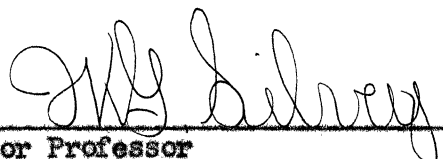




THE APPLICATION OF CHLORINE DIOXIDE TO
TASTES AND ODORS IN WATER SUPPLIES

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THE APPLICATION OF CHLORINE DIOXIDE TO TASTES
AND ODORS IN WATER SUPPLIES

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INTRODUCTION

The development of water resources and water supplies closely parallels the history of human society. In order for men to assemble in social units such as large towns or cities they found it necessary to provide an adequate water supply. This situation was realized in the time of the Roman Empire and was evidenced by the construction of large aqueducts. As human civilization began to assume a more orderly and diversified plan, the need for more and better water became evident. The French solved their problem by constructing aqueducts to transport water from the mountain springs into the cities. However, the first European people to investigate and employ chemical treatment of water was the Germans. As early as 1778 German industrialists realized that the demand for water was becoming acute in certain parts of their country. This initiated fundamental investigations into more efficient chemical and mechanical treatment of water. By 1850 German chemists and engineers had succeeded in establishing a number of water purification plants which were capable of reclaiming polluted river water.

The phenomenal growth of industry in the United States during the last half of the nineteenth century and its

continued development since that time demonstrates the importance of water in an industrialized nation. The City of St. Louis pioneered methods to improve its water supply as early as 1866. In 1887 and the following years the Massachusetts State Board of Health carried on experiments in the purification of water and sewage in connection with the water supply of Lawrence, Massachusetts. Most of these studies were concerned with filtration and flocculation. It is interesting to observe that rapid sand filtration introduced in Lawrence, Massachusetts, reduced the typhoid death rate 70 per cent in five years.

The removal of suspended and dissolved materials from raw water was of prime importance, but its purification for human consumption remained the primary consideration. The use of a specific chemical agent to destroy bacteria and to control aquatic plants was initiated by Moore (1904), when he employed copper sulphate in water supplies. Previous to this discovery, potassium permanganate was used in the purification of water, but it was generally regarded as unsafe for large scale application. Copper sulphate was shown to be a bactericide as well as an algacide and at present is being used for the latter purpose.

Chlorine was first introduced into the water purification process by Johnson (1908). This method has been so successful that it is standard operational procedure for most

of the water purification plants in this country. Chlorinated lime was first used as the source for chlorine, but now compressed gas (liquid chlorine) is preferred. Chlorination has been successful in controlling bacteria in water, but it has the disadvantage of producing disagreeable tastes and odors in certain waters. During the past ten years, industry has made an extensive search for chemical substances which would eradicate algae and remove tastes and odors from finished water. Ozone has been tried with encouraging results. Ozonation plants were installed at Long Beach, Hobart and Whiting, Indiana, in 1930, 1932, and 1938, respectively. The ozone treatment of these waters has been of aid in correcting serious taste and odor conditions. An installation (1949) of a 36 mgd. (million gallons per day) ozonation plant at Philadelphia, Pennsylvania, was made after several years of experimentation with a pilot plant demonstrated taste and odor reduction in the treatment of polluted river supplies. Sparse information is available regarding the bactericidal action of ozone in contaminated waters. Effective bactericidal reduction has been reported at Whiting, Indiana, and Philadelphia, Pennsylvania, but chlorine is used at each plant to insure adequate disinfection of the filtered water.

The installation of equipment for ozone generation requires an expenditure of considerable funds, which doubtless accounts for lack of interest on the part of industry and municipalities.

It has long been recognized that bromine and iodine have strong bactericidal properties; however, very little exact data are available on their use in water. Bromine has been used effectively for disinfection of swimming pool water and occasionally for small water supplies. It is more expensive and less available than chlorine, and its use has never become generally accepted. Iodine has been used in the form of tincture of iodine by military personnel for disinfection of small quantities of drinking water. Recently, table preparations containing available iodine have been developed for this purpose. Iodine is more expensive and less available than bromine and has not been used for disinfection of large quantities of water.

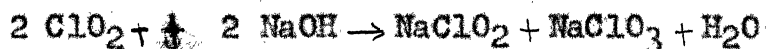
Many commercially prepared organic chloramines have strong bactericidal properties. None of these compounds, however, has been made available at a sufficiently low price to merit serious consideration for disinfection of municipal water supplies. A tablet preparation commercially termed "Halozone" has been widely used by military personnel for disinfection of individual and unit water supplies. Another preparation termed "Chloromelamine" has been preferred to chlorine or hypochlorities for use in sterilization of certain resin-type ion exchange equipment.

Ultraviolet light is employed for the disinfection of air, and numerous installations have been made for the

disinfection of swimming pools. There have been a few installations designed for the treatment of municipal supplies, but their use, as well as that of the swimming pool installations, is reported to have been discontinued because of the high cost of operation and maintenance.

In 1940, the Mathieson Chemical Corporation began an investigation into the industrial application of their oxygen-chlorine compound known as chlorine dioxide. Dienert (1928) had reported that chlorine dioxide might be a potential water purification agent that would answer part of the need for more reactive oxidizers. Since this compound can not be safely prepared as a compressed gas, its investigation proceeded slowly. In 1940, the Mathieson Chemical Corporation patented a new method for manufacturing sodium chlorite, the parent compound from which chlorine dioxide is produced. This discovery stimulated several investigators to look for new applications of chlorine dioxide. In July, 1950, following extensive laboratory determinations and experiments, Roy N. Aston and assistants installed chlorine dioxide generator in the water purification plant in Niagara Falls, New York. These investigators found that they could successfully control the phenolic tastes and odors present in the Niagara Falls raw water, and at the same time furnish a bacteria-free commodity to the consumer.

Chlorine dioxide is a yellow to red gas at ordinary temperatures, with a vapor density of about 2.4. It liquifies at 10 degrees C. under normal atmospheric pressure. It has an unpleasant odor, which becomes noticeable when it reaches a concentration of 15 parts of chlorine dioxide per million parts of air and becomes irritating at 45 ppm. It is soluble in water in concentrations of 2.8 grams per liter at room temperature and 30 mm. partial pressure. At elevated temperatures it decomposes into its elements with explosive violence. Its aqueous solutions are decomposed by light, forming perchloric and chloric acids and oxygen. In alkaline solutions, chlorite and chlorate are formed:



The most interesting property of chlorine dioxide is its remarkable oxidizing power. On a weight basis, expressed in terms of available chlorine, it has, theoretically, 2.5 times the oxidizing power of chlorine.

Previous studies (Ridenour 1949) have shown that chlorine dioxide possesses both bactericidal and virucidal properties as measured against E. Coli, common water pathogens and mouse adapted poliomyelitis virus. On the basis of orthotolidine-arsenite (OTA) residuals, the bactericidal properties of chlorine dioxide are greater than that of chlorine.

This problem was undertaken to determine the potentialities of chlorine dioxide as an algaecide and as an agent for

the removal of tastes and odors from fresh water. Since this compound has already been established as a water purification agent, the problem was one of perfecting new techniques of applications and perfecting new analytical methods.

METHODS AND MATERIALS

Laboratory Preparation of Chlorine Dioxide

Several methods have been developed for preparing chlorine dioxide. Probably the first method devised to produce chlorine dioxide consisted in mixing equal molecular portions of potassium chlorate and hydrochloric acid:



The same reagents may, under different conditions, yield potassium chloride and chlorine:



The disadvantage of this method is that chlorine is produced along with chlorine dioxide. The chemical and physical properties of these two gases are so closely related that separation is not practical.

Calvert and Davies (1859), using a mixture of potassium chlorate and oxalic acid, found the yield of chlorine dioxide dependent upon the proportions of the two reagents, but never obtained a theoretical yield based on the equation:



Becher (1933) described a method for producing chlorine dioxide by reacting dilute sulfuric acid with a chlorate:

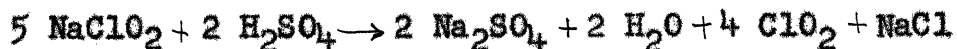


In the above reaction the oxalic acid serves both as an acid to produce a salt and also as a reducing agent. In practice, several times the theoretical amount of oxalic acid are required in order to obtain even a 50 per cent yield of chlorine dioxide. This process was long regarded as the classical laboratory method for preparing chlorine dioxide, since the carbon dioxide which was evolved rendered the chlorine dioxide relatively harmless.

