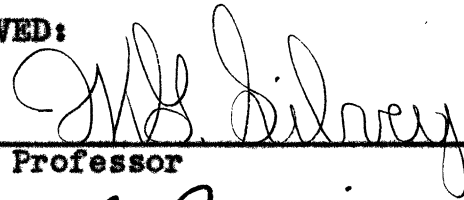


NEWER METHODS OF REMOVING TASTE AND ODOR
COMPOUNDS FROM WATER SUPPLIES


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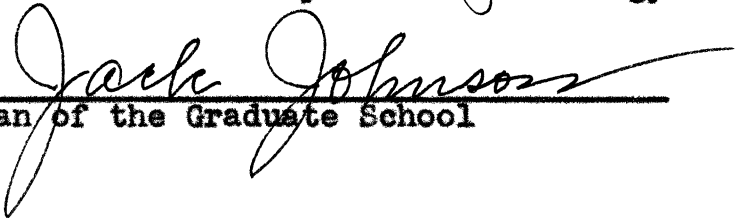
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NEWER METHODS OF REMOVING TASTE AND ODOR
COMPOUNDS FROM WATER SUPPLIES

THESIS

Presented to the Graduate Council of the
North Texas State College in Partial
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INTRODUCTION

The problem of tastes and odors in water supplies was not encountered by primitive man since his meager demands could be satisfied by the abundance of available water in natural streams and lakes. As man passed from the era of the stream-side village and the community well into one in which society demanded a palatable, abundant, and healthful water, the problems of supplying the consumer were multiplied. In areas where industry flourished, by-products from the plants were diverted into streams, rivers, and lakes, resulting in partial ruination of potential supplies. Many cities and towns were fraught with epidemics of water-borne diseases and other difficulties that were exhibited in populations consuming chemical wastes. Within the last twenty years many advances have been made in water purification so that today the average citizen is furnished a commodity that is free of disease producing organisms and generally healthful. However, the advancement in purification techniques has not attained sufficient skill to be able to produce an odorless, tasteless water at an economical figure. Many cities have water supplies that contain a concentration of odor and taste producing compounds that are reduced but not removed in the filtration process. Until this problem is solved, water plants are not accomplishing the tasks they were designed to complete.

In the Southwest rapid growth in population and industry made such demands on the natural water supplies, that municipalities found it necessary to impound rivers and streams in an effort to conserve and insure adequate supplies of water. These impoundments gave rise to reservoirs that assumed the characteristics of both a river and a lake. This type of ecological condition promoted a series of sporadic biological growths. Tastes and odors were multiplied many fold as a direct result of the increased biological activity. This sudden upsurge in the biota resulted not only in the abundance of higher plants and animals, but also in lower forms such as molds, algae, and actinomycetes.

Silvey (1950) reported that actinomycetes and their by-products were responsible for a high percentage of the tastes and odors encountered in surface water supplies in the Southwest. To augment this primary source, there were pollutive agents such as industrial waste, domestic sewage, and decomposition products of plant and animal remains contributing to tastes and odors. In an attempt to avert disaster, municipalities in this area have encouraged the investigation of potential methods of improving the present surface water and making more available.

The development of methods that would permit the use of surface water in city distribution systems has been in progress about a century and a quarter. The early history of this period has been reviewed by Hassler (1941) and the following chronology is summarized from his work.

Early purification efforts were directed principally toward producing a colorless or clear water which was thought to be safe for consumption. To supply this type of water, James Simpson installed the first slow sand filter in 1829 for the Chelsea Water Works in London. In 1832 Albert Stein designed and directed the installation of the first filters to be put into operation in the United States at Richmond, Virginia. Kirkwood's recommendation in 1860 was responsible for the use of sand filters by a half dozen Midwestern cities. Between the years 1832 and 1882 sixty-five cities installed filters that were similar to those operating at Richmond, Virginia. The filters were clearing the water; however, the taste and odor contents were not affected.

In 1884, A. R. Leeds, employed by Hackensack Water Company, was the first to introduce aeration as a method of odor reduction at Hoboken, New Jersey. In his design, compressed air was forced into the water in an attempt to hasten nature's scheme of odor removal by exposure of the water to air. Until 1905 aeration was the only method especially designed for the removal of tastes and odors from municipal water supplies.

The use of potassium permanganate for taste and odor reduction was suggested by Reidmeister in 1883; however, Fuller in 1900 first made use of the chemical for iron and odor reduction in Providence, Rhode Island. This method was popular during the first part of the twentieth century, but soon lost

favor because of its inability to eradicate a variety of odors. Carird in 1928 revealed that the action of potassium permanganate was largely effective on phenol odors such as those found at Rochester, New York. That experiment showed that potassium permanganate had power to oxidize phenols, but otherwise was limited in its ability to reduce tastes and odors.

The practice of coagulation in water treatment dates back hundreds of years. Possibly the Egyptians first used this method to precipitate mud and other suspended materials from the water of the Nile River. Tunnels Clark in 1841 first used lime and soda-ash coagulation in a London filtration plant. James A. Seddon in 1890 conducted a study using a combination of the previous ideas on purification plus sedimentation for the reduction of tastes and odors. The results obtained from this study led to investigations and subsequent use in the United States. The first use of softening and sedimentation in the United States was at Overland, Ohio, in 1905. The use of this process was soon adopted by other cities such as Columbus in 1908, New Orleans in 1909, and St. Louis in 1915.

Krokenke in 1884 suggested that the control of tastes and odors include methods which would prevent contamination as well as eliminate pollution already existing in the supply. To accomplish this task, Krokenke used copper sulfate in sufficient quantities to kill algae, thereby reducing the odors

in reservoirs. This work led to the use of copper sulfate as an odor control measure by Moore (1904) who also showed that the incidence of typhoid dropped in direct proportion to the amount and frequency of copper applied. This chemical is the most common algaecide in use today as a means of controlling tastes and odors in surface water supplies.

Bactericidal properties of ozone were first observed by Fox in 1873. Ohlmüller in 1893 employed ozone for purification of water but it was not until many years later that it was used for taste and odor control. Ozone plants were installed at Longbeach, Hobart, and Whitney, Indiana, in 1930, 1932, and 1938, respectively (Bartuska, 1941). The ozone treatment of these waters has been helpful in correcting serious taste and odor conditions. However, the equipment for ozone generation requires an expenditure of considerable funds, which doubtless accounts for the few installations in both industries and municipalities.

Credit for the invention of chloride of lime is given to Dr. Duik, a Belgian chemist. Chloride of lime was first used as a bactericidal agent at Boomtown Reservoir of the Jersey City Water Works in 1908. The invention of compressing chlorine gas into cylinders led to the use of an apparatus devised by Major C. R. Darnell in 1910 for diluting known amounts of chlorine gas into the water supply. Odor reducing properties of chlorine were accidentally found by Rideal in 1904 but the reasons for its success were unknown to him. Howard and

Houston in 1919 (Howard, 1922) conducted about three thousand experiments on the action of chlorine on different types of odors and found that the addition of greatly elevated levels of residual chlorine would destroy odors originally present and those resulting from the addition of smaller amounts of chlorine. Hale (1929) used this new process of "super-chlorination" in Jamaica, New York, with good results. This method never gained much favor because it is the most difficult to control of all procedures employed in water treatment.

