2 analysis - for further information regarding this interference, see reference 9.2). As shown in Table 8, a decrease in recovery (89.5%) occurred for the collection and IC analysis of ClO_2.

7. Detection Limit Study

Procedure: Low concentration samples were prepared by spiking solutions with standardized sodium chlorite. A 50-µL sample injection loop and a detector setting of 1 µS was used for all analyses.

Qualitative and quantitative detection limit:

A modification or derivation of the International Union of Pure and Applied Chemistry (IUPAC) detection limit equation (9.7) was used in this case. At the sensitivity level tested, blank readings and the standard deviation of the blank were equal to zero. The lack of a blank signal does not satisfy a strict interpretation of the IUPAC detection limit calculations. The detection limits for this method were calculated using a standard below the range of the expected detection limit as a substitute for the blank readings.

Results: The results are shown in Table 9 for qualitative and quantitative detection limits, respectively. The qualitative limit is 0.025 µg/mL as ClO_2^- (using a 50-µL sample injection loop) at the 99.8% confidence level. The quantitative limit is 0.082 µg/mL as ClO_2^-. Using a 120-L air volume and a 15-mL sample volume, the qualitative limit is 0.001 ppm and the quantitative limit is 0.004 ppm ClO_2.

8. Summary

The validation results indicate the method meets either NIOSH or OSHA criteria for accuracy and precision (9.5, 9.6). Collection efficiency, breakthrough, and storage stability are adequate; however, breakthrough did occur at approximately seven times the TWA PEL and the storage test at 0.07 ppm revealed an increase in recoveries as the test progressed. The reason for the increase in concentration is unknown. The stock standard should be standardized at least monthly. It was noted during testing that this standard solution decreases in concentration approximately 4% per month.

No significant difference in results was noted when sampling at different humidities. As shown in the mixture study, Cl_2 does not interfere with the sampling or ion chromatographic analysis of ClO_2 at the concentrations tested. Although a resultant 10% decrease in ClO_2 and 7% increase in Cl_2 concentrations occurred, this could have been due to the difficulty in generating both gases simultaneously. A mixture of ClO_2 and Cl_2 can be collected and analyzed together; however, Cl_2 measurements are considered for screening purposes only. Further work is necessary to validate the KI/buffer sampling and IC analysis for Cl_2.

Detection limits are adequate if samples are taken for 240 min at 0.5 L/min. Although no samples were taken to determine ability for Short-Term Exposure Limit (STEL) monitoring, the method appears capable of STEL determinations if a sampling rate of 0.5 L/min is used for at least 15 min. This sampling strategy gives a detection limit of 0.059 ppm for 15-min samples.

9. References

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Table 1
IC Analysis - Chlorine Dioxide

(OSHA-PEL) µg Taken	µg Found	F/T	n	Mean	Std Dev	CV_1	OE_a
(0.5 X PEL)							
16.56	17.21	1.039					
16.56	16.68M	1.007					
16.56	16.07	0.970					
16.56	17.14	1.035					
16.56	16.47	0.995					
16.56	15.81	0.955					
			6	1.000	0.034	0.034	6.8
(1 X PEL)							
33.12	31.81	0.960					
33.12	32.07	0.968					
33.12	32.07	0.968					
33.12	32.69	0.987					
33.12	32.10	0.969					
33.12	31.48	0.950					
			6	0.967	0.012	0.012	5.8
(2 X PEL)							
64.24	61.50	0.957					
64.24	62.00	0.965					
64.24	62.70	0.977					
64.24	63.81	0.993					
64.24	62.19	0.968					
64.24	60.13	0.936					
			6	0.966	0.019	0.020	7.4

Analytical Method Recovery (AMR) = 0.978

F/T = Found/Taken

OE_a = ± Overall Error (Analytical)

Bias = -0.022

CV_1 (Pooled) = 0.024

Overall Error (Analytical) = ±7.0%

Table 2
KI/Buffer Sampling and IC Analysis - Chlorine Dioxide
(0.5, 1, and 2 X PEL)

(OSHA-PEL) ppm Taken	ppm Found	F/T	n	Mean	Std Dev	CV_2	OE_s
(0.5 X PEL)							
0.058	0.076	1.310					
0.058	0.059	1.017					
0.058	0.058	1.000					
0.058	0.067	1.155					
0.058	0.065	1.121					
0.058	0.071	1.224					
			6	1.138	0.119	0.105	34.8
(1 X PEL)							
0.107	0.112	1.047					
0.107	0.106	0.991					
0.107	0.108	1.009					
0.107	0.110	1.028					
0.107	0.124	1.159					
0.107	0.116	1.084					
			6	1.053	0.061	0.058	16.9
(2 X PEL)							
0.202	0.192	0.950					
0.202	0.200	0.990					
0.202	0.200	0.990					
0.202	0.189	0.936					
0.202	0.205	1.015					
0.202	0.177	0.876					
			6	0.960	0.050	0.052	14.5

