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REPORT NUMBER 3

WATER DISINFECTION PRACTICE

FINAL REPORT

including

SUMMARY OF THE HARVARD REPORT ON THE DISINFECTION OF WATER

John T. O'Connor
Surinder K. Kapoor

August 31, 1969

Supported by

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Washington, D. C. 20315

Contract No. DADA 17-67-C-7062

University of Illinois
Urbana, Illinois 61801

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Summary of Accomplishments under the Contract on Water Disinfection Practice

This contract was initially undertaken to prepare and test a proposed new tablet for canteen water disinfection. Subsequently, it was decided that the testing and development of a new tablet might be costly and premature. As a result, the emphasis in the study was shifted to a review of the present practice of canteen water disinfection with suggestions for possible improvements or modifications in techniques. As part of this review, the contractor was requested to prepare a summation or condensation of an earlier work done in this area by investigators at Harvard University entitled, "Disinfection of Water and Related Substances, Final Report to the Committee on Medical Research," Cambridge, Massachusetts, (December 31, 1945).

Finally, the contractor was requested to conduct a search for new chemical products which might have potential as canteen water disinfectants.

1. Review of the Literature on Field Disinfection of Canteen Waters

A review of the available literature on canteen water disinfection incorporating the results of a recent survey of marines using the globaline purification tablet in Vietnam was prepared. Suggestions were made for possible modifications of the packaging and manufacturing techniques for the globaline tablet.

The review has been accepted for publication in the Journal of the American Water Works Association. Hopefully, the appearance of such a review may stimulate interest in problems related to military water supply. This has been little mention of military water supply or disinfection practices in the water works literature in recent years.

2. A Critique on Disinfection of Drinking Water

Prepared as a special report for limited distribution, the master's thesis written by Mr. Surinder K. Kapoor entitled, "A Critique on Disinfection of Drinking Water" is a general review of disinfection. It discusses the history of disinfection and the emergence of the present practices of municipal water disinfection. Emphasis is given to the disinfection of water using the halogens and ozone.

A paper based on this critique was presented at the annual meeting of the Illinois Section, American Water Works Association, in the spring of 1969.

3. Summary of the Harvard Report

Much of the substance of the Harvard Report on Water Disinfection has been lost, overlooked or forgotten. It has hitherto been published only in fragments. The resurrection of this report may help to bring this research to the attention of current researchers and, in this way, help in avoiding duplication or repetition by similar studies. The report is an essential primer for any researcher planning to study the chemical disinfection of water.

4. New Products for Water Disinfection

A search was conducted for new products for water disinfection by writing to chemical manufacturers and suppliers. There was little positive response to requests for information on such products. This poor response may indicate that chemical manufacturers are either unaware or are unconcerned with problems of military water disinfection.

5. Tangible Results of Present Research

It is difficult to ascribe technological developments to individual projects since, most often, many previous studies and other individuals contribute to such progress.

However, the current project hopefully has resulted in a re-examination of the practice and efficacy of canteen water disinfection. In turn, the following developments have taken place within the last two years.

1. Consideration is being given to new packaging techniques for globaline tablets.

2. A survey has been made of the response of marines to use of the globaline tablet in Vietnam. It has been somewhat adverse.

3. Studies have been made of the solution properties of the globaline tablet as currently manufactured.

4. Laboratory studies have revealed that the iodine released by the globaline tablet will react with reducing agents, such as ascorbic acid which is added to some beverage powders. In Vietnam, beverage powders are commonly added to canteen water to mask the taste imparted by iodine.

5. Questions have been raised concerning the effectiveness of iodine in inactivating virus particles. The "optimum" pH for the destruction of both virus and cysts may not correspond to the pH obtained by the solution of the buffer provided in the globaline tablet.

6. On the whole, the globaline tablet has been judged to be a reasonably effective and stable disinfecting agent. While there is no urgency about considering the development of new products or techniques for water disinfection, there is no reason to be complacent. This is particularly true since continuing research and experience demonstrates that some of our ideas about the relative resistance of organisms and the viability of organisms in water are incorrect. Moreover, there may be a greater problem regarding the user's acceptance of the globaline tablet than is generally recognized. It may be that a sweetening or masking agent could result in greater acceptance.

Introduction -- Summary of the Harvard Report

At the request of the U.S. Army, Medical Research and Development Command, Commission on Environmental Health and Hygiene, a summary has been prepared of the report submitted to the Office of Scientific Research and Development in 1945 by researchers at Harvard University. This report entitled, "Disinfection of Water and Related Substances, Final Report to the Committee on Medical Research," reported the results of studies by a team of researchers which included Dr. Gordon Fair, Dr. J. Carrell Morris and Dr. Shih L. Chang. The intensive effort which the report describes was made in an effort to develop a tablet for the disinfection of canteen waters. Many researchers agree that the work is a landmark in the field of water disinfection. Up to the present time, no similar coordinated team effort has been made in this area of research.

Despite the magnitude of the effort involved, this work has not become as well-known as it might have. This may have been due, in part, to the security regulations which governed publications during war-time. This summary or condensation has therefore been prepared, as a service to researchers, present and future, who wish to study processes for water disinfection.

The attached condensed version of what has come to be called the "Harvard Report" is about one-tenth as long as the original report. Some care has been taken, in editing the original report to this size, to preserve the terminology, meaning and even the wording. The summary is a reproduction of the original, but hopefully a faithful and accurate reproduction preserving the most important features. For the very serious investigator, however, there is no substitute for the complete work.

SUMMARY OF THE HARVARD REPORT ON THE DISINFECTION OF WATER

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SUMMARY OF THE HARVARD REPORT ON THE DISINFECTION OF WATER

Elements of Water Disinfection and Disinfecting Agents

The disinfection of water by chemical agents is a function of the following:

1. The concentration of the disinfectant in the water.

2. The time of contact between the disinfectant and the organism to be destroyed.

3. The resistance of these organisms to destruction by chemical agents.

4. The concentration of these organisms.

5. The temperature of the water.

6. The composition of the water.

Concentration of Disinfectant

The actual concentration of the disinfectant depends upon:

1. pH.

2. Halogen demand.

3. Side reactions of the disinfectant with substances present in the water that transform the active ingredients into a substance less potent than intended, e.g., chloramines.

Time of Contact

The time of contact necessary for disinfection

1. The time of solution: this is the time required for the agent to release its active ingredient to full attainable strength.

2. The time of kill: this is the time of effective contact between the disinfectant and the organism it is to destroy.

Resistance of Water-borne Pathogens

The following groups of pathogenic organisms are water-borne:

1. Non-sporulating pathogenic enteric bacteria such as *E. typhosa*, *S. dysenteriae*, *Vibrio comma*. However, experimental work on this group is often simplified by dealing with a non-pathogenic member of this group, *E.coli* which is somewhat more resistant to destruction than its pathogenic associates.

2. Pathogenic protozoa: *E. histolytica* is the most resistant.

3. Pathogenic viruses: only virus of infectious hepatitis has been accepted as water-borne so far. However, for lack of suitable experimental animal, the investigations were confined to the virus of mouse poliomyelitis and the virus of human poliomyelitis.

4. Pathogenic worms: among the many pathogenic parasites falling into this group, special interest has been focused on the cercariae of the Schistosomes.

Apart from the virus of infectious hepatitis, the cysts of *E. histolytica* appear to be the most resistant water-borne pathogens that must be dealt with in water disinfection and so appear to determine the pattern of accomplishment that must be established both in the laboratory and in the field.

Concentration of Organism

This report set the criterion for acceptable performance of a disinfectant from 100 million per 100 ml to less than 5 per 100 ml. This is a destruction of 99.999995%.

Assuming a *E. typhosa* to *E. coli* ratio as 100 to 1,000,000 which is quite a high figure, the above destruction of *E. coli* would leave but one *E. typhosa* in 200 canteens of water.

In case of E. histolytica, the maximum number of cysts in concentrated sewage comes to 10 per ml assuming endemicity to be as high as 50%. However, in these studies as many as 30 to 60 cysts per ml were employed.

Water Temperature

Water temperature affects a number of factors including, rate of solution, rate of kill and degree of ionization of disinfectant. Tests were run over a wide range of temperatures (0°C to 30°C).

Water Composition

Water composition affects the concentration of the disinfectant. Alkalinity and turbidity are of importance. While alkalinity is related to control of pH, turbidity in the form of suspended matter may occlude organism and so protect them against attack by the disinfectant.

Interrelationships

Certain generalizations drawn from the observed facts are:

1. The logarithmic order of death of organisms exposed to a given concentration of disinfectant.

Referred to as Chick's law, this relationship between number of survivors and time of exposure states that the proportion of organism destroyed in a unit of time at a given concentration of disinfectant is constant.

2. Inverse logarithmic proportionality of the time of equal percentage of kill, or direct logarithmic proportionality of the reaction velocity constant to the concentration of the disinfectant.

This relationship states that the product of time of kill and concentration of the disinfectant to a constant exponent is a constant.

3. Substantial conformity to the Van't-Hoff-Arrhenius equation of the effects of temperature upon rate of disinfection.

4. Conformity of the solution of a disinfecting agent in water to the normal physico-chemical equilibrium relationships as affected by pH, temperature and the presence of other dissolved impurities in the water.

Desirable Properties of Chemical Agents

A chemical water-disinfecting agent, intended for use by troops in time of war, should meet the following requirements:

1. It should be made available as a tablet of such size as to permit use of a single or at most two tablets per canteen or 5-gallon can and of a somewhat larger number of tablets or ampules per Lyster bag.

2. The technique of applying the disinfectant should be simple of management, substantially foolproof, and not unduly time-consuming.

3. The agent should disintegrate or dissolve quickly and liberate its active ingredients rapidly in order to free as much time as possible for the kill. A total contact time of 10 minutes for canteens and 30 minutes for 5-gallon cans and Lyster bags appears to be reasonable.

4. Dosage should preferably be such as to ensure disinfection of all kinds of natural waters to be treated without testing for residual concentrations of the disinfectant.

5. The treated water should be acceptable to troops. Odor, taste, and appearance of the water should not be objectionable; and foods and beverage powders or concentrates placed in the water should not be changed in normal appearance of flavor.

6. The treated water should not be toxic or otherwise undesirably physiologically active during periods of reasonable use. The water, furthermore, must not interfere with essential prophylactic or therapeutic medication.

7. The treated water should not be corrosive to water containers.

8. The disinfecting agent should be stable under conditions of storage and actual use.

9. The ingredients required in compounding the disinfectant should be economically and strategically available.

10. Manufacture of the chemical agent should lend itself to large-scale preparation with normally available chemical and pharmaceutical equipment.

Tablet Ingredients

1. Lubricating substance: this substance is added to the mixture to lubricate the punches of tablet-making machine. It may be talc or calcium or magnesium stearate. Sometimes this substance is also used to perform the additional function of increasing the bulk. In any case it should be easily soluble, inert to the active ingredients, cheap and should neither be physiologically active nor hygroscopic in character.

