The Treatment of Water by Certain Forms of Silver

JAMES GIBBARD, F.A.P.H.A.

Bacteriologist, Laboratory of Hygiene, Department of Pensions and National Health, Ottawa, Ont.

IN Canada and the United States one seldom hears of any process other than filtration and chlorination recommended for the treatment of polluted water supplies. Recently a new method involving the use of silver, has been receiving considerable attention, especially in Europe. The apparatus designed to apply this new process is now sold in Canada and presumably in the United States, and it is believed that patent rights for this new method have been issued.

This process depends upon the so-called oligodynamic action of silver. It is a well-known fact, first reported by Naegeli in 1893, that silver metal exerts an inhibitive action toward bacteria, algae and certain other forms of microscopic life. The term "oligodynamie," coined by Naegeli, is used to define that bactericidal action of silver, copper, mercury, etc., and their salts, which occurs in such a dilute concentration that a chemical determination is extremely difficult. In fact for many years the inhibitory action of the metals was thought to be mysterious, but it is now generally accepted that the metals act only through the solution of traces of salts or oxides on their surface. When water is exposed to metallic silver it develops oligodynamic properties reaching a maximum in about eight days, but if the area of metal exposed to water is increased many hundreds of times the time factor is greatly reduced.

In this new process silver with or without certain "activators" such as palladium or gold, is deposited on the surface of sand, porcelain, or filter candles. Water is then passed through the filter or allowed to remain in contact with the silvered porcelain for a certain time. Very striking claims are made for this method:

(1) There is no taste, odor or color to water treated by this method.
(2) Water which has been exposed to silver has the power of sterilizing other polluted water mixed with it.
(3) It is claimed to sterilize polluted water independent of the temperature of exposure.
(4) There is no reduction in the efficiency of this new process by the presence of minerals or organic matter in the water.
(5) The quality of the water is only of importance when it contains much suspended matter.
(6) It is recommended for the treatment of water in swimming pools, laundries, drains, ice plants, etc.
(7) Certain claims for medicinal application are made.

It will be seen that *if* this process is all that is claimed for it, we have available the ideal method of treating polluted water.

It is well at this stage to point out that although this process has important limitations, it has some points in its favor, and, in the author's estimation, is worthy of considerable further research.

As regards "oligodynamie" in gen-

eral, there have been at least 200 publications dealing with various phases of the problem.

Suckling [1, 2] studied this method of treating water and concluded that "it is a delicate process susceptible to interference by many factors such as temperature, turbidity, sulphides, chlorides, iron and organic matter. As far as public water supplies are concerned, the process is applicable to few and carefully selected cases. It is superior to chlorination in certain minor respects such as the entire absence of odor and taste production." He believes that it "may meet a long-felt need as a means of sterilizing water in the case of small supplies, country homes, etc."

It seemed desirable to obtain some first-hand data regarding this new process, while for comparison, studies on silver-plated porcelain, colloidal silver and silver nitrate were included.

One specimen of the commercial apparatus was obtained. The sterilizing elements consisted of small unglazed porcelain rings, each approximately 1.5 cm. in diameter, 1.5 cm. deep, the walls 0.2 cm. thick. These rings had silver in some form, presumably metallic, on the surface. Upon breaking a ring and heating it with H_2S, marked discoloration occurred at the surface only and it is therefore concluded that silver was deposited only on the surface. A quantitative determination of silver on 1 ring indicated 7.5 mg. There is undoubtedly considerable variation, as microscopic and macroscopic examination showed a considerable unevenness in deposit. The apparatus, which was designed to treat, by contact, 1,300 c.c. of water, contained approximately 400 rings. The directions were simply to rinse the jar, fill with water, allow to stand two hours, when the water would be found to be sterile unless it had approached sewage in its degree of contamination, in which case 6 to 7 hours would be necessary.

