Public Health Aspects of the Treatment of Water and Beverages With Silver*

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PUBLIC health workers have been greatly interested for many years in the presence of metallic substances such as arsenic and lead in foods and more recently in the presence of antimony. These substances have usually gained entrance to foodstuffs either accidentally or by technical methods designed to produce better quality foods. In general, however, such substances have not been deliberately added with the full knowledge that the consumer will ingest regular and definite quantities.

We now have another member of the metallic group, namely, silver, which certain commercial organizations are recommending for use as a bactericidal and preserving agent. Before the general use of a method designed to add silver becomes widespread, public health authorities should consider whether or not the public health hazard from the ingestion of silver is comparable to the known dangers from other metallic compounds and, if so, what concentration of silver can be considered safe in foods and in drinking water.

From a bacteriological viewpoint, silver is one of the most active ions, exceeded only by mercury. Silver nitrate, colloidal silver, and certain other silver compounds are among the most generally used bactericidal agents, while metallic silver has been used in surgical technics for many years. One of the reasons for such widespread use is that even very small amounts of silver possess bactericidal action and even relatively high dosage does not produce any immediate pathological or physiological change.

The peculiar growth-inhibiting or bactericidal action of silver was first noted by Naegeli in 1893. Since that time there have been a great many publications dealing with various aspects of the bactericidal action of silver. Some 200 publications, mostly dealing with various theories to explain the action of silver, have been consulted. Unfortunately, many of the more recent papers have been obviously presented with the commercial aspects to the fore. It was therefore decided that with a few exceptions the literature should be eliminated from our considerations and the principles involved should be studied first-hand.

In general, there are 3 commercial

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methods of using silver. One corporation has patented various methods of exposing water and other liquids to silver deposited on sand, porcelain and various types of filtering devices. A method of applying silver by electrolysis has also been patented. Another commercial process combines heat in addition to the difference in E.M.F. which exists between silver and nickel electrodes when kept at different temperatures in the material to be treated, and may be considered to be a modified pasteurization process. In all cases which have come to our attention the objective is the same, namely, to secure the solution of silver. Apparatus has been designed and recommended for the treatment of water, ice, milk, beer, vinegar, wine, alcohol for perfumes, liqueurs, gin, whiskey, brandy, cider, and fresh fruit juices—in fact, there is hardly a food industry in which water plays any part that silver treatment has not been recommended as a valuable agent.

It does not seem reasonable that such methods should be permitted general or widespread use until we have some very definite knowledge as to exactly how efficient they may be under a great variety of conditions. The common method of heat preservation should not be lightly thrown aside for this process, which, at least on this continent, has been given little serious attention up to the present.

Our department became interested in the problem first in reference to the application of silver as a method of treating domestic water. This aspect of the problem was studied and a résumé published by the author.[1] At that time it was concluded that the application of the oligodynamic action of metallic silver to the treatment of water could not be recommended for practical use. Since then we have had to take cognizance of the extension of this process to the preservation of fruit juices, vinegar, etc. Certain fundamental research has been carried out in our laboratory, the results of which will be presented as briefly as possible. The exact technical details will not be given here, but can be made available to those interested.

EXPERIMENTAL

The majority of the following experiments were conducted in glass containers, but a sufficient number of controls in quartz containers was also carried out to indicate the validity of the results.

1. *Metallic Silver*—Silver metal possesses marked oligodynamic or bactericidal power, which may be clearly demonstrated by embedding a piece of metal in an agar plate seeded with *B. coli*. The oligodynamic action may be seen by the absence of growth in a small area surrounding the metal. The width of the zone may be increased by treating the metal with nitric acid, and may be decreased by careful cleaning. Fused silver chloride or horn silver, silver chloride, and various concentrations of silver nitrate show a similar oligodynamic activity.

On the assumption that the bactericidal properties of silver might be due to ionized silver, probably from silver oxide, the following experiment was set up: Small pieces of pure silver metal were melted in a home-made quartz furnace. Each piece was subjected to a different treatment with the following results:

A. Silver melted in air and cooled in hydrogen, or melted in hydrogen and cooled in hydrogen showed no evidence of any inhibitive action. Silver cooled in hydrogen had not regained its bactericidal properties 3 months after such treatment, although kept at room temperature exposed to the air (Figures I and II).

B. Silver metal heated in air and cooled in air, or heated in hydrogen and cooled in air

showed a zone of inhibition about 3 mm. wide, but if cooled by dropping into water the zone was at least 6 mm. wide.