2. Swelling agent: Bentonite is a colloidal clay which promotes disintegration of tablets and causes them to burst. Starch can't be used, unfortunately, as it is not inert to halogens.

3. Buffering agent: If the activity of the disinfecting ingredient is promoted by the reaction of the water, buffering agents are included in the tablet mixture. Generally the filler serves as a buffer too. Certain phosphates are ideal for this purpose.

Undesirable Effects on Water Quality

Following are the characteristics generally affected by the disinfecting agent:

1. Odor and taste.
2. Color.
3. Turbidity.
4. Foaming.
5. Corrosiveness.
6. Toxicity.

Of these, toxicity is the most important.

All these aspects must be carefully scrutinized. In addition, tablet ingredients must not interfere with essential prophylactic or therapeutic medication.

Keeping Qualities

The compound used for the disinfection in the form of a tablet must:

1. remain unimpaired in sealed containers over long periods of time.
2. maintain full strength while the contents of the container are being used up.
3. stand firm against high temperatures and humidities.

Theoretical Chemistry of Water Disinfectants

This report deals with only three of the halogens, i.e., chlorine, bromine and iodine. Flourine was found to react with water so vigorously to release oxygen that its use seems impractical.

These halogens may react in a number of ways with water, but there are only two general reactions which have any importance during the time allowed for reaction. The first of these is hydrolysis with water and second one is the ionization of the hypohalous acid formed. These reactions are immediate and equilibrium conditions are reached almost at once in which varying quantities of the possible active species X_2, XOH and OX^- are present where "X" represents the halogen. Further, each of these species has the same oxidizing power per molecule and hence any of the usual analytical methods will determine the sum of the quantities of these three compounds present in the solution. Nevertheless, it is possible to determine the amounts of each of these species from a knowledge of the equilibrium constants for the reactions and of the total analytical concentration of oxidizing halogen. Various equations are:

$$X_2 + H_2O \rightleftharpoons HOX + H^+ + X^- \tag{1}$$

$$HOX \rightleftharpoons OX^- + H^+ \tag{2}$$

$$\frac{[HOX]\ (H^+)[X^-]}{[X_2]} = K_h \tag{3}$$

$$\frac{(H^+)[OX^-]}{[HOX]} = K_I \tag{4}$$

$$C = [HOX] + [OX^-] + [X_2] \tag{5}$$

where K_h = hydrolysis constant

K_I = ionization constant

C = total analytical concentration of the oxidizing halogens in moles/liter

and square brackets [ ] stand for molar concentration of the enclosed materials.

A solution of the above equations on the basis of the knowledge of the following is possible:

i) hydrolysis and ionization constants,
ii) pH of the solution,
iii) total concentration of active halogen, and
iv) halide ion concentration.

The only one of these that offers difficulty is the halide ion concentration.

Application of the Equations to Chlorine

The values of K_h and K_I were taken from the research works of other authors and correction for activities were made wherever necessary.

Calculations for chlorine for all concentrations used in water disinfection showed that the percentage of Cl_2 is so small that it may be disregarded. This has been proved experimentally by some authors also. Consequently chlorine is not a factor in water disinfection and only HOCl and OCl^- need be considered. The authors have thus drawn figures for the relative amounts of HOCl and OCl^- at various pH values.

Below pH 5, the titrable chlorine is present almost entirely in the form of HOCl. As the pH is increased above 6, the fraction present as HOCl decreases very rapidly until above pH 10 the titrable chlorine is practically all OCl^- ions. Since HOCl is considerably more effective than OCl^- ion as a disinfectant, one would expect this change to be paralleled by a change in the disinfecting power of chlorine solution, as is the case.

The authors have also calculated the amounts of total chlorine at various pH values necessary to produce a given concentration of HOCl. They also find that these agree very closely with the relative amounts of titrable chlorine required to kill bacteria and cysts at the corresponding pH values.

Chemistry of Chloramines

The chemical relationships of the chloramines are very imperfectly known. The authors, however, assume that the HOCl reacts completely with the ammonia and that this occurrence of mono- or dichloramine is governed by the equations:

$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$ (1)

$2NH_2Cl \rightarrow NH_3 + NHCl_2$ (2)

$NH_3 + H^+ \rightarrow NH_4^+$ (3)

On the basis of these equations and some experimental data, the following results are derived:

i) the equilibrium constant, $Ka = \frac{(NH_3)\ (NHCl_2)}{(NH_2\ Cl)^2}$

ii) relative amounts of chlorine in the form of monochloramine and dichloramine at various pH values;

iii) calculated effect of the molar ammonia-chlorine ratio on the relative amounts of the chloramines at a number of pH values;

iv) variation of dichloramine with pH for some of the chlorine-ammonia weight ratios employed in practical water disinfection.

Application of the Equations to Bromine

The values of the constants for the hydrolysis of bromine and the ionization of hypobromous acid are not well established. However, the values of these constants are such for bromine that within the range of pH values found in water supply work, any one of the three possible species may predominate. More experimental work is recommended.

The numerical evaluation of the fundamental equations has been carried out for titrable bromine concentrations ranging from 0.1 to 1000 ppm, for pH values from 3 to 11 and at a temperature of 20°C. The values of these species show that the influence of Br_2 should be noticeable at the concentrations required to kill bacteria and cysts only below a pH of five and that above a pH of seven decreased effectiveness of bromine as a disinfectant should become noticeable because of the formation of OBr^-.

The practical decrease in effectiveness, especially at long contact times, may be even greater than above because of formation of bromide and bromate from OBr^-.

Formation of Bromamines

There is no evidence for the formation of compounds between bromine and ammonia in water solution. Compounds in which bromine is combined with the nitrogen atom in amine- or amide-type organic substances are known, but these substances are completely hydrolyzed at the concentration employed in water work and hence the activity of bromine solution should not be affected by nitrogenous organic matter except for the organic demand.

Application of Equations to Iodine

Iodine is much less hydrolyzed in solution than either chlorine or bromine. Consequently, over much of the practical range the active species is I_2 molecule rather than hypohalous acid as in case of chlorine or bromine. At high pH values where the hydrolysis becomes important, the reaction to form iodide and iodate is so rapid that after a short period of time these are the only species present.

Although there is lot of disagreement over hydrolysis and ionization constants, both these values are so small that the ionization of HOI is not a factor at the pH values attained in water disinfection. However, the formation of triodide by the combination of iodine and iodide ions is of considerable importance in case of iodine whereas similar reactions in case of chlorine and bromine are negligible.

The equilibrium iodide ion is affected by three factors:

1. the amount of iodide ion introduced with the iodine to make the iodine soluble;

2. the amount of iodide formed in the hydrolysis of the iodine;

3. the amount of iodide removed by the formation of tri-iodide.

It may be mentioned here that almost all of the iodine preparations to be used for disinfection have contained iodine and iodide in equimolar ratios, the amounts found in pure tri-iodide preparations.

On the basis of the above applied to general equations mentioned earlier, the authors calculated the percentage of elemental iodine, the chief disinfecting agent, plotted against the total titrable iodine at various pH values. The figures demonstrate that pH should have little effect on the disinfecting efficiency of iodine at a 5 ppm level below a pH of 7, that 25 to 30% more titrable iodine should be required at a pH of 8, and that the efficiency should decrease rapidly above pH 8. Since the HOI formed by hydrolysis is a fairly good germicide, the change in efficiency should not be as marked as with chlorine or bromine solutions.

Formation of Iodamines

There is no evidence for the reaction of iodine with ammonia or amine type substance in water solution.

Interhalogen Compounds

The interhalogen compounds, BrCl, ICl, and IBr may also be expected to show disinfecting action in water. While they show the same type of hydrolysis and ionization reactions as the simple halogen but the hypohalous acid formed as a result of hydrolysis is always that of the less electronegative element, so that BrCl gives HOBr and Cl^-, while ICl and IBr give HOI and Cl^- and Br^- respectively. All these compounds are rather highly hydrolyzed at concentrations of a few parts per million, for the hydrolysis constants are comparable with those of chlorine. These materials in dilute solution will show disinfecting action appropriate to the hypohalous acid formed by hydrolysis.

The authors worked on the germicidal activity of ICl in detail and show that its activity gives a good measure of the activity of HOI, and since the ionization constant of HOI is so small that practically no dissociation occurs below pH 10, the disinfecting activity of HOI (ICl) should be constant between pH values of 3 and 10.

Solid Materials Liberating Halogen or Hypohalous Acid in Water Solution

Because of the physical state of the halogens, they are not of themselves suitable portable materials for the disinfection of canteen-size quantities of water. The gaseous nature of chlorine and the fact that bromine is a corrosive, volatile liquid eliminates these elements from consideration. Iodine, to be sure, is a solid, but is so volatile and so slowly soluble in the elementary condition that its use is also impractical. These facts demand that only stable and solid materials which will react with water to liberate these elements or their hypohalous acids are required.

Chemistry of Hypochlorites

Out of a number of commercial products in the form of hypochlorites, $Ca(OCl)_2$ and Li-OCl have been found to be quite stable. Their reactions are:

$$Ca(OCl)_2 \xrightarrow{\text{in water}} Ca^{++} + 2OCl^-$$

$$OCl^- + H^+ \longrightarrow HOCl$$

The formation of HOCl shows that the hypochlorites produce disinfecting solutions of the same nature as those of chlorine.

In the hydrolysis reaction, however, the pH of the water is increased, since the hydrolysis uses up H^+ ions. Since the higher the pH value, the greater the dose of titrable chlorine required for disinfecting action, addition of hypochlorites to water tends to defeat its own purpose by raising the pH into ranges where the pH is less effective.

The authors developed the following mathematical expression for evaluation of pH on addition of doses of hypochlorite in excess of 1 ppm:

$$pH = -\frac{1}{2} (\log K_1 + \log K_w - \log C + \log 7.15 \times 10^4)$$

where K_1 = ionization constant of HOCl

K_w = ion product of water

C = dose in ppm of $Ca(OCl)_2$

On this basis, calculations were made for the effect of different doses of $Ca(OCl)_2$ in distilled water on pH and consequent fractions of cysticidal dose attained. These figures show that the increase in pH due to addition of hypochlorite costs a lot more in the form of additional dose than if the pH had remained at the original value. This means that if $Ca(OCl)_2$ or any other hypochlorite is to be used for water disinfection, some form of acid material should be used with it to neutralize the hydroxyl ion formed by hydrolysis.

Chemistry of Organic Compounds Containing Oxidizing Halogen

When an N-halogen compound is dissolved in dilute solution in water, hypohalous acid is liberated, thus giving the solution disinfecting powers. Some of the N-chlor compounds have been found to be toxic to bacteria themselves, but the cysticidal effect is apparently almost wholly dependent upon the amount of HOCl liberated by hydrolysis. A brief outline of the various types of N-halo compounds is given in Table-I.