Preliminary experiments were done with the sterilizer as sold by the manufacturers. The jar was filled with tap water to which enough of broth culture of *B. coli* or *B. typhosus* was added to give approximately 1 million viable organisms per c.c. The test was conducted at 22° C. At half-hour intervals 5 c.c. of water were removed from the jar and inoculated into Smith fermentation tubes of lactose broth. Growth occurred from samples removed after one hour, but all cultures were negative after two hours' exposure. Those tubes which showed no growth were then reinoculated with the test organism, in order to determine whether or not enough of the inhibitive material might be carried over to prevent growth. In every case excellent growth took place. It was concluded that the process warranted further study.

It was considered advisable to remove the silvered rings from the apparatus for experimental purposes, and place them in 400 c.c. pyrex beakers for further study, in order that they would not all be affected by some special experiment. In addition broken porcelain insulators and later porcelain rings, plated with silver by one of the usual chemical reduction methods, were used in identical experiments.

Distilled water suspensions of 24 hour broth cultures of *B. coli* were used. Five c.c. amounts of the suspension were removed at half-hour intervals and inoculated into lactose broth Smith fermentation tubes. In this report "sterility" means that growth did not occur when the sample was inoculated into lactose broth and incubated at 37° C. for 48 hours.

At room temperature (22° C.) water with approximately 2 million *B. coli* per c.c., was sterilized by silvered commercial rings in slightly less than four hours; at 37° C. in two hours, while at 10° C. not even after 22 hours. Identical results were obtained with the

silvered rings prepared in the laboratory.

A variety of experiments was conducted, during which it seemed as if both the commercial and the laboratory rings were losing their efficiency, so a comparison was made with new rings. Sterility was obtained at room temperature within four hours with the used rings, but in two hours with the new ones.

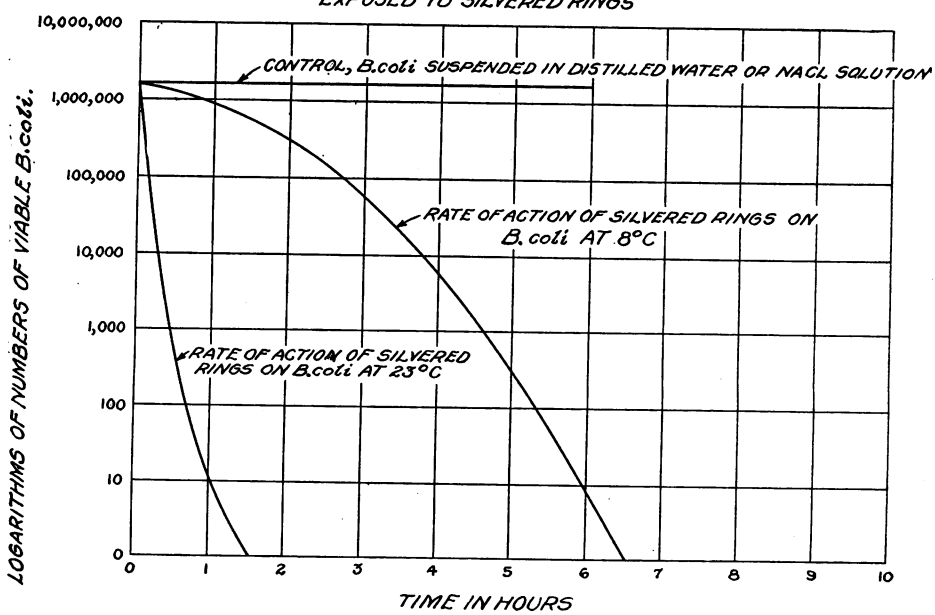
These results were repeated several times and indicated that under continued use there is a gradual loss of efficiency of both commercial and laboratory rings. It was believed that the use of broth cultures in preparing the suspensions of *B. coli* for test purposes might be a factor through the addition of organic matter. Only 1 to 2 c.c.'s of a broth culture were used to prepare a litre of suspension, and this quantity of broth would represent very little organic matter. In order to avoid objections on this point, all further suspensions were, unless otherwise stated, prepared from *B. coli* grown on an agar slant and filtered through paper. Even under these conditions there is a gradual loss of efficiency of the rings.