A new source of chlorine dioxide was made available in 1940 when sodium chlorite, NaClO_2 , was produced commercially.

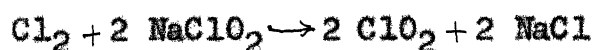
Sodium chlorite is a pink powder, stable in both solid and aqueous solutions. It is apparently intermediate in properties between hypochlorites and chlorates, and contains approximately 158 per cent available chlorine. The technical product is flaked and contains approximately 82 per cent chlorite.

Several methods have been developed to produce chlorine dioxide from sodium chlorite. The earliest of these methods was an electrolytic method based on the reaction:



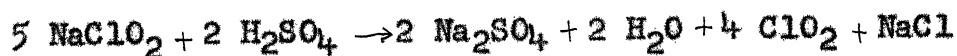
This process produces chlorine dioxide when the concentration of the reagents, heat and pressure, are controlled. This process also required complicated electrical apparatus, and because of this it has been abandoned in favor of other more efficient methods.

Recently a method of generating chlorine dioxide has been developed which utilizes chlorine. A mixture of chlorine and air is passed through two stone towers, lined with stone ware, and filled with flake sodium chlorite. The generated chlorine dioxide is then swept out by a stream of air. The reaction may be represented by the following equation:



This reaction proceeds rapidly at room temperature, and if the partial pressure of chlorine dioxide does not exceed 50 mm., no hazardous condition is said to exist. For many processes, such as the bleaching of flour and tallow, this process is very satisfactory; however, it was not used in this investigation.

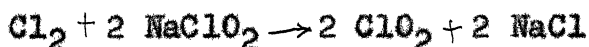
A pure solution of chlorine dioxide used in laboratory investigations may be prepared by slowly adding a 10 per cent solution of sulfuric acid drop wise to a 10 per cent solution of sodium chlorite. The liberated gas is scrubbed out of solution into a small volume of triple distilled water by a slow stream of air induced by an aspirator. A solution of 3000 ppm. chlorine dioxide as chlorine dioxide can be prepared in this manner. The reaction involved in this method of making chlorine dioxide is:



This reaction has been partially confirmed by determining the quantity of chlorides produced from a known amount of sodium chlorite.

Generating Chlorine Dioxide for Water Treatment

For water treatment the method of generating chlorine dioxide is based upon the reaction of chlorine with a solution of sodium chlorite:



The chlorite solution and the chlorine water solution are fed continuously into a reaction chamber, and the resulting solution is fed into the water system.

As applied in water plants today, the installations employ commercial chlorinators to supply the stream of chlorine water. The discharge line from the chlorinator is connected to the lower end of the reaction chamber into which the sodium chlorite solution is fed by means of a metering pump. The purpose of the chamber is to insure complete mixing of the chlorite and chlorine solutions and a complete conversion of the chlorite to chlorine dioxide before it is discharged into the water supply. The main portion of the reaction chamber is a 4-inch glass chamber, 12 inches long, filled with unglazed Richig rings. This is reduced at the lower end to a 1-inch tube for chlorine inlet, and similarly at the top for the chlorine dioxide outlet. The chlorite is fed through a T-tube at the lower end of the chamber above the chlorine inlet.

There is considerable freedom in the operation of the generator, the major consideration being the completeness

of the reaction to form chlorine dioxide. Certain factors must be taken into consideration such as the pH of the raw water and an accurate maintenance of pH of the solution in the reaction chamber. The pH of the solution is directly dependent upon the chlorine concentration and hence may be controlled by regulating the amount of chlorine entering the reaction chamber.

This method of producing chlorine dioxide has certain advantages. It utilizes the existing items of equipment in the water plant and requires only the addition of a glass reaction tower and a small metering pump. Plant operators are capable of operating the generator after it has been installed and demonstrated. Possibly the main disadvantage in this method is that the complete elimination of chlorine is not achieved even though the concentration of free chlorine in the final solution may be low if careful control is practiced.

A modification of the above method, in which sulfuric acid is employed instead of chlorine, has proven very successful in laboratory tests, and has the advantage of assuring chlorine free chlorine dioxide. In water contaminated with actinomycete by-products, chlorine in extremely small concentrations may completely nullify the otherwise beneficial effects of chlorine dioxide in removal of tastes and odors.

Methods of Analysis of Chlorine Dioxide and Chlorine

A simple procedure for determining chlorine dioxide has been the object of considerable research. Chlorine dioxide present in treated water may be distinguished from free chlorine by conventional laboratory tests.

Haller and Listed (1948) developed a procedure for determining chlorine dioxide by employing an amperometric titration. This method aided in the development of analytical procedure for chlorine dioxide but has not proved useful in water plant control. The above described technique is largely a research tool for use in laboratories with highly trained personnel.

A. T. Palin (1948) reported an adaptation of the OTA method of analysis currently employed in the determination of chlorine. In this procedure ammonium chloride was used to react with the free chlorine, thus leaving chlorine dioxide which could be measured by the OTA test. Unfortunately, the procedure will not give consistent results since all free chlorine will not combine to form chloramine in sufficient quantities to prevent color interference.

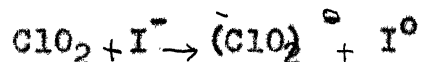
The Mathieson Chemical Corporation research laboratories working along the lines indicated by Palin, developed an adaptation of the OTA test which is applicable for use as a control method. Schmidt (1932) demonstrated that chlorine dioxide would not react with oxalic acid, even though the

latter was readily oxidized to carbon dioxide and water. The fact that chlorine will oxidize oxalic acid suggested its use to tie up the chlorine present, leaving only the chlorine dioxide to be measured by the OTA test. This modification proved successful, and after many tests it was found that chlorine and chlorine dioxide could be differentiated quantitatively in this manner. Since any investigation of the biological properties of chlorine dioxide, i. e., its ability to reduce tastes and odors and its ability to control algae would depend upon its concentration, it was decided that a standard method of quantitative analysis should be established. Following the methods inaugurated by Palin and the research staff of the Mathieson Chemical Company, investigation of all previous analytical methods was conducted. The results of this study indicated that starch iodine titration and the modified OTA test would serve the needs of this investigation.

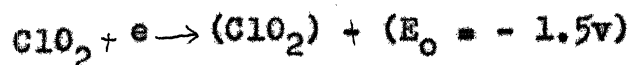
Starch-Iodine Titration

Chlorine dioxide is a compound containing oxygen, so that its oxidation capacity is more dependent upon pH than in the case of chlorine. For example, an alcoholic solution of potassium iodine, when added to an aliquot pure solution of chlorine dioxide buffered to a pH of 7.18 with 200 ppm. of sodium bicarbonate, will liberate one fifth as much iodine (measured by sodium thiosulfate and starch indicator) as

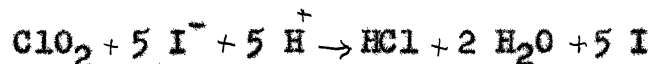
when concentrated hydrochloric acid is added to a similar aliquot of the chlorine dioxide solution. This difference can be explained by the reaction of the chlorine dioxide with potassium iodine at pH 7.8.



or:



In this reaction a chlorite ion is formed from chlorine dioxide by the uptake of one of the five possible electron changes of the chlorine dioxide. However, the complete breakdown of all five electron changes of the chlorine dioxide requires the presence of the hydrogen ion:



This relationship shows the importance of maintaining proper conditions when measuring chlorine dioxide. Laboratory studies have indicated that pH 1.5 is the highest numerical value that will allow the development of the full oxidative capacity of chlorine dioxide to iodide. Glacial acetic acid as sometimes proposed for chlorine, will not produce a pH low enough to develop the complete oxidative capacity of chlorine dioxide. Hydrochloric acid is sufficiently strong to lower the pH and does not interfere with the titration, hence it is used for this purpose. One ml. of concentrated hydrochloric acid in a 25 ml. sample will lower the pH of the solution sufficiently to develop the full oxidative capacity of chlorine dioxide. The step-by-step procedure followed in

making starch-iodide titrations is as follows:

1. A 25 ml. sample of the solution under investigation is placed in a small flask, to which is added 20 ml. of 10 per cent potassium iodide.

2. One ml. of concentrated hydrochloric acid is added.

3. The sample is titrated with N/10 sodium thiosulfate until the solution loses its yellow appearance, at which point 1 ml. of a 2 per cent solution is added and the titration is continued until the blue color disappears.

