DISINFECTION—WATER AND WASTEWATER

J. Donald Johnson

DISINFECTION

WATER AND WASTEWATER

edited by

J. DONALD JOHNSON

Professor of Environmental Chemistry
Department of Environmental Sciences and Engineering
School of Public Health
University of North Carolina
Chapel Hill, N.C.

ANN ARBOR SCIENCE
PUBLISHERS INC
P.O. BOX 1425 • ANN ARBOR, MICH. 48106

Copyright © 1975 by Ann Arbor Science Publishers, Inc.
P. O. Box 1425, Ann Arbor, Michigan 48106

Library of Congress Catalog Card No. 74-14425
ISBN 0-250-40042-1

Manufactured in the United States of America
All Rights Reserved

PREFACE

This book describes the chemical and microbiological basis of the treatment of drinking, swimming and wastewater with chlorine, bromine, iodine and ozone. The main concern of water disinfection practice long has been with chlorine and its effectiveness in killing bacteria. Today, toxic compounds formation as a result of chlorination, and the questionable efficiency of chlorine as a bactericide and also as a cyst- and virucide, prompt the need for critical analysis of the alternatives to water disinfection by chlorine. The primary objective is better control of water chlorination and/or disinfection with other chemicals—to produce a minimal impact on man and our environment. Control of water disinfection practice is presented by discussing analytical methods available to assure that the minimum concentration of disinfectant has been added, consistent with the combined objectives of microbiological safety and minimum environmental impact.

Chemistry of water chlorination is discussed because the analytical methodology measures the effective disinfectant forms of free available chlorine, hypochlorous acid, as well as many relatively poor disinfectants such as hypochloride ion and the chloramines. Judging the effectiveness of microbiological disinfection depends on the quantitative assessment of the germicidal efficiency of the disinfectant. The concentration of the effective chemical species of disinfectant, multiplied by the time that this concentration has been in contact with the microorganism to be disinfected, equals the total dose. However, this total dose response to disinfection processes is not simple, but requires careful treatment and analysis.

This volume answers the question of how to assess efficiency of disinfection so that the process can be controlled with an analytical method of required selectivity, at the minimum necessary and desirable concentration (avoiding cost and toxicity problems caused when excess disinfectant is used).

Unfortunately, many problems are associated with the safety of handling gas chlorine, such as toxicity, tastes and odor, and also the ineffectiveness

of chloramine residual. This makes it necessary to continue the search for better disinfectants and application methods in water and wastewater treatment. Bromine, bromine chloride, iodine and ozone have recently enjoyed considerable renewed interest as possible alternates to chlorination. The chemistry and microbiological efficiency of these disinfectants is discussed and compared (among themselves, and especially with chlorine) in their effectiveness against the more difficult to disinfect microbiological systems: viruses and cysts.

Sanitary engineers, chemists and biologists, as well as water and wastewater treatment plant personnel will find practical data on how to do a better job in treating their water and wastewater. Tools are also presented for developing a more critical understanding of the disinfection process, for the classical old as well as the new, soon to be tried water disinfectants.

Much of this volume evolved from conferences sponsored by the division of environmental chemistry of the American Chemical Society. Considerable additional material then was required to make a complete and useful book.

J. Donald Johnson
Chapel Hill, June 1975

此为试读,需要完整PDF请访问: www.ertongbook.com

CONTENTS

CHAPTER 1

ASPECTS OF THE QUANTITATIVE ASSESSMENT OF GERMICIDAL EFFICIENCY

J. Carrell Morris

Division of Engineering and Applied Physics
Harvard University
Cambridge, Massachusetts

Although the bases for the quantitative expression of the effectiveness of germicidal agents have been known for more than 60 years, there has been relatively little application to the systematic tabulation of the relative potencies of disinfectants. Only a very small fraction of the total published literature on germicidal action is sufficiently complete or in form suitable for satisfactory quantitative analysis. Moreover, there is no consensus on which method of tabulation is most convenient. Probably the most common technique is to list the concentrations required to give a fixed percentage of kill with a given time of contact, but there is no unanimity with regard to either the percentage or the time. Other workers prefer to use the Chick's Law constant as a measure of relative effectiveness.