It was therefore concluded that pure silver metal has no bactericidal or inhibitory action, and that the inhibitive properties of ordinary silver are probably due to silver ions coming from silver oxide which develops during the cooling process when most of the oxygen absorbed by the silver is released.[2]

These conclusions are in agreement with those of Buhrmam,[3] Bushke, Jacobson, and Klopstock,[4] Doerr,[5, 6, 7, 8] Felippe and Martins,[9] Freundleck and Sollner,[10] Kling,[11] LaCava,[12] Leitner,[13] Markvoort and Wieringa,[14] Wernicke[15, 16, 17]; although Lakhovsky,[19] Saxl,[20] and Tamman,[21] do not agree.

2. *Silver Salts in Distilled Water*—Silver, whether in the form of silver nitrate, silver oxide, silver chloride, and electrically dispersed colloidal silver exerts similar bactericidal actions against *B. coli* suspended in distilled water, thus:

1 p.p.m. of silver as silver nitrate killed *B. coli* (1 million per c.c.) within ½ hour at 20° C.

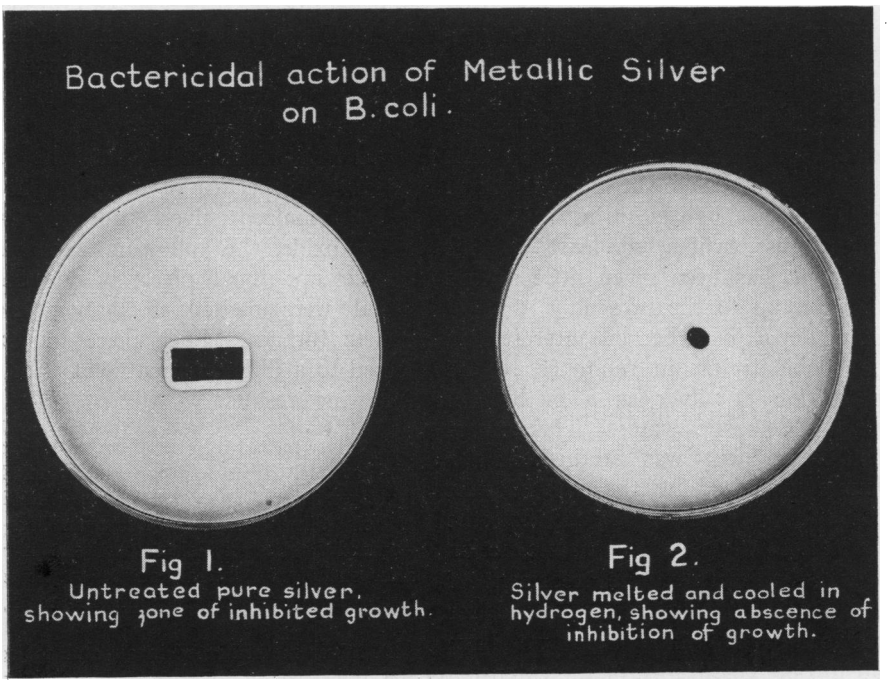
1 p.p.m. of silver as silver oxide killed *B. coli* (1 million per c.c.) within ½ hour at 20° C.

1 p.p.m. of silver as silver chloride killed *B. coli* (1 million per c.c.) within 1 hour at 20° C.

1 p.p.m. of silver as electrically dispersed colloidal silver killed *B. coli* (1 million per c.c.) within 2 hours at 20° C.

A commercial apparatus consisting of silver deposited on porcelain had a similar action, but since the amount of silver in solution steadily increases with time, it is not practical to express our results in the same manner.

3. *The Effect of Peptone and Grape Juice on Silver Nitrate*—In the presence of peptone and grape juice, silver nitrate, silver oxide, and colloidal silver show a marked reduction in bactericidal activity.



10 p.p.m. of silver as silver nitrate were required to kill *B. coli* (1 million per c.c.) within 3 hours in the presence of 2 per cent peptone.

10 p.p.m. of silver as silver nitrate were required to kill *B. coli* (1 million per c.c.) within 3 hours in the presence of 10 per cent grape juice, although in the presence of 1 per cent grape juice 2 p.p.m. were effective within 3 hours.

Considerably more than 10 times the amount of silver effective against *B. coli* in distilled water is required to produce a similar bactericidal action in 2 per cent peptone and 10 per cent grape juice.