F/T = Found/Taken

OE_s = ± Overall Error (Sampling and Analysis)

Bias = +0.050

CV_2 (Pooled) = 0.075

CV_T (Pooled) = 0.076

Overall Error (Total) = ±20.1%

Table 3
KI/Buffer Sampling and IC Analysis - Chlorine Dioxide
(All concentrations)

Test Level	Air Vol	Found	Taken	Statistical Analysis				
	(L)	ppm	ppm	n	Mean	Std Dev	CV_2	Recovery (%)
0.3 X PEL	120	0.030	0.028					
(25 °C &	116	0.026	0.028					
50% RH)	118	0.029	0.028					
	120	0.024	0.028					
	91	0.037	0.028					
	107	0.023	0.028					
				6	0.028	0.005	0.18	101
0.6 X PEL	118	0.076	0.058					
(25 °C &	114	0.059	0.058					
28% RH)	117	0.058	0.058					
	119	0.067	0.058					
	120	0.065	0.058					
	106	0.071	0.058					
				6	0.066	0.007	0.105	114
0.7 X PEL	118	0.069	0.071					
(25 °C &	115	0.066	0.071					
80% RH)	117	0.070	0.071					
	119	0.065	0.071					
	120	0.068	0.071					
	119	0.094*	0.071					
				5	0.068	0.002	0.031	95.2
0.7 X PEL	116	0.074	0.072					
(25 °C &	114	0.077	0.072					
50% RH)	117	0.081	0.072					
	117	0.077	0.072					
	119	0.078	0.072					
	129	0.088	0.072					
				6	0.079	0.005	0.062	110
1 X PEL	120	0.112	0.107					
(25 °C &	116	0.106	0.107					

26% RH)	118	0.108	0.107					
	120	0.110	0.107					
	122	0.124	0.107					
	124	0.116	0.107					
				6	0.113	0.007	0.058	105
1 X PEL	118	0.094	0.087					
(25 °C &	115	0.094	0.087					
80% RH)	117	0.093	0.087					
	119	0.090	0.087					
	120	0.092	0.087					
	119	0.129*	0.087					
				5	0.093	0.002	0.018	106
1.3 X PEL	116	0.133	0.130					
(25 °C &	116	0.133	0.130					
50% RH)	112	0.128	0.130					
	116	0.128	0.130					
	117	0.126	0.130					
	119	0.115	0.130					
				6	0.126	0.006	0.047	97.1
2 X PEL	119	0.241	0.212					
(25 °C &	116	0.241	0.212					
28% RH)	118	0.240	0.212					
	119	0.244	0.212					
	121	0.243	0.212					
	122	0.234	0.212					
				6	0.241	0.004	0.015	113
2 X PEL	90	0.192	0.202					
(25 °C &	115	0.200	0.202					
50% RH)	119	0.200	0.202					
	120	0.189	0.202					
	120	0.205	0.202					
	116	0.177	0.202					
				6	0.194	0.010	0.052	96.0
2 X PEL	118	0.174	180					

(25 °C &	115	0.176	0.180					
80% RH)	118	0.184	0.180					
	120	0.176	0.180					
	121	0.183	0.180					
	120	0.259*	0.180					
				5	0.179	0.005	0.026	99.2
3 X PEL	119	0.319	0.330					
(25 °C &	117	0.315	0.330					
50% RH)	119	0.317	0.330					
	119	0.324	0.330					
	122	0.314	0.330					
	116	0.236*	0.330					
				5	0.318	0.004	0.012	96.3
3 X PEL	118	0.312	0.288					
(25 °C &	114	0.310	0.288					
80% RH)	118	0.299	0.288					
	119	0.309	0.288					
	120	0.312	0.288					
	122	0.326	0.288					
				6	0.311	0.009	0.028	108

* Outlier - not used in statistical analysis

All concentration levels

CV$_2$ (pooled) = 0.072
Bias = +0.033
Overall Error = ±18%

Table 4
Summary - Comparison of Methods for Chlorine Dioxide
(CPR vs. IC)