In recent years interest in germicidal research has been stimulated by concern for disinfection of wastewaters and inactivation of pathogenic viruses. A growing fraction of these studies give full attention to the dynamics of the germicidal process, providing the sort of information that can lead to fundamental tabulations.

It is time to try to achieve some general acceptance of terminology and forms for presentation of germicidal data. Proposals will be made in this paper in the hope that any discussion initiated will lead to a rational, systematic, and broadly accepted concordance of disinfectant efficiency for aqueous solutions.

THE SPECIFIC LETHALITY COEFFICIENT

Let us begin with a presentation of hypothetical but typical germicidal data in which the logarithms of the surviving populations of organisms, N, are plotted as a function of t, the time of contact of germicidal agent with the organisms, as shown in Figure 1-1. Often the data points for such a study are made to relate by a smooth curve of some sort, such as that of the dashed trace in Figure 1-1. Any such smoothed curve represents some degree of conceptualization, however; the soundest way to relate such data is empirically to connect the adjacent points by straight lines, as shown by the solid traces in Figure 1-1.

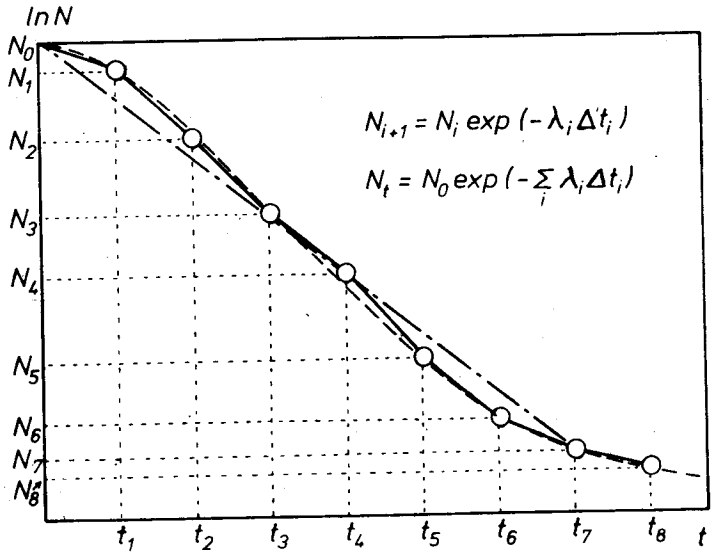

Figure 1-1. Graphical representation of model germicidal data.
N = numbers of viable organisms per standard unit sample
t = time of action of germicidal agent.

Each line segment connecting adjacent points may be represented by an equation

$$\ell n\,(N_{i+1}/N_i) = -\lambda_i\,(t_{i+1} - t_i)$$
$$= -\lambda_i\,\Delta t_i \qquad (1)$$

where $-\lambda_i$ is the slope of the line. These equations may also be written

$$N_{i+1} = N_i \exp(-\lambda_i \Delta t_i) \qquad (2)$$

Moreover, the total decrease in N over the total t intervals of time is given by the expression

$$N_t = N_o \exp \left(-\sum_{i=1}^{t} \lambda_i \Delta t_i\right) \qquad (3)$$

There is no requirement that the successive λ_i values be the same. When they are, the data conform to Chick's Law, but in the general case the λ_i may vary with the course of the germicidal action as a result of changing response of the organisms, of changing concentration or form of germicide, of changing temperature, or possibly other factors. Depending on the situation λ may be treated as a function of the time or as a function of the surviving fraction of organisms, N_t/N_o.

It should be noted also that, in common with other first-order processes, the summation of equation (3) gives the same result as would be obtained if all the intermediate points were ignored and equation (2) were written simply for N_t and N_o.

The parameter, λ, is a reflection of the ease or rapidity with which the organisms are destroyed or inactivated. It may, therefore, be termed, appropriately, the susceptibility coefficient. It contains, as some kind of factor, the concentration of the germicidal agent, the dependence being generally expressed in the form

$$\lambda_i = \Lambda_i C_i^n \qquad (4)$$

where n is called the coefficient of dilution. Substitution of this relation into the term $\Sigma\lambda_i\Delta t_i$ of equation (3) then gives the expression

$$\sum_i \lambda_i \Delta t_i = \sum_i \Lambda_i C_i^n \Delta t_i \qquad (5)$$

When C_i is unity, the right side of this equation reduces to $\sum_i \Lambda_i \Delta t_i$.

