

DETERMINATION OF CHLORINE DIOXIDE IN WORKPLACE ATMOSPHERES




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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 midjet 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 <sub>2</sub> <sup>-</sup> ) 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 <sub>T</sub> :	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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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 sample collection and analysis of airborne chlorine dioxide (ClO<sub>2</sub>). 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<sub>2</sub> in the workplace involved collecting samples in 0.01 N sodium hydroxide (8.1). Because this method was also used to collect chlorine (Cl<sub>2</sub>) and could not discriminate between the two species, a better method was needed. The scientific literature contains few articles addressing Cl<sub>2</sub> and ClO<sub>2</sub> analysis. A method proposed by NIOSH was a spectrophotometric technique based on the decolorization of chlorophenol red (CPR) by ClO<sub>2</sub> (8.2). Another method was proposed by the Workers' Compensation Board of British Columbia as the N,N-Dimethyl-p-phenyldiamine sulfate (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<sub>2</sub> and ClO<sub>2</sub> 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:

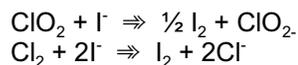
- a) Chlorine produces a significant positive interference;
- b) The stock solution used for ClO<sub>2</sub> analysis is very difficult to prepare and extremely unstable.

A comparison of the CPR and NNDP method indicated a disagreement in results below 0.3 ppm ClO<sub>2</sub>; 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<sub>2</sub>. 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<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub>) buffer solution. Chlorine dioxide as well as chlorine are trapped and converted to chlorite (ClO<sub>2</sub><sup>-</sup>) and chloride (Cl<sup>-</sup>), respectively, in neutral or a weak basic solution according to the following chemical reactions:



The collected ClO<sub>2</sub> (as ClO<sub>2</sub><sup>-</sup>) 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<sub>2</sub> collected can be estimated as Cl<sup>-</sup>; however, the evaluation of this method did not include a full validation of the sampling and analysis of Cl<sub>2</sub>. Therefore, results for Cl<sub>2</sub> are only used as a screening tool. For further information regarding sampling and analysis of Cl<sub>2</sub>, 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<sub>2</sub>.
- 1.3.2 The method is simple, rapid, and easily automated.
- 1.3.3 The analysis is specific for ClO<sub>2</sub> (determined as chlorite ion, ClO<sub>2</sub><sup>-</sup>), in the presence of Cl<sub>2</sub>.
- 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<sub>2</sub> 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 <sub>2</sub>
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<sub>2</sub> 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

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Note: Information listed within this section is a synopsis of current knowledge of the physiological effects of ClO<sub>2</sub> and is not intended to be used as the basis for OSHA policy.

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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<sub>2</sub> below 0.1 ppm, combined with about 1 ppm Cl<sub>2</sub>, 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<sub>2</sub>) when using a 15-mL solution volume. This corresponds to 0.001 ppm ClO<sub>2</sub> for a 120-L air volume.
- 2.3 The quantitative detection limit was 0.082 µg/mL or 1.23 µg (as ClO<sub>2</sub>) when using a 15-mL solution volume. This corresponds to 0.004 ppm ClO<sub>2</sub> 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 x 10<sup>6</sup> area units per 1 µg/mL when using the instrumentation mentioned in Section 6.2.

## 3. Method Performance (8.9)

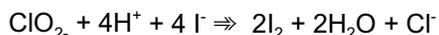
- 3.1 This method was compared to the NIOSH chlorophenol method for ClO<sub>2</sub> (8.2). All results were obtained using the NIOSH reference method results as known values. Bias and overall error values are reported below as compared to the NIOSH method.
- 3.2 The pooled coefficient of variation (CV<sub>T</sub>), 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 (≤ ±25%) at ±20%.
- 3.3 The CV<sub>2</sub>(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<sub>2</sub> was 100%. Samples were collected at a generated concentration of 0.202 ppm ClO<sub>2</sub> for 240 min.
- 3.5 A breakthrough test was performed at a concentration of 0.33 ppm ClO<sub>2</sub>. 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<sub>2</sub> 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<sub>2</sub>.
- 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<sub>3</sub>-), sulfate (SO<sub>4</sub><sup>2-</sup>), and phosphate (HPO<sub>4</sub><sup>2-</sup>), do not interfere. However, very large amounts (> 100 µg/mL) of Cl<sup>-</sup> may interfere with the determination of ClO<sub>2</sub>. The possibility of collecting this quantity of Cl<sup>-</sup> in the workplace is minimal.