Solid Mixtures Liberating Elemental Iodine

A. Tri-iodides:

Elemental iodine has the property of combining with iodide ion to form tri-iodides, pentaiodide and so on. This tendency is much more in concentrated solutions.

All these, but particularly I_3^-, will combine with appropriate cations to give salt-like solids which dissociate when dissolved in water.

It has been found experimentally that the stability of the alkali tri-iodides with respect to the reaction

$$MI_3 \text{ (solid)} = MI \text{ (solid)} + I_2 \text{ (gas)}$$

varies directly with the square root of the diameter of the cation with which the tri-iodide ion is associated. Thus cesium, the largest of the alkali metal ions, forms the most stable tri-iodide in this series. Tri-iodide ions are found more in complex ions where many atoms contribute to the overall diameter, e.g., substituted ammonium ions, Werner or hydrate type ion in which the central metallic ion is combined with several neutral molecules by dative bonds. Unfortunately, for almost all such compounds the <u>increase in stability is accompanied by a decrease in solubility</u>. This difficulty can be avoided with the Werner-type compounds if tri-iodide contains a cation which is readily decomposed by water into simpler substances. This breaking up of the cation greatly enhances the solubility, since it decreases the concentration of the cation which is required for formation of the solid salt.

A number of the tri-iodides have properties well suited for water-disinfecting tablets. Choice among them must be based on practical considerations

TABLE-I

S. No.	Name of Compound	General Formula	Typical Compound	Conclusions Drawn
1	Organic Chloramines	$R{-}N\genfrac{}{}{0pt}{}{H}{Cl}$ or $R{-}N\genfrac{}{}{0pt}{}{Cl}{Cl}$ or $\begin{matrix}R_1{-}N{-}Cl\\R_2\end{matrix}$	methyl dichloramine	Very unstable in general
2	Organic Chlorimines	$R{=}N{-}Cl$	Quinone-Dichlorimine	Very insoluble
3	Organic Chloramides	$(i)R{-}\overset{\overset{O}{\|}}{C}{-}N\genfrac{}{}{0pt}{}{Cl}{Cl}$	None	Liquids--not considered
		$(ii)R{-}\overset{\overset{O}{\|}}{C}{-}N\genfrac{}{}{0pt}{}{H}{Cl}$	Chloracetamide	Poor disinfectant
4	Organic chlorimides	$R_1{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{Cl}{|}}{N}{-}\underset{\underset{O}{\|}}{C}{-}R_2$	N-chlor Succinimide	Poor disinfectant
5	Chlorsulfonamides	$(i)R{-}SO_2{-}N\genfrac{}{}{0pt}{}{H}{Cl}$		
		$(ii)R{-}SO_2{-}N\genfrac{}{}{0pt}{}{Na}{Cl}$	Chloramine-T	Feeble disinfectant
		$(iii)R{-}SO_2{-}N\genfrac{}{}{0pt}{}{Cl}{Cl}$	Halozone	a. 50% disinfectant activity compared to chlorine b. Less soluble at low pH values
6	Ring Compounds and Miscellaneous Structures	---	---	No general conclusions can be drawn

---

A. The same classes exist for bromine and iodine but none of the compounds are of great practical importance.

B. R is an alkyl or aryl radical.

TABLE-II

EQUILIBRIUM CONSTANTS

Element or Compound	Hydrolysis Constant-K_h	Ionization Constant - K_1 for hypohalous acid	$Ka = \frac{(NH_3)(NHCl_2)}{(NH_2Cl)^2}$
Chlorine	4.48×10^{-4} at 25°C	3.3×10^{-8} at 20°C	0.013 at room temperature
Bromine	5.8×10^{-9} at 25°C	1.78×10^{-9} at 20°C	----
Iodine	1×10^{-13} at 25°C	2.3×10^{-11} to 4.5×10^{-13} at 20°C	----

of humidity resistance, ease of manufacture, physiological action, and cost.

B. Adsorption Materials:

Iodine combines physically with a great variety of carbohydrate materials, e.g., starch, by a mechanism not yet completely understood. The effect of adsorption of the iodine is to reduce its vapor pressure and thus stabilize it against loss thru vaporization. In addition the iodine is molecularly dispersed and dissolves readily when brought into contact with water. Such materials offer the advantage that all the iodine present is in active elemental form so that the physiological uptake of iodine for a given active dose is less than in any other iodine preparation. The authors tested a number of iodine-restraining compounds but found sodium carboxy methyl cellulose to be most practical in view of good stability and solubility of the reaction product. Moreover this product does not produce a blue color as with starch and is free from strong tastes and odors in solutions.

C. Reacting Systems Which Produce Iodine:

The most extensively used reacting system consists of a metallic iodide with potassium iodate, a strong oxidizing agent. The particular advantage of this type of tablet is that it has high resistance to thermal deterioration but at the same time the material must be kept perfectly dry to prevent the chemical reaction before use. It has also been found that:

1) the reaction will proceed only if the solution is more acid than pH 6.

2) the rate of reaction is proportional to the fourth or fifth power of the reactants.

3) even in moderately dilute solutions the reaction speed is quite slow unless catalysts are present.

4) in practice, a complete reaction is not obtainable.

5) Iodine intake is high.

D. Synthetic Detergents:

None of the synthetic detergents has shown good disinfecting efficiency below 25 ppm. At this concentration in solution they have considerable foaming qualities, and a brackish, bitter taste is imparted to the water. It is apparent that while these synthetic detergents show promise, much more theoretical and practical investigation of this class of compounds is needed before they can be used as drinking-water disinfectants.

Review of Tablets

The following tablets were extensively studied under the project:

1. Standard Halazone Tablet

The composition of this tablet is:

Halazone (p-dichlorosulfonamidobenzoic acid) - - - 5.3 mg

Soda Ash, dried - - - - - - - - - - - - - - - - - - - 5.18 mg

Boric Acid -11.92 mg

NaCl - 114.00 mg

Weight per tablet 136.4 mg

One tablet per quart of water produces a titrable chlorine concentration of 2.3 ppm and a maximum concentration of HOCl (as Cl_2) of 1.1 ppm. This tablet was used by U. S. Army during the second World War.

2. Experimental Halazone Tablet

This tablet has essentially the same composition as the standard Halazone tablet except that it contains 5% of dried starch and its Halazone content is 4.4 mg.

3. Extra-Strength Halazone Tablet

Its composition is:

Halazone -20.0 mg

Sodium Borate -30.0 mg

Potassium Nitrate - - - - - - - - - - - - - - - - -77.5 mg

Starch - 2.0 mg

Magnesium Stearate - - - - - - - - - - - - - - - - - 0.5 mg

Weight per tablet - - - - - - - - - - - - - - - - - 130.0 mg

This tablet was tried because four standard Halazone tablets per liter constitute a cysticidal dose.

4. Perchloron/Hood Chlor/HTH

This high-test hyporchlorite yields about 70% of available chlorine by weight.

5. Chlor-Dechlor

This consists of a vial containing (1) 130 mg of powder containing Halazone, designed to liberate about 17 ppm of titrable chlorine in a quart of water, and (2) a tablet of sodium sulphite, coated with cellulose acetate butyrate to retard dissolving of this tablet until the chlorine has had time to be effective. This coating delays the dechlorination by about 9 minutes.

6. Dactin RH-1001 and RH-1001-A Tablet

These are tabletized forms of "Dactin" or dichlorodimethyl hydantoin. About 25% of a titrable chlorine is hydrolized to HOCl.

Composition of the tablets by weight is:

	RH-1001		RH-1001-A
Dactin	10.0%		9.00%
$Na_2H_2P_2O_7$	83.5		60.75
Saccharin	1.0		0.25
Talc	5.5	Boric Acid	5.00
		$CaCO_3$	10.00
		Succinic Acid	15.00
	100.0%		100.00%

The data provided includes the weight and manufacturers' ratings for disintegration time also.

7. Lambert #202

This tablet is compounded of succinchlorimide and potassium bromide. One quart of water needs a dose of 3 tablets and 20 minutes contact time to be cysticidal. The composition is:

Succinchlorimide	13.0 mg
KBr	2.3 mg
Succinic Acid	20.0 mg
Potato Starch, dried	1.3 mg
KNO_3, USP	93.4 mg
Weight per tablet	130.0 mg

8. Special Tablet No. E-6890

This tablet provides one ppm of residual chlorine in a quart of water. The tablet contains succinchlorimide and an anionic detergent but exact composition is not known.

9. Activated Chloramines

This tablet contains:

Methane dichlorsulfanamide	14 mg
$Na_2H_2P_2O_7$	100 mg
Talc	10 mg

No other data is given.

10. Japanese Water Purifying Liquid

This liquid is principally an aqueous solution of NaOCl, plus a small amount of organic matter. One drop of this liquid provided 0.1 to 0.3 mg of chlorine.

11. Burroughs Wellcome Tablet No. 4

This tablet has the following composition:

Potassium Iodide	20 mg
Potassium Iodate	10 mg
Potassium Permanganate	1 mg
Citric Acid Anhydrous	20 mg

Sodium Chloride - - - - - - - - - - - - - - - - - - -150 mg

Bentonite - 10 mg

Magnesium Stearate - - - - - - - - - - - - - - - - - - 1 mg

Weight per tablet - - - - - - - - - - - - - - - - - -212 mg

Available Iodine per tablet - - - - - - - - - - - - 21 mg

This tablet is unstable at high humidity.

12. Bursoline Tablet

Four formulations were developed at Harvard:

Composition	#1	#1A	#2	#3
Diglycine Hydriodide, mg	11.0	10.4	13.0	18.0
Iodine, mg	5.4	5.0	6.3	8.2
Sodium dihydrogen-pyrophosphate mg	110.0	81.0	54.0	82.1
Talc, mg	4.0	-	4.0	4.0
Aerosol OT (100%), mg	-	19.0	-	-
Weight per tablet, mg	130.4	115.4	77.3	112.3
Titrable Iodine, ppm (One tablet per quart)	4.6	-	5.8	7.4

Bursoline 2 and 3 differ essentially from #1 only in increased amount of iodine to take care of iodine demand by natural and polluted waters. The aerosol included in tablet 1A was found to make the tablet too hard to dissolve and produces a bad odor.

13. Bursoline Mud Tablet

The composition of this tablet is:

Diglycine hydriodide - - - - - - - - 16.8
Iodine - - - - - - - - - - - - - - - - - 8.0
} Bursoline Mud = 24.8 mg

Talc - - - - - - - - - - - - - - - - - - 3.5 mg

$Na_2H_2P_2O_7$ - - - - - - - - - - - - - - 91.7 mg

Weight per tablet - - - - - - - - - -120.0 mg

No other data is provided.