Values of Λ_i relate to the germicidal process in two ways: one, they indicate the sensitivities or resistances of organisms to inactivation; two, they give the relative potencies of disinfectants at unit concentration. Accordingly, Λ may have two designations, one the *specific susceptibility coefficient* when organisms are compared, the other the *specific lethality coefficient* when germicides are compared.

Since there is no dependence on concentration of germicide in Λ, any variation in this parameter at constant temperature should involve the properties of the organisms being inactivated. Indeed, the most likely explanation for the variations in the logarithmic rate of inactivation at constant temperature and concentration of germicidal agent that are commonly observed in laboratory studies of disinfection appears to be a clumping or aggregation of the organisms. Yet it is not at all clear that this behavior is a fundamental property of the organisms, for the methods

employed to culture and purify highly concentrated populations of microorganisms so that large N_o values may be realized may serve also to induce clumping.

If this is the case, then natural populations of the microorganisms should exhibit Λ values more nearly constant throughout the disinfection process, with values characteristic of isolated rather than clumped organisms. As a xeroth approximation and to facilitate additional considerations, it will be assumed throughout the remainder of this paper that Λ is a constant for a given reagent and organism at a specified temperature. The objective of quantitative germicidal studies then becomes the evaluation of values for Λ–specific lethality coefficients.

A problem that remains is the establishment of a single parameter equivalent to Λ for germicidal reactions in which λ is found to vary significantly during the course of the action. Methods are available for particular forms of variation; some of these appear in articles in *Disinfection*."[1] Discussion of such individual evaluations is beyond the scope of this chapter.

THE GERMICIDAL DOSE

If Λ is constant throughout the course of germicidal action, then equation (3) becomes

$$\ell n(N_o/N_t) = \Lambda \sum_i C_i^n \Delta t_i \tag{6}$$

The latter part of this expression, $\sum_i C_i^n \Delta t_i$, which can also be written as $\int C^n dt$ for situations in which the concentration of agent changes continuously as a function of time, may be termed the germicidal dose. Then

$$\text{dose} = D = \sum_i C_i^n \Delta t_i = \int_o^t C^n dt \tag{7}$$

E. L. Hall has fruitfully utilized this concept of dose to assess the effectiveness of chlorination in waters with considerable demand.[2] In his presentation, however, the additional simplification was made that $n \doteq 1.0$, so that equation (7) was reduced to

$$D = \sum_i C_i \Delta t_i = \int C dt$$

Hall justified this simplification at some length for the germicidal species and organisms with which he was concerned. The simplification appears broadly applicable to other systems, at least in approximate fashion and provided the data are used for the same order of magnitude of concentrations as those from which they were obtained. Most of the evidence for

此为试读,需要完整PDF请访问: www.ertongbook.com

n values much different from unity with potent aqueous germicides is based on scanty or unreliable data. It is difficult to carry out experiments over a wide range of concentrations to establish n reliably without encountering serious problems of bias in the measurement of time or of concentration.

TABULATION OF SPECIFIC LETHALITY COEFFICIENTS

Whether the simplification that n = 1.0 is used, the fundamental germicidal equation with Λ constant can be written in the form

$$N_t = N_0 \exp(-\Lambda D)$$

where D is the dose as defined previously. For further discussion the simplified formulation $D = \int C dt$ will be used, however.

The particular dose, $D_L = \Lambda^{-1}$, can now be called a *lethal unit* or a *lethe* of the germicide under consideration. It is the dose required to reduce N_0 to N_0/e. So, it is equal to the constant concentration needed to reduce N_0 to N_0/e within unit time. The specific lethality coefficient, Λ, then is also the number of lethes provided by unit concentration for unit time.

There is a question of units for parameters like Λ and D_L. For practical reasons of size, intelligiblity and ease of application, I favor the use of mg/l and minutes as the standard concentration and time units respectively. Molar units of some sort are needed for theoretical comparisons, but such units are not likely to have broad engineering utility.

