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Chlorine and Chlorine Dioxide in Workplace Atmospheres



Method No.:	ID-126SGX
Matrix:	Air
OSHA Standard:	0.1 mg/m ³
Collection Procedure:	2% KI in an impinger
Recommended Air Volume:	100 liters
Recommended Sampling Rate:	0.1 to 1.0 L/min
Analytical Procedure:	Titration with 0.01 N sodium thiosulfate
Detection Limit:	1.0 mg/m ³ for a 10 L sample
Precision:	Unknown
Method Classification:	PV

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Note: OSHA no longer uses or supports this method (2021)

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1. Introduction

1.1. Scope

1.1.1. This method describes the sampling and analysis of high levels of chlorine and chlorine dioxide by titration with 0.01 N sodium thiosulfate.

1.2. Advantages and Disadvantages

1.2.1. Both chlorine and chlorine dioxide can be analyzed together.

1.2.2. Little instrumentation is necessary.

1.2.3. The analytical technique is not sophisticated.

1.2.4. The analysis suffers from many interferences.

1.2.5. This method is accurate for levels of chlorine and chlorine dioxide above 1.0 µg/mL for a 10 L sample.

1.2.6. The collection of oxidants can be monitored by observing the color change of the 2% KI solution.

1.2.7. The method gives a very precise measure of total available strength of a solution in terms of its ability to liberate iodine from iodide. (Reference 7.1)

1.2.8. Temperature and strong light affect solution stability. Minimum ClO₂ losses occur when the determination is completed immediately at the site of sample collection.

1.3. Principle

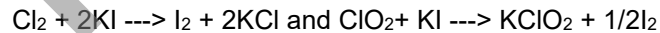
1.3.1. The sample is collected using an impinger or Liquid Media Sampler (LMS) containing 2% KI.

1.3.2. The sample is then titrated with 0.01 N sodium thiosulfate with starch as an indicator to a colorless endpoint.

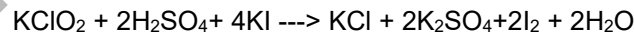
1.3.3. 5 mL of 1 N sulfuric acid is then added to the sample and the sample is again titrated with 0.01 N sodium thiosulfate to a colorless endpoint.

1.3.4. The concentrations of chlorine and chlorine dioxide are then calculated.

1.3.5. In a neutral solution of 2% KI:



In an acid solution of 2% KI:



2. Range and Detection Limit

2.1. The detection limit is 1.0 µg/mL for a 10 L air sample. The range is 100 µg to 50 mg.

3. Precision and Accuracy

3.1. Unknown

4. Interferences

4.1. Any compounds capable of oxidizing KI to I₂ will interfere with the analysis.

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5. Sampling

5.1. Apparatus

- 5.1.1. Personal sampling pump.
- 5.1.2. Impinger or Liquid Media Sampler.
- 5.1.3. 2% KI collection solution.
- 5.1.4. Glass fiber pre-filters to remove particulates.

5.2. Procedure

- 5.2.1. Sampling is done in accordance with current instructions contained in OSHA directives to the industrial hygienist.
- 5.2.2. The sample is collected in a 2% KI solution using a flow rate of 0.1 to 1 liters per minute. A glass fiber filter should be used to remove any particulates. The net weight collected in micrograms is then divided by the air volume in liters.
- 5.2.3. Enough air must be collected to cause the clear 2% KI solution to turn yellow or red.
- 5.2.4. If the samples are to be sent to the lab for analysis, they must be protected from heat and light. Wrap the impingers with tape, pack in ice, and ship air express.

6. Analytical Procedure

6.1. Apparatus

- 6.1.1. 50-mL Class A burette with Teflon stopcock.
- 6.1.2. Glass volumetric pipettes.
- 6.1.3. Micropipettes with tips.
- 6.1.4. 125-mL Erlenmeyer flask.
- 6.1.5. Mechanical stirrer.

6.2. Reagents: All chemicals should be ACS reagent grade or equivalent, and the dilution water must be boiled in accordance with Reference 7.1.