Particulate chloride contamination will present a positive interference for the screening determination of  $\text{Cl}_2$ . Care must be exercised to not contaminate the collection solutions with chloride salts if screening for  $\text{Cl}_2$  is desired.

- 4.4 When other compounds are known or suspected to be present in the air, such information should be transmitted with the sample.
- 4.5 Altering the pH of the collection solution to more acidic conditions will alter the reaction of  $\text{ClO}_2$  to  $\text{ClO}_2^-$ . 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:



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  $\pm 5\%$  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  $\text{Na}_2\text{CO}_3$ /1.5 mM  $\text{NaHCO}_3$ ):  
Dissolve 0.636 g  $\text{Na}_2\text{CO}_3$  and 0.504 g  $\text{NaHCO}_3$  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 workshift 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, labcoat, 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 micromembrane suppressor, Dionex).
- 6.2.6 Disposable syringes (1 mL) and filters.

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(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).

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- 6.2.7 Miscellaneous volumetric glassware: Micropipettes, buret, 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 ( $\text{Na}_2\text{CO}_3$ )  
Potassium iodide (KI)  
Sodium chloride (NaCl)  
Sulfuric acid

- 6.3.1 Eluent 1: Deionized water (DI  $\text{H}_2\text{O}$ ) with a specific conductance of less than 10  $\mu\text{S}$ .
- 6.3.2 Eluent 2 (10 mM  $\text{Na}_2\text{CO}_3$ ):  
Dissolve 2.12 g  $\text{Na}_2\text{CO}_3$  in 2.0 L of DI  $\text{H}_2\text{O}$ .
- 6.3.3 Eluent 3 (10 mM  $\text{NaHCO}_3$ ):  
Dissolve 1.68 g  $\text{NaHCO}_3$  in 2.0 L of DI  $\text{H}_2\text{O}$ .
- 6.3.4 Buffer solution (1.5 mM  $\text{Na}_2\text{CO}_3$ /1.5 mM  $\text{NaHCO}_3$ ):  
Dissolve 0.636 g  $\text{Na}_2\text{CO}_3$  and 0.504 g  $\text{NaHCO}_3$  in 4.0 L of DI  $\text{H}_2\text{O}$ .
- 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  $\text{H}_2\text{SO}_4$ ):  
Place 1.14 mL concentrated  $\text{H}_2\text{SO}_4$  into a 2-L volumetric flask which contains about 500 mL DI  $\text{H}_2\text{O}$ . Dilute to volume with DI  $\text{H}_2\text{O}$ .
- 6.3.7 Chloride stock standard (1,000  $\mu\text{g}/\text{mL}$ ):  
Dissolve 1.6479 g dried NaCl and dilute to the mark in a 1-L volumetric flask with DI  $\text{H}_2\text{O}$ .
- 6.3.8 Chloride standards (100, 10, and 1  $\mu\text{g}/\text{mL}$ ):  
Perform serial dilutions of the 1,000  $\mu\text{g}/\text{mL}$  chloride stock standard with collection solution. Prepare weekly. [Note: Prepare only if necessary. These standards are only used to screen  $\text{Cl}_2$  (as  $\text{Cl}^-$ ) concentrations.]
- 6.3.9 Chlorite stock standard (1,000  $\mu\text{g}/\text{mL}$ ):  
Dissolve in a 1-L volumetric flask approximately 1.7 g sodium chlorite ( $\text{NaClO}_2$ ) in 500 mL DI  $\text{H}_2\text{O}$ . Dilute to the mark with DI  $\text{H}_2\text{O}$ . 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  $\mu\text{g}/\text{mL}$ ). Dilute 10 mL of the 1,000  $\mu\text{g}/\text{mL}$  chlorite stock standard to 100 mL with collection solution. Prepare monthly.
- 6.3.11 Chlorite standard (10  $\mu\text{g}/\text{mL}$ ). Dilute 10 mL of the 100  $\mu\text{g}/\text{mL}$  chlorite stock standard to 100 mL with collection solution. Prepare weekly.
- 6.3.12 Chlorite standard (1  $\mu\text{g}/\text{mL}$ ). Dilute 10 mL of the 10  $\mu\text{g}/\text{mL}$  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 ( $\pm 0.5\%$  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 that has aged significantly.