4. *Effect of Glucose on Silver Nitrate*—Further studies showed that silver nitrate is not markedly affected by glucose.

1 p.p.m. of silver as silver nitrate killed *B. coli* (1 million per c.c.) within 1 hour in the presence of 4 per cent glucose, while heating a glucose-silver nitrate solution increased the time required to 1½ hours.

It was, therefore, concluded that the sugar in the grape juice was not the factor affecting the action of silver nitrate but rather the protein fractions.

5. *Silver Oxide*—Silver oxide prepared by the method of Johnston, Cuta, and Garrett [22] behaved in a similar manner to silver nitrate in distilled water, peptone solution, and in grape juice. However, it was found that glucose has a marked effect upon silver oxide. This was to be expected from the work of Whitby,[23] who used the reduction of silver oxide to colloidal silver by sugar as a means of determining small amounts of silver.

When tested bactericidally it was found that:

1 p.p.m. of silver as silver oxide killed *B. coli* (1 million per c.c.) within ½ hour in the presence of 2 per cent glucose, but when the oxide-glucose mixture was heated to increase the rate of reduction the solution failed to kill *B. coli* (1 million per c.c.) within 24 hours.

6. *Colloidal Silver*—The experiments conducted with silver oxide were repeated, using electrically dispersed colloidal silver [18] and silver oxide reduced with hydrogen (Kohlschutter's sol), with similar results. Certain physical chemists believe that the stability of an electrically dispersed silver sol depends upon silver oxide. It would appear from our studies of the bactericidal action of colloidal silver that such is the case. Further studies along this line may provide the physical chemists with definite proof of their theory.

7. *Silver Chloride*—A few experiments were conducted with silver chloride in distilled water. The results are essentially similar to those obtained with other forms of silver. The relative insolubility of silver chloride limits the amount of work that can be done, and as a result we did not actively pursue this phase of the work.

8. *Electrolysis of Silver*—Silver electrodes were immersed in an agar plate seeded with *B. coli* and an E.M.F. of 1.5 volts applied for varying intervals. The electrodes were then removed and the plates incubated in the usual way. It was found that a zone of inhibition of growth surrounded the hole in the agar made by the anode, but that when a carbon electrode was substituted for the silver electrode no inhibition occurred. In no case were there any signs of inhibition surrounding the hole made by the cathode.

9. *Commercial Silver Apparatus*—The results previously reported by the author [1] dealing with a commercial method of applying silver to water through the use of silver deposited on porcelain rings have been confirmed and need not be repeated at this time. In general, the temperature at which water is exposed to the action of silver has a marked effect on the time necessary to kill *B. coli*. At 10° C. (50° F.)

it may require 7 hours to kill the same number of organisms killed at 22° C. (71° F.) in 1½ hours. Organic and inorganic constituents also markedly increase the length of time necessary to kill *B. coli*.

At a recent meeting of the New England Waterworks Association, Hale and Shapiro [24] reported on the use of silver in treating swimming pools. They stated that ammonia present in the water prevented the bactericidal action of silver; also, that the 37° C. total count is not affected, and among those bacteria may be disease germs affecting the eye, ear, nose, and throat. Furthermore, the required time for sterilization is too long, at least 2 hours. Attention is drawn to the relative costs of silver and chlorine treatment.

10. *Silver in Certain Food Materials* —The presence of silver in certain food materials has been studied by J. Dick of this department. Mr. Dick has made a series of spectrographic analyses and has kindly permitted me to present the material in Table I.

TABLE I

Fresh Fruit	*Silver Parts per 1,000 Million*
Tomato Juice	0
Australian Oranges	0
Jamaica Oranges	0
California Oranges	0
Lemons	0

Commercial Fruit Juices, Vinegar etc.	*Container*	*Silver Parts per 1,000 Million*
Grape Juice	Glass	less than 5
Grape Juice	"	" " 5
Apple Cider	"	" " 5
Tomato Juice	Tin	" " 5
Tomato Juice	"	" " 5
Cider Vinegar	Glass	" " 5
Cider Vinegar	"	25
Malt Vinegar	"	less than 5
Malt Vinegar	"	" " 5
Malt Vinegar	"	50
Spirit Vinegar	"	less than 5
Distilled White Vinegar	"	50
Evaporated Milk	Tin	less than 10
Milk, Sweetened, Condensed	"	11
Maple Syrup	Glass	less than 5

It is obvious that silver does not occur in significant quantities in this class of foods. Further data on this subject will be collected in the near future. Commercially, it is understood that the amount of silver to be added to various food materials will vary between 0.05 p.p.m. and 1 p.p.m., which, as will be readily seen, constitutes a definite addition of silver.