In the search to find a cheaper method for sterilizing water, Race in 1916 noted that chloramine was not only a good sterilizing agent, but also that it had good odor reducing properties. Howard (1922) reported acceptable results from laboratory experiments using chloramine as an odor eradicating compound. McAims in 1926 employed chloramine in plant operations at Greenville, Tennessee, with splendid results. Experiments conducted by Houston in 1929 (Gainey and Lord, 1952) indicate that this process frequently "back fires" in that the odor producing compounds are reformed and magnified.

One of the better methods of taste and odor control was introduced by Spaulding (1930) when he demonstrated that active carbon could correct taste conditions in municipal water supplies at a very moderate cost. According to Wrench (1935), by 1935 the use had extended to 700 communities. This process is still widely used throughout the United States, even though the expense of carbon to destroy high threshold odors may become impractical.

Realizing that it is not financially feasible to treat large quantities of high threshold odor water with the activated carbon process, competitors turned to further chlorination studies. One of these studies was introduced by Griffin (1944) in 1939 in his report to the New Jersey section of the American Water Works Association on a new process called "break-point" chlorination. Break-point chlorination has been used for a variety of taste and odor problems and has yielded variable results.

One of the more recent developments in taste and odor control is the application of chlorine dioxide. Mathieson Chemical Corporation began a search to develop methods for preparing and applying chlorine dioxide gas to water supplies. Roy N. Aston (1947) and his assistants installed the first chlorine dioxide generators at Niagara Falls, New York, in 1944 by feeding a solution of sodium chlorite into the discharge line of the chlorinator, then passing the mixture of chlorine and chlorite through a reaction chamber to facilitate the formation of chlorine dioxide. Chlorine dioxide was successful in oxidizing the phenol compounds and thus reducing tastes and odors to a minimum at that site. In looking at results reported from laboratory and plant experimentation there are undoubtedly many other specific reactions which occur when chlorine dioxide is administered directly to water.

Although many investigations have been conducted on methods for taste and odor control, no standards exist that

indicate how much of any product is required to control a particular type of odor. Lack of such standards posed the first problem in this investigation.

Secondarily, it seemed desirable to investigate many compounds in an attempt to find an inexpensive material or formula that would control tastes and odors in surface water supplies. After many experiments, a compound which is an activated vegetable extract was found that appeared to have possibilities and which could be readily used in laboratory investigations. By comparing this compound with other compounds used in taste and odor control, results would indicate the real value of the new material. The major part of the problem deals with investigations that reveal the value of the new compound in control of tastes and odors in filtration plants.

METHODS

A review of the literature indicated that previous investigators have used raw water samples for determining the amounts of odor reducing materials necessary to eradicate tastes and odors. These samples doubtlessly contained many varieties of odor producing compounds from numerous sources. Consequently, their methods yielded variable results that had no quantitative or formulative bases for comparison of odor treatments to be applied in different localities. Therefore, the first step in the present investigation was to produce a standard odor bearing water for all determinations so that quantitative and qualitative methods could be applied to such problems in the Southwest.

Actinomycetes and their metabolic by-products, according to Silvey (1950), produce a high percentage of the tastes and odors found in the surface waters of North America. Since actinomycetes and their decomposition odors are variable, different strains of actinomycetes were raised in culture so as to have a representative sample of the odors attributable to actinomycetes and algae. The strains of actinomycetes used in the study were first plated from raw, untreated water samples taken from various reservoirs containing actinomycete odors. The water samples were thoroughly mixed and two milliliters of water were pipetted into a sterile petri dish

containing fifteen milliliters of double strength nutrient agar. The plates were rotated gently to insure a water film distribution, then permitted to solidify, inverted, and incubated at room temperature for fourteen to twenty-one days. Transfers were made until actinomycetes were free of bacterial and fungal contaminations. The isolated colonies of the actinomycetes were then transferred to prepared nutrient agar slants for stock cultures. Transfers were made from these cultures to Erlenmeyer flasks containing one hundred fifty milliliters of nutrient broth and incubated at room temperature for five days or until well developed pellicles were floating on the broth. Several of the larger pellicles were placed in a tissue homogenizer and ground into a pulverized, semi-solid state. The by-products were added to carboys containing five gallons of odor free distilled water in concentrations sufficient to obtain a threshold odor of forty.

Diversion or seepage of industrial wastes such as effluent from a formaldehyde, alcohol, or similar plants are common causes of tastes and odors problems. In an effort to reproduce this type of water, chemically polluted water samples having odors similar to those found in sections of the Trinity River in Texas, parts of the Mississippi River, the Ohio River, and streams in Northeastern Oklahoma were procured from streams which carried the wastes of cracking plants. The samples contained known amounts of short chain aldehydes, ketones, amines, and aromatics. Small amounts of these

concentrates were added to a carboy containing five gallons of odor free distilled water until a threshold of forty was attained.

There have been few satisfactory methods employed for treating phenolic tastes and odors. This odor is perplexing to municipalities in highly industrial sections of the Midwest and North. The economic and social importance of this type of chemical pollution makes it desirable for further investigation to be followed on control of phenolic wastes. Sufficient amounts of primary hydroxy benzene (phenol) were added to carboys containing five gallons of odor free distilled water so that the threshold odor of the sample was forty.

The method used for determining threshold odors was the technique described by Spaulding (1930). The procedure consisted of comparing varying dilutions of odor bearing water samples with an odor free standard. The highest dilution at which odor could just be detected was called the threshold point. The odor at the threshold point is expressed quantitatively by the threshold number, which is simply the number of times the odor bearing sample is diluted with odor free water.

The preparation of odor free water used in the threshold determination was accomplished by allowing distilled water to flow by gravity through a 1000 milliliter separatory funnel filled with activated carbon.

The writer found that a properly activated chlorophyll-containing vegetable material, if used in correct proportions, would remove essentially all of the taste and odor compounds. Although a hydrated chlorophyll-containing vegetable material was satisfactory for the purpose of a product, a dehydrated chlorophyll-containing vegetable material was preferred as a constituent of the composition of the odor reducing compound since proper dehydration by removal of water reduced the experimental problems without reducing its effectiveness. There are a number of known processes for removal of most of the water content of chlorophyll-containing vegetable material without causing disintegration of the chlorophyll-molecule. The dehydration methods differ essentially in the amount of vacuum used or the type of dehydration accomplished. The chlorophyll-containing vegetable material may be dehydrated under any conditions which dehydrate the material without breaking down the chlorophyll-molecule. In other words, the resultant chlorophyll content must permit saponification to yield activated materials.

In order to permit proper activation of the selected vegetable material, the composition of the product must contain proper proportions of a suitable alkaline material. Alkaline materials that activate these vegetable materials can be, for example, magnesium hydroxide, calcium oxide, and calcium hydroxide. Of these, hydrated lime or calcium hydroxide was preferred. The reasons for this preference were: it

is generally undesirable to add magnesium to water and sodium oxide, sodium hydroxide and the corresponding potassium compounds are very strong caustics and exceptionally deliquescent. The preferred alkaline material, namely calcium hydroxide, when dry mixed in proper proportions with the vegetable materials does not pick up sufficient water to bring about hydration of the vegetable material and therefore does not result in premature formation of active substances. Premature activation has been found to lower the effectiveness of the compositions of the active product.