14. <u>TGHI Tablet</u>

The composition of this tablet is:

TGHI powder	19.2 mg
Talc	3.8 mg
$Na_2H_2P_2O_7$	97.0 mg
Weight per tablet	120.0 mg

Titrable iodine (one tablet per quart) - 7.8 ppm

TGHI powder is a result of grinding one mole of diglycine hydriodide and one mole of iodine with an extra mole of glycine in the presence of alcohol.

This tablet is more stable than "Bursoline Mud" tablet.

15. <u>Globaline Tablet</u>

This tablet has as its principal ingredient "Globaline" which was then thought to be triglycine hydroperiodide. The composition of the tablet is:

Globaline (40% I_2)	19.3 to 21.3 mg
$Na_2H_2P_2O_7$	82.5 to 92.3 mg
Talc	not more than 6 mg
Weight per tablet	110 to 120 mg

Titrable Iodine (one tablet per quart) - approx. 8 ppm

This is the tablet which was finally standardized and is now used by the U.S. Army.

16. <u>Alure Tablet and Alure Nitrate Tablet</u>

Sample composition of this tablet is:

Alure	27.2 mg
$Na_2H_2P_2O_7$	81.6 mg
Talc	3.2 mg

Weight per tablet	112.0 mg

Titrable Iodine (one tablet per quart) - 7.8 ppm

Alure is aluminum hexacarbamide sulfate tri-iodide Alure Nitrate is aluminum hexacarbamide dinitrate tri-iodide.

17. <u>IFI Tablet</u>

The active component of this tablet is sodium carboxymethylcellulose iodine (IFI). Sample composition of this tablet is:

IFI	66.5 mg
Tartaric Acid	45.0 mg
$NaHCO_3$	8.0 mg
Talc	8.0 mg
Weight	127.5 mg

Titrable Iodine (one tablet per quart) - 8.0 ppm

The following tablets were prepared or analyzed but no extensive testing was carried out because of one defect or another:

1. Chloramine T and Sodium Sulphite Dechlorinating Tablets
2. Succinchlorimide (SCI) Tablets
3. Lithium Hypochlorite Powder
4. N-Chloro Succinimide Tablets
5. Russian Disinfectant
6. Burroughs Wellcome Modified Tablet A-88
7. Halazone and Succinchlorimide Tablets
8. Succinimide Periodide Tablets
9. Iodosuccinimide Powder

Chemical Analytical Methods

This chapter provides definitions of a number of terms used in the report as well as various analytical methods employed for the purposes of the project.

Definitions:

The following two terms have been extensively used in this report:

I. Titrable chlorine.

This term is also referred to as "Available Chlorine" or "Total Active Chlorine." These terms represent total oxidizing power of a material or solution under consideration which is effective in oxidizing iodide ion to iodine in dilute acetic acid solution, expressed as ppm of elemental chlorine. For the most part it refers simply to the sum of $HOCl$, OCl^- and chloramine chlorine present.

The determination of titrable iodine was most frequently done by the "starch-iodide" method which was found to have greater precision in the high doses necessary to kill cysts. O-Tolidine method was used whenever lower doses (less than 1 ppm) were employed.

II. Free Chlorine.

Free chlorine is defined as that chlorine present in solution as hypochlorous acid or hypochlorite ion.

III. Chloramines.

Chloramine is that oxidizing chlorine in the compound which is attached to nitrogen atoms.

Methods employed for "Free Chlorine" and "Chloramines"

A. Amperometric Method

B. Orthotolidine-Arsenite Method

C. p-Amino Dimethylaniline (Amidian) Method

D. Flourescein-Bromide Method

E. Arsenite Titration with external indicator

The report describes these procedures in detail and also discusses the advantages and disadvantages of each of them. The quantities of free chlorine and chloramine indicated by each method were compared with actual quantities added.

IV. Elemental Iodine.

Methods employed for the determination are:

A. Starch-Iodide Method

B. Extraction Method

C. Amidian Method

D. Potentiometric Titration Method

These methods have been described in detail along with their advantages and disadvantages.

V. Total Iodine

Total iodine is a sum of iodide as well as elemental iodine. A number of methods were developed to determine total iodine:

A. Iodate Method

B. Nitrite Method

C. Chlorine Oxidation Method

Physical and Chemical Properties of Halogen Containing Disinfectants

Hypochlorites

The following samples of commercial hypochlorites were tested for their solution properties, the extent to which they raised the pH of waters, and the ease with which their solutions could be acidified by solid acids:

A. HTH from Matheson Alkali Co.

B. HTH from Pennsylvania Salt Co.

C. Hoodchlor from Hood Chemical Co.

D. Lithium Hypochlorite from Solvay Process Co.

Samples A, B, and C contain calcium hypochlorite as the active ingredient.

Dissolving properties - Out of these four, sample D alone gave a perfectly clear solutipn; others gave cloudy solution to varying degrees.

Regarding solubility, results were as below:

Sample	A	B	C	D
% Titrable chlorine	67.4	67.2	72.2	81.0

Effect of hypochlorites on pH - The lithium hypochlorite showed the least tendency to increase pH of the water. The results of the tests carried out on the use of 10 mg/liter in distilled water with original pH equal to 6.2 were as follows:

Sample	A	B	C	D
pH	7.6	7.9	7.5	7.4

On the basis of solubility tests as well as its effect on pH, lithium hypochlorite would have been preferred but it was found to be too hygroscopic.

Effect of Acidification - It was found that a mixture of HTH and acid decomposed rapidly. As a result, these constituents must be kept separately. The quantity of acid added must react not only with the alkalinity of the raw water but also with the alkalinity produced by the addition of the HTH. When tests were carried out to see the effect of a number of solid acids such as citric, tartaric, $Na_2H_2P_2O_7$, etc. on alkaline water containing 25 ppm of HTH, citric acid was found to be the most effective in depressing pH being closely followed by tartaric acid. Either of these acids in 100 mg per liter concentration would lower the pH of a water containing 250 ppm of bicarbonate alkalinity and 25 ppm of HTH to less than 7. Neither of these acids have a measurable effect on the titrable chlorine at the concentrations used in the time required for disinfection.

N-Chloro Compounds - The so called "break point phenomenon" was observed when halazone and methandichlorsulfonamide were dissolved, the decomposition apparently resulting from the action of the free HOCl liberated by the solution of the material on the remaining monochlor or dichlor compounds. It was also seen that the decrease in titrable chlorine which occurred on standing with solutions of these compounds was largely accounted for in terms of loss of free HOCl. Thus, halazone which has lost half of its titrable chlorine strength, therefore, has probably lost 90-95% of its cysticidal efficiency.

This decomposition of halazone was tested at various pH values and it was observed that it is more rapid at higher pH values. Since an alkaline buffer is used in the manufacture of halazone tablets, break-point reaction may be responsible, at least partially, for the low values of free chlorine released by these tablets.

The fact that very little decomposition occurred at low pH values suggests that the halazone and methandichlorsulfonamide do not hydrolyze to give HOCl in this range. Actually the solubility was low and constant up to pH of about 4. Above this the solubility increased quite rapidly. It should, therefore, be possible to prepare a soluble halazone tablet buffered at pH 6 rather than 8 or 9, a condition which would greatly increase the disinfecting efficiency of halazone. Such a tablet was not attempted.

Iodine Compounds

The stability of iodine containing materials was listed in terms of vapor pressure of iodine over the solid of which the stability was being determined. This data has been provided in the report for 11 compounds including globaline and bursoline.

The solubility of globaline along with three other iodine-containing compounds was determined. Globaline appears to have a solubility of 380 gm/liter.

Each of the materials; bursoline, globaline, alure, and alure nitrate produces a pronounced lowering of the pH when dissolved in water. Globaline depresses pH because of the HI constituent in it which is liberated in solution. In addition, in the tablets prepared with these ingredients, 80 to 100 mg/tablet of disodium dihydrogen pyrophosphate has been incorporated which is sufficient to lower the pH of "quite" alkaline water below 7.5. The combined effects of the two acidifying ingredients will, therefore, lower the pH well below 7.5, above which iodine solutions may decrease in disinfecting efficiency in practically all natural waters.

Chlorine and Iodine Demand of Water and Related Substances

For the purposes of this project, the halogen demand of water is defined as the difference between the concentration of titrable halogen added and titrable halogen remaining at the end of a given contact time or disinfecting period. This demand is exercised in part by the organisms that are to be destroyed and in part by chemical and organic substances that reduce the halogen.

From the studies conducted on iodine and chlorine demands, the following conclusions can be arrived at:

1. Iodine demand of natural waters are of approximately the same magnitude as chlorine demands on a ppm basis. On a molar basis, iodine demands are about 28% of the chlorine demands.

2. Halogen demand increases with increasing concentration of halogen.

3. Halogen demand of surface waters is correlated directly with color content.

4. Leaf-extract solution of high color content exerts considerable halogen demand.

5. Chlorine and iodine demands of solutions of organic acid are greater in basic solutions than at lower pH values.

6. Ammonia and urea exert no appreciable effect upon iodine and do not form iodoamines.

7. Plastic canteens exert an iodine demand upon one bursoline tablet of about 15% in 20 minutes, but after prolonged use of a plastic canteen, its iodine demand is satisfied, because the plastic surfaces become oxidized.

8. Synthetic beverage powders exert such high halogen demands that they should never be mixed with water until the iodine or chlorine disinfectant has had time to act.

9. Many detergents and organic acids exert a high iodine demand.

Survival of Micro-Organisms in Water at Varying pH Values

Studies of the literature at the time of the Harvard Report indicated the following effects of acids and bases on various micro-organisms:

1. Destruction of bacteria by mineral acids is a function

of the hydrogen ion concentration; the lower the pH value, the quicker is the destruction of the bacteria.

2. With organic acids, the pH values observed at comparable germicidal levels were definitely higher than those recorded when mineral acids were employed. This suggests that the germicidal activity of organic acids is due not only to the hydrogen ions but probably also to the anions and undissociated molecules.

3. The destruction of bacteria, at least _E. coli_, by hydrogen ions seems to be bounded by a critical level, below which no destruction is expected even when the contact time is greatly increased.

4. _Staphylococcus aureus_ and _Eber. typhosa_ are definitely less resistant to germicidal action by acids than is _E. coli_.

5. Generally speaking, the germicidal activity of alkalies is chiefly a function of the hydroxyl-ion concentration.

6. With _E. coli_ and _E. typhosa_, germicidal activity is observed at pH values of 11.0 or higher.

Harvard Studies

These tests were made to gauge the effect of hydrogen-ion concentration on the survival of _E. coli_ and _E. typhosa_ and of cysts of _E. histolytica_ in water in addition to the effect of the disinfectants. From these tests the following conclusions were drawn:

1. The survival of _E. coli_ and _E. typhosa_ in water was apparently not affected by the hydrogen or hydroxyl-ion concentrations as measured by pH values in the range of 4.0 and 11.0 and 5.0 to 10.0, respectively. Beyond these limits, bactericidal effects became progressively more pronounced.

