Small-Scale Generation of CHLORINE DIOXIDE

Three methods are described for the small-scale generation of chlorine dioxide, based on the gaseous chlorine–solid chlorite process. The selection of the method for any specific application depends on the purity of the chlorine dioxide desired, the amounts needed, the feasibility of batch or continuous production, the accuracy of control required, and the partial pressure of chlorine dioxide needed in the ClO_2–air mixture generated. All three methods produce chlorine dioxide at low partial pressures at substantially atmospheric pressures and temperatures.

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CHLORINE dioxide is rapidly finding a place among the more important oxidizing and bleaching agents. Its widespread use in the past was retarded by the lack of economical and convenient sources of the gas. Availability of chlorites in commercial quantities has made possible the plant-scale generation of chlorine dioxide in several ways, as recently described by Woodward, Petroe, and Vincent (*4*).

Since chlorine dioxide and equipment for its generation and distribution are now available at reasonable prices, numerous plants and laboratories are interested in trying the reagent in their processes or for bleaching their products. Because no suitable method is available in the literature for the small-scale production and handling of this highly reactive oxidizing gas, the purpose of this article is to describe small-scale methods for the production of chlorine dioxide that have proved useful in experimental work on the bleaching of flour in small quantities.

The number of available methods for producing the gas under accurately controlled conditions was found to be extremely limited. The electrolytic process described by Logan (*3*) was given extensive trial, in which chlorine dioxide is produced from a sodium chloride and sodium chlorite solution. The chlorinated brine method of Cunningham and Losch (*1*) was also tried; it consists of introducing chlorine diluted with air into a solution of sodium chlorite. The difficulty inherent in these continuous processes is mainly a control problem when small quantities of the gas are generated. The time for an output equilibrium to be established for any given level of chlorine dioxide concentration in the effluent gas was lengthy and uncertain.

The chief difficulties with the wet processes are corrosion of the equipment and the solubility of chlorine dioxide in aqueous solutions which makes necessary the achievement of an equilibrium between the chlorine dioxide generated, that in solution, and that stripped from the solution by air or other inert gases. Such an equilibrium is difficult to achieve and maintain, either on starting the generator or in changing the output of chlorine dioxide from one level to another. Another drawback is the necessity for the complete stripping of the chlorine dioxide from the chlorite solution to prevent undue corrosion of the equipment when it is not in use. This is a slow and wasteful process.

Early in the experimental work on flour bleaching, a need became evident for a simple method of generating small amounts of chlorine dioxide which could be precisely controlled. A successful method was found which depended on the reaction of accurately metered dry chlorine obtained from a cylinder, with substantially dry, powdered sodium chlorite according to the equation:

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

This process was described by Hutchinson and Mecham (*2*).

Three methods were developed for the utilization of this process in the laboratory. The selection of the method to be used for any specific application depended on the purity of chlorine dioxide desired, the amounts needed, the feasibility of batch-scale or continuous production, the accuracy of control needed, and the partial pressure of chlorine dioxide in the ClO_2–air mixture produced. These methods will be given in detail to facilitate the small-scale production of the gas for use in any reactions involving chlorine dioxide diluted with air or other inert gas at substantially atmospheric pressures and temperatures.

NONCONTINUOUS PRODUCTION ADMIXED WITH INERT GASES AND CHLORINE

This method yields chlorine dioxide and chlorine in the effluent gases. For flour bleaching, and probably for many other uses, the action of the excess chlorine to ensure completion of the reaction is of slight or no consequence when compared to the oxidizing power of the chlorine dioxide produced. For example, in flour bleaching the amount of chlorine dioxide generally used on a patent flour is about 1.5 grams per 196-pound barrel. The

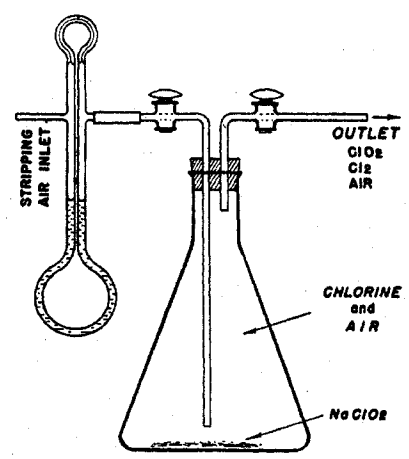

Figure 1. Apparatus for Small-Scale Production of Chlorine Dioxide Gas

chlorine required to produce 1.5 grams of chlorine dioxide, calculated from the reaction equation, is 0.79 gram. Since 100% excess of chlorine gas is used for the reaction, the amount of chlorine introduced to the flour along with 1.5 grams per barrel of chlorine dioxide would be 0.79 gram per barrel (0.028 ounce). The color removal effect of this amount of chlorine would be too slight to be determined by the usual methods of flour color analysis. To

