Laboratory Preparations Of Chlorine Dioxide Solutions

There are two common methods used to prepare laboratory solutions of chlorine dioxide. The choice of method depends upon required purity of the resultant solution. Method I produces a material equivalent to that produced by most commercial chlorine dioxide generators. Method II produces a reagent grade, chlorine dioxide solution with no free chlorine and is used for instrument standards and for studies where free chlorine would interfere.

Chlorine dioxide solutions should be protected from sunlight (ultraviolet light) and heat. Chlorine dioxide solutions can be stored in amber bottles in a refrigerator for some time. A gradual decrease in chlorine dioxide concentrations will occur due to volatilization and decomposition.

Precautions: *The chlorine dioxide solution concentrations produced in these procedures are high enough that a small amount of chlorine dioxide gas may escape to the air. Since chlorine dioxide is an irritating oxidizer, always work in a well-ventilated hood.*

Method I: Preparation of Technical-Grade Chlorine Dioxide Solutions.

Purpose: To prepare chlorine dioxide solutions (approx. 2000 ppm) typical of those produced by most chlorine dioxide generators. These solutions may be used for studies that do not require "chlorine-free" chlorine dioxide solutions.

Summary: Chlorine dioxide (ClO_2) is produced from the oxidation of sodium chlorite ($NaClO_2$) by hypochlorous acid (HOCl). Hypochlorous acid is prepared by combining solutions of sodium hypochlorite (NaOCl) and hydrochloric acid (HCl):

$$NaOCl + HCl \rightarrow HOCl + NaCl$$

Then:

$$2NaClO_2 + HOCl + HCl \rightarrow 2ClO_2 + 2NaCl + H_2O$$

Combined Equation:

$$2NaClO_2 + NaOCl + 2HCl \rightarrow ClO_2 + 3NaCl + H_2O$$

Equipment and Reagents:

- 3-Volumetric Flasks, 1 liter
- Graduated cylinder, 25 ml
- Graduated cylinder, 100 ml
- 4-Amber reagent bottles, 1 liter
- Graduated cylinder, 50 ml
- Graduated cylinder, 250 ml
- Sodium hypochlorite solution, 5.25%
- Technical sodium chlorite solution, 31.25 (25%)
- Concentrated hydrochloric acid, 12N

Solutions:

Solution I: Dilute Sodium Hypochlorite Solution
Dilute 63 mls of 5.25% sodium hypochlorite solution to 1 liter with DI water (store in amber bottle).

Solution II: Dilute Hydrochloric Acid Solution
Add 8 mls of concentrated (12N) hydrochloric acid to 500 mls of water in a 1 liter volumetric flask. Mix and make up to volume with DI water (store in an amber bottle).

Solution III: Dilute Sodium Chlorite Solution
Dilute 26 mls of Technical Sodium Chlorite Solution 31.25% to 1 liter with DI water (store in an amber bottle).

Procedure:

1. Prepare the dilute solutions shown above.
2. Pour 250 mls of dilute sodium hypochlorite solution into a 1 liter amber reagent bottle.
3. Add 250 mls of dilute hydrochloric acid solution to the reagent bottle, mix.
4. Add 250 mls of dilute sodium chlorite solution to the reagent bottle, mix.
5. Store the chlorine dioxide solution in a closed amber bottle in a refrigerator. Properly stored solutions may be used for weeks, but should be standardized daily, prior to use, by an approved method[1].