One to three parts by weight of calcium hydroxide were added for each ten parts of vegetable material. The most satisfactory mixture in this range is one which employs a very high grade lime and a high chlorophyll-containing vegetable material. To attain maximum activation of vegetable material sufficient amounts of the mixture were added to water to obtain a pH range from 11.1 to 11.8.

In order to demonstrate that maximum activation was obtained, in an aqueous solution between pH 11.1 to 11.8, varying amounts of calcium hydroxide were added to 100 milligram samples of dehydrated vegetable material and placed in 100 milliliters of water. The amounts of caustic added produced a pH range of from 9.5 to 12.5 in steps of 0.1 pH factor making a total of thirty samples. After a contact period of five minutes with vigorous agitation, samples of fluid were centrifuged and the densities were read in a Beckman DU

Spectrophotometer, using a slit width of 0.06 millimeters at a wave length of 402 millimicrons.

To be certain that readings of optical density were a true measure of the active substances that removed tastes and odors, a further series of experiments was performed. Aqueous solutions containing progressively increasing amounts of the preferred composition, that is, four parts by weight of lime for each twenty-one parts by weight of dehydrated vegetable material, were made up to obtain a pH range of from 9.5 to 12.5 in steps of 0.1 pH factor. After sufficient time for activation, samples of water containing actinomycetes products and having a threshold odor of forty were treated with each of the made-up activated vegetable samples in an amount equivalent to five parts per million of the dry mix.

When the dry product composition was added to water for the purpose of activation, the time and temperature of activation were of importance. To illustrate the effects of time and temperature upon activation, four 100 milligram samples of the dry mix product were added to four 250 milliliter beakers containing 100 milliliters of distilled water each and was thoroughly mixed for five minutes. Two of the samples were read in the Beckman DU Spectrophotometer at hour intervals for a period of eight hours and again at the end of twenty-four hours. The remaining samples were subjected to temperatures ranging from thirty-five degrees Fahrenheit to boiling to demonstrate effects upon activation as well as degeneration.

In order to duplicate various water plant operations in chemical treatments and show the effects of these treatments upon the odor reducing properties of activated vegetable material and activated carbon, the following procedures were employed. One-gallon, wide mouthed glass jars were chosen as containers for the three-liter samples to be used in the study. Six standard actinomycete water solutions were placed into one-gallon jars. Three of these were treated with activated vegetable material in amounts varying from fifteen to one hundred twenty milligrams (five to forty parts per million). The remaining samples were treated with activated carbon in amounts varying from thirty to one hundred eighty milligrams (ten to sixty parts per million) and then allowed to stand for two hours to insure complete sedimentation. Approximately four hundred milliliters of each were filtered through a two by eight inch column of anthrafilt into odor free glass stoppered containers. Threshold odor values were determined by the above described method, giving a clear comparison of the odor reducing properties of activated vegetable material and carbon under these circumstances. Henceforth, this practice will be referred to as sedimentation and filtration.

A second group of actinomycete water standards was taken from the carboy and placed in six one-gallon jars. Each sample was pre-chlorinated by the addition of seven and a half milligrams of chlorine (two and one-half parts per million). A time interval of ten to twenty minutes was given for chlorine

to disperse itself through the sample. Three of the samples were treated with activated vegetable material in amounts varying from thirty to sixty milligrams (ten to twenty parts per million), while the remaining three were treated with activated carbon in amounts varying from thirty to one hundred twenty milligrams (ten to forty parts per million). These mixtures were stirred slowly using an electrically powered paddle stirrer for a period of five minutes to insure a thorough mixing of the materials with the water. The electrodes of the Beckman pH meter were placed in the water throughout the following operations for the purpose of continually recording the pH. A sufficient amount of aluminum sulfate was added to the samples to give a pH reading of approximately 6.5. After the aluminum sulfate was completely dissolved, another pH reading was taken to make sure that the pH had not fallen below six. Upon increasing the speed of the stirrer, calcium hydroxide was added in sufficient amounts to bring the pH to eight or initiate the formation of a white flocculent precipitate of aluminum hydroxide. The vigorous agitation of this mixture, referred to in water plant operation as "flash mix," was continued until the precipitate was very evident. The paddle stirrer was turned to a slow speed allowing the sample to roll slowly, encouraging additional flocculation. The samples were removed from the stirrer at the end of five minutes of slow stirring and allowed to stand for a period of two hours to give the suspended precipitate, now

referred to as "floc," sufficient time to settle to the bottom of the jar. Approximately 400 milliliters of the supernatant of each was filtered through anthrafilt as described above. Threshold odor determinations were run on each sample. Further account of this procedure will be referred to as pre-chlorination, flocculation, sedimentation, and filtration.

A third group of actinomycete standard samples was placed in six one-gallon jars. Each was flocked, allowed to settle, and filtered as described above, and then post-chlorinated by the addition of one and one-half milligrams of chlorine (0.5 parts per million). Threshold odors were determined in the prescribed method. This practice will be referred to as the post-chlorination method throughout this paper.

The other standard odor bearing samples were given an identical sequence of treatments as those employed above in the treatment of actinomycete standards. The amounts of odor reducing materials were varied with respect to the standard treated. The raw water samples obtained from Cincinnati, New Orleans, and Philadelphia were pre-chlorinated by addition of three parts per million chlorine. Varying amounts of activated vegetable material were necessary for reducing the odors liberated by these raw water samples. These samples were flocculated and filtered by the above described methods. Threshold odor determinations were run on these samples in order to note the reduction or alteration of the odors.

RESULTS

As a basis for the testing of the previously described experimental design, a quantitative measurement of the activity or odor reducing potential of the activated vegetable material was essential. Varying concentrations of the activated vegetable material were measured as reciprocals of transmitted light or optical densities with the Beckman DU Spectrophotometer. These solutions were then added to water containing a threshold odor of forty. A retrogressive or inversely proportional relationship between optical density as odor reducing potential and actual reduction of the threshold odors is shown in Table 1.

In order to control experimental error, variable environmental factors that might influence the activity of the vegetable material were tested. When one of these, the pH of the solution, is changed, concentration or activity is altered (Table 1). Since optical densities are the greatest for a given solution between a pH range of 11.1 to 11.8, all treatment solutions were adjusted to this range.