2. At all pH levels in the bactericidal ranges, the reduction

of the number of survivors in the course of time could be formulated as a unimolecular reaction, i.e. destruction progressed in logarithmic order. When the killing was very rapid, an initial high rate of reduction was followed by a slow rate of reduction extending over many hours.

3. The relative rate of kill associated with different pH values in the bactericidal range could be expressed in terms of a first order reaction velocity constant, K, as determined by this equation

$$K = \frac{-\log p}{0.4343\ t}$$

where p is the fraction surviving after time, t, minutes.

Values of K for survival of E. coli and E. typhosa in water at low and high pH values have been calculated and presented in the report. The relations of percentage of these organisms killed in one hour to various pH values have also been graphically reported. In addition to this, the survival of cysts of E. histolytica in water at high and low pH values at 23°C has also been studied.

The results obtained indicate that cysts are more resistant to high and low pH values than are either E. coli or E. typhosa. The cysts were not killed at pH values as low as 0.5; they were killed by exposure for 10 minutes or longer at pH 14.0.

The bactericidal results recorded both for coliform and typhoid organisms seem to indicate that the effects of both hydrogen-ion and hydroxyl-ion concentration became manifest at the same relative level, namely 10^{-2} for E. coli and 10^{-3} for E. typhosa. However the OH^- ions seemed to be slightly more bactericidal than H^+ ions since the values of K at pH 2 for E. coli and E. typhosa were 0.023 and 0.20 respectively, while the value for K at pH 12.0 were 0.042 and 0.62 respectively.

E. typhosa was observed to be less resistant then E. coli, the difference being less marked when the killing rate was high and more marked when it was low. The difference may be due to a more reactive cell membrane allowing the H^+ ions and OH^- ions to enter the organism at lower concentrations. Amoebic cysts have a resistant cystic wall and are also more resistant to H^+ions and OH^-ions.

Destruction of Cysts in Water by Halogen Compounds Other Than Calcium Hypochlorite and Ammonia - Chloramines

The substances studied for cysticidal efficiency under this section included:

1. Aqueous solutions of elemental iodine with varying amounts of KI ($I_2:I^-$ ratios from 1:0 to 1:10).
2. Burroughs-Wellcome tablet No. 4
3. Bursoline tablet No. 3
4. Alure tablet
5. Globaline tablet
6. IFI tablet
7. Iodosuccinimide
8. Succinimide periodide
9. Iodoacetic acid
10. Morpholine hydroperiodide
11. Iodine chloride
12. Standard halazone tablet
13. Halazone tablet No. 307
14. CDC (Halazone - Dechlor) capsules
15. Halazone - fixanol tablet
16. Succinchlorimid tablet (Lambert)
17. A solution of powdered succinchlorimid in distilled water
18. A succinchlorimid and bromide mixture
19. Halazone - Succinchlorimid mixture
20. Lithium hypochlorite

21. Bromine water

22. N - Chloracetamide

23. Hexachloramelamine

24. Chloramine - B

25. Chloramine - T

The report has presented the cysticidal doses of these compounds for different cyst densities and contact times at different pH conditions. In addition the effect of temperature has also been studied in some cases.

Conclusions

In the destruction of amoebic cysts by halogens or halogen compounds, two controlling factors should be considered: 1) oxidizing power, and 2) diffusibility.

In preliminary tests on the diffusion of halogens and halogen compounds through a cellophane membrane, the elemental halogens were found to diffuse more rapidly than their anions. The high cysticidal efficiency of HOCl may be associated with its high oxidizing power. The observed, equally high, cysticidal efficiency of elemental iodine, on the other hand, may result from high diffusibility at relatively lower oxidizing power. On the other hand, the poor cysticidal activity of Succinchlorimid - a substance with high oxidation potential (normal oxidation potential about 1300 mv) - may be due to its large molecular size and its failure to hydrolize to HOCl. The very poor cysticidal activity of chloramine - B, chloramine - T, and N-Chloracetamide may be associated with their poor diffusibility (large molecular size) and poor oxidizing power. As reported elsewhere, even monochloramine was found to possess better cysticidal efficiency than these organic monochloramines. Since NH_2Cl was found to have low oxidation -

reduction potential, the cysticidal efficiency of monochloramine may be related to its small molecular size and good diffusibility.

Destruction of Amoebic Cysts by HTH

These studies were conducted to obtain information on the relationships that exist between requisite concentration of HTH and the following factors:

1. pH
2. temperature
3. time of contact

Effect of pH:

The following relationship was developed:

$$R = A \frac{1 + \frac{K}{[H^+]}}{1 + B \frac{K}{[H^+]}}$$

where

R = titrable cysticidal residual chlorine in ppm

A = cysticidal concentration of equivalent HOCl in ppm of Cl_2 (given approximately by R at pH 4)

B = ratio of the cysticidal power of OCl^- ion to that of unionized HOCl

K = ionization constant of HOCl, varying with temperature

$[H^+]$ = hydrogen-ion concentration

Effect of temperature:

To define the variation in magnitude of A and B with temperature, the values of A and B have been plotted against different temperatures. Values of energy of activation, E, and temperature coefficient Q_{10}, have also been presented for various temperature ranges.

These data show that with rising temperatures, less titrable residual chlorine is required to destroy the cysts of E. histolytica.

Effect of Contact time:

The data presented is so limited that no conclusive decisions could be made. However, the following could be deduced:

1. At low pH values approximately three times the titrable chlorine residual is needed to kill cysts in 10 minutes as is required to do so in 30 minutes.

2. At high pH values, the corresponding factor is about two.

Destruction of Amoebic Cysts by HTH in Tap Water with Added Impurities:

A number of different tests were run for the following purposes:

1. evaluating the influence of pollutional substances upon the effectiveness of HTH;

2. attaining the short-time destruction of cysts by high doses of HTH;

3. exploring ways and means for the effective application of HTH in the disinfection of water in Lyster bags.

These studies indicate that the principal influence of pollutional substances upon disinfection is to increase the required dosage by an amount equal to their own chlorine demand. It has also been revealed that superchlorination can result in rapid destruction of cysts provided the pH value of water is kept below neutral.

Effective Utilization of HTH:

The overall conclusions drawn with regard to the effective utilization of HTH for the destruction of amoebic cysts can be summarized as follows:

1. Superchlorination to assure the destruction of amoebic cysts and reduce operating controls;

2. Acidification of the water to be disinfected, in order to reduce excessive dosages;

3. Dechlorination to assure palatability of the treated water.

The estimated amount of HTH at pH 7.5 at 10°C and for 30 minutes of contact is composed of the following:

Required cysticidal residual chlorine - 7.5 ppm

Estimated chlorine demand of polluting substances other than ammonia and amino nitrogen - 15.0 ppm.

Amount of chlorine needed to destroy ammonia and amino-nitrogen- 15.0 ppm.

Total - 37.5 ppm

The most obvious substance for dechlorination would be sodium sulfite, its calculated dose being 1.77 ppm per ppm of titrable chlorine.

Destruction of Amoebic Cysts by Ammonia - Chloramines

Although the chloramines are not as efficient disinfectants as HOCl, they are nevertheless very powerful cysticidal agents. Because of the formation of OCl^- ion in free chlorine solutions at high pH values, the chloramines are actually more effective cysticides than free chlorine for a 30 minute treatment at pH values above pH 7.5.

The variations in cysticidal results for chloramine with pH have been adequately explained on the basis of an equilibrium constant derived from chemical experiments on a distribution of chloramines under various conditions. In obtaining values for cysticidal doses of solutions of mixed chloramines, an equation involving the harmonic mean of the cysticidal doses of pure monochloramine and dichloramine reproduces the experimentally observed results. This equation is based on three other equations.

$$\frac{(NH^+_4)}{(NH_3)(H^+)} = K_1 \text{ --------------------1}$$

$$\frac{[NH_3]\,[NHCl_2]}{[NH_2Cl]^2} \quad K_2 \text{ ------------------2}$$

$$1/D = N/A + \frac{1-N}{B} \text{ --------------------3}$$

where

K_1 = ionization constant of NH_4OH and depends upon temperature

K_2 = equilibrium constant for NH_3, $NHCl_2$, and NH_2Cl and does not appreciably change with temperature

= 0.0135

D = cysticidal chlorine residual

A = cysticidal chlorine residual for pure dichloramine

B = cysticidal chlorine residual for pure monochloramine

N = fraction of titrable chlorine present as dichloramine

The report also establishes disinfecting constants for the above and other substances which represent quantitatively their relative cysticidal efficiencies. The Cysticidal Constant has been defined as the number of liters of water with an initial population of 30 cysts per ml that one gram of a chemical will disinfect. This constant will depend upon temperature and time of contact, which must be specified for a given cysticidal constant. For an exact chemical comparison, a somewhat modified constant, the Molar Cysticidal Constant is preferable. This is defined as the number of liters of water one mole of the chemical will disinfect.

A third variation for use with chlorine-containing compounds is also useful, since the strength of such solutions is ordinarily based on the ppm of titrable chlorine present rather than the ppm of solid compound used. This may be called the Cysticidal Constant (as Cl_2).

The report also shows how this concept can be used for standard evaluation and testing of germicidal substances. For example, let us calculate cysticidal constants, at 23°C and 30 minutes contact time for various species.

Substance	Cysticidal Dose ppm Cl_2	Cysticidal Constant liters/g	Molar Cysticidal liters/mole	Cysticidal Constant (as Cl_2)
HOCl	1.2	1130.00	59000	833
OCl^-	480.0	2.87	148	21
$NHCl_2$	2.0	825.00	71000	500
NH_2Cl	5.5	251.00	12900	182

From the constants one may calculate the disinfecting value for cysts of any combination of these ingredients by summing the concentrations of the disinfecting materials in ppm, each multiplied by its cysticidal constant.

This additive principle can be extended carefully for different disinfectants at various conditions of temperature and contact time.

DESTRUCTION OF BACTERIAL SPORES BY HALOGENS

Studies were conducted on the destruction of the spores of *B. anthracis* and *B. metiens* with the following purposes in view:

1. to determine the resistance of bacterial spores as a group in the scale of organisms that may be present in water to be disinfected;
2. to shed light upon the mechanism of cell destruction by halogens;
3. to investigate the possibility of substituting spores for cysts of *E. histolytica* in pilot experiments on water disinfection.

The results obtained can be summarized for various disinfecting chemicals:

Solutions of Chlorine and HTH

It was found that:

1. Within a pH range of 4 to 9, the active ingredient in solutions of chlorine and HTH is the unionized HOCl, and that the basic residual requirements to kill 1250 anthrax spores per ml for 10 minutes contact time is almost six times as much HOCl as is needed to kill 30 cysts of *E. histolytica* per ml. For 30 minute kill the corresponding increase is less than twofold.
2. For given contact periods (between 10 and 60 minutes) the required titrable chlorine residuals, in the form of HOCl, vary inversely as the three halves power of the contact times; conversely, for given residuals the required contact periods vary inversely as the two-thirds power of the residual.