4. Calculation:

$$\frac{(\text{ml. of sodium thiosulfate}) (\text{normality of sodium thiosulfate})}{1000}$$

$$\times \text{equivalent wt. of } \text{ClO}_2 \text{ or } \text{ClO}_2 = \text{gms. chlorine dioxide per ml. of sample}$$

$$\underline{\quad 5 \quad}$$

The starch iodide titration method for chlorine dioxide residual determination can be carried out with a high degree of precision on samples containing 20 ppm. or more. This method, however, is inaccurate to use for determining low residuals in raw water. Moreover it is not adaptable to use in the field procedure.

OTA Modification as Adapted for Determining Chlorine Dioxide

A method widely adopted for the quantitative differentiation of chlorine dioxide and chlorine is the OTA test which employs oxalic acid in addition to the reagents used

for the chlorine determination. The compounds produced at different pH values as well as concentrations have been described by Chamberlin (1942). If one adds sufficient amount of orthotolidine at a low pH, it appears as a yellow holoquinone in the standard colorimetric test used for chlorine. As the pH of the final color mixture rises, increasing proportions of blue meriquinone are found. This is a result of the incomplete oxidation of the orthotolidine, and the color may be any shade from yellow to blue. In order to minimize the chances of a different color, it is necessary to control both the amount of the orthotolidine reagent and the pH of the reagent. It has been known for many years that the amount of acid in the original orthotolidine reagent was insufficient to prevent the formation of blue and red quinones; thus, modified orthotolidine reagent was specified in Standard Methods of the American Public Association which contained more acid than the original reagent. Consequently, the modified OTA test used in this investigation could be employed to measure the amount of chlorine (i.e., hypochlorite, hypochlorous acid and/or molecular chlorine), combined chlorine, (e.g., chlorine substituents or ammonia and chloro-derivatives or organic compounds), and chlorine dioxide.

This technique for measuring chlorine dioxide utilized sodium arsenite and oxalic acid. The reaction of free chlorine dioxide and chlorine with the orthotolidine is

known to be rapid, while the reaction with chloro-derivatives is slow. Thus by adding sodium arsenite, the chloramines and/or chloro-derivatives may be destroyed. The reaction between the arsenite and the combined chlorine compounds is not complete and errors from this may be as much as 7 per cent. However, this method does have great value both as a control and as a research tool in this study, and in actual plant practice.

Previously mentioned, it is the purpose of this oxalic acid to react with the free chlorine present in the sample and leave the chlorine dioxide free to react with the orthotolidine reagent to produce color. Thus by using oxalic acid and sodium arsenite to tie up most of the other compounds encountered in this test, it is possible to determine chlorine dioxide by colorimetric methods.

In this determination either visual standards or a photo-electric colorimeter may be employed. The accuracy and precision obtained in either of these methods will depend upon the accuracy of the standards. The standards used in this study were prepared immediately before readings were made. Only pure stock solutions of chlorine dioxide (prepared by scrubbing the gas out of an acidified sodium chlorite solution) were used in all laboratory investigations. The temperature of these solutions and all the subsequent solutions used as standards were never permitted to deviate from 20° C.

The determination for purity of the stock solution was made by using a Beckman model pH meter. It was found that if the pH of the original solution was determined as soon as it had been collected in triple distilled water and noted that a determination of the pH made at regular intervals after this, record of the purity of the solution could be kept, any deviation in pH being an indication of the relative purity of the solution.

Throughout the experimental work leading to the development of the method hereunder presented, the starch-iodide-thiosulfate titration as given in the above discussion was taken as the standard method for comparison and determination of standards.

The new method utilizes all of the existing solutions as prescribed for the OTA determination in Standard Methods of Water and Sewage. The procedure is as follows:

1. A chlorine dioxide solution of unknown concentration is placed in the refrigerator and held until it attains 18° C.
2. A 100 ml. sample of the solution is placed in a Nessler tube and 1 ml. of saturated oxalic acid is added.
3. Five minutes is allowed to elapse from the time when the oxalic acid is added until the next reagent is introduced.
4. At the end of five minutes 1 ml. of orthotolidine solution is added.

5. Within five seconds 1 ml. of sodium arsenite reagent is added.

6. The maximum color is produced at the end of 1 minute. The color produced remains constant for at least 30 minutes. (Care should be taken to note that the sample is 20° C.)

7. A sample from the Nessler tube is poured into a cuvette from the Beckman DU spectrophotometer and the transmission is read at 437 millimicrons. The transmission reading is matched against a standard curve.

The accuracy of the method which we have referred to as OTO has been tested many times with various solutions at temperatures from 1 to 30° C. It was observed that 20° C. gave the only constant readings and that concentrations determined at 20° C. matched those readings previously determined by starch-iodine titrations. Thus, the method described above was adopted for routine laboratory research. Since spectrophotometers are not generally available for field use it was decided that field methods should be developed. Samples of water containing ClO_2 were placed in 10 ml. quantities in the Wallace and Tiernan comparator block use for chlorine determinations. One ml. of saturated oxalic acid was added to the sample and at the end of five minutes the regular OTA test was run. Thus, this procedure followed the OTO technique and by employing chlorine

dioxide solutions previously determined in the Beckman spectrophotometer it was found that readings on the color comparator divided by two gave the residual chlorine dioxide as available chlorine dioxide. If a reading of .4 ppm. were observed on a comparator the actual contents was .2 ppm. chlorine dioxide as chlorine dioxide.

Methods to Determine Algacidal Properties of Chlorine Dioxide

An important part of the investigation of chlorine dioxide was to determine its algacidal properties. It is well known that chlorine, copper sulphate, and a number of new copper compounds as well as hypochlorites, chlorinated lime, and other compounds have been used to eradicate algae from rivers, streams, reservoirs, lakes, cooling towers, and certain other mechanical devices.

The initial methods employed in studying the algacidal properties of chlorine dioxide was to place small amounts of a solution containing chlorine dioxide gas in perfusion chambers containing algal cells. If deterioration was observed then large cultures of algae were produced so that actual quantitative and qualitative determinations could be completed. If the algae did not appear to be affected by chlorine dioxide in concentrations as high as 10 ppm., further investigations were not considered economically sound.

It should be observed that the laboratories at this institution have been interested in algae populations in reservoir lakes for over fifteen years. Excellent distribution records are available so that one may refer to the files and thereby have information on when specific types of algal blooms are to occur in certain bodies of water. The investigator employed this information to secure samples of algae from Lake Dallas, Lake Waco, Eagle Mountain Lake, Lake Hefner, and other small reservoirs and streams throughout Texas and Oklahoma. The algae samples were placed in large aquaria with sufficient nutrient and agitation to sustain them. After the culture was in apparent equilibrium liter samples were filtered through a regular Sedgewick Rafter concentrating funnel so that milligram weights per liter could be measured. These data gave actual quantitative results with regard to destruction of algae by specific amounts of chlorine dioxide. Concurrently, areal unit counts were made on identical samples so that numerical reductions of algae provoked by specific amounts of chlorine dioxide could be stated.

The actual testing was ordinarily accomplished in 1 gal. glass jugs to which a definite number of milligrams and a specific number of areal unit organisms had been added. Twenty 1 gal. jugs composed a series. Ten of the jugs received chlorine dioxide in concentrations in .1 to 10 ppm. The other 10 received either copper sulphate or chlorine.

Small samples were removed from each experimental jug at the end of the first 10 minutes, at the end of 30 minutes, and, subsequently, at intervals of 1 hour, 4, 8, 12, 48, and 96 hours. At the end of the experiment a liter of each sample was concentrated in the milligrams of remaining algae recorded. It is appropriate to observe that our results on copper sulphate and chlorine demands were not consistent in many instances as reported by Hal in 1942. Since the work involves chlorine dioxide, not copper sulphate and chlorine, the results, Table 9, carry only chlorine dioxide required to eradicate the organism and do not attempt to change previously indicated requirements of copper sulphate and chlorine.

Similar samples of algae were tested with sodium chlorite using both CP and technical grades. The intent of this investigation was to find if chlorite would serve as an inhibitor of algae in cooling towers. On occasions the experiments were continued for as long as three months in order to find if the chlorite would remain in circulating water for that period of time. Residual chlorites were determined by acidification of small samples with subsequent OTO tests and calculation of residual chlorite.