- a) Sodium thiosulfate solution ( $\text{Na}_2\text{S}_2\text{O}_3$ ), 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.
- b) Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), concentrated.
- c) Sulfuric acid, dilute.  
Slowly and cautiously add 40 mL of concentrated  $\text{H}_2\text{SO}_4$  to a 200-mL volumetric flask which contains 150 mL DI  $\text{H}_2\text{O}$ . Allow to cool, then dilute to volume with DI  $\text{H}_2\text{O}$ .
- d) Potassium iodide (KI).
- e) Starch indicator solution, (1% w/v): Gradually add about 5 mL of DI  $\text{H}_2\text{O}$  to 1 g soluble starch, with stirring, until a paste is formed. Add the paste to 100 mL of boiling DI  $\text{H}_2\text{O}$ . 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)

- a) Add 10 mL of dilute  $\text{H}_2\text{SO}_4$  into a 125-mL Phillips beaker which contains 20.0 mL of  $\text{NaClO}_2$  stock solution (1,000  $\mu\text{g}/\text{mL}$ , from Section 6.3.9).
- b) Add 1 g of KI and 40 mL of DI  $\text{H}_2\text{O}$ .
- c) Titrate with standardized 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  until a color change to a light straw color is achieved.
- d) Add 2 mL of 1% starch indicator. A blue color should appear.
- e) Titrate again with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  until the blue color completely disappears.
- f) For blank sample(s), repeat steps 1 through 5 except use 20.0 mL DI  $\text{H}_2\text{O}$  instead of 20.0 mL of the  $\text{NaClO}_2$  stock solution.
- g) Calculate  $\mu\text{g}/\text{mL}$  chlorite as follows:  
where:

$$\mu\text{g}/\text{mL ClO}_2^- = \frac{(A-B)(C)(D)}{E}$$

A = mL of the standardized  $\text{Na}_2\text{S}_2\text{O}_3$  solution required to titrate the sample  
 B = mL of the standardized  $\text{Na}_2\text{S}_2\text{O}_3$  solution required to titrate the blank  
 C = normality of the standardized  $\text{Na}_2\text{S}_2\text{O}_3$  solution (meq/mL)  
 D = (16.875 mg/meq  $\text{ClO}_2^-$ )(1,000  $\mu\text{g}/\text{mg}$ ) =  $16.875 \times 10^3$   $\mu\text{g}/\text{meq}$  of  $\text{ClO}_2^-$ .  
 E = mL of  $\text{ClO}_2^-$  used = 20 mL

6.4.2 Working standard preparation:

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

Working std $\mu\text{g}/\text{mL}$	Standard Solution $\mu\text{g}/\text{mL}$	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

b) Pipette appropriate aliquots of standard solutions (prepared in Section 6.3) into 10-mL volumetric 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 filtercap 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<sub>2</sub>O  
Eluent 2: 10.0 mM Na<sub>2</sub>CO<sub>3</sub>  
Eluent 3: 10.0 mM NaHCO<sub>3</sub>  
Pump pressure: approximately 900 psi  
Flow rate: 2 mL/min

Time min	Flow mL/min	Eluent			Comments
		%1	%2	%3	
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	
14.1	2.0	70	0	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.