3. The temperature effect may be expressed in terms of Van't Hoff-Arrhenius equation where the energy of activation is about 7800 calories with a Q10 of 0.62, signifying that the required contact time decreases by 38% for an increase in temperature of 10°C. Also the Q10 for dosage is 0.49, signifying that the required dosage decreases by 51% for every rise in temperature of 10°C.

4. The complete formulation of the requisite titrable chlorine residual needed for 100% kill of anthrax spores by solutions of chlorine or HTH is

$$R = 99 \frac{1.073^{(25-T)} N^{2/9}}{t^{3/2}} \left(1 + \frac{K}{[H^+]}\right)$$

R = the required titrable residual chlorine in ppm

T = temperature of the water in °C

t = time of contact in minutes

N = number of spores per ml

K = ionization constant of HOCl

$[H^+]$ = hydrogen-ion concentration of treated water

Solutions of Chloramines

The pH reaction exerts a profound effect upon the disinfecting power of the chloramines. Depending upon pH, varying proportions of monochloramine or dichloramine are formed. It has been shown that the controlling sporicidal ingredient is $NHCl_2$.

On the basis of contact time, 1 ppm of titrable chlorine in the form of $NHCl_2$ will take 4.2 times as long to kill anthrax spores as 1 ppm of titrable chlorine in the form of HOCl.

Comparison of Different Halogens

Within the limitations of the experiments, the following comparisons can be set up to indicate the relative efficiency of the four halogens against the spores of anthrax. All values are for water temperatures of 25°C and average spore concentrations of 26,000 to 39,000 per ml.

Halogen	Spores per ml	Time required to achieve 100% kill *B. anthracis* at a residual concentration of 10 ppm (minutes)
HOCl	26,000	14
$NHCl_2$	37,000	67
HOBr	39,000	38
I_2	30,000	35 (for 90% kill)

According to these figures the order of sporicidal effectiveness of the four halogens is HOCl, HOBr, $NHCl_2$, and I_2 at a concentration of 10 ppm. Iodine, although coming off worst in this comparison, possesses the outstanding advantage over the other halogens that its effect is substantially independent of pH. Unless pH is controlled, the requisite amounts of chlorine and bromine must be much higher at higher pH values.

Destruction of Spores of *B. metiens*

The time (minutes) required to kill the spores of *B. metiens* at a residual halogen concentration of 25 ppm, at 25°C for different species is given below:

Halogen	Spores per ml	Time for 90% kill, mins.
HOCl	12,000	1.3
HOBr	21,000	13
I_2	8,800	73
Succinchlorimide	9,500	29

It may be mentioned here that this data is less reliable than for B. anthracis for statistical reasons.

Comparison of Test Spores

Laboratory data showed that the time required to destroy the anthrax spores is about three times as long as for the spores of B. metiens. The time-concentration relationship for B. anthracis and B. metiens are $R^{0.9}$ t = 63 and $R^{0.67}$ t = 65 which indicates that the length of exposure is relatively more important for B. anthracis than dosage.

DESTRUCTION OF NON-SPORULATING ENTERIC BACTERIA IN WATER BY CHLORINE COMPOUNDS

The primary aims of these studies were:

1. Comparison of the bactericidal efficiencies of available chlorine compounds.

2. Determination of the effect of hydrogen-ion concentration on the release of active chlorine.

3. Investigation of the susceptibility of the various chlorine compounds to interfering substances such as carbonaceous and nitrogenous materials of plant and animal origin that are commonly present in polluted waters.

4. Determination of the effect of water temperature on the rate of bactericidal action.

5. Determination of the relative resistance of typical non-sporulating enteric bacteria organisms.

Bactericidal efficiencies of the following chlorine compounds were investigated:

1. chlorine
2. HTH
3. standard halazone tablets
4. chloramines
5. succinchlorimide tablets
6. 1-chloro -5, 5-dimethyl - hydantoin (RH-915)
7. chlorine dioxide
8. N-chlor saccharin
9. Japanese water disinfectant

Comparison of Compounds Tested

In general, for a given pH and temperature, the bactericidal efficiencies of all chlorine compounds that hydrolize to HOCl are of the same order of magnitude. To compare the required dosages of various disinfectants at 25°C., the reduction in bacterial population from 100 million per 100 ml to 5 per 100 ml in 10 minutes was considered.

Agent	Bactericidal Dose	Final pH
Chlorine	3 ppm	7.5
HTH	4.4 ppm (as Cl_2)	8.2
Standard Halazone	2 tablets per liter (5 ppm as Cl_2)	7.8
Chloramine	> 3 ppm Cl_2: 3 to 13.5 ppm NH_3	7.9
Succinchlorimide	1 tablet per liter (6.5 ppm Cl_2)	7.2
RH-915	4 ppm as Cl_2	7.4
Chlorine Dioxide	2 ppm (as ClO_2)	7.5
N-Chlor Saccharin	> 6 tablets per liter (6 ppm Cl_2)	6.6
Japanese Disinfectant	> 2 drops per liter	7.8

In addition the following conclusions were drawn or confirmed:

1. Lowering of pH brings about an increase in bactericidal efficiency.

2. In accordance with Van't Hoff-Arrhenius Law, the rate of disinfection decreased with temperature.

3. E. Coli is more resistant to chlorine than Salmonella Schottmulleri, S. dysenteria and E. typhosa, and as such is justified as the test organism.

4. The presence of ammonia in water decreases the rate of bactericidal action of added chlorine considerably.

5. Organic pollution decreases the bactericidal efficiency of chlorine by competing with the bacteria for the available chlorine and, in some cases, by providing protection for bacteria enmeshed in clumps of debris.

DESTRUCTION OF NON-SPORULATING ENTERIC BACTERIA IN WATER BY IODINE PREPARATIONS

The principal aims of this study were: (1) To ascertain, for canteen water sterilization, the minimum amount of elemental iodine required for effective destruction of non-sporulating enteric bacteria in contact periods of not more than 10 minutes; (2) To determine under similar conditions of test the relative bactericidal efficiencies of different tablet preparations of elemental iodine so as to find the most effective preparation for field use; (3) To determine the susceptibility of various iodine preparations to interfering substances such as organic materials of animal and plant origin, clays that are commonly present in polluted natural water, and also of carbonate alkalinity; (4) To determine the effect of water temperature on the bactericidal efficiency of iodine preparations.

Organisms tested:

1. *Esch. coli*
2. *Eber. typhosa*
3. *Sh. dysenteria*
4. *Sal. Schottmulleri*
5. *Vibrio Comma*

Compounds or tablets tested:

1. Aqueous solutions of elemental iodine
2. Bursoline tablet No. 1
3. Bursoline No. 2
4. Bursoline No. 3

5. Globaline tablet
6. Alure tablet
7. IFI
8. Burroughs Wellcome tablet No. 4

Discussion of results

The standard of effectiveness was set on a reduction of bacteria from a number of 100 million per 100 ml of water to 5 per 100 ml in 10 minutes of contact time. The following facts are revealed by this analysis of the data published in this report.

1. Effect of Iodine and Iodide Concentration on Bactericidal Activity of Elemental Iodine: Iodide is required for stabilization of tablet preparations and for quick liberation of elemental iodine. It was observed the iodide contents of the tablets do not affect noticeably the bactericidal activity of iodine. It was also seen that 5 ppm of initial and 3 ppm of residual iodine will ensure effective destruction of E. coli in "warm" tap water.

2. Bactericidal Efficiencies of Bursoline Tablets: Whereas Bursoline No. 1 and 2 failed to produce effective destruction of E. coli and other organisms, one Bursoline No. 3 tablet was effective in their complete destruction in a liter of tap and natural water and even killed coli-aerogenes in 10 percent filtered sewage above a temperature of 7°C. Below this temperature, 20 minutes of contact were required.

3. Bactericidal Efficiency of Globaline, Alure, and IFI Tablets: All three tablets have essentially the same bactericidal efficiency as that of Bursoline No. 3 under the same conditions (discussed

above). It was, however, observed that wherever there was "heavy" iodine demand in the water, one tablet of Globaline per quart would not insure safety and two tablets were required.

4. *Effect of Interfering Substances Present in Naturally Polluted Water*: It was observed that the natural river, brook and pond waters and tap or distilled water containing 10 percent sewage had some iodine demand but this did not seriously affect the bactericidal efficiency of any of the compounds or tablets tested.

5. *Rate of Destruction of Bacteria and Effect of Temperature*: The data obtained on Bursoline No. 3, Globaline, Alure, and IFI tablets show that the greatest bactericidal activity takes place in the first minute of contact, and that most of the destructive work is accomplished in the first 5 minutes. After this the survivors die off more slowly. This is true at all temperatures tested (3°C to 25°C), although the death rate is slightly reduced as the temperature is lowered. It may be mentioned here that the effect of temperature on the rate of kill is not as great for bacteria as it is for amoebic cysts.

6. *Bactericidal Efficiency of Burroughs Wellcome Tablet No. 4*: The data obtained shows that the bactericidal efficiency of this tablet, when properly used, is essentially the same as that of other iodine preparations.

7. *Difference in Resistance of Different Species of Pathogenic Bacteria*: The data obtained shows that *E. coli*, *E. typhosa*, *Sh. dysenteria*, and *Sal. Schottmulleri* are almost equally resistant to iodine tablets but *Vibrio Comma* is definitely less resistant then *E. coli*.

RELATIVE BACTERICIDAL POWER OF HALOGEN COMPOUNDS

The relative bactericidal power of the halogen compounds and their mechanism of cell destruction were evaluated by a series of tests at low concentrations of disinfecting agents and with small numbers of *E. coli*. Because of the small amounts of disinfectants involved, modifications in the preparation of the suspending fluid were necessary to remove all external halogen demand.

COMPOUNDS: The compounds tested fall into five groups.

Group 1

a. HTH
b. Dactin
c. Halazone

Group 2

a. Elemental Bromine

Group 3

a. N -iodosuccinimide
b. Iodine chloride

Group 4

a. Succinchlorimide
b. Chloramines -Class 1
c. Chlorine Dioxide
d. Monochloramine - T
-Class 2
e. Azochloramide
f. N-Chloracetamide -Class 3

Group 5

a. Elemental Iodine

b. Succinimide periodide

Discussion of Results

For the hydrolyzing chlorine compounds of Group 1, the liberated hypochlorous acid is the major bactericidal agent. While HTH is practically 100 percent hydrolyzed at pH 7, the observed molar concentrations of Dactin and Halazone can be adjusted to equivalent HOCl concentrations by multiplying them by their relative hydrolysis constants, 30 percent and 45 percent, respectively.