Uses of Chlorine Dioxide for Removal of Tastes and Odors from Water Supplies

It is common knowledge among water plant operators, engineers, and, frequently, consumers that the characteristic taste and odor of drinking water will vary from time to time. Infrequently the newspaper will carry small stories on the types of organisms in the raw water that are producing tastes and odors. Since 1846 the algae have been accepted as contributing the taste and odor compounds to surface water. After approximately 100 years, it was found that algae did not contribute the tastes and odors to water but that compounds produced by actinomycetes were responsible for naturally occurring tastes and odors in water containing dissolved oxygen. Septic conditions are not caused by algae nor by actinomycetes but, doubtless, by bacteria and possibly other fungi. The comments thus far have no reference to pollution since many chemical products used in industry find their way into water that ultimately is passed to the consumer. The reader should understand that reference to tastes and odors refers to those varieties that have been previously attributed to algae.

The actinomycetes growing in or on algae produce primary amines, aromatic compounds, saturated fatty acids, and aldehydes. The concentration of these compounds in natural water is probably measured in parts per billion and on the surface would appear to be of very little importance.

As long as these compounds are not exposed to chlorine, their odor is not too apparent. As soon as they combine with chlorine to form chloro-derivatives the odors become strong and repulsive. One might describe such odors as musty, manurial, rotten hay, rotting wood, marshy, or geranium. The reason for the variation in odors may be attributed to different concentrations of the major groups of organic compounds produced by the actinomycetes in their normal physiology. Laboratory records of the research group at this institution show distribution of these organisms from Venezuela, to as far north as Chicago, and as far east as Philadelphia. It is the contention of the research group working on these organisms that practically all tastes and odors in water supplies that are not pollutive or septic in nature arrive from actinomycetes. A considerable proportion of the research on chlorine dioxide rotated around the actinomycete by-products and the efficiency of chlorine dioxide in oxidizing them.

The first method of approach to the investigation of the application of chlorine dioxide to the removal of actinomycete by-products was purely experimental. Actinomycetes were reared in deep culture and the by-products were extracted. These by-products were added to odorless, tasteless water in different concentrations so as to produce a series of samples having different threshold odor numbers. The

threshold number was determined by methods prescribed by Standard Methods for the Analysis of Water and Sewage, ninth edition. Threshold odor numbers varied from 2 to 500 throughout the series of experiments. Chlorine dioxide was added in varying concentrations from .1 to 10 ppm. It was employed as a pre-chlorination practice, and samples were later flocced and filtered. On other samples they were first subjected to flash mixing, floccing, clarification, and filtration before chlorine dioxide was added. Many of the experiments involved the addition of chlorine to chlorine dioxide while others involved the addition of activated carbon to chlorine dioxide. The purpose of the rather elaborate experimentation was to determine if chlorine dioxide was a suitable agent to be employed to remove tastes and odors from water supplies. Where actinomycete by-products are present chlorine enhances taste and does not, under any conditions, remove the chloro-derivatives formed. Activated carbon in very fine mesh has been rather successfully employed either in conjunction with chlorine or alone. All types of combinations were set up in our laboratories in order to arrive at a definite conclusion. The results of this elaborate set of experiments may be observed further on in this paper.

Methods for Testing the Effects of Chlorine Dioxide
on Actinomycete By-Products

As indicated above, actinomycetes in their normal physiology produce several groups of organic compounds. If the oxygen content is high, the major compounds produced are aromatic forms closely allied to phenol. Since we have not actually determined the true chemical nature of the aromatic compound produced, we have chosen to use phenol for experimental purposes. This compound was dissolved in carbon tetrachloride to which known quantities of chlorine dioxide were added. The reason for employing carbon tetrachloride was to enable us to make use of the Beckman infra-red spectrophotometer. It is well known that carbon tetrachloride will permit the transmission of infra-red light where water will absorb infra-red light very rapidly. If we were to determine the changes that occurred in phenol, it was necessary that we have a medium that would not absorb infra-red. The routine analytical procedure involved taking a solution of carbon tetrachloride and adding small amounts of phenol, transferring this solution to the infra-red cuvette and making a scan usually from 2.2 to 15 microns. Known amounts of chlorine dioxide were then added in carbon tetrachloride to the phenol solution. After a reaction time the treated sample was again exposed to the infra-red spectrophotometer and a scan was made from 2.2 to 15 microns. A comparison of the curves in the scan would

show at what point reaction occurred. By referring to the literature we could predict whether phenol had been changed or not and in some instances what changes had occurred. Similar samples were fractionated and the by-products were collected and chemical determinations were made to see if the chemical characteristics had changed and what by-products were formed.

Since no definite proof had previously been established pertaining to the effects of chlorine on actinomycete by-products, investigation was instituted to treat phenol with chlorine in the manner described above and determine the effect of that compound on phenol so that comparisons of the effects of chlorine dioxide and chlorine could be made. It is not necessary to repeat the procedure indicated above, but the reader should hold in mind that all tests were rigidly controlled and the findings shown in the section on results reveal some interesting by-products and reactions.

In addition to phenol we studied certain of the amines that are known to be produced by the actinomycetes. The major compounds studied in this procedure were methyl, dimethyl amine, and N-butyl amine. These compounds were studied for reaction with chlorine and chlorine dioxide. In the fatty acid group we investigated the effects of chlorine and chlorine dioxide on oelic acid, palmitic acid, isovaleric acid, and beta hydroxy butyric acid. The only aldehyde

known to occur as an actinomycete by-product is isovaleraldehyde. This compound was also tested with chlorine and chlorine dioxide.

It was the belief of the investigator that if these compounds known to occur in water and to be responsible for a large proportion of tastes and odors could be oxidized by chlorine dioxide and not by chlorine that ample proof would be sustained and that guess-work in water treatment would be obviated. The results of these findings are shown in Tables 9 and 10.

Practical Methods

Bird Creek and Barnsdall Reservoir, North Eastern Oklahoma.---A small stream by the name of Bird Creek arises north and west of the city of Pawhuska, Oklahoma, and runs for a distance of approximately 20 miles before skirting the southern borders of the Oklahoma town. At the outskirts of the city limits of Pawhuska the effluent from the city disposal plant is introduced into Bird Creek. The course of the stream continues to the southeast approximately 16 miles, at which point City Service Oil Company had constructed a chemical plant for the production of formaldehyde, acetaldehyde, methynol, and acetone. The creek continues in a more southernly direction below the chemical plant for about 2 miles at which point it is impounded by a small dam into a body of water known as the Barnsdall Reservoir. Water

is pumped from the reservoir by the Bareco Oil Company into their wax plant in the City of Barnsdall, Oklahoma, and water consumed by the city itself is pumped by the same main over into the purification plant.

Bird Creek is a deep basin stream which runs during wet weather but during the dry season it forms elongated lagoons that are isolated one from another. The lagoon that occurs in front of the City Service Chemical Plant may be isolated for periods of several months. The volume of this lagoon is roughly thirty million gallons when no flow of water is evident. The Barnsdall Reservoir just south also becomes isolated and contains approximately the same volume of water. Water from the lagoon or stream is used to cool gas engines, condensers, other coolers, and other types of machinery in the chemical plant. Large boilers take up about 100,000 gallons of water per day, convert about 95,000 gallons of water into steam, and turn the blowdown water concentrate back into Bird Creek. Waste products other than the ones mentioned above are polymer resins which are pumped in brass pipes across the creek, forced into stone kilns, and burned. Waste from the formaldehyde and acetaldehyde plants, which contain some aldehyde and polymer resins are pumped into a waste well which is approximately 2,600 feet deep. During high water periods or well repair, some of these wastes escape and get into Bird Creek.

Water from Bird Creek which is dispensed to the population of Barnsdall, Oklahoma, receives the following treatment in this order: aeration, coagulation using alum and lime, sedimentation, activated carbon and chlorine is added to the finished water in the clear well. The retention time for this plant is approximately 30 minutes. The pumping capacity of this plant is 120,000 gallons per day.

The initial installation of chlorine dioxide in the Barnsdall water treatment plant was made on August 29, 1949. At this time the water in the Barnsdall Reservoir was very black and had a septic smell and a BOD of 150 ppm. The threshold odor of the water in the reservoir was 240 and treatment of this water in the plant reduced it to 200.

A chlorine dioxide generator of the type previously described was installed in the second floor of the Barnsdall water plant and was immediately placed in operation. The chlorine dioxide produced by this installation was introduced into the clear well by means of a plastic tube. Chlorine was added to the clear well by providing an excess of this element in the reaction of chlorine and sodium chlorite.