A series of fruit juices supposedly preserved by silver process were secured for study, and the results may be briefly summarized by stating that significant amounts of silver were not found spectrographically, as will be noted by Table II.

TABLE II

Juices Supposedly Treated by Silver Process	*Container*	*Silver Parts per 1,000 Million*
Strawberry	Glass	10
Tomato	"	less than 5
Black Currant	"	" " 5
Cherry	"	" " 5
Apple	"	" " 5
Gooseberry	"	40

Two of the bottles from samples supposedly treated by silver were drained, but not rinsed, and then treated with warm nitric acid, the solution concentrated and spectrographed. No silver was found in significant traces to suggest silver precipitated on the glass.

Furthermore, studies of the death rate of *B. coli* suspended in these fruit juices showed that there was no significant difference in the death rate in silver treated grape juice as compared with fresh, normal grape juice prepared without silver, or in a citrate buffer of the same pH. It was also found that the growth curve for yeast inoculated into this commercial grape juice was almost identical with the

curve obtained in fresh, normal grape juice. The obvious conclusion is that the silver treatment was either inefficiently applied or that the method used did not permit of solution of silver.

SOME PUBLIC HEALTH ASPECTS

Argyria is a well known although not very common clinical manifestation of silver poisoning. Gaul and Staud [25] have reported on the development of argyria following treatment with silver arsphenamine, and in a later publication [26] dealt with some 70 cases of argyria which developed after the use of other forms of silver medication. These authors have determined from biopsy materials the amount of silver present in normal persons. They state that "normally, an individual in the fifth decade of life has a silver retention equivalent to from 1 to 2 gm. of silver arsphenamine." If silver compounds have been used this quantity will be greatly increased. They also state that argyria becomes evident after a silver retention approximating an equivalent of 8 gm. (1.2 gm. silver) of silver arsphenamine. Therefore, the more silver an individual has accumulated the less it will take at a later date to produce argyria. It is obvious that this amount will constitute an individual problem.

Argyria, so far as one can determine from the literature, does not seem to produce any serious effect on the body outside of the discoloration of exposed parts. It should, however, be clearly pointed out that very little is known concerning the actions of silver when ingested. Most of the references in the literature refer to poisoning by silver compounds following the ingestion of rather large quantities, or the development of argyria after prolonged treatment with silver preparations. No data are available as to the amount of silver retained following the administration of small doses. Cases of argyria are very seldom met with and, so far as can be determined from the literature, no systematic study of mortality rates, physiological disturbances, etc., have been made.

It is definitely known that the salts of heavy metals have a strong inactivating action on enzymes. Waksman and Davidson [27] have discussed this aspect. For example, 0.005 mg. of mercuric chloride per liter, or 1 part in 200 million, is sufficient to reduce by 50 per cent the activity of many catalase preparations. It is stated that silver nitrate is 3 times as active against diastase as mercuric chloride. These authors also say that "the action of silver nitrate is similar but greater than that of the mercurial salt." Enzyme inactivation by salts of heavy metals may be reactivated by certain neutral salts of the alkalis and alkali earths. It is obvious, therefore, that the effect of silver on enzymes should be very carefully studied before any definite opinion is given as to whether or not similar inactivation occurs in the digestive tract.

The amount of silver ingested in foods and water treated by silver must be considered. The commercial apparatus (silver deposited on porcelain rings) liberated, in our experiments, 0.03 p.p.m. of silver in 1 hour and 0.5 p.p.m. in 8 hours. The electrical method of applying silver will liberate varying quantities, depending upon the current. According to Faraday's law 1 ampere flowing for 1 hour will liberate 4.023 gm. of silver. The electrical method of applying silver provides a more certain method of controlling the rate of solution of silver, but it has a disadvantage in that the rate can be greatly increased by the operator. If under practical conditions it is found that the usual dosage is not producing

the required preservative or bactericidal action, a much greater concentration of silver can be applied by simply increasing the current. If there is any health hazard in the use of silver, it is obvious that unscrupulous persons could expose the public to relatively high dosages of silver. Commercial recommendations as to the amount of silver required to treat water and food vary from 0.05 to 1.0 p.p.m. (1 p.p.m. is equal to 1 mg. per liter.)