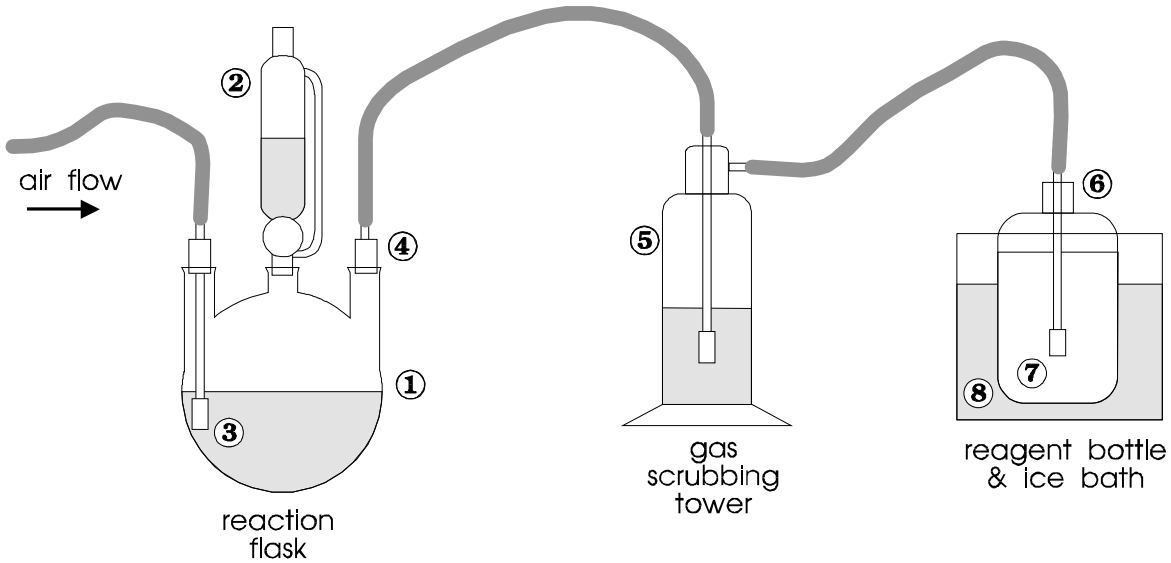

Figure 1 Generation Setup for Method II

<u>Method II:</u> Preparation of Reagent-Grade Chlorine Dioxide Solution.

Purpose: To prepare low concentration (<1000 ppm), chemically pure, chlorine dioxide solutions for use as instrument standards or for studies, like trihalomethanes (THM) abatement studies, where the possibility of any chlorine contamination must be avoided.

Summary: Chlorine dioxide (ClO_2) is produced by the acidification of sodium chlorite ($NaClO_2$) solution with sulfuric acid (H_2SO_4):

$$4NaClO_2 + 2H_2SO_4 \rightarrow 2ClO_2 + HCl + HClO_3 + 2Na_2SO_4 + H_2O$$

Chlorine dioxide is removed from the reaction flask solution as gas by air stripping, purified by scrubbing with sodium chlorite solution and recovered by absorbing in chilled deionized (DI) water.

Equipment and Reagents:

- Three-neck reaction flask, 1-liter (1)
- Pressure equalizing addition funnel, 125-mls (2)
- air inlet tube, with adapter (3)
- gas exit adapter (4)
- gas scrubbing tower, 1-liter (5)
- amber reagent bottle, 1 liter (6)
- air inlet tube, without adapter (7)
- ice bath (8)
- flexible tubing (rubber or Tygon®)
- Technical Sodium Chlorite Solution 31.25
- concentrated sulfuric acid, 36N

Procedure:

1. Assemble the generator setup as shown in Figure 1. To ensure airtight assembly use standard taper glassware and silicon grease if possible. Rubber stoppers are an acceptable alternative.

2. Fill the reaction flask and gas scrubbing tower with 500 mls of approximately 2.5% (wt) $NaClO_2$ solution. Make certain all gas inlets are submerged. (2.5 % $NaClO_2$ solution may be prepared by diluting OxyChem Technical Sodium Chlorite Solution 31.25 1:10 with DI water).

3. Prepare 50 mls of 10% (vol) sulfuric acid solution and place this solution in the addition funnel. **WARNING: Always add acid to water; never add water to acid.**

4. Fill the amber reagent bottle with 500 to 750 mls. of DI water and place in an ice bath.

5. Turn on the air flow to the generation setup (there should be bubbles in all three solutions.) If there are not, check the setup for leaks.

6. Once there are no leaks, slowly add the acid solution (5 to 10 mls at a time). Wait 5 minutes between additions. Continue the air flow for 30 minutes after the final addition.

7. Store the chlorine dioxide solution in a closed amber bottle in a refrigerator. Properly stored solutions may be used for weeks, but should be standardized daily, prior to use, by an approved method[1].

Safety and Handling

The following summary of health and safety information is not intended to be complete. For complete information, read the current Material Safety Data Sheet (MSDS). To obtain a MSDS, contact OxyChem Technical Services, or visit the OxyChem website at www.oxy.com .

Toxicological Properties
Sodium chlorite is toxic by ingestion. Sodium chlorite may cause anemia by oral exposure and has low toxicity by dermal exposure. OxyChem sodium chlorite has an oral LD_{50} (rat) of 165 mg/kg. Sodium chlorite has a dermal LD_{50} (rabbit) of greater than 2 g/kg. Sodium chlorite can produce severe irritation or burns to the skin and eyes. Corneal damage can occur if not washed immediately from the eyes.

Personnel Protection
When handling sodium chlorite solutions, chemical goggles, face shield, neoprene gloves, apron, and boots should be worn. Wear a NIOSH/MSHA approved acid gas respirator with a dust/mist filter if any exposure is possible. Additionally, for dry sodium chlorite, wear a chemically impervious suit. Local exhaust is required where exposure to dust or mist might occur. If sodium chlorite is spilled on clothing, remove and wash contaminated clothing at once to avoid the potential of fire.