Breckenridge, Texas.--The City of Breckenridge, Texas, receives its raw water from a shallow lake known as Lake Daniel. Lake Daniel has approximately 2,000 acres of surface area and a mean depth of 5 feet. The raw water from

this source is transported to the Breckenridge water treatment plant by means of a small stream. Lake Daniel is a relatively shallow body of water and experiences several considerable variations in water level during the year. In dry seasons the shoreline has a heavy growth of vegetation, which is later inundated during the wet season. Moreover the stream which connects Lake Daniel with the Breckenridge water treatment plant is subject to a large pollution load caused by the decay of vegetation along its banks and some domestic sewage that finds its way into this stream.

Water treatment at the Breckenridge water treatment plant is very similar to the processes employed at Barnsdall, Oklahoma. Aeration, coagulation, activated carbon, sedimentation and sterilization with chlorine are the principal steps and methods employed in this plant. This plant has an average treatment capacity of 1,000,000 gallons and a retention time of approximately one hour.

Initial investigation of the Breckenridge water treatment plant was made on August 14, 1950. At this time the incoming raw water to this plant was receiving approximately 150 pounds of alum, 120 pounds of lime, and approximately 50 pounds of activated carbon per day for 750,000 gallons of water. The pH of the raw water was 8.2 and the pH of the finished water was 8.5 in the clear well, and it was about 8.4 in the west part of Breckenridge. The residual chlorine

in the clear well was .5 ppm. and .1 ppm. on the west side of town.

The odor of the finished water is best described as being the odor of decaying vegetation. This odor was so pronounced that it was offensive in cold water. The ecological conditions that exist in Lake Daniel and in the stream seem to favor the growth and development of actinomycetes. Recent investigations by Silvey et al seem to bear out this statement and further indicate that the odor in the Breckenridge water was due to the substances produced by these organisms.

Chlorine dioxide was installed in the Breckenridge plant on August 14, 1950. The equipment used for this purpose is the same as described earlier in this paper. Chlorine was completely removed from the clear well and was used in connection with the chlorine dioxide generator to produce chlorine dioxide. Preliminary laboratory investigations disclosed that chlorine dioxide could effectively reduce the odor produced in the raw water but would not reduce the odor in finished chlorinated water. This initial installation lasted for a period of 16 hours. During this time a total of 20 pounds of sodium chlorite and 8 pounds of chlorine was fed into the clear well of the treatment plant. The residual of chlorine dioxide in the clear well was 3 ppm. at the end of one hour's operation and the residual in the line on the west part of Breckenridge was .08 ppm.

RESULTS

Quantitative Determination of Chlorine Dioxide

A spectrophotographic technique for the determination of chlorine dioxide in water was proved by employing the Beckman spectrophotometer. Solutions of chlorine dioxide in variable dilutions were treated as previously described with oxalic acid followed by the OTA test. Absorption curves were run from 350 to 600 mw. It was found in this investigation that 437 mw. was the point of maximum absorption and of quantitative accuracy. The accompanying quantitative curve (Figure 1) demonstrates that chlorine dioxide may be accurately measured from 0 to 3.3 ppm. and that the test is sensitive to .02 ppm. Numerous rechecks of the above curve demonstrates that it is accurate and so far is the most effective method found. In the event chlorine dioxide exceeds 3.3 ppm. dilutions of the stock solution may be made before the OTO test is run. The addition of chlorine, hypochlorites and other chlorinous compounds does not interfere with the test if it is run correctly.

The quantitative determination of chlorine dioxide was also run on the Coleman spectrophotometer model 11, and the results agree with those found on the Beckman so that the accompanying curve may be used with either instrument.

34-a

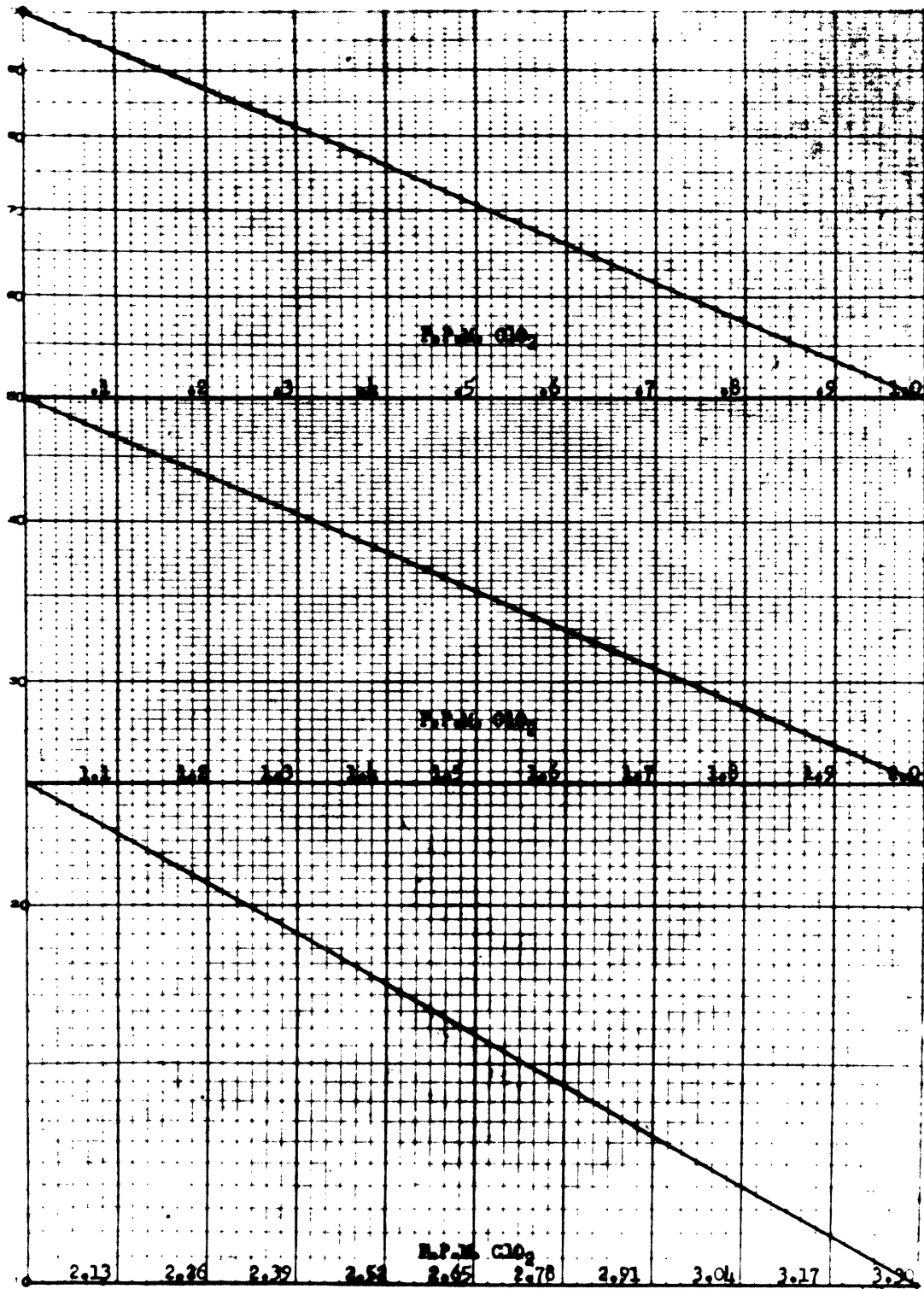


Fig. 1—Quantitative Curve C.T.O. for ClO₂

Algacidal Investigations on Chlorine Dioxide

Sixty-five genera of algae were studied in order to determine the dose of chlorine dioxide necessary for complete destruction of the algae. The lethal dose was judged by observation of the algae under the microscope as well as by loss in weight amounted to as much as 50 per cent and if the number of dead algae in a 96-hour period comprised as much as 80 per cent of the sample, that specific amount of chlorine dioxide was listed as the lethal dose.

It is not necessary to include each series of experiments in regard to weight loss and number reduction, but, rather, it is most appropriate to include the specific amounts of chlorine dioxide required to eradicate particular genera of algae. The writer has taken occasion to use the original list of algae compiled by Hale (1942) to quote the concentrations of copper sulphate and chlorine required to destroy the algae and in the third column to list the quantities of chlorine dioxide required to kill the various genera of algae. Table 1 lists the results of the investigation.