It is important to know how much of the silver ingested will be retained in the body. So far as can be learned there are no data available and it is, therefore, just as incorrect to assume that most of the ingested silver is absorbed as to assume that it is excreted. It is more important to know whether or not such amounts will have any effect on enzymes in the digestive tract, and finally it is essential that if this process is to be permitted some definite limit as to the amount of silver permissible in foods and water be established.

Public health officials have considered it necessary to establish limits governing the amount of lead (2.5 p.p.m.) and arsenic (1.5 p.p.m.) in food materials. Whether or not silver can be considered in the same category must be decided on further scientific evidence. It should be emphasized that we are not dealing with the accidental occurrence of silver in foods but with a commercial process designed to add silver as a preserving agent. In this respect, the situation is entirely different from that which obtains in connection with lead and arsenic and, therefore, needs special consideration.

Another possible hazard in the use of silver as a preserving agent in foods is that the bactericidal effect may gradually disappear through formation of inactive compounds, with the result that the public would have a false sense of security as to the safety of foods.

The general principle of adding chemical preservatives to foods has been one of the most contentious problems of food and drugs administration. The addition of silver to foods is chemical preservation and, therefore, it is incumbent upon public health officials to ascertain whether or not this method constitutes a health hazard.

It must also be determined whether the silver treatment is safe from the standpoint of food preservation. In the meantime it is recommended that official approval be not given pending further studies.

CONCLUSIONS

1. As a result of many experiments with metallic silver, colloidal silver, silver oxide, and certain commercial methods of using silver, the conclusion has been reached that silver metal possesses bactericidal action by reason of the solution of silver ions, probably from silver oxide. It is believed that this conclusion is strengthened by the fact that reduction by glucose substantially lessens the bactericidal action of electrically dispersed silver (colloidal silver), and silver oxide. In other words, the bactericidal activity of silver is due entirely to ionized silver.

2. Silver nitrate, silver oxide, electrically dispersed colloidal silver, when diluted on the basis of silver concentration, all possess a similar bactericidal or oligodynamic activity.

3. The bactericidal activity of silver nitrate or of silver oxide is markedly reduced by the presence of proteins or glucose.

4. Grape juice purported to have been commercially treated by a silver process did not show significant amounts of silver either spectrographically or bacteriologically.

5. Attention is called to the reported effect of silver on enzymatic action, and the occurrence of argyria is discussed.

6. Silver in certain normal food materials has been estimated by spectrographic analysis, and in the substances examined was not found to be present in significant proportions.

7. It is recommended that the use of silver as a preserving agent in foods, or as a method of treating polluted water, be carefully considered by public health officials, and that the method be not used until all doubts concerning the health risk are removed by indisputable evidence to the contrary.

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University of Michigan Public Health Engineering Courses

THE following information has been received from the University of Michigan, Ann Arbor, Mich.:

Programs of study in Public Health Engineering are now being offered in accordance with the "Preliminary Report of the Sub-committee of the Qualifications of Public Health Engineers" (*American Journal of Public Health*, 26, 6 (June), 1936). Two new courses are scheduled for the second semester of the school year 1936–1937.

1. *Civil Engineering 37*—"State Health Department Sanitary Engineering Practices" in the College of Engineering is a study of state laws, regulations and policies under which sanitary engineering activities of state departments of health are conducted, current procedures, practices and standards, regulatory functions, consultation services to local official agencies in both urban and rural sanitation, and the further application of sanitary engineering science in the field of public health.

2. *Hygiene*—"Public Health Engineering Laboratory" in the Division of Hygiene and Public Health is a study of the applications of sanitary biology and chemistry in the control and operation of water purification and sewage treatment processes, and the study of Stream pollution and industrial wastes. The course includes lectures, demonstrations, and laboratory exercises.

The above courses are designed for engineers of state health departments and should be taken concurrently.

In addition to the courses given in the College of Engineering and the Division of Hygiene and Public Health, other courses are available in other departments from which elections may be made to meet the special needs of the student. Since the problem of training Public Health Engineers falls within the joint province of engineering and public health, the two units directly concerned—Division of Hygiene and Public Health and College of Engineering—will engage in a joint educational program. The object is to equip the student for administrative and technical work in the many engineering problems which concern the public health worker. The problems include, in addition to the generally recognized fields of water purification, sewage disposal, garbage disposal, etc., such fields as industrial sanitation, illumination, state and municipal engineering practices and others.