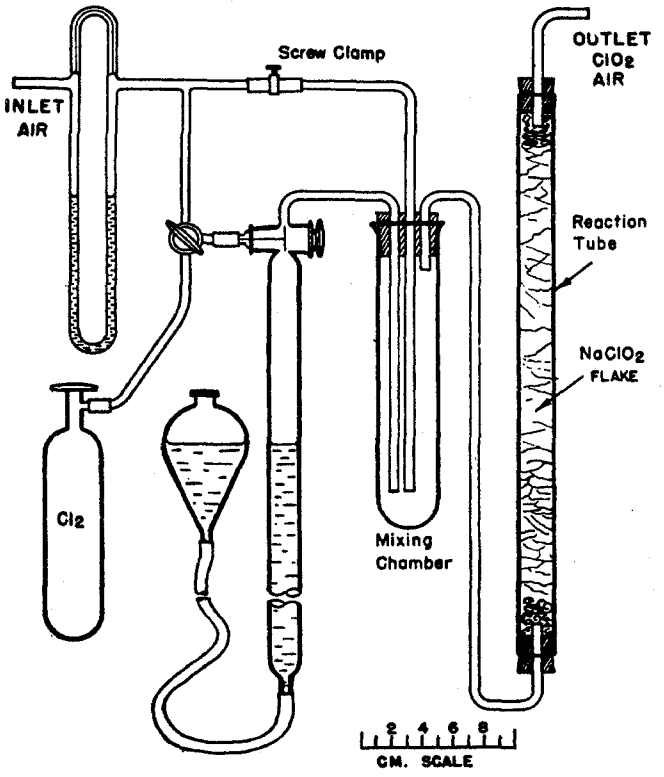

Figure 2. Apparatus for Production of Pure Chlorine Dioxide Gas in Admixture with Inert Gases

equal the color removal effect of 1.5 grams chlorine dioxide per barrel, the chlorine would have to be used at a rate of about 43 grams (1.5 ounces) per barrel. Thus on a weight basis chlorine dioxide is about thirty times as effective as chlorine for flour color removal.

To generate the desired amount of chlorine dioxide, a weighed amount of sodium chlorite is reacted with an excess of chlorine gas. The reaction to produce any desired amount up to 0.1 gram of chlorine dioxide may be carried out in a 1-liter flask equipped with inlet and outlet stopcocks as shown in Figure 1. Rubber stoppers for apparatus to produce chlorine dioxide should be coated with a chlorinated lacquer or kept in a strong atmosphere of chlorine for a few hours. Whenever possible, the stoppers should also be protected by glass wool. As an alternative, ground glass joints can be used; but it is not believed necessary. To generate approximately 0.1 gram chlorine dioxide, about 0.13 gram of substantially dry, powdered sodium chlorite (approaching 100% purity) is distributed over the bottom of the liter Erlenmeyer flask. The flask is partially evacuated by a water pump, and metered chlorine gas is admitted to the flask, partially releasing the vacuum. Air is then admitted until the vacuum is wholly released. The amount of chlorine required is about 100% in excess of the theoretical amount indicated by the reaction equation. The excess is used to ensure that all the sodium chlorite is reacted in a reasonable time. It also eliminates the need for controlling the quantity of chlorine dioxide produced by the metering of such minute quantities of chlorine gas, and throws the burden of control on weighing the chlorite on an analytical balance. The amount of chlorite needed is calculated on a moisture-free basis and corrected for the purity of the chlorite salt with respect to the percentage of sodium chlorite present. The reaction goes to completion in about 3 hours; during this time the flask must be kept in the dark, since chlorine dioxide is photochemically active. After reaction, the resulting gaseous mixture is stripped from the flask and conducted to the point of application by a stream of air at a velocity of about 300 cc. per minute.

The reaction is about 94% efficient at a chlorine dioxide partial pressure of 30 mm. mercury, since a small amount of the sodium chlorite is converted to sodium chlorate. Chlorate formation becomes less as the partial pressure of chlorine dioxide is decreased. The greatest efficiency for the process is therefore found for the lower partial pressures of chlorine dioxide. The exact efficiencies for any given set of conditions may be checked by titrating for the purity of the sodium chlorite and by analyzing the effluent gases.