The relationship of time and temperature to activation was revealed by the results of previously described methods. A minimum time necessary for complete activation of the vegetable material at seventy degrees Fahrenheit was found to

TABLE 1

THE RELATIONSHIP OF OPTICAL DENSITY AS ACTIVITY
OF STANDARDIZED VEGETABLE MATERIAL TO
THRESHOLD ODOR REDUCTION AND TO PH

| pH | Optical Density | Threshold Odor |
|------|-----------------|----------------|
| 9.5 | .16 | 14 |
| 9.6 | .16 | 14 |
| 9.7 | .16 | 14 |
| 9.8 | .27 | 13 |
| 9.9 | .17 | 13 |
| 10.0 | .17 | 13 |
| 10.1 | .19 | 12 |
| 10.2 | .19 | 12 |
| 10.3 | .19 | 12 |
| 10.4 | .23 | 11 |
| 10.5 | .26 | 11 |
| 10.6 | .26 | 11 |
| 10.7 | .30 | 10 |
| 10.8 | .32 | 10 |
| 10.9 | .34 | 9 |
| 11.0 | .38 | 7 |
| 11.1 | .40 | 5 |
| 11.2 | .44 | 2 |
| 11.3 | .45 | 2 |
| 11.4 | .46 | 2 |
| 11.5 | .46 | 2 |
| 11.6 | .46 | 2 |
| 11.7 | .45 | 3 |
| 11.8 | .44 | 3 |
| 11.9 | .30 | 4 |
| 12.0 | .28 | 4 |
| 12.1 | .23 | 6 |
| 12.2 | .21 | 8 |
| 12.3 | .21 | 10 |
| 12.4 | .21 | 10 |
| 12.5 | .18 | 10 |

be approximately twenty-five seconds. At ninety degrees Fahrenheit, complete activation occurred in fifteen seconds. At thirty-five degrees Fahrenheit, complete activation required two minutes. When aqueous solutions of activated vegetable material containing proper proportions of dry mix were allowed to stand for long periods of time, the odor reducing activity became less efficient. Optical densities taken at regular intervals indicated a progressive decrease in activity (Table 2). Thus, activated vegetable material in solution lost more than half of its effectiveness within twenty-four hours.

TABLE 2

RELATIONSHIP OF TIME TO RELATIVE ACTIVITY MEASURED AS
OPTICAL DENSITY OF STANDARDIZED ACTIVATED
VEGETABLE MATTER

| Time in Hours | Optical Densities |
|---------------|-------------------|
| 0 | .46 |
| 1 | .46 |
| 2 | .45 |
| 3 | .45 |
| 4 | .44 |
| 5 | .43 |
| 6 | .41 |
| 7 | .40 |
| 8 | .37 |
| 24 | .22 |

The graphic representation of results obtained when standard water samples were submitted to various chemical treatments and odor reducing materials will be discussed briefly because the curves do not show all integrations of the data.

When the actinomycete odor standards were treated with varying amounts of activated vegetable material and/or activated carbon, followed by sedimentation and filtration, as shown in Part A, Figure 1, the activated vegetable material reduced the threshold odor number to a value of three in concentrations as great as fifteen parts per million. The amount of activated vegetable material added to obtain a threshold odor number of three is calculated on the basis of dry weight of the mixture of vegetable materials and caustic rather than its weight in the aqueous solution. However, water having a threshold odor of forty could not be treated with activated carbon, since inefficient odor reduction was observed even at sixty parts per million. Thus samples were substituted with a threshold odor number of twenty-five. In these samples, forty parts per million of carbon lowered the odor to a threshold number of eight. The results obtained when an excess of activated vegetable material was added indicate that there is an upper limit to the amount of activated vegetable material which may be used without obtaining undesirable results. This feature of the product is evident in each graph of all aspects of the study. This upper limit is around fifteen parts per million. In fact, if the amount added is too much in excess of this concentration, the resultant threshold odor of the treated water may be greater than that of the raw or untreated water.

When samples of standard actinomycete water were treated with activated vegetable material and/or activated carbon

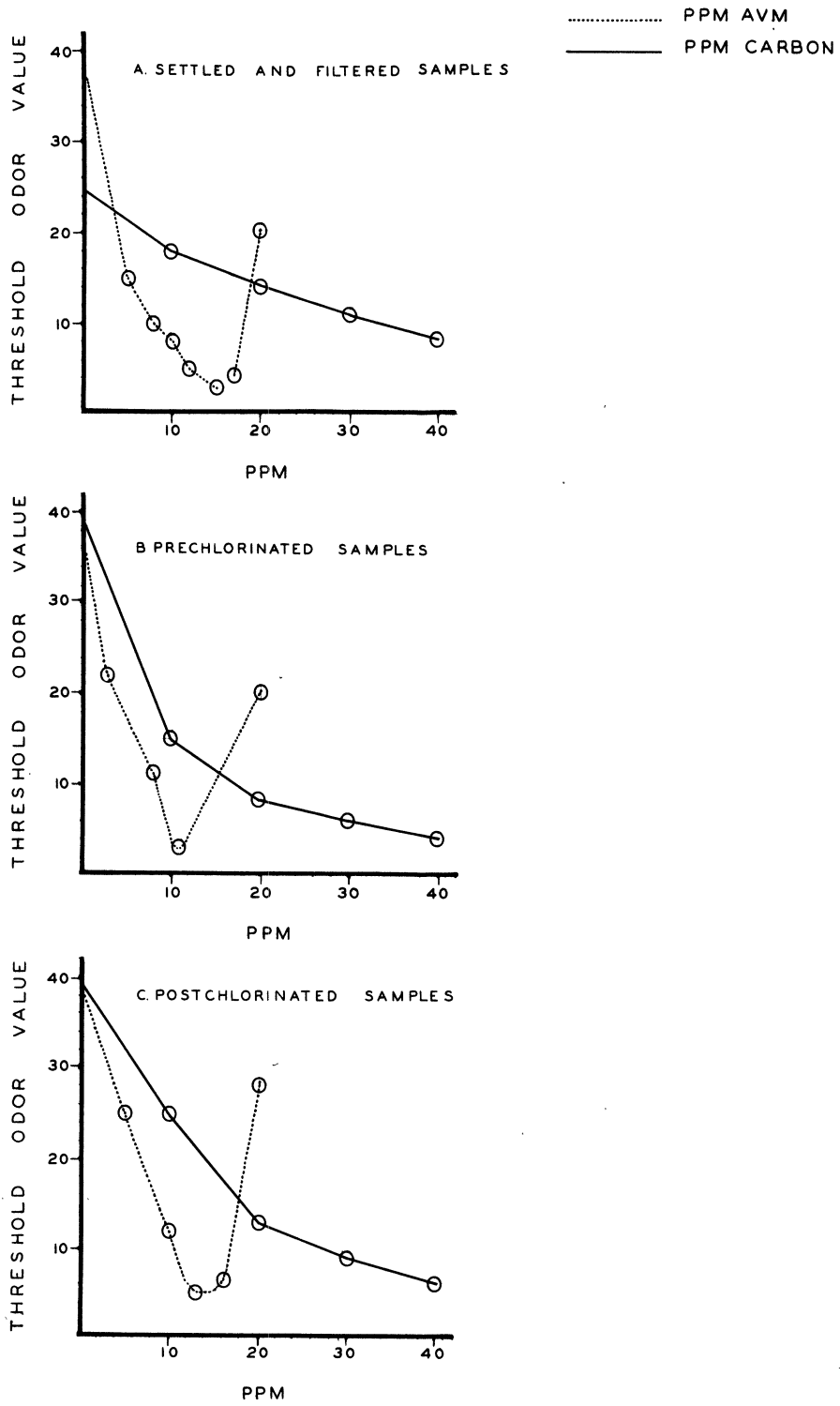


FIG. 1. TREATMENTS OF ACTINOMYCETE ODOR STANDARDS

then subjected to pre-chlorination, flocculation, and sedimentation (Part B, Figure 1), the threshold odor in the samples treated with activated vegetable material was reduced to five when twelve parts per million were used. Also, activated carbon at a concentration of forty parts per million reduced the threshold odor to six.