	CPR	*IC*	*IC/CPR*
(a) 30% RH & 25 °C			
n	6	6	
Mean (ppm)	0.058	0.066	1.14
Std Dev (ppm)	0.004	0.007	
CV_2	0.069	0.105	
n	6	6	
Mean (ppm)	0.107	0.113	1.05
Std Dev (ppm)	0.007	0.007	
CV_2	0.067	0.058	
n	6	6	
Mean (ppm)	0.212	0.241	1.13
Std Dev (ppm)	0.006	0.004	
CV_2	0.029	0.015	
(b)50% RH & 25 °C			
n	6	6	
Mean (ppm)	0.028	0.028	1.01
Std Dev (ppm)	0.002	0.005	
CV_2	0.079	0.18	
n	6	6	
Mean (ppm)	0.072	0.079	1.10
Std Dev (ppm)	0.002	0.005	
CV_2	0.029	0.062	
n	6	6	
Mean (ppm)	0.130	0.126	0.969
Std Dev (ppm)	0.010	0.006	
CV_2	0.077	0.047	
n	6	6	
Mean (ppm)	0.202	0.194	0.960
Std Dev (ppm)	0.019	0.010	
CV_2	0.095	0.052	

n	6	6	
Mean (ppm)	0.330	0.318	0.963
Std Dev (ppm)	0.013	0.004	
CV_2	0.039	0.012	
(c) 80% RH & 25 °C			
n	6	5	
Mean (ppm)	0.071	0.068	0.958
Std Dev (ppm)	0.002	0.002	
CV_2	0.031	0.031	
n	6	5	
Mean (ppm)	0.087	0.093	1.06
Std Dev (ppm)	0.003	0.002	
CV_2	0.033	0.018	
n	6	5	
Mean (ppm)	0.180	0.179	0.992
Std Dev (ppm)	0.006	0.005	
CV_2	0.034	0.026	
n	6	6	
Mean (ppm)	0.288	0.311	1.08
Std Dev (ppm)	0.026	0.009	
CV_2	0.089	0.028	
All Levels			
CV_2 (pooled)	0.035	0.072	

Table 5a
Collection Efficiency - Midget Fritted Glass Bubblers
(2 X PEL, 25 °C & 50% RH)

	ppm Chlorine Dioxide		
Sample No.	First Bubbler	Second Bubbler	% Collection Efficiency
1	0.192	ND	100
2	0.200	ND	100
3	0.200	ND	100
4	0.189	ND	100
5	0.205	ND	100
6	0.177	ND	100

Note: (1) Sampled at 0.5 L/min for 240 min

(2) Sampling solution = 25 mL

(3) ND = None detectable, < 0.02 ppm ClO_2

Table 5b
Breakthrough Study
(25 °C and 50% RH)

	ppm ClO_2 Found		
Sample No.	1st Bubbler	2nd Bubbler	% Breakthrough
1	0.319	ND	0
2	0.315	ND	0
3	0.317	ND	0
4	0.324	ND	0
5	0.314	ND	0
			no breakthrough
6	0.686	0.076	9.97
7	0.682	0.066	8.82
8	0.666	0.081	10.84
9	0.680	0.062	8.36
10	0.680	0.062	8.36
11	0.633	0.057	8.26
			9.1% breakthrough

n = 6

Mean = 9.10

Std Dev = 1.06

CV = 0.12

Note: (1) Sampled at 0.5 L/min for 240 min

(2) Sampling solution = 25 mL

(3) ND = None detectable, < 0.02 ppm ClO_2

Table 6
Storage Stability Test - Chlorine Dioxide

Test Level	Air Vol	Found	Taken	Statistical Analysis				
0.13 ppm ClO_2	(L)	ppm	ppm	n	Mean	Std Dev	CV	Recovery (%)
Day 1	116	0.133	0.130					
	112	0.128	0.130					
	116	0.128	0.130					
	117	0.126	0.130					
	119	0.115	0.130					
	104	0.127	0.130					
				6	0.126	0.006	0.047	97.1
Day 5	116	0.125	0.130					
	112	0.122	0.130					
	116	0.117	0.130					
	117	0.123	0.130					
	119	0.125	0.130					
	104	0.118	0.130					
				6	0.122	0.003	0.028	93.6
Day 15	116	0.133	0.130					
	112	0.129	0.130					
	116	0.127	0.130					
	117	0.125	0.130					
	119	0.131	0.130					
	104	0.157*	0.130					
				5	0.129	0.003	0.025	99.2
Day 30	116	0.126	0.130					
	112	0.130	0.130					
	116	0.130	0.130					
	117	0.128	0.130					
	119	0.125	0.130					
	104	0.161*	0.130					
				5	0.128	0.002	0.018	98.3
Day 48	116	0.131	0.130					