- 6.2.1. 1.0 N Sulfuric Acid: Slowly add 28 mL H_2SO_4 to about 500 mL freshly boiled deionized water, stir and let cool. Dilute to 1 L with boiled deionized water.
- 6.2.2. Starch indicator solution: To 5 g starch add a little cold water and grind in a mortar to a thin paste. Pour into 1 L of boiling distilled water, stir, and let settle overnight. Decant the clear supernate. Preserve with 4 g zinc chloride.
- 6.2.3. 0.1 N Sodium Thiosulfate: Dissolve 25 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 1 L freshly boiled deionized water and standardize against potassium dichromate after at least 2 weeks storage. This initial storage is necessary to allow oxidation of any bisulfite ion present. Add a few mL chloroform to minimize bacterial decomposition.
- 6.2.4. 0.1 N Potassium Dichromate: Dissolve 4.904 g anhydrous $\text{K}_2\text{Cr}_2\text{O}_7$ of primary standard quality, in distilled water and dilute to 1 L. Store in a glass stoppered bottle.
- 6.2.5. 0.01 N Sodium Thiosulfate titrant: Improve the stability of 0.01 N sodium thiosulfate by diluting an aged 0.1 N solution of sodium thiosulfate (6.2.3) with freshly boiled deionized

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water. Add 4 g sodium borate and 10 mg mercuric iodide per liter. For accurate work, standardize daily.

6.2.6. 2% Potassium Iodide: Add 20 g of KI crystals to 500 mL freshly boiled deionized water and dilute to 1 L. Store in a brown glass-stoppered bottle and discard the solution when a yellow color has developed.

6.2.7. 0.01 N Potassium Dichromate: Dilute 10 mL of the 0.1 N potassium dichromate (6.2.4.) to 1 L with deionized water.

6.3. Sample Preparation

6.3.1. Take a 1 to 15 mL aliquot of sample and transfer to a 125-mL erlenmeyer flask. Add boiled deionized water to make the total volume 30 mL. The sample aliquot size will depend on the intensity of the color of the collecting solution.

6.4. Standard Preparation

6.4.1. Standards need not be prepared for a calibration curve for each analysis. If standards are wanted see the chlorine dioxide generation system described in the chlorine dioxide backup report.

6.5. Analysis

6.5.1. Standardize the 0.01 N sodium thiosulfate (6.2.5) with the 0.01 N potassium dichromate (6.2.7) using the following procedure. To 50 mL of freshly boiled deionized water add 10 mL of the 0.01 N potassium dichromate (6.2.7), 1 mL of concentrated sulfuric acid, and 1 g potassium iodide crystals. Allow the mixture to stand 6 minutes in the dark before titration with the 0.01 N sodium thiosulfate solution (6.2.5). Standardize prior to use.

Calculation of Normality:

Normality $\text{Na}_2\text{S}_2\text{O}_3 = 1/\text{mL } \text{Na}_2\text{S}_2\text{O}_3 \text{ consumed}$

6.5.2. Record the initial volume of 0.01 N sodium thiosulfate and titrate the sample until the yellow color almost disappears.

6.5.3. Add 0.5 mL of the starch indicator (6.2.2). A blue color will appear.

6.5.4. Titrate with 0.01 N sodium thiosulfate until the blue color just disappears. Record the volume of thiosulfate. This is the neutral endpoint.

6.5.5. Add 5 mL of 1 N sulfuric acid. The blue color will return and the solution should be very dark.

6.5.6. Titrate with 0.01 N sodium thiosulfate until the blue color just disappears. Record the volume of thiosulfate. This is the acid endpoint.

6.6. Calculations

6.6.1. Subtract the initial volume of sodium thiosulfate from the volume at the neutral endpoint. This is the volume to the neutral endpoint. Multiply this volume by the standardized normality of the thiosulfate solution to give the number of neutral equivalents.

6.6.2. Subtract the initial volume of sodium thiosulfate from the volume at the acid endpoint. This is the volume to the acid endpoint. Multiply this volume by the standardized normality of the thiosulfate solution to give the number of total acid equivalents.