In the additional actinomycete standard odor samples which were flocked, filtered, and post-chlorinated, treated with activated vegetable material and/or activated carbon, concentrations of between ten and twelve parts per million of activated vegetable material removed most of the odor from the water (Part C, Figure 1). In order to lower the threshold odor to two and one-half, a concentration of sixty parts per million of activated carbon was necessary.

Figure 2 shows the results obtained by the addition of activated vegetable material and/or activated carbon to a series of the chemical standard odor water samples. Activated vegetable material in a concentration of from six to seven parts per million reduced the threshold odor number to four; whereas, carbon in concentrations of sixty parts per million reduced the threshold odor number to two in those samples which were not chlorinated. A threshold odor number of two or three is not usually noticeable in domestic water.

In the second group of chemical standard odor water samples which were pre-chlorinated, a concentration of six parts per million activated vegetable material reduced the

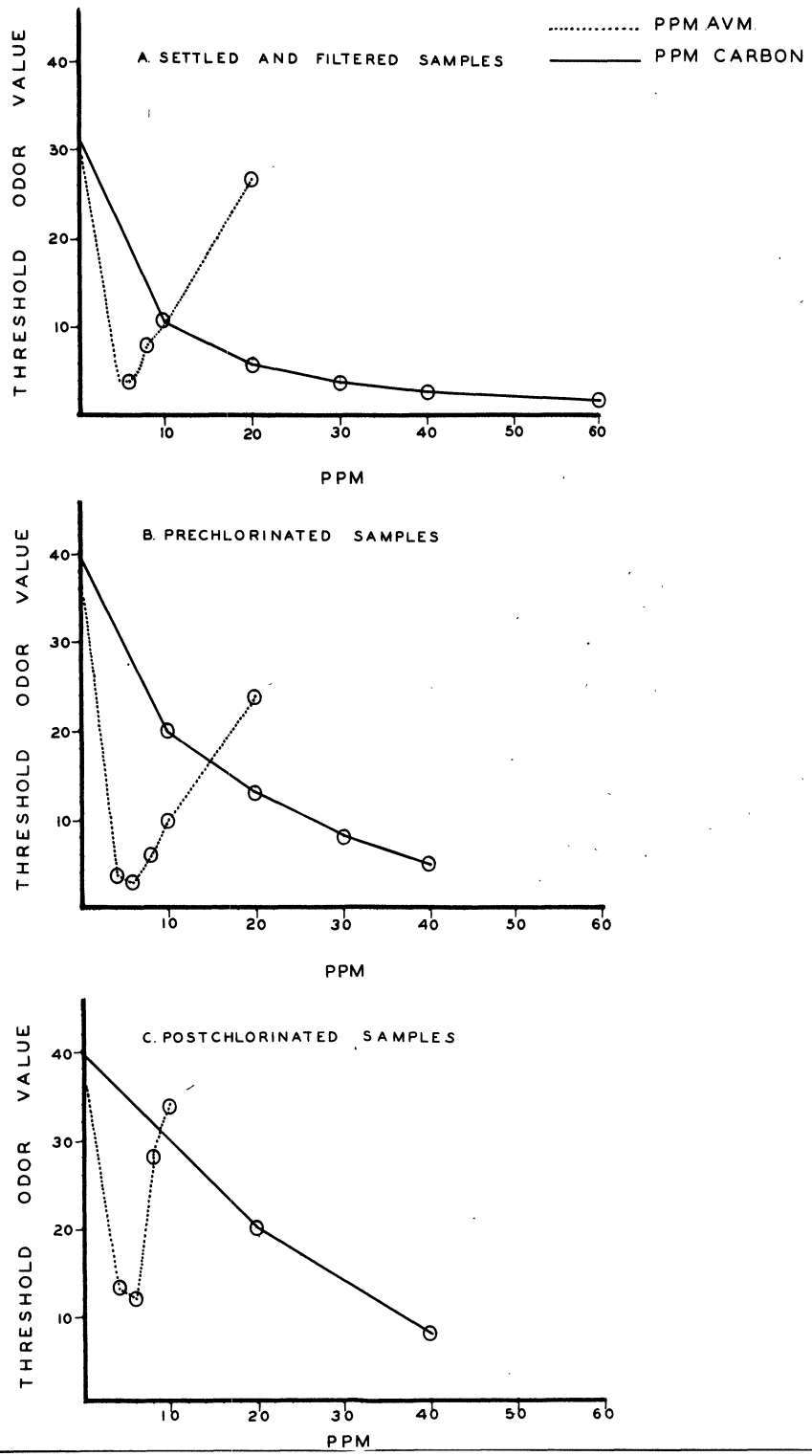


FIG. 2. TREATMENTS OF CHEMICAL ODOR STANDARDS

threshold odor to twelve (Part B, Figure 2). Forty parts per million activated carbon reduced the odor to eight.

For those samples of water of the same make-up as those employed above which were treated with activated carbon and/or activated vegetable material and subsequently subjected to flocculation, sedimentation, and post-chlorination, the addition of activated vegetable material at a concentration between four and six parts per million reduced the threshold odor from forty to three (Part C, Figure 2). Activated carbon at a concentration of forty parts per million reduced the odor to five.

The phenol odor standards, after treatment as in the other sequences with post-chlorination, showed that the lowest threshold odor was obtained with the activated vegetable material (Part B, Figure 3). This odor was reduced from forty to twenty-one at a concentration of ten parts per million. The activated carbon in concentrations of forty parts per million reduced the threshold odor slightly below thirty-five. The odors of phenol samples of the same make-up as those used above, as shown in Part A, Figure 3, were more effectively reduced by pre-chlorination regardless of odor-reducing compounds. However, activated carbon in concentrations of forty parts per million lowered the threshold odor to fifteen; whereas, activated vegetable material in concentrations of between ten and twelve parts per million reduced the threshold odor to only twenty.