	112	0.131	0.130					
	116	0.127	0.130					
	117	0.128	0.130					
	119	0.127	0.130					
	104	0.164*	0.130					
				5	0.129	0.002	0.016	99.1
Day 96	116	0.137	0.130					
	112	0.132	0.130					
	116	0.128	0.130					
	117	0.133	0.130					
	119	LIA	0.130					
	104	0.161*	0.130					
				4	0.133	0.004	0.028	102

LIA = Lost in Analysis

[*] Outlier - not used in statistical analysis

Table 7
Humidity Test - Chlorine Dioxide
(1 X PEL & 25 °C)

% RH		26	50	80
ppm ClO_2 Taken		0.107	0.130	0.087
ppm ClO_2 Found		0.112	0.133	0.094
		0.106	0.128	0.094
		0.108	0.128	0.093
		0.110	0.126	0.090
		0.124	0.115	0.092
		0.116	0.127	0.129*
n	=	6	6	5
Mean (ppm)	=	0.113	0.126	0.093
Std Dev (ppm)	=	0.007	0.006	0.002
CV	=	0.058	0.047	0.018
Ave Recovery	=	105%	97.1%	106%

* Excluded from statistical analysis as an outlier.

At the 95% confidence level:Fcrit = 3.68 Fcalc = 3.39 (2, 15 degrees of freedom) Fcrit > Fcalc; therefore, a significant difference in results was not noted across the humidity levels tested.

Table 8
Chlorine Dioxide and Chlorine Mixture Study
(25 °C & 50% RH)

	Chlorine		Chlorine Dioxide	
	Taken[*]	Found[**]	Taken[***]	Found[**]
Air Vol, L	ppm	ppm	ppm	ppm
29	1.56	1.62	0.556	0.488
27	1.56	1.72	0.556	0.497
29	1.56	1.70	0.556	0.481
29	1.56	1.71	0.556	0.514
28	1.56	1.66	0.556	0.499
26	1.56	1.60	0.556	0.506

n	=	6	6
Mean	=	1.67	0.498
Std Dev	=	0.05	0.012
CV	=	0.03	0.024
Recovery	=	107%	89.5%

[*] MFGB samples containing KI/buffer. These samples were collected from the chlorine atmosphere immediately before mixing. They were analyzed by IC.

[**] MFGB samples containing KI/buffer. These samples were collected after mixing the chlorine and chlorine dioxide. They were analyzed by IC.

[***] CPR samples. These samples collected after mixing and then analyzed using NIOSH CPR method. This result is corrected for the influence of chlorine.

Note: Samples were also taken using the CPR method immediately before mixing. The results of all CPR samples indicated:

1) CPR samples taken of only the generated chlorine gave 0.133 ppm as chlorine dioxide.

2) CPR samples taken of the mixture gave 0.689 ppm as chlorine dioxide.

3) Therefore, the correction for the chlorine dioxide Taken ppm was:

0.689 - 0.133 = 0.556 ppm

Table 9
Qualitative and Quantitative Detection Limits (IUPAC Method)

		Chlorine Dioxide (as ClO_2) Level		
		0.10 µg/mL	0.20 µg/mL	0.50 µg/mL
Sample No.		PA	PA	PA
1		0.966	2.806	14.05
2		1.187	4.338	14.87
3		0.890	3.391	15.56
4		1.210	3.986	14.27
5		1.619	3.064	15.54
6		1.520	3.368	15.79
n	=	6	6	6
Mean	=	1.232	3.492	15.01
Std dev	=	0.291	0.573	0.732
CV	=	0.236	0.164	0.049

PA = Integrated Peak Area (ClO_2^-)/100,000

Using the equation: $C_{ld} = k(sd)/m$

where:

C_{ld} = the smallest reliable detectable concentration an analytical instrument can determine at a given confidence level.

k = 3 (Qualitative Detection Limit, 99.86% Confidence)

= 10 (Quantitative Detection Limit, 99.99% Confidence)

sd = standard deviation of the 0.1 µg/mL standard readings.

m = analytical sensitivity or slope as calculated by linear regression.

C_{ld} = 3(0.291)/35.35 = 0.025 µg/mL ClO_2^- for the qualitative limit.

C_{ld} = 10(0.291)/35.35 = 0.082 µg/mL ClO_2^- for the quantitative limit.

Qualitative detection limit = 0.38 µg ClO_2^- (15-mL sample volume) or 0.001 ppm ClO_2 (120-L air volume).

Quantitative detection limit = 1.23 µg ClO_2^- (15-mL sample volume) or 0.004 ppm ClO_2 (120-L air volume).