It was also found that when the bacterial content was greatly increased, there was a corresponding increase in the time necessary for sterilization. Water with 500,000 *B. coli* might be sterilized at room temperature within 1½ hours, but with 10,000,000 per c.c. may take ten hours. Although it is possible that the same rate of action on *B. coli* took place in both samples, the result was a greatly increased time.

Temperature plays an important rôle in sterilization. Distilled water containing a suspension of *B. coli* may be sterilized in from 1½ to 2 hours at 22° C., while at 8° it may require six or seven hours, indicating that even with the most favorable type of water the temperature is a very important factor.

Sixteen experiments were conducted to determine rates of reduction in the

FIGURE 1.
RATE OF REDUCTION IN NUMBERS OF VIABLE B. coli EXPOSED TO SILVERED RINGS



number of *B. coli* suspended in distilled water when exposed to silvered rings at room and refrigeration temperatures. Control experiments were conducted on *B. coli* suspended in distilled water and 1 per cent sodium chloride. The cultures for these control tests were grown on either sodium chloride free agar or 1 per cent sodium chloride agar. A semi-logarithmic graph (Figure 1) shows these results to the best advantage.

Table I shows the silver content of water exposed to silvered laboratory and commercial rings. The spectrograph was employed.

TABLE I

SPECTROGRAPHIC QUANTITATIVE DETERMINATIONS OF SILVER IN WATER *

Water exposed to silvered commercial rings	*Silver in parts per million*
After 1 hr. exposure	0.03 p.p.m.
After 2 hrs. exposure	0.07 p.p.m.
After 4 hrs. exposure	0.15 p.p.m.
After 8 hrs. exposure	0.5 p.p.m.
Water exposed to silver plated laboratory rings	
After 1 hr. exposure	0.125 p.p.m.
After 4 hrs. exposure	0.2 p.p.m.

* Acknowledgment is gratefully expressed to Mr. J. Dick for conducting these analyses.

It will be seen that the quantity of silver in the water increases with the length of exposure.

Silvered commercial and laboratory rings which have become inactivated can be revived by treating with 10 per cent HCl for one hour and then thoroughly washing. It is difficult to determine whether or not this so-called oligodynamic effect is metallic in nature or due to traces of soluble salts or oxides on the surface. Hydrogen ion concentration was not a factor after this treatment.

The effect of light on silver plated laboratory rings was studied at room temperature. Two dishes with 1 layer of rings were prepared. One was kept in a dark room and 1 in daylight, but away from direct sunlight. The temperature, bacterial count, condition of rings and method of sampling were as nearly identical as possible. It was found that the rings were not as active in the light as in the dark. The difference in time necessary to sterilize a *B. coli* suspension varied considerably, and was found to be as much as one hour longer for those rings kept in the light. Unfortunately, rate curves were not prepared. It was quite evident that there is some photo-effect which needs further study.

When comparisons were made between sterile raw water and sterile distilled water to which was added a filtered 24 hour culture of *B. coli* to approximate 1 million per c.c., the organisms suspended in distilled water were killed or rendered inactive more quickly by silver plated rings than those in raw water. This indicates that the nature of the water treated markedly affects the results. That this difference was not due to distilled water against raw water is shown by the normal death rate of *B. coli* suspended in distilled water (Figure 1).

Several experiments were conducted in an attempt to determine whether or not the organisms are actually killed by exposure to silver. Thus far it has not been possible to obtain any definite evidence of revival, although doubtful results were obtained in one test. Further work is indicated in light of the reported revival of organisms exposed to copper.

Sterile distilled water was exposed to silvered laboratory porcelain rings for several hours, removed and its action against *B. coli* determined. It was found that it had acquired considerable sterilizing effect, as would be expected from the spectrographic determination

of the silver content of exposed water (*vide supra*).