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Column & Sample Injection	
Column:	HPIC-AS4A
Column temperature:	ambient
Sample injection loop:	50 µL
Chromatogram	
Run time:	18 min
Peak retention time:	
ClO <sub>2</sub>	approximately 2 min
Cl <sup>-</sup>	approximately 3 min

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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<sub>2</sub> and 0.5 µg/mL Cl<sup>-</sup> 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:

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

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<sub>2</sub> and Cl<sub>2</sub> in each air sample is expressed in ppm.

$$\text{ppm ClO}_2 = \frac{\mu\text{gC Analyte} \times \text{Molar volume}}{\text{Air volume} \times \text{Molecular weight}}$$

$$\text{ppm Cl}_2^* = \frac{\mu\text{gC Analyte} \times \text{Molar volume}}{\text{Air volume} \times \text{Molecular weight}}$$

where:

µg/mL ClO<sub>2</sub> or Cl<sup>-</sup> = Amount found from the curve

Solution volume (mL) = Amount of sample (from Section 6.5.1)

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

Molecular weight for ClO<sub>2</sub> = 67.5

Molecular weight for Cl<sub>2</sub> = 71.0

\* Note: Results for Cl<sub>2</sub> 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 chlorine may be used as information to the industrial hygienist. Additional sampling for chlorine may be recommended using OSHA method no. ID-101.

## 8. References

- 8.1 Occupational Safety and Health Administration Analytical Laboratory: Chlorine Dioxide (Tentative), Internal Document. Salt Lake City, UT, 1971 (unpublished).
- 8.2 National Institute for Occupational Safety and Health: Methods Development for Sampling and Analysis of Chlorine, Chlorine Dioxide, Bromine, and Iodine - Research Report for Chlorine Dioxide by W.K. Fowler and H.K. Dillon. Birmingham, AL: Southern Research Institute (Contract no. 210-80-0067), 1982.
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Chromatogram of a Mixture of 5 µg/mL ClO<sub>2</sub> and 0.5 µg/mL Cl<sup>-</sup>

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

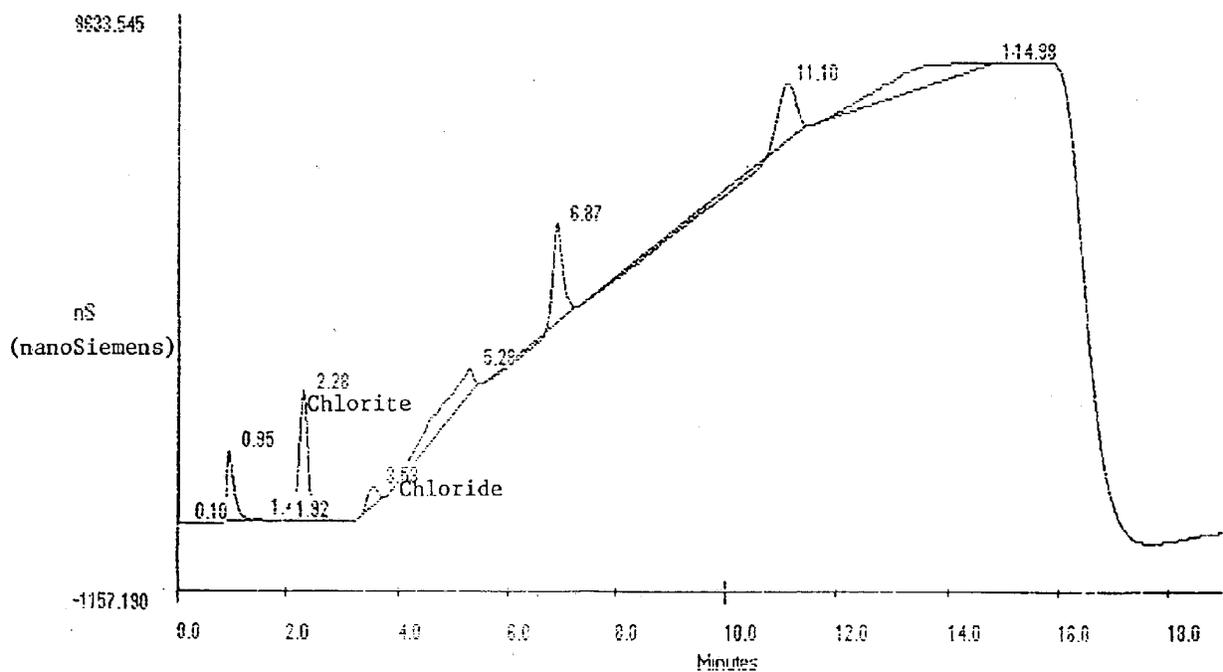


Figure 1