Group 2 contains elemental bromine only which was at least 99.9 percent hydrolyzed to HOBr at the concentrations and pH values employed. Disinfecting action must be, therefore, ascribed to HOBr released.

Group 3 compounds hydrolyze almost completely to hypoiodous acid and thus should give equivalent kills at equal concentrations of iodine or HOI.

Comparing the first three groups which include hydrolyzing halogens, it is observed that the mode of action exhibited by the hypohalous acids is similar, but the individual groups decrease in efficiency from HOCl through HOBr to HOI in the order of their occurrence in the periodic table.

Group IV contains three types of non-hydrolyzing chlorine:

1. A class of relatively high oxidation potential, class 1.
2. A class of relatively low oxidation potential, class 2.
3. A class of very feeble oxidation potential, class 3.

Class 1 is seen to possess about 100 times the bactericidal efficiency of class 2 and about 1000 times that of class 3. However, insufficient knowledge of a chemical properties of these compounds precludes any further generalization.

Tests with compounds of group 5 illustrate the disinfecting action of elemental iodine or the I_3^- ion. While the mode of occurrence of iodine in solution is not comparable to that of the more usual halogen hypoacids, the resulting disinfecting action is stronger than would be predicted either on the basis of oxidation potential or relative size of molecule. There is either a specific action of the iodine, or the element in its simplest molecular form is a more efficient penetrating agent than HOI, molecular weight notwithstanding.

Summing up, it is felt that while the halogen compounds tested seem to show a common mode of destruction of bacteria in water, the differences in bactericidal efficiency between the various compounds and the marked differences between the several groups of compounds strongly suggest that at least two main factors govern the activity of these compounds, namely:

1. The penetrating or diffusion efficiency of the compound. This property is probably governed by the size of the molecule, the ionic configuration, and whether the substance is in its elemental state.

2. The oxidizing activity of the compound. This may be measured by the oxidation potential.

SURVIVAL IN WATER AND SEWAGE, AND DESTRUCTION IN WATER BY HALOGEN COMPOUNDS, SYNTHETIC DETERGENTS, AND HEAT, OF Leptospira icterohaemorrhagiae

Leptospirosis, also known as infectious jaundice, or Weil's disease, may occur sporadically as an occupational disease particularly among fish cutters, slaughterhouse workers, miners, and sewer workers or as a waterborne disease. The primary source of infection is chiefly, if not solely, the sewer rat.

Very little information is available on the resistance of the organism responsible for leptospirosis, *L. icterohaemorrhagiae*, to disinfectants. In view of this situation, carefully controlled experiments were performed to determine the survival in water and sewage, as well as the resistance to disinfectants and heat, of *L. icterohaemorrhogiae*.

The results of this study may be summarized as follows:

1. Culture-produced *L. icterohaemorrhaogiae* may survive in water and related fluids from 12 hours to over 3 months, depending upon the nature of the fluids.

2. In tap water without bacterial contamination, the leptospira survived for over 4 weeks at neutral pH when a small amount of food substance was present. The survival time is expected to be considerably shorter in the absence of food. In tap water with air contamination, the survival period of leptospira was almost cut in half.

3. Both low and high pH values (5.0 and 8.5) were detrimental to leptospira, especially the low values.

4. The presence of bacteria and other microorganisms probably was detrimental to leptospira. In sewage the survival of leptospira was only 12 to 14 hours but rose to 7 to 8 days when the sewage was diluted with tap water to one percent of its strength. The addition of food substances in the presence of bacteria was harmful to the survival of leptospira because bacterial activities were increased.

5. A high salt concentration is probably detrimental to leptospira. The survival of leptospira in sea water was reduced to 18 to 20 hours where the salt content was 2.2 percent.

6. Normal water temperatures affected the survival of leptospira in three ways. At low temperature, multiplication was retarded, but the life span of individual organisms was increased; at higher temperatures, multiplication was favored, but the life span of individual organism was shortened; and an increase in temperature in the presence of bacteria shortened survival by favoring bacterial growth.

7. Halazone (in solution) at neutral pH value and 25-26°C, killed all leptospira in 3 minutes when the titrable chlorine content was 1.0 ppm. Its leptospiral efficiency was better than that of iodine.

8. Calcium hypochlorite solutions at 25-26°C destroyed all leptospira at pH 5 in 1 and 3 minutes with titrable residual chlorine concentrations of 0.5 and 0.3 ppm respectively. At pH 8 the leptospiricidal titrable chlorine residuals for 1 and 3 minutes of contact were raised to 6.0 and 3.0 ppm respectively.

9. Cationic detergents like Ceepryn, Finanol and Sapamine at neutral pH and 25-26°C killed all leptospira in 5, 10, 30 and 60 minutes at dosages of about 30, 20, 10 and 7 ppm respectively.

10. The thermal death points of *L. icterohaemorrhagiae* in distilled water were 25-30 minutes at 45°C, 5-10 minutes at 50°C, 10 seconds at 60°C, and less than 10 seconds at 70°C.

11. On the whole, this organism is definitely less resistant to disinfectants and heat than are most of the non-sporulating pathogenic bacteria.

INACTIVATION OF THE VIRUS OF POLIOMYELITIS BY BURSOLINE NO. 3 AND HALAZONE IN WATER

Although statistically significant kills of virus were obtained both with Bursoline No. 3 and Halazone, an examination of the experimental findings led to the conclusion that the conditions of experimentation imposed by use of the Lansing strain of poliomyelitis did not permit the statement of clear-cut conclusions. In substance it can be said that treatment with halogens "probably" destroys the exposed virus but fails to reach the protected virus.

VIABILITY AND DESTRUCTION BY HALOGEN COMPOUNDS OF THE VIRUS OF MOUSE POLIOMYELITIES (THEILER'S VIRUS) IN WATER

In order to obtain more precise information concerning the survival and resistance to halogen compounds of a virus in water, experiments were conducted under a variety of conditions to evaluate the effect of certain controllable factors on the survival of Theiler's virus on the viricidal efficiency of certain halogen compounds. Theiler's virus was selected for the experiments for the following reasons:

1. This virus is not infrequently found in the intestinal canal of healthy mice and so may represent a virus of enteric origin in the absence of a better agent.

2. Intracerebral inoculation of this virus into mice produces a fatal disease with characteristic symptoms even at high dilutions. Hence a highly purified suspension may be prepared without losing much of a potency of the test preparation.

Conclusions

The viability of virus in clean unpolluted water appears to be very great. Available information indicates that the survival is longer than that of amoebic cysts and non-sporulating enteric bacteria such as *Eber. typhosa*. As for parasitic bacteria and protozoa, survival of virus is greater in clean water than in polluted water. Foraging and enzymatic activities of saprophytic organisms may be responsible for the more rapid kill in polluted water. Temperature effects, to some extent, can be explained in the same terms.

The destruction of virus by disinfectants appears to be of the same order of magnitude as that of most pathogenic non-sporulating bacteria. "Discovery" of the fundamental rates of kill, however, is obstructed by the nature of the virus preparation with which tests must be conducted. Unless a virus suspension free from protoplasmic masses can be obtained, it is not possible to determine the resistance of the naked virus. If, under natural conditions in water, on the other hand, virus is found imbedded in protecting particulate matter, complete destruction of such virus by chemical disinfectants alone poses a problem that may be difficult to solve. Physical removal of the sheltering masses by coagulation and filtration would then offer a possible means for the protection of drinking-water supplies.

RESIDUAL CONTAMINATION AND COINCIDENTAL DISINFECTION OF THE LIP AND NECK OF CANTEENS

When a standard Army canteen is filled by dipping it into a contaminated body of water, the outside lip and neck are contaminated and, under normal conditions of use, remain so even though the water in the canteen itself is disinfected by adding a suitable disinfecting tablet to the collected water. This fact was amply proved by a number of tests conducted in the laboratory.

Coincidental Disinfection of the canteen lip and neck

Three methods for insuring the disinfection of the canteen lip and neck were investigated:

1. Cork wafer removed from cap to prevent full seating of the cap in the lip.
2. Small hole (1/16 inch) drilled through the neck.
3. Cap not screwed home during disinfection.

All of these methods proved to be effective, but the third method appeared to be the most practical one, since it prevented undesired leakage from the canteen in use.

Recommendation

To insure coincidental disinfection of the lip and neck of the canteen, it is recommended that the canteen cap be replaced loosely after the disinfecting tablet has been added in order to allow a little leakage from the canteen when it is shaken. After shaking, the canteen cap may be screwed home.

To insure automatic disinfection, a modification in the design of canteen is suggested. This modification involves:

1. extension of the canteen neck about 3/4" above the threaded portion; and

2. provision of a cap that leaves an open space of 1/16" to 1/8" around the lip and outer neck.

3. To afford a tight seal and prevent leakage, a sealing ring should be inserted, to bear against the upper threads in much the same way that the cork wafer bears against the lip of the present canteen.

In this canteen, water to which a disinfecting tablet has been added should wash the lip and neck either during initial shaking or by splashing during marching or riding. With modified design, no reliance need be placed upon the user's ability to read and follow instructions.

TOXICITY OF IODINE AND IODINE COMPOUNDS

Since iodine is a physiologically active element, the use of this element as a water disinfecting agent is a questionable matter. Consideration need also be given to the compatability of the disinfecting compounds with the use of various commonly used drugs. In this connection studies were conducted by the following authorities:

1. Dr. Otto Krayer, Dept. of Pharmacology, Harvard Medical School;
2. Division of Pharmacology, Food and Drug Administration;
3. U. S. Army Medical Research Laboratory, Fort Knox, Kentucky

The report on the first of these investigations is reproduced in this report. All these studies and the experiments done at Harvard indicate that ingestion of iodine-disinfected water by healthy male adults should have no injurious effect.

DISINFECTING PROPERTIES OF SYNTHETIC DETERGENTS

The synthetic detergents are organic compounds of relatively large molecular size. Although they exhibit hydrophobic properties, they are soluble in water. Since the adhesive force between these substances and water is greater than their intermolecular cohesive force, they lower the surface tension of the water and tend to concentrate at liquid-liquid, liquid-solid, and liquid-gas interfaces. Hence, they are also known as surface-active agents, surface tension depressants, and wetting agents. The synthetic detergents are classified as neutral, cationic, or anionic detergents, depending upon whether they are undissociated, dissociated with cationic hydrophobic radicals, or dissociated with anionic hydrophobic radicals, respectively.

A number of detergents of all kinds were studied for their disinfecting properties and related aspects. Some of the conclusions drawn were as follows:

1. Of the synthetic detergents studied, at least seven of the cationic substances were found to be effective cysticides, the single neutral detergent was somewhat less efficient, and three anionic detergents showed no promise.

2. For the disinfection of drinking water, the safe cysticidal dosage of the most effective substances tested was about 30 ppm for contact periods of 10 minutes, and the required dosage was decreased to 10 ppm as the contact period was lengthened to two hours.