The purity of sodium chlorite is determined by the following procedure: An accurately weighed sample of about 2 grams is dissolved in a liter of water, and an aliquot of 25 ml. is taken for titration. To this aliquot are added 2 ml. of 50% potassium iodide solution and 10 ml. of glacial acetic acid. The reaction is allowed to proceed in the dark for 5 minutes; the liberated iodine is then titrated with 0.1 N standard sodium thiosulfate solution using starch as indicator. The reaction equation is:

$$NaClO_2 + 4HC_2H_3O_2 + 4KI \rightarrow NaCl + 2I_2 + 4KC_2H_3O_2 + 2H_2O \quad (1)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \quad (2)$$

Thus 1 mole of sodium thiosulfate is equivalent to 0.25 mole of sodium chlorite, the milliequivalent weight of the sodium chlorite being 0.0226. The equation for the percentage of sodium chlorite in the original sample follows:

% $NaClO_2$ = (ml. standard thiosulfate × normality × milliequivalent wt. of $NaClO_2$ × 100)/(wt. of sample in aliquot soln.)

The mixed gas may be analyzed according to the procedure of Woodward, Petroe, and Vincent (4).

No more than 0.135 gram of 95–97% sodium chlorite should be reacted in a liter flask since the partial pressure of the resulting chlorine dioxide will be approximately 26 mm. mercury at usual room conditions of temperature and pressure. This is about the highest concentration recommended by the authors for this type of apparatus, since at a partial pressure of 36 mm. of mercury (20° C.) Woodward, Petroe, and Vincent (4) indicated that chlorine dioxide can be exploded by an electric spark. However, chlorine dioxide does not appear to decompose spontaneously at room temperature but only when it comes in contact with easily oxidized material. Thus the recommended maximum concentration is given as a precaution. The gas may be produced at somewhat higher concentrations if the apparatus is kept free of all oxidizable materials and protected against damage due to questionable conditions. It must be remembered that these reagents are moderately strong oxidizing agents and should be handled as such. For generating greater amounts of the gas, a number of flasks may be used or the gas may be produced in a larger chamber. In the latter case, more time should be allowed to ensure diffusion of the chlorine to the chlorite for the reaction.

In many applications other than flour bleaching, the presence of chlorine would probably not interfere; but in numerous cases chlorine admixed with the resulting chlorine dioxide would preclude the use of this method.

NONCONTINUOUS PRODUCTION ADMIXED WITH INERT GASES

If larger amounts of chlorine dioxide free from chlorine as a contaminant are desired, a method in which output of the dioxide is controlled by chlorine input may be utilized. The required amount of chlorine is metered in a buret, using a salt solution saturated with sodium chloride and chlorine as the metering fluid. This chlorine is slowly introduced into a mixing chamber; from there it is swept by a continuous stream of air (about 200 to

300 cc. per minute) through a column, as shown in Figure 2; the column is approximately 0.75 inch in diameter and 8 to 16 inches long, and is filled with substantially dry, flaked chlorite. As the chlorine is metered into the mixing chamber, the dilution air flow is through the central tube leading into the mixing chamber (Figure 2). However, after all chlorine has been displaced from the buret, the air flow is directed through the three-way stopcock and the buret stopcock, the screw clamp being closed. This procedure ensures that all metered chlorine is flushed into the reaction tube. The effluent gases are then conducted to the point of application. No chlorine is present in the effluent gases, which are composed of chlorine dioxide in admixture with air. The dioxide is preferably kept at a partial pressure of 30 mm. mercury or less, depending upon the usage to which the gases are to be put.

The reaction is practically instantaneous, and the output gas is chlorine dioxide and air, with no chlorine present until about two thirds or more of the sodium chlorite is reacted and the chlorine channels through the salt. The absence of chlorine in the effluent gases can be assured by testing the output stream with ammonium hydroxide fumes, since chlorine, but not chlorine dioxide, produces the typical white cloud of ammonium chloride.

The input chlorine and air flow is so adjusted that the partial pressure of chlorine dioxide in the effluent gas-air mixture is held at or below 30 mm. mercury. Thus, according to the reaction equation, if 5 cc. of chlorine are used per minute, chlorine dioxide will be produced at a rate of 10 cc. per minute. The amount of air which must be used for diluting the chlorine at 740 mm. mercury barometer pressure to obtain chlorine dioxide at 30 mm. mercury partial pressure will be:

$$\text{Air/minute} = \frac{10\text{ cc. } ClO_2\text{/min.} \times 740\text{ mm. Hg bar. press.}}{30\text{ mm. Hg partial press. } ClO_2} - 10\text{ cc. } ClO_2\text{/min.} = 237\text{ cc./min.}$$

The air should be flushed through the chlorite column for several minutes after all chlorine has been swept through it to ensure complete stripping of all chlorine dioxide from the chlorite column.