A number of experiments on chlorine dioxide are not quoted because the concentration of organisms in milligram weight was not reduced noticeably, and we could not judge by appearance whether the algae were dead. Where the algae were in pure culture free from bacteria and other organisms, it was a relatively simple matter to evaluate, particularly when transfers from samples could not be cultured.

TABLE 1

CHEMICALS REQUIRED FOR TREATMENT OF DIFFERENT GENERA

Organisms--Odor	Copper Sulfate p.p.m.	Chlorine p.p.m.	Chlorine Dioxide p.p.m.as ClO ₂
Cyclotella:		1.0	.4
Faintly aromatic			
Melosira	0.20	2.0	.8
Navicula	0.07		.2
Synedra	0.36-0.50	1.0	.7
Chlorophyceae:			
Cladophora	0.50		1.2
Closterium	0.17		1.4
Dictyosphaerium		0.5-1.0	1.2
Grassy, fishy, nasturtium			
Eudorina	2.00-10.00		1.6
Faintly fishy			
Palmella	2.00		2.0
Pandorina	2.00-10.00		3.8
Faintly fishy			
Scenedesmus	1.00		1.6
Spirogyra	0.12	0.7-1.5	.3
Staurostrum	1.50		.8
Grassy			
Ulothrix	0.20		.3
Cyanophyceae:			
Anabaena	0.12-0.48	0.5-1.0	1.2
Moldy, grassy, vile			
Coelosphaerium	0.20-0.33	0.5-1.0	.6
Sweet, grassy			
Gloeocapsa	0.24		.4
(red)			
Microcystis	0.20		.5
Oscillatoria	0.20-0.50	1.1	.5
Protozoa:			
Ceratium	0.24-0.33	0.3-1.0	.5
Fishy, vile (rusty brown)			
Chlamydomonas	0.36-1.0		1.6

TABLE 1--Continued

Organisms--Odor	Copper Sulfate p.p.m.	Chlorine p.p.m.	Chlorine Dioxide p.p.m. as ClO ₂
Dinobryon	0.18	0.3-1.0	1.5
Aromatic, violets, fishy			
Euglena	0.50	1.9	.8
Synura	0.12-0.25	0.3-1.0	.4
Cucumber, musk-melon, fishy, bitter taste			

If contaminating organisms were present with the algae the results were discarded. Certain varieties of algae are readily isolated and grown in pure culture, others are particularly difficult to isolate and even more difficult to culture. Because of these circumstances a number of the forms investigated gave inconclusive results and are not mentioned in these results.

By way of observation, it now appears that the odors previously ascribed to these algae are probably in considerable error. We know, for example, that Eudorina will not always produce a faint fishy odor. It may produce a rotting hay or a musty odor, depending upon the other microorganisms with which it is associated. The same may apply to all of the other forms studied. We point this out so the

the reader may know that the odors attributed to these various forms were previously described by other workers, and we have not taken the liberty to make any changes.

Applications of Chlorine Dioxide for the Removal of Tastes and Odors from Water Supplies

In an earlier section of this paper attention was called to the fact that the major taste and odor-producing compounds in unpolluted water in the Southwest was due to by-products of actinomycetes. Also reference was made to the fact that experimental work was done by using these concentrates and treating them with chlorine, chlorine dioxide or activated carbon, and assembling the data from the experimental work.

Cultures of actinomycetes were set up with air flowing continuously through the media into containers of triple distilled water. The taste and odor-producing compounds were concentrated in the water and these concentrates were used for all testing reported in this section. Since no other compounds were present in the water in addition to the actinomycete by-products, any alteration in their chemical composition could be discerned in the threshold odor test run on all samples.

One series of experiments was a set of dilutions of the strong compound so that each sample of water had a threshold odor number of 40. Each of the 10 samples received quantities of chlorine dioxide varying from .1 to 8.0 ppm.

The residual was run at the end of one hour as was the threshold odor on each sample. The results of this series of experiments may be seen in Table 2. It should be

TABLE 2
ODOR REDUCTION OF ACTINOMYCETE BY-PRODUCTS WITH ClO_2

Sample	1	2	3	4	5	6	7	8	9	10
T.O.*	40	40	40	40	40	40	40	40	40	40
ClO_2 ppm.	.1	.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
Residual ClO_2 ppm. end 1 hr.	0	0	0	0	.3	1.0	1.2	1.4	1.54	1.68
T.O. end 1 hr.	38.0	28.0	23.0	20.0	16.0	12.4	10.2	8.0	6.0	4.2

* Threshold odor.

mentioned that similar series were run on several occasions and results quoted are averages for all such experiments. It is noted that the maximum amount of chlorine dioxide, namely 8 ppm., reduced the threshold odor to 4.2 and that the residual chlorine dioxide 1.68 ppm. was relatively high. The idea of this series was to find what amount of chlorine dioxide would be demanded for water having an odor number of 40. (Table 2).

Similar sets of samples were set up and received like quantities of chlorine dioxide. At the end of one hour the samples were flocced and filtered. Threshold odors and chlorine dioxide residuals were run. As in the series mentioned above, numerous duplicates of this experiment were run before final averages were assembled. It is apparent from the results in Table 3 that in water containing as much actinomycete by-products as these samples that about 8 ppm. chlorine dioxide will be required to oxidize the compounds present.

TABLE 3
ODOR REDUCTION OF ACTINOMYCETE BY-PRODUCTS WITH
ClO₂ AND FLOCCING

Sample	1	2	3	4	5	6	7	8	9	10
T.O.	40	40	40	40	40	40	40	40	40	40
ClO ₂ ppm.	.1	.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
flocced and fil- tered	28.0	24.0	20.0	18.0	16.0	12.0	8.0	6.0	3.8	2.0
Residual ClO ₂	0	0	0	0	0	0	.3	.6	.8	1.1

Since a considerable amount of experimental work was done on chlorine, it is appropriate to include the average finding from this as indicated in Table 4. This series of samples with an original threshold odor of 40 shows a continuous rise in threshold odor numbers in all samples 1 through 10 as a result of the addition of chlorine.

TABLE 4

EFFECT OF CHLORINE ON ODOR VALUES WITH BY-
PRODUCTS OF ACTINOMYCETES

Sample	1	2	3	4	5	6	7	8	9	10
T.O.	40	40	40	40	40	40	40	40	40	40
Cl ₂ ppm.	.5	2.0	4.0	6.0	9.0	12.0	14.0	17.0	18.5	20.0
Residual total Cl ₂ end 1 hr.	.2	1.8	3.8	5.9	8.8	11.6	13.4	16.6	18.0	19.0
T.O.	48	62	84	106	123	140	162	174	189	206

TABLE 5

EFFECT OF ClO₂ ON ODOR VALUES WITH ACTINOMYCETE
BY-PRODUCTS

Sample	1	2	3	4	5	6	7	8
T.O.	20	40	80	160	310	380	440	500
ClO ₂ ppm. added	10	10	10	10	10	10	10	10
Residual end 1 hr	4.5	2.6	1.4	.2	0	0	0	0
T, O. end 1 hr.	0	0.4	2.6	3.4	6.4	10	16	20

There are additional data not included in this paper that show if the chlorine content is extended up to 200 ppm. there is still no break point. The chloro-derivatives that are formed by the action of chlorine reacting with the

actinomycete by-products do not appear to be destroyed by high concentrations of free chlorine.

In order to have a general scan of the effect of a constant amount of chlorine dioxide on samples with variable threshold odors, we chose to add 10 ppm. of chlorine dioxide to each one of eight samples having threshold odor numbers of from 20 to 500. One may observe that 10 ppm. will lower the threshold odor in all samples, even in the sample containing a threshold odor of 500. We believe this information which is assembled from a number of experiments may be used by workers in the field as a general reference for the amount of chlorine dioxide required. (Table 8)

By way of comparison, a number of samples were run using activated carbon with a mesh number of 320 and a phenol number of 15. Typical results from these experiments may be observed in Table 6.

TABLE 6
EFFECT OF CARBON ON ACTINOMYCETE BY-PRODUCTS

Sample	1	2	3	4	5	6	7	8	9	10
T.O.	20	20	20	20	20	20	20	20	20	20
Carbon ppm.	4	6	8	10	12	14	16	18	20	22
T.O. after 2 hrs. stirring	12	12	11	11	9	8	8	6	4	3.5
T.O. after floc. and filter	9	9	8	7	6	4	3.5	3.0	2.0	1.5

The writer chose to use a threshold odor of 20 rather than 40 since such threshold odor numbers may be rather commonly encountered in water plant practice. Threshold odor numbers of 40 are relatively rare although they may occur during times of copious actinomycete growth. One may observe that 22 ppm. of fine mesh activated carbon was required to reduce the threshold odor number to 1.5 which is an acceptable content of taste or odor in drinking water. It is also interesting to observe (Table 7) that under similar conditions with a series of 10 samples having a threshold odor of 20 and to which chlorine dioxide had been added the concentrations of .1-2.0 ppm. that 2 ppm. chlorine dioxide produced similar results.