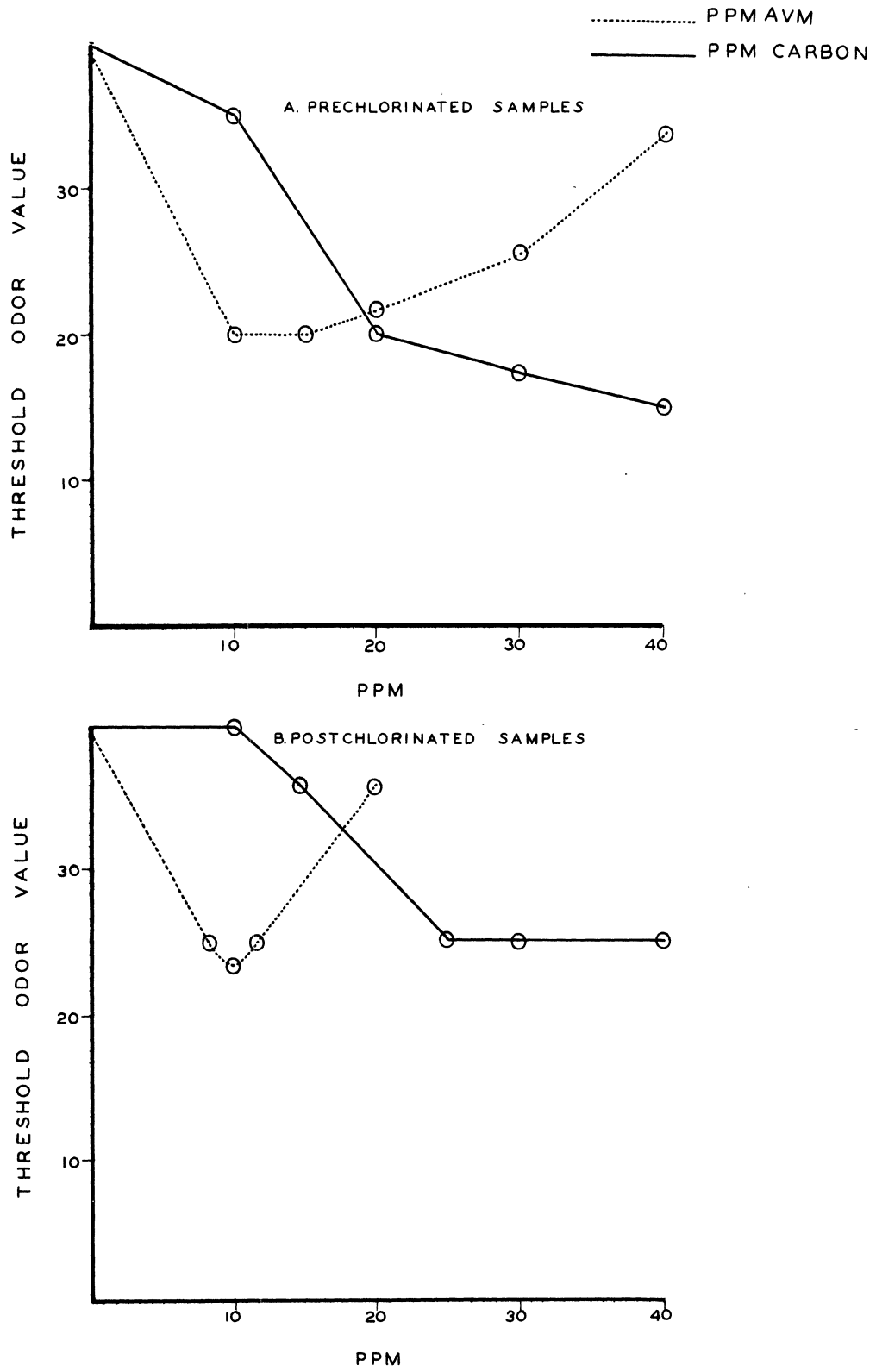


FIG. 3 TREATMENTS OF PHENOL ODOR STANDARDS

After pre-chlorination, raw water samples from the Ohio River, the Mississippi River at New Orleans, and Philadelphia Water Supply were treated with five, five, and twelve parts per million activated vegetable material, respectively (Figure 4). Results show that after the samples were flocculated and filtered the Ohio River raw water was reduced from a threshold odor value of sixty to ten. The New Orleans raw water threshold odor value was lowered from sixteen to four. The raw sample from Philadelphia water supply was reduced from a threshold odor value of forty to four.

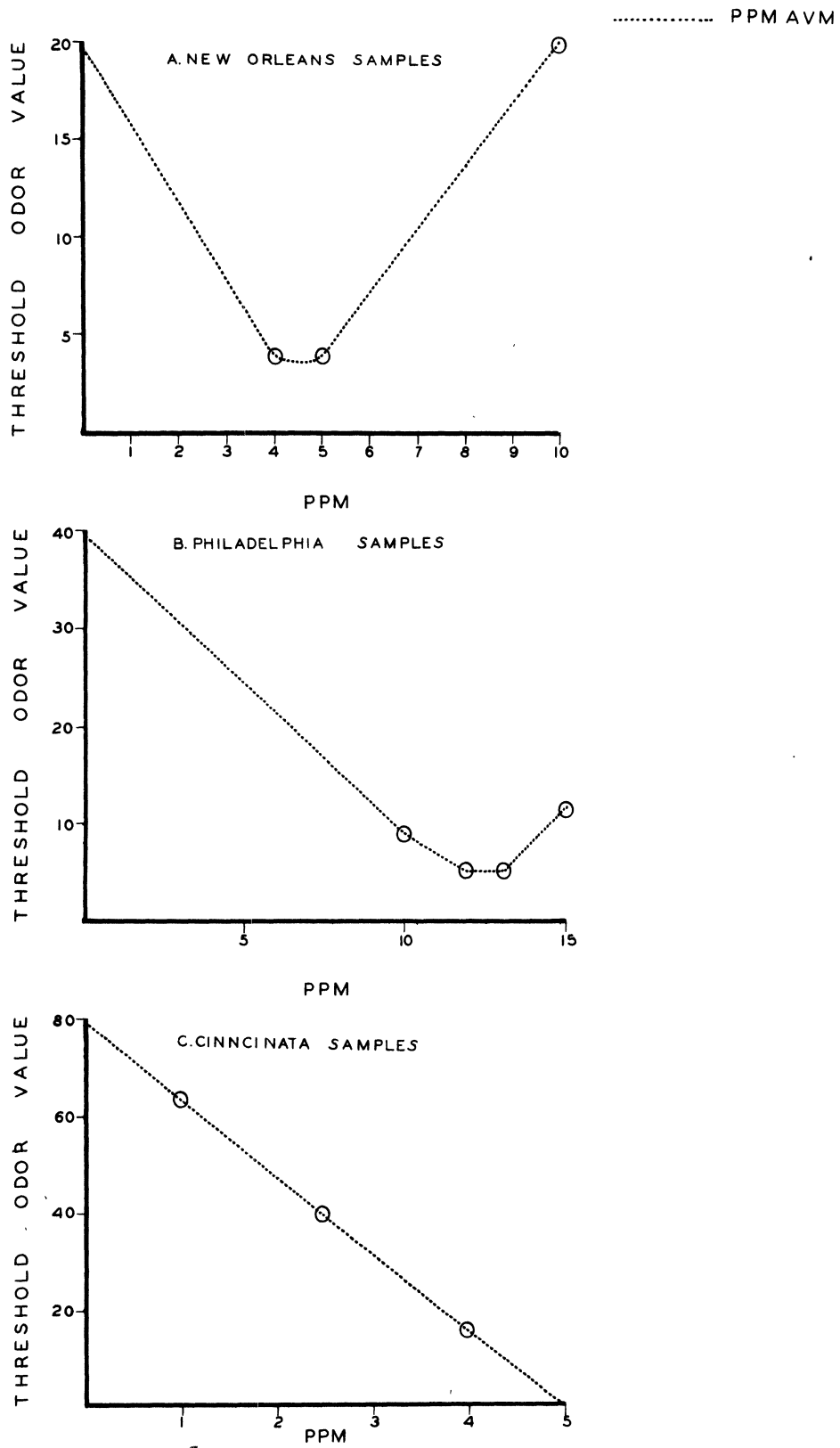


FIG.4. RAW WATER SAMPLES PRECHLORINATED AND TREATED WITH AVM

DISCUSSION

Under controlled quantitative conditions, activated vegetable material was conclusively an excellent odor reducing compound when used to eradicate common types of odor that may be encountered in water supplies, because of the wide-ranged magnitude of its reductions. Furthermore, this compound yielded as great or greater odor reductions than the best types of odor reducing practices used today regardless of the type of chemical treatment used in conjunction with this compound. Also, the experimental evidence substantiated its effectivity as being far beyond the limits of experimental error in that in almost all cases an objectionable threshold odor of forty was reduced to a level which is not often discernible by the consumer. When activated vegetable material was compared to activated carbon, this new material was a more effective odor reducer for most odors. Although the experimental results show its superiority for most given situations that would be encountered in different water plants using various operations, maximum production of relatively odor-free water can be assured by a controlled use and treatment procedure with this compound.