CONTINUOUS PRODUCTION ADMIXED WITH INERT GASES AT CONTROLLED PARTIAL PRESSURES

This method is preferred to those cited above in cases where large amounts of chlorine dioxide are desired, where it is necessary to have chlorine dioxide at a carefully controlled partial pressure, or where a continuous stream of the dioxide diluted with inert gases is desirable. In this case the amount of chlorine dioxide applied to a process or product may be controlled; or the product may be immersed in or treated with an atmosphere of chlorine dioxide at a controlled partial pressure for a given time by running the dioxide stream through a chamber from which partially spent gas is constantly withdrawn. The partial pressure of chlorine dioxide in the effluent gases from the chamber is less than in the input gaseous mixture.

A suitable generator for carrying out this process will be described. Quantities, dimensions, and flows may be altered to suit the equipment or the usage under consideration. The generator will serve for many uses requiring less chlorine dioxide than its minimum output by carefully proportioning the effluent gases at a given dioxide production rate. The waste gas may be exhausted to the air or absorbed in caustic solution.

Control in this process depends upon the chlorine input; the chlorite is in excess and sufficient is used to allow operation over a relatively long period of time.

Two or more glass tubes, about 2.5 inches in diameter and 4 to 5 feet long, are filled with technical grade sodium chlorite flakes and connected in series with glass tubing. Chlorine and air or other inert gases to generate a considerable quantity of chlorine dioxide at 30 mm. mercury partial pressure are introduced at the bottom of the first tube and pass through the two tubes in series. The effluent gases are then conducted to a mixing chamber where they are diluted to any desired concentration with air. The generator is sketched in Figure 3. For flour bleaching, the apparatus was designed to deliver as high as 1.3 grams chlorine dioxide per barrel to a 16-barrel-an-hour flour stream at a partial pressure of about 2 mm. mercury for about 20 hours per tube. This is equivalent to 20 grams per hour for 20 hours or about 400 grams chlorine dioxide per charge of sodium chlorite per tube.

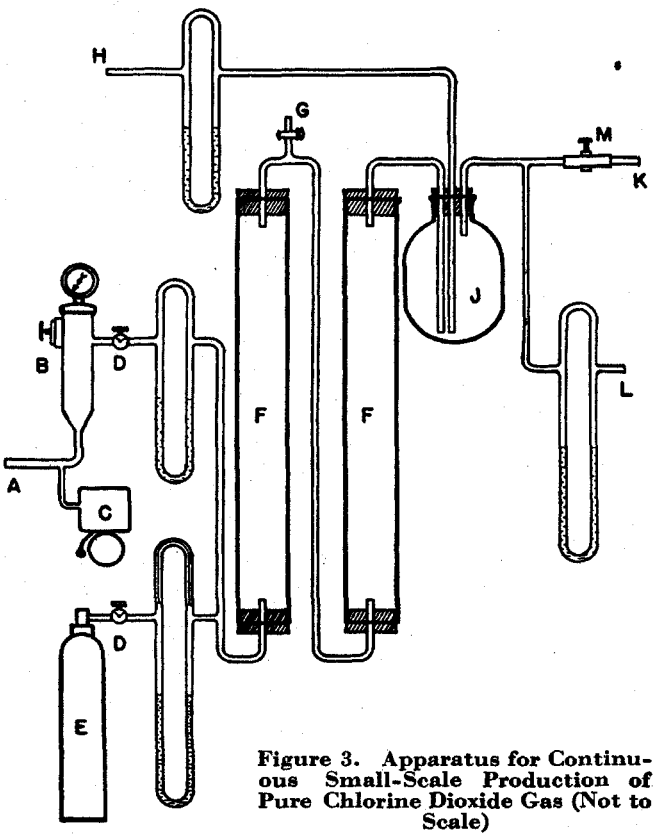

Figure 3. Apparatus for Continuous Small-Scale Production of Pure Chlorine Dioxide Gas (Not to Scale)

A.	Compressed air inlet	*G.*	NH_4OH test point for Cl_2
B.	Pressure-reducing valve	*H.*	Dilution air
C.	Pressure-operated signal	*J.*	Mixing bulb
D.	Needle valves	*K.*	Main flow outlet
E.	Chlorine cylinder	*L.*	Effluent gas proportioning meter
F.	Reaction tubes	*M.*	Screw clamp or valve

As the sodium chlorite becomes exhausted, tubes with fresh charges may be inserted in the line to make the process continuous. The chlorine flow for this apparatus is controlled by a needle valve and a U-tube differential manometer containing sulfuric acid. The other manometers contain water as the fluid medium.

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