TABLE 7
EFFECT OF ClO_2 ON ACTINOMYCETE BY-PRODUCTS

Sample	1	2	3	4	5	6	7	8	9	10
T.O.	20	20	20	20	20	20	20	20	20	20
ClO_2 ppm.	.1	.2	.4	.6	.8	1.0	1.3	1.5	1.8	2.0
T.O. after 2 hrs.	18	17	16	14	12	10	7.2	5.8	4.6	3.5
T.O. after floc and filter	13	12	12	11	8	4	3.8	3.3	2.2	1.5
Residual ClO_2 ppm.	0	0	0	0	0	0	.02	.07	.08	.1

TABLE 8

ClO₂ AND CARBON REQUIRED TO REDUCE ODOR OF
ACTINOMYCETE BY-PRODUCTS

Sample	1	2	3	4	5	6	7	8	9
T.O.	10	20	30	40	50	60	70	80	90
ClO ₂ ppm. required	1.3	2.0	4.8	7.6	8.8	10.1	12.2	14	18
Small mesh carbon ppm.	12	25	40	48	59	70	92		106

After a number of samples of water had been run through the routine described in this section, it became apparent that certain threshold odor numbers produced by actinomycete by-products would, under normal conditions, be eliminated or controlled by specific amounts of chlorine dioxide and/or 320 mesh carbon. The writer therefore has taken this occasion to show the amounts of chlorine dioxide required to oxidize the odor and taste producing compounds in nine different samples varying in concentration from 10 to 90 threshold odor. The same table (8) shows the requirements in activated carbon. For example, we note that it takes 2 ppm. chlorine dioxide or 25 ppm. activated carbon to control a threshold odor number of 20 produced by actinomycete by-products. One reason that we did not take threshold odor numbers higher than 90 is the fact that such concentrations

rarely, if ever, appear in surface samples in this section of the country. The reader, of course, will hold in mind that the threshold odor numbers are mere dilutions of the original water so that a threshold odor number of 50 indicates that the water diluted 50 times has no detectable odor but if it were diluted one less time it would have evidence of the odor. We believe this knowledge to be fundamental in that it will be possible for individuals to predict the amount of chlorine dioxide or activated carbon that will be demanded in actinomycete contaminated water. Naturally more demand will be present in natural waters than in the laboratory samples since of the chlorine dioxide will be consumed by other materials that are present in natural water. The requirements for both chlorine dioxide and carbon are based on finished water that has been passed through a softening process so as to have a final pH of 10.2. Waters that are not softened may have more or less odor depending on the quantity of the amines that are present. The reader will observe that no comment is made on chlorine, but it should be understood that if chlorine is used as a pre-chlorination practice and then activated carbon is used for odor removal that about twice the amount of carbon will be demanded since some of it is lost in consuming the chloro-derivatives formed by chlorine in conjunction with the actinomycete by-products.

The Effects of Chlorine Dioxide and Chlorine on the Actinomycete By-Products

In the course of the investigation on actinomycete by-products certain compounds were identified from culture media as well as from water extracts. These compounds have been shown to be responsible for the major tastes and odors in water supplies. As discussed in the section on methods, each of the known compounds was dissolved in carbon tetrachloride and scanned on the infra-red spectrophotometer. They were then reacted with chlorine dioxide and chlorine in different samples and the effects of these two chemicals were noted.

The results of the effects of chlorine dioxide on the various compounds may be seen in Table 9. It is interesting to observe that the primary and secondary amines were oxidized by chlorine dioxide while the tertiary amines were not altered. We have not actually isolated any tertiary amines from actinomycete metabolism. This compound was included because it was available. The fatty acids used in this series of experiments show differential results. Isovaleric and beta hydroxy butyric acid were not affected by chlorine dioxide. Oleic acid was oxidized to the point that the carbon chain was broken as double bonds with the subsequent formation of short-chained acids and aldehydes. It should be pointed out that the by-products of oleic acid did not produce obvious tastes and odors. Palmitic acid

was broken down into a number of short chained acids, only one of which had any offensive tastes and odors. It should be mentioned that neither oleic or palmitic acids have been identified as by-products of actinomycete metabolism.

TABLE 9

PRODUCTS TESTED WITH ClO_2

Material Studied	Results and Comments
1. Methyl amine	Amino group attacked. No nitrogen chloride derivatives formed.
2. Di methyl amine.	Amino group attacked. No nitrogen chloride derivatives formed.
3. Tri methyl amine	No reaction.
4. Oleic acid	Carbon chain broken at double bond and various short chain acids and aldehydes formed.
5. Iso-valeraldehyde.	Iso-valeric acid and Iso-valeric chloride formed.
6. Palmitic acid	Acetic acid, Butyric, Propyl and Valeric acids formed.
7. Iso-valeric acid	No reaction.
8. N-Butyl amine	Amino group oxidized. Formed chloropicrin and N-Propyl chloride.
9. B-hydroxy butyric acid	No reaction.
10. Phenol	Formed oxalic, maleic and small quantity of formic acids.

The phenolic compound was oxidized to oxalic acid, maleic, and small quantities of formic acids. In hard water with a high calcium content the oxalic acid would be

precipitated out, the maleic and formic would be in such low percentages as to be of no importance.

The only aldehyde formed in the actinomycete investigation was iso-valeraldehyde. When this substance was tested with chlorine dioxide, the aldehyde was converted to iso-valeric acid and iso-valeric chloride. More chloride was formed than acid which resulted in a noticeable reduction in odor when compared with the amount produced by the aldehyde. Since iso-valeric acid is not affected by chlorine dioxide there was no manner by which this compound could be further reduced.

The major odors produced by the actinomycetes are due to amines, aromatic compounds such as phenols, and the aldehydes, such as iso-valeraldehyde. Since all of these are oxidized by chlorine dioxide, particularly the amines and aromatic compounds, it can be stated that chlorine dioxide serves very appropriately for eradication of odors and tastes produced by specific chemicals that result from the metabolism of actinomycetes.

In the study of the various compounds, chlorine was also reacted with the various specific chemicals, the results of which may be observed in Table 10. It is interesting to observe that the results here showed either no reaction or the formation of nitrogen chloride derivatives or chlorine substitution in some form or fashion. As a result of the various

substitutions and reactions of chlorine, it is immediately observed that the addition of chlorine to any of the chemicals produced by actinomycetes may result in compounds with more intense tastes and odors. It is possible that these compounds may, under certain conditions, be highly toxic. It is not appropriate to make further comments on that point at this time.

TABLE 10

PRODUCTS TESTED WITH Cl_2

Material Studied	Results and Comments
1. Methyl amine	Reaction. Nitrogen chloride derivatives formed.
2. Di methyl amine	Reaction. Nitrogen chloride derivatives formed.
3. Tri methyl amine	No reaction.
4. Oelic acid	No reaction.
5. Iso-valeraldehyde	Chlorine substitution.
6. N-Butyl amine.	Chlorine is substituted on to the amine group.
7. Palmitic acid	Chloro-derivatives of this acid formed.
8. Iso-valeric acid	No reaction.
9. B-hydroxy butyric acid	No reaction.
10. Phenol	Chloro-phenols produced.

The Effect of Chlorine Dioxide on Barnsdall City Water

In the section on practical methods a description was given of the Bird Creek situation in Northeastern Oklahoma and the condition of the water when it arrived at the small town of Barnsdall. It was noted that the threshold odor of the raw water was 240 at the time chlorine dioxide was installed. During the first few days of operation residuals as high as 30 ppm. of chlorine dioxide were carried in the clear well. By taking samples from taps on the different parts of the distribution system, we were able to show that no chlorine dioxide was traveling in the distribution system as far as three blocks. By the fifth day of operation 1 ppm. residual chlorine dioxide was found in the business district three blocks from the filtration plant. On the tenth day only 10 ppm. chlorine dioxide residual was being maintained in the clear well and the distribution system in all sections of the city was showing from .3 ppm. to 1.5 ppm. chlorine dioxide. The writer assumed that the long chained polymeric aldehydes from the chemical plant were probably clinging to the sides of the pipes of the distribution system and must be oxidized before chlorine dioxide could maintain a residual in the system. In a matter of 30 days 1.5 ppm. residual chlorine dioxide was being maintained in the clear well and all parts of the distribution system showed residuals from .3 to .8 ppm.