In addition to its odor reducing efficiency, it would be more advantageous to use activated vegetable material in filtration plants than activated carbon. Only one-fifth as

much activated vegetable material as carbon is necessary for accomplishing odor reduction. Thus, less bulk would simplify the existing problems of handling and its costs as well as the actual cost of the material. Furthermore, the activated vegetable material does not offer any of the objectionable problems associated with the use of activated carbon. Carbon is not always available because of several difficulties allied with its manufacture; whereas, the production of activated vegetable material appears to be less complex. Moreover, many plants have found activated carbon hard to store because it is difficult to locate carbon at some place in the plant where it is accessible and at the same time does not cover the entire area with a layer of soot. Filtration plant officials have partially alleviated soot deposition by using wet storage. This solution involves an expensive installation and higher operational costs. Since activated vegetable material does not present such a soot problem and there is no need for wet storage basins, these expenditures are eliminated.

Substantiation of the odor-reduction characteristics of activated vegetable material may be shown more specifically by the experimental results. One of these was the reduction of the actinomycete odor without chlorination from a threshold value of forty to an undetectable odor of three where fifteen parts per million activated vegetable materials were used. This reduction is significant because most odors encountered in water supplies of the Southwest are of this

type and because carbon effected no significant reduction of this type with concentrations up to sixty parts per million. However, when the samples were pre-chlorinated the reduction of a threshold value of forty was approximately the same by activated vegetable material and activated carbon. Again as in the non-chlorinated samples similar patterns of reduction were apparent in post-chlorinated samples. Thus it would be impractical to use carbon in plants where it is either unnecessary to chlorinate the water or where post-chlorination practices are essential. In any event activated vegetable material will give more effective reduction for this type of odor.

In water polluted by sewage and chemical water from industries, odor-free water could only effectively be produced beyond the level of detectability by using activated vegetable material with post-chlorination. Where pre-chlorination is employed a very high concentration of activated carbon is more effective than activated vegetable material; however, maximum reduction by carbon was to an ineffective level of eight. Because of carbon's greater adsorption of esteric compounds, such as are commonly found in chemical wastes, activated carbon would produce an odor-free water without chlorination, but it is improbable that water containing chemical wastes could be processed without chlorination.

In localized areas where industries are highly concentrated and divert their total wastes into a stream, the phenolic compounds are sometimes encountered. These are particularly troublesome because their odors are detectable in concentrations as low as forty to sixty parts per billion. Neither the type of odor reducing compound, the chlorination practice, nor the concentration of the two compounds used reduced the threshold odor level of the samples to a significant point. Activated vegetable material was slightly more efficient than activated carbon with post-chlorination; whereas, in pre-chlorinated samples the role of these two compounds was reversed. In pre-chlorination practices, chlorophenol, which has a low base exchange capacity, is formed and is undoubtedly the reason for less reduction. Nevertheless, phenol threshold odor was halved by activated vegetable material with only one-third as high a concentration as that of activated carbon. Such a reduction would be significant in those instances where phenol odors are unduly high and great quantities of carbon would be necessary to effect any amount of odor amelioration. Thus the use of activated vegetable material would allow an application closer to the filter and in appreciable lower quantities.

The standardization and separation of the odors together with the application of water chemical procedures, served a useful purpose in the determination of the capacity of activated vegetable material as an odor adsorber and its comparison

to the activity of carbon. However, actual field application was desirable and with water from problem areas regardless of threshold level or odor type. The reductions of odor in the pre-chlorinated Ohio River water of 83 per cent, in the New Orleans water of 75 per cent, and in the Philadelphia water of 90 per cent suggest that the use of activated vegetable material would be highly practical. When such percentages of odor reduction can be effected with a cheaper, easier to handle and cleaner agent, existing compounds and methods should be revised.

Several recommendations can be made for the use of activated vegetable material in a conventional water plant to facilitate maximal results in operational control and to be functional as a mean resolution of odor and taste variance. Since pre-chlorination practice is preferable in some instances, in accordance with the use of activated vegetable material, the addition of properly activated product is desirable just after the pre-chlorination step, that is, just before flocculation. Although it is possible to add this product to the flocculators or even the clarifiers, preferred results are obtained when the activated vegetable material is added earlier in the treating process. In the event that a particular water purification plant has only primary sedimentation without the application of chemicals, then the product should be added at the point of primary sedimentation or if possible, on the raw water line, followed by chlorination.

When tastes and odors are attributable to chemical effluents and/or to actinomycetes or their decomposition products, pre-chlorination practices, as revealed in the data, reduced the threshold odor number even lower than that obtained with the use of activated product alone. Since these types of odors are the most commonly encountered, it would be wise to pre-chlorinate in conjunction with activated vegetable material for the removal of most of the odors encountered. To make sure that the proper amounts of activated vegetable material are added to give optimum results, a mean amount of the product has been calculated. For most general types of odors which are attributable to actinomycetes and/or chemical by-products, one part per million activated vegetable material will reduce a threshold odor value five units. For example, eight parts per million activated vegetable material are required to effectively reduce a threshold odor of forty below the level of detectability. Therefore, since most odors of the above described type will not exceed a threshold odor value of forty and if present will not fall below a threshold value of twenty-five to thirty, a mean of six to eight parts per million activated vegetable material can safely be added to most waters with common types of odor to produce a relatively odor free water. Also, this mean amount is well below those concentrations of activated vegetable material that give an increase in threshold values.

It is of the utmost importance in the use of activated vegetable material to maintain a pH of from 11.1 to 11.8 of the treating solution. When distilled water is employed, a treating solution containing 5000 parts per million of activated vegetable material will attain a pH of approximately 11.6. When using the average raw water of the Southwest, the same proportions will result in a pH of 11.8. In most natural waters tested from, for example, the Ohio River, the Mississippi River, the Canadian River, the Trinity, and reservoirs of the Trinity water shed, the pH obtained using 5000 parts per million of the dry mix formula has been approximately 11.6 to 11.7. During the time when threshold odor numbers are low and smaller amounts of activated chlorophyll compounds are needed for the removal of tastes and odors, smaller quantities of the dry mix may be employed in making up the treating solution. For example, when 1000 parts per million of this particular dehydrated vegetable material and calcium hydroxide are added to raw waters such as those mentioned above, a treating solution having a pH of approximately 11.2 will result. Preferably, the solutions produced from the compositions of activated vegetable material should not contain less than 1000 parts per million nor more than 5000 parts per million of the dry mix. Between these varied qualities, pH values are sufficient to produce a maximum activated state of vegetable material. One further precaution to be observed in the use of activated vegetable

material would be to control the rate at which the activated vegetable material is injected into the water system. If the dry mix plus water is injected into the system immediately, there is insufficient activation because optimum results are obtained when a maximum of approximately two minutes is allowed for the alkaline material to activate the vegetable material in solution. On the other hand if the operators allow the activated liquid to stand for any length of time, a progress decrease in activity will occur.