Block Diagram of the Laboratory Generation System

The system shown below provided a means for generating dynamic test atmospheres. The system consists of four essential elements: a flow-temperature-humidity control system, a chlorine dioxide (and chlorine) vapor generating system (see Figure 2), a mixing chamber, and an active sampling manifold.

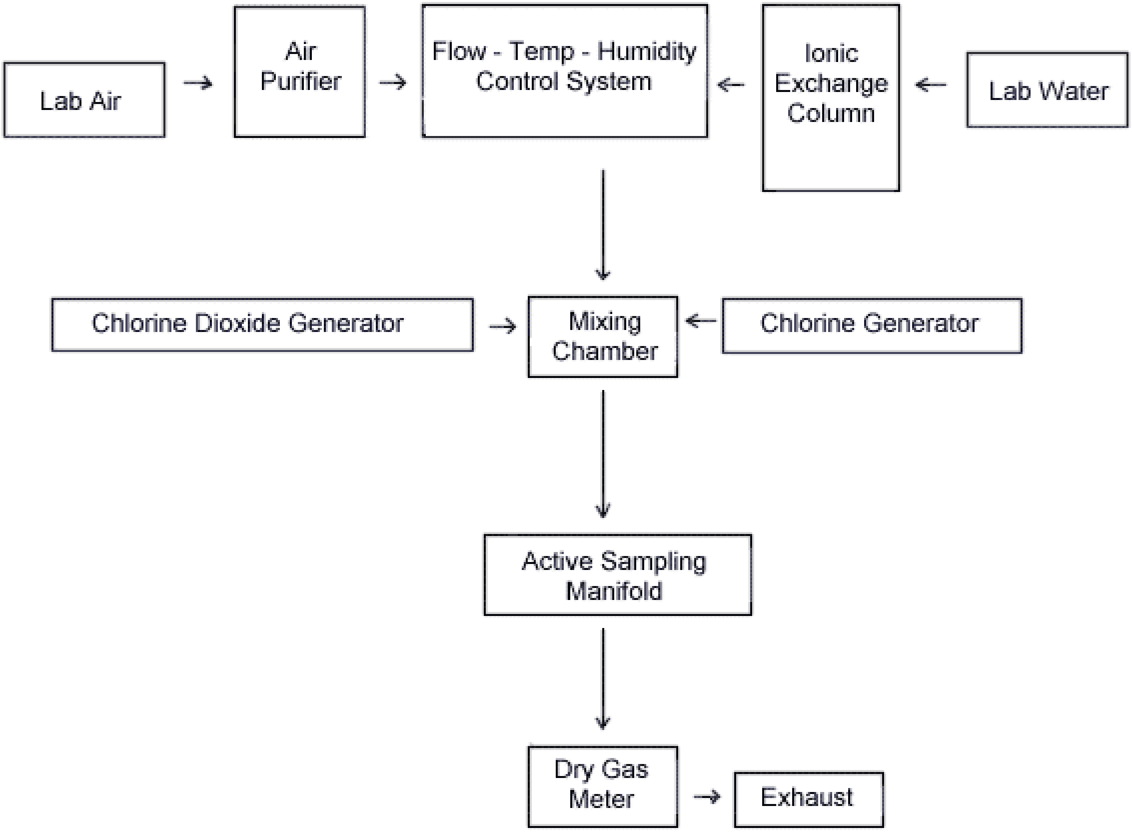
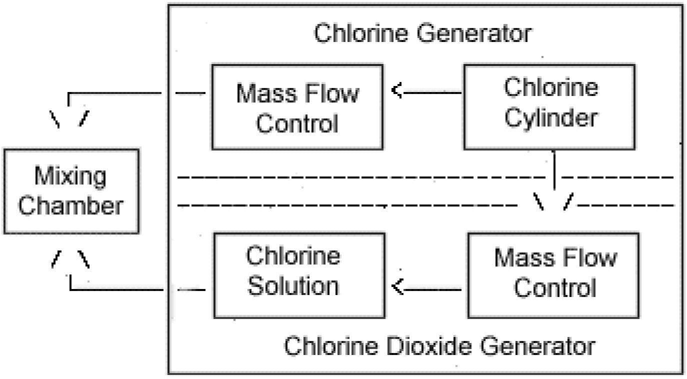


Figure 1

Block Diagram of the Chlorine Dioxide (and Chlorine) Generator

The equipment shown below provided a means for dynamic generation of chlorine dioxide and chlorine test atmospheres.



* 10 g $NaClO_2$ in 25 mL deionized water

Figure 2