First Aid
Eyes: Immediately flush eyes with large amounts of water for at least 15 minutes while frequently lifting the upper and lower eyelids. Consult a physician immediately.

Skin: Remove contaminated clothing. Immediately flush exposed skin areas with large amounts of water for at least 15 minutes. Consult a physician if burning or irritation of the skin persists. Contaminated clothing must be laundered before re-use.

Ingestion: DO NOT induce vomiting. Drink large quantities of water. Consult a physician immediately. DO NOT give anything by mouth if the person is unconscious or having seizures.

Inhalation: Move patient to fresh air and monitor for respiratory distress. If cough or difficulty in breathing develops, administer oxygen, and consult a physician immediately. In the event that breathing stops, administer artificial respiration and obtain emergency medical assistance immediately.

Notes to Physician: Chlorine dioxide vapors are emitted when this product contacts acids or chlorine. If these vapors are inhaled, monitor patient closely for delayed development of pulmonary edema which may occur up to 48-72 hours post-inhalation.

Following ingestion, neutralization and use of activated charcoal is not indicated.

Storage and Handling
Do not contaminate sodium chlorite with incompatible materials such as dirt, organic matter, oxidizers, reducing agents, chemicals, soap products, solvents, acids, paint products, or combustible materials. Do not store or transport sodium chlorite with incompatible materials. Contamination may start a chemical reaction with generation of heat and emission of chlorine dioxide (a poisonous, explosive gas). A fire or explosion may result. Rinse empty containers thoroughly with water and dispose of in accordance with label instructions.

Dry sodium chlorite. Do not expose to moisture during storage. Store in the original container, in a cool, dry, well ventilated area away from direct sunlight. Always replace cover tightly. Mix only into water using a clean, dry metal scoop reserved for this product alone.

Keep away from flame or any burning material (such as a lighted cigarette). If fire occurs, extinguish with plenty of water. Cool any unopened drums near the fire by spraying water on them.

Sodium chlorite solutions. Store in clean, closed, non-translucent containers. Exposure to sunlight or ultra-violet light w

Do not allow solution to evaporate to dryness; this product becomes a fire or explosion hazard if allowed to dry and can ignite in contact with combustible materials.

Spill and Leak Procedures
In the event of a spill or leak, remove all sources of ignition. Wear NIOSH/MSHA approved positive pressure, self-contained breathing apparatus with a chemically impermeable, fully encapsulated suit. Follow OSHA regulations for respirator use (see 29 CFR 1910.34).

Sodium chlorite, dry, is a fire or explosion hazard if contaminated with combustible material. Clean up in a manner to avoid contamination. Spilled material should be picked up, by using a clean, dry, scoop or shovel and placed into a clean, dry, container. Do not return spilled material to the original container. Isolate the recovery container outside or in a well-ventilated area and hold for proper waste disposal. Do not seal the container. Flush any residual material with large quantities of water.

Sodium chlorite, solution, also becomes a fire or explosion hazard if allowed to dry and can ignite on contact with combustible material. Continue to keep damp. Contain spilled material by diking or absorbing with clay, soil or non-flammable commercial absorbents. Do not return spilled material to original container. Place in a clean container and isolate outside or in a well-ventilated area. Do not seal the container. Flush any residual material with large quantities of water.

Disposal

Spill residues may be a hazardous waste as defined in 40 CFR 261. The EPA hazardous waste designation for dry sodium chlorite waste would be D001 and sodium chlorite solution waste would have the waste designation of D002. As a hazardous waste, it is subject to the Land Disposal Restrictions under 40 CFR 268 and must be managed accordingly. As a hazardous waste solution or solid, it must be disposed of in accordance with local, state, and federal regulations in a permitted hazardous waste treatment, storage and disposal facility.

Shipping Information

Technical sodium chlorite is available in 100 lb. drums. Technical sodium chlorite solution 50 is available in tank trucks. Technical Sodium Chlorite Solution 31.25 is available in 55 gallon drums, 275-gallon non-returnable totes and tank trucks. Special blends are available upon request. OxyChem technical sodium chlorite is registered with the EPA for a number of pesticidal applications under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).

Further Information

More detailed information on sodium chlorite is available on request through the OxyChem Chemicals Technical Service Department. Call or write to:

Technical Service Department
OxyChem
6200 South Ridge Road
Wichita, KS 67277
800-733-1165
www.oxy.com

Reference:

1 Method 4500-ClO_2, *Standard Methods for the Examination of Water and Wastewater*., 20th Ed., APHA, Washington, D.C., 1998, pp 4-73 to 4-79

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