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6.6.3. From the equations in 1.3.5, it can be seen that 1/5 of the chlorine dioxide and all of the chlorine reacts in the neutral solution. Four fifths of the chlorine dioxide reacts in the acid solution.

6.6.4. To calculate the number of milligrams of chlorine dioxide use the following formulas:

$$\text{equivalents } ClO_2 = \frac{5(\text{total acid equivalents} - \text{neutral equivalents})}{4}$$

$$\text{milligrams } ClO_2 = \frac{(\text{equivalents } ClO_2)(1 \text{ mole} \times 67.5 \text{ grams} \times 10^2 \text{ mg})}{5 \text{ equivalents} \times \text{mole} \times \text{gram}}$$

6.6.5. To calculate the number of milligrams of chlorine use the following formulas:

$$\text{equivalents } Cl_2 = (\text{total acid equivalents} - \text{equivalents } ClO_2)$$

$$\text{milligrams } Cl_2 = \frac{(\text{equivalents } Cl_2)(1 \text{ mole} \times 70.9 \text{ grams} \times 10^2 \text{ mg})}{2 \text{ equivalents} \times \text{mole} \times \text{gram}}$$

7. References

- 7.1. Standard Methods for the Examination of Water and Wastewater, 15th Ed., pg 304 (1980).
- 7.2. Methods Development for Sampling and Analysis of Chlorine, Chlorine Dioxide, Bromine, and Iodine, by the Southern Research Institute for NIOSH, project 4558-R1.
- 7.3. Fritz and Schenk, Quantitative Analytical Chemistry, pg 278.

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CHLORINE DIOXIDE BACKUP REPORT

1. Introduction

1.1. Scope

1.1.1. This report describes the chlorine dioxide generation system used to make chlorine and chlorine dioxide standards.

1.2. Principle

1.2.1. Chlorine dioxide is produced when chlorine vapor is passed through a concentrated aqueous solution of sodium chlorite.

2. Construction of test atmosphere generator

2.1. Apparatus

2.1.1. Chlorine, 99% pure.

2.1.2. Chlorine regulator, Model 660.

2.1.3. 250-mL impinger.

2.1.4. Sodium chlorite, reagent grade.

2.1.5. Two flowmeters, accurate to within 1%. These flowmeters must be made of inert materials like glass or Teflon.

2.1.6. Tubing--glass, Teflon, or other inert materials, and tubing connectors.

2.1.7. Mixing and sampling chamber, Teflon.

2.1.8. Separate air source capable of providing dilution air at various temperature ranges.

2.1.9. Pure nitrogen gas with regulator.

2.2. Design

2.2.1. The generator is designed such that any range of chlorine dioxide can be generated from 50 to 50,000 PPM.

2.2.2. A 250-mL impinger containing 80 grams sodium chlorite in 200 mL deionized water is used as a chlorine to chlorine dioxide conversion chamber.

2.2.3. Teflon tubing is used to connect the chlorine tank to the chlorine flowmeter and the nitrogen tank to the nitrogen flowmeter.

2.2.4. Teflon tubing is used to connect the chlorine flowmeter to one leg of a "T" connector. Tubing is also run from the nitrogen flowmeter to another leg of the "T" connector. The third leg of the "T" will go to the chlorine dioxide conversion chamber.

2.2.5. Connect Teflon tubing from the output of the chlorine dioxide conversion chamber to the output of the dilution air source.

2.2.6. The diluted chlorine stream is then directed to the mixing and sampling manifold using Teflon tubing.

2.2.7. For an 800 PPM chlorine dioxide atmosphere, set the chlorine flowmeter to 17 mL/min, the nitrogen flowmeter to 2 L/min, and the dilution air to 40 L/min.

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- 2.2.8. To prepare lower concentrations of chlorine dioxide use a tank of 400 PPM chlorine in nitrogen instead of pure chlorine and increase the chlorine flowmeter while cutting back on the flow of dilution air.

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