3. Detergent requirements became greater as the density of the cysts to be killed was increased.

4. Hydrogen-ion concentration appeared to have little influence on the cysticidal activity of the detergents examined.

5. The presence of suspended organic matter was of some significance.

6. Temperature effects were marked, as in all chemical disinfection systems.

7. Water containing minimal cysticidal dose of one of the effective detergents had a tendency to foam when shaken. The resulting suggestive appearance and general sliminess of the water elicit an unsatisfactory physiological responses.

More important than any of above findings is a lack of information on the physiological effects that the synthetic detergents may have on human beings. Until these matters are fully explored, use of the synthetic detergent for the disinfection of drinking water must necessarily remain in an experimental stage.

CHEMICAL AND PHYSICAL PROPERTIES OF DISINFECTING TABLETS STUDIES IN THE PROJECT

A good water disinfecting tablet must have the following properties:

A. Packaged tablets during shipment, storage and use

  1. High thermal stability
  2. High resistance to humidity
  3. High resistance to mechanical disintegration

B. Tablets removed from container and added to water

  1. Rapid dissolution
  2. Full release of active ingredient

Let us consider each of these factors in order of their importance.

Time of Dissolution of Tablets

Some acceptability tests carried out on the soldiers in the field indicated that any soldier would be impatient with a disinfecting agent if it takes more than 10 minutes to complete its germicidal effect. Thus, the ideal tablet must dissolve as well as disinfect the water in less than 10 minutes.

Experiments were conducted to compare the times of dissolution of the various agents under consideration. These agents include the following:

1. Alure nitrate
2. Burroughs Wellcome No. 4
3. Bursoline tablets
4. Globaline tablet

5. IFI tablet
6. Standard halazone tablet
7. Extra strength halazone tablet
8. Lambert tablet
9. Chlor-dechlor tablet
10. Chloramine T tablet
11. TGHI

The results indicate that tablets of Alure, Bursoline No. 3, Bursoline mud, Globaline and TGHI disintegrated and dissolved in less than one minute, and that IFI and Burroughs Wellcome No. 4 tablets took somewhat longer. Standard halazone required 7½ minutes. It may be pointed out that these dissolution times are for one liter of water at 23°C where the one liter volumetric flask was inverted end-over-end continuously, causing the tablet to drop through water until it was dissolved. It is also important to note at this point that the disintegration of most of the tablets is not primarily a function of the disinfecting ingredient but rather of the filler and expanding agents used in the tablets.

Effects of Storage and Humidity on Dissolution Time

In general, storage at room temperature and under 100 percent humidity increased the time of dissolution of most of the tablets but storage at 140°F and room humidity did not appear to affect the dissolving characteristics of the tablet.

Effect of Temperature on Dissolution Time

In general all compounds obeyed Van't Hoff-Arrlenius rule substantially but iodine compounds dissolved much faster at all temperatures.

Effect of Pooling on Dissolution Time

"Pooling" means the creation of a zone of increased concentration of the dissolved materials and as a consequence more rapid occurrence of intended chemical reactions. All iodine tablets containing tri-iodides are not affected by "pooling" which is actually disadvantageous under field conditions since it is impossible to assure pooling under conditions of tablet uses (Tri-iodide dissolved most rapidly in the absence of pooling).

Thermal Stability of Tablets

Water disinfecting tablets designed for global use must be capable of withstanding not only prevailing extreme air temperatures but also the heat developed in storage warehouses, in the holds of vessels, or under a tarpaulin in the tropical sun. The agents under consideration were subjected to accelerated storage tests at 140°F and room humidity to determine the rate at which the tablets decompose and at what rate the active ingredients are dissipated.

Thermal Stability of Iodine Compounds

Thermal stability was determined by placing flat dishes containing iodine powders or tablets in an oven at 140°F and observing the rate at which weight was lost. The order of stability was as below:

1. Alure
2. IFI
3. Globaline
4. Bursoline

Thermal Stability of Chlorine Compounds

At 140°F and room humidity the chlorine compounds studied, with the exception of halazone tablets and vials of chlor-dechlor, were found to be unstable. There was no appreciable loss in available chlorine in the case of halazone even after 20 days. On the other hand HTH powder exposed for 25 days lost 100 percent of its available chlorine. In fact, all hypochlorites tested were found to be extremely unstable.

Resistance to Humidity

To determine the relative stability of tablets and compounds in humid atmosphere, such as those encountered in jungle warfare, a series of experiments were conducted at 100 percent, 79 percent and 55 percent humidities. That resistance to humidity must be fundamentally incompatible with rapid time of dissolution seems obvious; yet the experiments showed that some of the fastest dissolving tablets, notably globaline and IFI are more resistant to humidity than slow dissolving tablets such as halazone.

The tests were based on a comparison of gain in weight at 100 percent humidity at room temperature. Out of Bursoline, Alure, IFI, TGHI and Globaline, the last is the least hygroscopic. During similar experiments with chlorine compounds, standard halazone was found to be extremely hygroscopic.

Similar tests were conducted with various tablets at 79 percent and 55 percent humidity. Again, globaline was found to be far superior to halazone.

Simulated High Humidity Field Tests

In order to gage resistance to humidity and thermal stability during actual use in the field, bottles of bursoline, globaline and halazone tablets, with and without cotton plugs, were placed in a control room held at 80 to 90 percent humidity and approximately 80°F. Every two hours during the day each bottle was opened for a minute and a tablet was withdrawn. Over a three-week period, none of the compounds showed an appreciable loss of strength, and there was little variation between the bottle with or without cotton plugs.

Corrosion of Canteens

To compare the corrosive action of iodine with that of chlorine preparation on G. I., aluminum and steel canteens, a series of experiments was conducted with solutions of globaline tablets and halazone tablets. The normal dosage recommended for use in water disinfection were quadrupled in order to accelerate corrosion. Thus, globaline treated water contained 32 ppm of titrable iodine and halazone treated water contained 20 ppm of titrable chlorine.

Drip Tests

These tests involved the flushing of the halogen treated water upon experimental metals for about 9 hours over a period of 30 to 50 days. The same solution was used over and over again, but it was freshly reconcentrated each day with halazone or globaline tablets, so that the corrosion products of metal would accumulate in the solution. The loss in weight of the metal was taken as a measure of corrosion. These tests were conducted on steel and aluminum canteen metals.

The results showed that upon aluminum, globaline appears to be more corrosive than halazone, although upon steel, the action of globaline is less pronounced than that of halazone.

LABORATORY ANALYSES FOR TASTES AND ODORS AND FIELD TESTS FOR ACCEPTABILITY OF WATER DISINFECTING AGENTS

A series of laboratory experiments was conducted to measure the nature and intensity of tastes and odors produced by halogen-liberating compounds, and field tests were instituted by the Army and Marine Corps to ascertain the general acceptability of the compound by troops. Results of the two series of tests are summarized below.

Tastes and Odors

For cysticidal dosage, it was decided that under normal field conditions iodine compounds must liberate approximately 8 mg of elemental iodine while halazone must be added in sufficient amounts to release 10 ppm of titrable chlorine. The following tablets were tested:

1. Bursoline No. 3
2. Globaline
3. Alure
4. IFI
5. Standard halazone

These tests were conducted on 7 to 14 observers and the results indicate that in the "pH range commonly encountered" and for comparable cysticidal power, iodine-liberating compounds were more acceptable than halazone. In particular, globaline was found to be objectionable only when 200 percent of normal cysticidal dosage was applied to water at pH 5 and 7. In the case of the halazone tablet, objectionable thresholds were reached in the pH range of 4 to 9 at dosages anywhere between 25 to 50 percent of the normal cysticidal dosage. These experiments were performed using boiled distilled water at 23°C.

Evaluating the effect of temperature upon tastes and odors, all observers agreed that the coldest drink was the most palatable and that water at 30°C is unpleasant to drink even without disinfectants. Addition of the disinfecting tablets, however, did not make the water objectionable.

Effect of Disinfection Tablets on Beverage Powders

One of the uses to which water from a canteen is put in combat areas is as a solvent for the beverage powders which are consumed by soldiers both cold and hot. That the accepted disinfecting tablet should not react unfavorably with these beverage powders should be a desirable requirement. To this end, laboratory experiments were conducted with bursoline tablets (one and/or two per quart) upon bouillon, lemon, orange, grape and coffee powders. The bouillon and coffee powders were tested at 52°C as well as at 23°C. In no instance did the iodine compound interfere noticeably with the tastes and/or odors of the cold beverages. For hot beverages, a few observers recognized a very faint iodine taste with two tablets per quart, but none with one tablet.

Acceptability in Field Tests

This report records three different series of field tests conducted at different places. The summary of their findings is as follows:

British South East Asia Command

During Second World War, field tests were conducted with bursoline on British and Indian troops located in Burma. With bursoline "about 90 percent of the men agreed that there was no taste to the water, and the remaining 10 percent stated that they could taste a bit of chlorine." In an officers' mess, bursoline was first tried without informing the consumers of the drinks. No adverse criticism was heard. When this group was retested and informed beforeheand that bursoline was being used, only about 10 percent of the officers could detect any appreciable taste. In these instances the taste was described as slightly medicinal but not unpalatable.

Medical Field Research Laboratory

These tests were made with bursoline tablets, chlor-dechlor (CDC) vials, bromine-iodine mixture and tincture of iodine. Among 151 marines who completed the test by taking different compounds each day, the response was as follows:

79 percent preferred bursoline
12 percent preferred CDC
6 percent preferred bromine-iodine
3 percent preferred tincture of iodine

Reasons for selecting bursoline were primarily: (1) least disagreeable taste and odor; (2) ease of application; (3) short contact period.

Army Quartermaster Field Test

In the summer of 1944, field experiments were conducted by the Quartermaster Corps in Florida for the purpose of comparing the acceptability of bursoline and halazone.

Out of 48 men who purified their canteens with the two types of tablets for five days each, 96 percent chose bursoline and only

4 percent selected halazone. The stated reasons for the choice of bursoline were: (1) less time was required to purify the water; (2) in one case the iodine taste particularly appealed to the man.

From these tests, they concluded that bursoline tablets were "satisfactory in regard to taste, adequacy of printed instructions, voluntary use in field, absence of toxic effects, and general acceptability."

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13. ABSTRACT

Summary

The final report on military water disinfection practice includes a brief review of the accomplishments of the project and a detailed summary of the renowned "Harvard Report" on water disinfection.

The following reports have been prepared as part of the contract:

1. Review of the Literature on Water Disinfection
   The review is scheduled for publication in the Journal of the American Water Works Association.
2. A Critique on Water Disinfection
   The critique was prepared on the general subject of water disinfection.
3. Summary of the Harvard Report
   The "Summary" is a condensation of the most detailed research study of water disinfection ever conducted.

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