SILVER NITRATE

The action of silver nitrate was also studied. The dilutions are expressed on the basis of the silver ion-content.

It was found that in a dilution of 1 in a million silver nitrate sterilized water containing a million and a quarter *B. coli* per c.c. in less than ½ hour, while a 1 in 10 million required 1½ to 2 hours at 22° C. and 2½ to 3 hours at 8° C. The effect of temperature on the action of silver nitrate on *B. coli* is not as great as in the case of either the silvered rings or colloidal silver. It was noted, strangely enough, that 0.1 per cent normal horse serum seemed to increase the rate of action.

The effect of light was also studied but no difference could be noted between experiments conducted in the dark and those conducted in the light.

Another series of interesting experiments was conducted with silver nitrate. Tubes of lactose broth were prepared with a 1 in 100,000 concentration of silver nitrate. A definite number of organisms was added to each tube and incubated at 37° C. No growth was obtained in any tube inoculated with less than 200,000 *B. coli*, while all inoculated with 200,000 or more grew. A concentration of 1:10,000 $AgNO_3$ prevents growth in a tube inoculated with 100 million *B. coli*. A set of tubes was prepared with 1:100,000 silver nitrate and allowed to stand at incubator temperature for 48 hours and at room temperature for ten days. They were then inoculated with varying numbers of *B. coli*. A control set without silver nitrate was inoculated with a similar number of *B. coli*. All of the control tubes showed growth within 24 hours. Those which had silver nitrate added, and were inoculated with 200 or more showed excellent growth, but growth was prevented when only 20 *B. coli* were used. The difference noted between this experiment and the first one described suggests that the combination of $AgNO_3$ with something in this broth results in inactivation.

COLLOIDAL SILVER

The action of silver sols on bacteria has been studied by Marshall.[3] He reported that silver nitrate was more active than silver sols, *i.e.*, that silver nitrate calculated as 1 part of silver in 3,200,000 killed *B. typhosus* in 10 minutes, whereas a silver sol containing 1 part silver in 25,000 failed to kill in 15 minutes, but killed in 30 minutes. Marshall used Bredig's method, which produces particles of various sizes, most of which are so large that they readily precipitate. In this research a new electric dispersion method described by Fraser and Gibbard[4] was used, by which a clear, yellow, silver sol was prepared. It was found that the concentration of silver in an effective silver sol was of the same order as the concentration of silver as silver nitrate, producing similar results. In addition, the concentration of silver in water exposed to silvered commercial rings or silver plated rings was also of the same order. A concentration of silver (colloidal silver) of one in 10 million in distilled water produces sterility in 3½ hours at 23° C., and in 6 hours at 8° C. It was found that the action of colloidal silver on *B. coli* is affected by the presence of organic matter and temperature of exposure.

It is believed, therefore, that colloidal silver has an inhibitory or oligodynamic action similar to that of silvered commercial rings, or silver plated porcelain.

SILVER CHLORIDE AND FUSED SILVER CHLORIDE (HORN SILVER)

The effect of silver chloride was studied in a few experiments, with results similar to those obtained with

silver nitrate. A concentration of 1 part of AgCl in a million parts of distilled water sterilized a million *B. coli* per c.c. in 2½ hours.

Horn silver, or fused silver chloride, had a more rapid action, producing sterility in ½ to ¾ of an hour. However, quantitative determinations of the solubility of fused silver chloride were not made; consequently the results are not quite comparable.

METALLIC SILVER

The action of metallic silver in agar plates heavily seeded with *B. coli* was studied.

Pure sheet silver was obtained (99.98 per cent pure); a small strip as first obtained was placed in an agar plate. A zone of inhibition ¼ inch wide surrounded the silver after 24 hours' incubation. Another experiment was set up in which strips ¼ inch wide and 1 inch long were used. One strip was cleaned by fine emery paper, another was heated to a red heat in a bunsen flame and a third was held above the tip of the flame for about one minute. Neither the cleaned silver nor that heated to redness gave any zone of inhibition, while one held over the flame gave a zone of inhibition at least ¼ inch wide. The inference is, of course, that the inhibitory or oligodynamic action on *B. coli* is due entirely to traces of salts, oxides or sulphides on the surface.