SUMMARY AND CONCLUSIONS

1. A review of the methods and practices of water purification suggested that municipal water supplies are relatively free of water-borne disease organisms and chemical impurities but that techniques for the production of odorless and tasteless water are inadequate at an economical figure.

2. The most common odor reducing compound in use today is activated carbon which is expensive, hard to handle, and ineffective for most odors and tastes except at very high concentrations.

3. A new activated vegetable compound which is cheaper and cleaner than carbon was synthesized and activated.

4. To investigate odor and taste reducing capacity and efficiency of the new compound as compared to carbon, quantitative bases were set up for standardization of different types of odors encountered in water, such as actinomycete by-products, chemical wastes and phenols; level of threshold odor; and measurement of activity of the compound.

5. The comparative studies involved the preparation of sets of samples with threshold values of forty for each of the three types of odors. In each of these three series to duplicate various water plant operations in chemical treatment, three duplicate sets of samples were flocced and

filtered; two sets were pre- or post-chlorinated and the third was not chlorinated. Prior to flocculation one half of the samples in each series were treated with activated vegetable material and one half with activated carbon and their reductions of odor recorded.

6. In addition, raw water samples from odor problem supplies with varying threshold levels and odor types were pre-chlorinated and treated with activated vegetable material to test the practical application of this new product.

7. In all of the sequences activated vegetable material proved as effective as or superior to carbon in threshold odor reductions with one third as much material. The most common types of odors were reduced from a high level to an undetectable level using activated vegetable material in conjunction with pre-chlorination.

8. Recommendations are given for the control and application of activated vegetable material in a conventional water filtration plant.

BIBLIOGRAPHY

- Adams, C. D., 1946, "Control of Taste and Odor from Industrial Wastes," Journal of American Water Works Association, Vol. 38, pp. 702-12.
- Anon. 1948, "Chlorine Dioxide, A Summary of the Developments of its Uses for Water Works Purposes," Journal of American Water Works Association, Vol. 40, p. 1235.
- Aston, R. N., 1947, "Chlorine Dioxide Use in Plants on the Niagara Border," Journal of American Water Works Association, Vol. 39, No. 7, pp. 687-690.
- Aston, R. N., 1950, "Developments in the Chlorine Dioxide Process," Journal of American Water Works Association, Vol. 42, p. 151.
- Aston, R. N., 1948, "Progress Report on Chlorine Dioxide in Taste and Odor Control," Southwest Water Works Journal, December, 1948.
- Bailey, H. E., and Studley, J., 1948, "Activated Carbon Treatment of an Open Reservoir," Water and Sewage Works, Vol. 94, pp. 219-22.
- Bartuska, James F., 1941, "Ozonation at Whiting, Indiana," Journal of American Water Works Association, Vol. 33, p. 2035.
- Besozzi and Vaughn, 1949, "Experimental Studies of Odor Control at Whiting, Indiana," Journal of American Water Works Association, Vol. 41, p. 1035.
- Billings, L. C., 1939, "Activated Carbon Performance," Taste and Odor Control Journal, Vol. 5, No. 10, pp. 1-8.
- Duke, Donald, 1952, "The Ohio River Presents a Severe Odor Problem," Taste and Odor Control Journal, Vol. 18, No. 9, pp. 1-4.
- Gainey, P. L., and Lord, T. H., Microbiology of Water and Sewage, New York, Prentice-Hall, Inc., 1952.
- Griffin, A. E., 1944, "Chlorination, A Five-year Review," Journal of North East Water Works Association, Vol. 53, p. 322.

- Griffin, A. E., 1946, "Break-Point Chlorination," Technical Publication, No. 213, Wallace and Tiernan Co., Inc., Newark, New Jersey.
- Hale, F. E., 1929, "Taste and Odor in the New York City's Supplies," Journal of American Water Works Association, Vol. 10, pp. 829-837.
- Hann, Victor, 1947, "Ozone Treatment for Removal of Tastes, Odors, and Color From Water," Journal of North East Water Works Association, Vol. 61, pp. 247-52.
- Hann, V., 1943, "Ozone Treatment of Water," Journal of American Water Works Association, Vol. 35, p. 585.
- Hassler, J. W., Active Carbon, New York, Chemical Publishing Co., 1951.
- Hassler, W. W., "A History of Taste and Odor Control," Journal of American Water Works Association, Vol. 33, p. 2124, 1941.
- Hasville, Morgan, and Mauzy, 1942, "Practical Application of Ammonia-Induced Break-Point Chlorination," Journal of American Water Works Association, Vol. 34, p. 275.
- Howard, N. J., 1922, "Modern Practice in the Removal of Taste and Odor," Journal of American Water Works Association, Vol. 9, pp. 766-782.
- Howard, N. J., 1946, 1947, "Progress in the Treatment of Water for Taste and Odor Correction," Water Treatment and Sewage, Vol. 84, pp. 11-14.
- Howard, N. J., 1947, "Super-chlorination and De-chlorination," Journal of American Water Works Association, Vol. 39, p. 1241.
- Langlier, W. F., 1932, "The Theory and Practice of Aeration," Journal of American Water Works Association, Vol. 24, P. 62.
- Lawson, Haynes, 1945, and Wallace, Grant, 1945, "Water Treatment to Reduce Chemical Odors," Water Works and Sewage, Vol. 92, pp. 331-34.
- Middleton, Braus, Ruchhoft, 1952, "Fundamental Studies of Taste and Odor in Water Supplies", Taste and Odor Control Journal, Vol. 18, No. 10, pp. 1-12.

- Silvey, J. K. G., Russell, James C., Redden, David R., McCormick, William, 1950, "Actinomycetes and Common Tastes and Odors," Journal of American Water Works Association, Vol. 42, No. 11.
- Spalding, G. R., 1930, "Experimental Studies of Taste and Odor Control", Journal of American Water Works Association, Vol. 22, p. 646.
- Standard Methods for the Examination of Water and Sewage, Ninth Edition, New York, American Public Health Association, 1946.
- Tarzwel, C. M., and Palmer, C. M., 1951, "Ecology of Significant Organisms in Surface Water Supplies," Journal of American Water Works Association, Vol. 43, No. 7.
- Taylor, Frank S., 1948, "Taste and Odor Problems at Oklahoma City," Taste and Odor Control Journal, Vol. 14, No. 10, pp. 1-15.
- Theroux, Eldridge, Mallmann, Analysis of Water Sewage, Third Edition, New York, McGraw-Hill, 1943.
- Thomas, Harold A., Jr., 1943, "Calculations of Threshold Odor," Journal of American Water Works Association, Vol. 35, pp. 751-69.
- Vincent, C. P., 1946, "Drinking Water Made Palatable by Chlorine Dioxide," The Frontier, March, 1946.
- Welch, W. A., 1952, "Mixed Drinks from Pollution Problems," Taste and Odor Control Journal, Vol. 18, No. 8, pp. 1-4.
- Williams, D. B., 1949, "A New Method of Odor Control," Journal of American Water Works Association, Vol. 41, p. 441.
- Wrench, J., 1935, "Carbon in the Removal of Tastes and Odors," Engineering Contract Record, Vol. 50, p. 610.