Since the installation in August of 1949 chlorine dioxide has been in continuous use at the Barnsdall Water Purification Plant. The threshold odors of the finished water are maintained around a 3 or 4, the water is palatable and bacteria free. No other compound tried by previous investigators on the same problem had been able to handle the situation as appropriately as did chlorine dioxide. It is noted that activated carbon in this instance was completely ineffective. Additions of fine mesh carbon as high as 50 ppm. did not appear to reduce greatly the taste and odor in the finished water.

Breckenridge, Texas

The application of chlorine dioxide to the water plant in Breckenridge, Texas, on August 14, 1950, was doubtless one of the briefest periods that this compound has been used with such phenomenal success. As indicated in the section on methods, only 20 lbs. of sodium chlorite was available at the time the installation was made and in a period of 16 hours the chemical had been depleted and the residual chlorine dioxide in the clear well had reached a maximum of 3 ppm. In the distribution system the residuals varied from .75 to .08 ppm. Twelve hours after the chlorine dioxide addition had terminated the taste and odor in the water had disappeared. Since that time the City of Breckenridge has established its own chlorine dioxide feed system by employing

a generator and a pump. The longest period required for the removal of actinomycete by-products since the installation has been a period of 48 hours in the fall of 1951. The chlorine dioxide is not used regularly in the plant since the periodicity of the actinomycetes is very brief and the amount of by-products appears to be small. The installation is now used for emergency work. Colleagues of the writer have made installations of chlorine dioxide in several other purification plants in Texas and have done considerable work at Waco, Texas, where actinomycetes have established themselves in the distribution system. In all instances the chlorine dioxide has proved most appropriate and has not appeared to be any more expensive than chlorine and carbon.

DISCUSSION

In the Southwestern section of the nation additional water supplies are being established on various rivers and streams as population increases. With the advent of more surface water supplies new problems arise in taste and odor control. For some years the major taste and odor problems were appropriately handled by break-point chlorination in connection with the addition of high concentrations of carbon. It appears that the cause of tastes and odors in the

Southwest had altered somewhat from the original types of twenty years ago. This may be due to a change in the fertility of the water or to the introduction of new organisms.

At any rate, chlorine dioxide appears, from the experimental work in our laboratory, to be the most successful method for removing the actinomycete by-products. The writer has indicated that laboratory results on water samples tested for threshold odor demonstrated that the obnoxious odors could be removed with chlorine dioxide but could not be reduced with chlorine. Laboratory analysis on the actual isolated chemical compounds produced by the actinomycetes have shown that the specific chemicals responsible for tastes and odors in most instances may be completely oxidized. In a similar group of experiments, demonstrations have shown that chlorine alone will not oxidize the compounds but may substitute on

them in various forms or fashions to give rise to complex, and, in many instances, more volatile and offensive compounds. Thus one may conclude from this mass of experimental work that chlorine dioxide has a useful purpose in public health work, particularly as an emergency method for the eradication of tastes and odors. It should be pointed out that chlorine dioxide would be more appropriately used in water systems if it were generated with sulphuric acid rather than with chlorine. Our laboratory work indicates that a mixture of 2.2 lbs. of technical grade sodium chlorite with 1 lb. of chlorine in water at a pH of 8.2 may result in high concentrations of chlorine dioxide and low concentrations of chlorine. In order to produce chlorine dioxide with no chlorine it is necessary to add 3 lbs. of chlorite to 1 lb. of chlorine. In this instance, however, there is unreacted sodium chlorite in the water supply. The writer does not feel that the quantity of sodium chlorite would be sufficient to be dangerous but it is wasteful. Therefore, there is reason to contend that it is best to generate chlorine dioxide by using sodium chlorite and sulphuric acid. It is appropriate to point out that chlorine plus chlorite produces a higher percentage of chlorine dioxide than chlorite plus sulphuric acid. The difference on a percentage basis is approximately 16 per cent. On the other hand, if enough chlorite is used with

chlorine so as to have no chlorine present, there is a wastage of 18 per cent chlorite. It would seem best to suggest this to the operator so he would know that the addition of the gas would not enhance tastes and odors if he substituted sulphuric acid for chlorine. On a cost basis sulphuric acid will be much cheaper than chlorine and even though less productive from a chlorine dioxide standpoint, on a large scale basis, the plant would save money by using the sulphuric acid. The writer has observed many laboratory demonstrations of this principle and thinks it appropriate to call it to the attention of the water plant operators who are interested in producing an odor-free commodity for the consumer.

There are a number of instances in cities where encrustations have formed on the inner sides of pipes of the distribution systems. These encrustations are composed largely of deposited calcium compounds and in many instances give rise to luxuriant growths of blue-green algae. The latter organisms demand no light; they require mainly a supply of nitrogen and calcium. After the algae are well established, spores of the actinomycetes pass through the filters and enter the distribution system. When the temperature of the water and pipes rises to around 17° C. spores imbed themselves in the blue-green algae and actinomycetes flourish in the distribution system. The operator may produce an odorless, tasteless water at the water plant only to find

his consumers highly dissatisfied with the vile tastes and odors in their finished water. When these occasions arise the only available treatment is chlorine dioxide. If this gas is added in concentrations as high as 7 ppm., mycelia of the actinomycetes are killed and the by-products are oxidized by the available chlorine dioxide resulting in odorless, tasteless water. This dosage does not necessarily have to be maintained for a period of time longer than it takes for water to pass from the filtration plant through the distribution system. The dosage of the chlorine dioxide will not kill the spores but the germination period of a normal spore is approximately five days, thus a large dose of chlorine dioxide every five days will result in overcoming the difficulty that heretofore has not been adequately handled in any of the city distribution systems.

When the writer first started assisting in laboratory work on chlorine dioxide, it was the belief of the principal investigator that the gas would be useful in the Southwest since that was the major area of actinomycete contamination.

Since the beginning of the original work on chlorine dioxide, distribution of the actinomycetes has been extended to include the cities of Chicago and Philadelphia. Only recently actinomycetes were isolated from the Bryn Mawr filtration plant in the City of Philadelphia. These are identical with the forms found in Waco which means that in all

probability the organisms will act in the fashion observed in Waco, that is, growing in the pipes of the distribution system. The superintendent of filtration at the water plant has recently tested chlorine dioxide and has shown that it will remove the tastes and odors while chlorine will enhance them. That was shown in our laboratories four years ago, but it is still important to the filtration engineer in Philadelphia. Chicago from time to time suffers from mild actinomycete tastes and odors. After isolation of the organisms from finished water the principal chemist at the South District Filtration Plant is aware of the fact that he has a tool to combat the tastes and odors should they rise to an obnoxious concentration. Certain work that we have been able to do on polluted water, particularly those containing phenols, has demonstrated that chlorine dioxide will oxidize the phenols resulting in by-products that are innocuous. This is obviously an advance towards reclaiming certain waters that heretofore were thought to be useless for human consumption.

Attention should be called again to the fact that sodium chlorite alone is a good algacide and that it is a fairly effective bactericide and fungicide. If the waters are alkaline, the sodium chlorite will last for considerable periods in cooling towers or in enclosed circulating systems or blow-down towers and even though it is expensive to add, the

stability of the compound in basic water makes it useful. Chlorine dioxide may also be employed as an algicide although it is not nearly so stable as chlorite but serves particularly well in swimming pools and other areas where algae eradication is required. It is advisable to mention that the lack of nitrogen trichloride and chloramines when chlorine dioxide is employed in swimming pools is a high recommendation for the use of this gas.

SUMMARY AND CONCLUSIONS

From these investigations on chlorine dioxide one may make the following conclusions:

1. The modified OTA as presented in this paper is accurate and concise enough to warrant usage as a research and plant practice.
2. ClO_2 is not significantly different from CuSO_4 or Cl_2 in its algacidal abilities.
3. ClO_2 is an effective odor reducing agent when used to reduce odors due to actinomycete by-products.
4. ClO_2 is not a "cure all" for all odor problems; however, it may find application in many odor problems.
5. ClO_2 is most effective in cases where Cl_2 is kept at a minimum.
6. ClO_2 may be safely used by a plant operator.

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