After some days a plate which had shown a zone of inhibition was seen to have colonies growing in the clear zone. It is suggested that there is a distinct possibility of developing silver-resistant strains of *B. coli*. This point has not been studied, but will be kept in mind in future work.

MISCELLANEOUS EXPERIMENTS

One. A number of flasks and beakers, some of which were etched with hydrofluoric acid, were plated with silver by the same chemical reduction process used for plating the porcelain. It was found that quite good oligodynamic action was secured. The rate of action was definitely co-related with the ratio between the capacity of the beaker and its wall area. The narrower the ratio between surface and volume the more quickly were the organisms affected. The suspension contained 700,000 *B. coli* per c.c. The experiment was conducted at room temperature. The main objection to this process from a practical point of view is that the silver plating on polished or etched glass did not adhere under the usual washing and cleansing conditions with soap and water.

Two. Double distilled water exposed to silver plated laboratory rings forty hours was boiled down from 500 c.c. to 10 c.c. and immediately diluted to 500 c.c. A suspension of *B. coli* was added to give a count of approximately 2 million per c.c. In addition, two control experiments were conducted with water exposed to silver which had not been boiled. The test was conducted at 22° C. It was found that while *B. coli* failed to grow after six hours' exposure to the control "silver" water, excellent growth was obtained after 24 hours' exposure to the boiled "silver" water.

SUMMARY

1. Distilled water suspensions of *B. coli* are apparently killed by exposure to silvered porcelain rings, without affecting color, odor or taste of the water.

2. There is a very definite time factor for silvered commercial rings and silvered laboratory rings to affect *B. coli* even under optimum conditions.

3. Although definite evidence of revival of organisms exposed to silver has not been obtained, further investigation is necessary before any final conclusion can be made.

4. The quantity of silver in water ex-

posed to silvered commercial rings, or to silver plated laboratory rings increases with the time of exposure, introducing another variable factor.

5. The presence of organic matter markedly increases the time of exposure necessary to prevent subsequent growth of *B. coli*.

6. The temperature of exposure markedly affects the rate of action of silvered rings, the sterilizing time increasing with lowered temperatures.

7. Rings which become inactive may be reactivated by treating with dilute HCl.

8. Silvered laboratory rings are more active in the dark than in the light.

9. Water which contains silver after exposure to silver plated porcelain has, as would be expected, the ability to inactivate *B. coli* added to it.

10. The effect of light on the action of silver nitrate on *B. coli* was studied, but it was found that under the most carefully controlled conditions there was no difference.

11. The concentration of silver in water exposed to silvered rings which is effective against *B. coli* is of a similar order as the effective concentration of silver in a silver nitrate or silver chloride solution and colloidal silver.

12. In general those factors which affect the so-called oligodynamic effect of silver metal also affect the action of the other forms of silver studied.

CONCLUSIONS

It may be concluded, as a result of these laboratory studies, that although the application of the oligodynamic action of metallic silver to the treatment of water has some points of considerable interest, it cannot at the present time be recommended for practical use. Temperature, organic and inorganic constituents definitely influence the "oligodynamic" action of silver toward *B. coli* to a degree which renders the results unsatisfactory for practical application.

Furthermore, the definite, rather prolonged time factor which markedly increases under unfavorable conditions, necessitates constant and careful bacteriological control. The lack of a simple, delicate test for silver would require water to be stored until a bacteriological analysis could be completed.

REFERENCES

1. Suckling, E. V. *Water & Water Eng.*, Dec. 21, 1931.
2. *Ibid*, Jan. 20, 1932.
3. Marshall, C. R. *Proc. Roy. Soc. Edinburgh*, 39:143, 1919.
4. Fraser and Gibbard. *Canad. J. Res.*, VII:133, 1932.