The use of specific lethality coefficients or some similar parameter for comparison of the potencies of germicides has the major advantage that the number is greater the more potent the agent, whereas tabulations of concentrations yielding a specified fraction of inactivation in a certain time exhibit the inverse relation. So, also, do tabulations of times required for a specified fraction of kill at a standard concentration.

Values of Λ can, however, be obtained readily from the other types of data. For example, this author presented in 1967 a tabulation of concentrations giving 99% inactivation of organisms within 10 minutes.[3] The equation

$$N_t/N_0 = \exp(-\Lambda C t)$$

then becomes

$$0.01 = \exp(-10\,\Lambda\, C_{99:10})$$

from which

$$10\,\Lambda\, C_{99:10} = 4.6$$

$$\Lambda = 0.46/C_{99:10}$$

Values of Λ so computed from the 1967 tabulation are shown in Table 1-1.

Table 1-1. Values of Λ at 5°C

Λ in (mg per ℓ)$^{-1}$ (min)$^{-1}$

Agent	Enteric Bacteria	Amoebic Cysts	Viruses	Spores
O_3	500	0.5	5	2
HOCl as Cl_2	20	0.05	1.0 up	0.05
OCl^- as Cl_2	0.2	0.0005	< 0.02	< 0.0005
NH_2Cl as Cl_2	0.1	0.02	0.005	0.001

THE KILLING TIME

One of the problems encountered in simplifying the results of germicidal studies is the lack of an adequate concept of complete kill or inactivation, either practically or theoretically. Theoretically the percentage of inactivation according to standard equations is always something less than 100. Practically, the number of surviving organisms is reported as less than one per so many milliliters because of limitations of test methods and sample sizes.

There is a way around this dilemma, making use of the idea of a "whole-life" developed by H. A. Thomas for radioactive decay processes,[4] but equally applicable to any other first-order process with constant λ. The presentation that follows is essentially his, with some embellishments and emendations.

Assume a population of N_o particles—organisms in this instance—with a die-away parameter, λ, such that

$$-d\,\ell n\, N/dt = \lambda$$

The probability that a given organism will survive for a time period of zero to t is $\exp(-\lambda t)$. The probability that it will die or be inactivated is then equal to $1 - \exp(-\lambda t)$. With an initial N_o organisms at t = 0, the probability that exactly x of these will have died or been inactivated for the interval zero to t is the product of the probabilities for each of x organisms to die and each of $(N_o - x)$ to survive. This is given by

$$P(x) = \binom{N_o}{x} (1 - e^{-\lambda t})^x\, e^{-\lambda t(N_o - x)} \qquad (9)$$

The probability that *all* the organisms will have been inactivated in time t, is

$$P(N_o) = \binom{N_o}{N_o} (1 - e^{-\lambda t})^{N_o} e^{-\lambda t(N_o - N_o)} = (1 - e^{-\lambda t})^{N_o} \qquad (10)$$

Set $P(N_o) \equiv \alpha$. For example, α might be 0.5, in which case there would be equal probability for complete disinfection and for incomplete disinfection. The previous inability to describe a complete killing time is shifted to a less than unit probability of complete kill, but this latter concept is easier to handle for it is used all the time intuitively in daily living.

The rationale for this approach is, in part, the fact that the mathematical equation relates to a continuum whereas the particles decaying or organisms being devitalized are a collection of discrete unitary individuals. When the numbers involved are small and particularly when the mathematical equations yield numbers indicating survival of a fraction of an organism, then the numbers must be interpreted on a statistical basis. Results can then be expressed either as a most probable number, as is done with standard tube methods, or as the probability of finding one or more survivors. The accuracy of data or computations is not decreased by expressing them in either of these ways. The true significance and variability are made explicit.

Equation (10) may be solved for t in terms of the chosen value for α, and known or specified values for λ and N_o. The resulting time, designated $\tilde{t}$ or t_{100}, may be considered the "killing time" (Thomas's "whole life") for the population, N_o.

From equation (10) and $\alpha \equiv P(N_o)$

$$\alpha^{(1/N_o)} = 1 - \exp(-\lambda \tilde{t}) \qquad (11a)$$

$$\lambda \tilde{t} = -\ell n[1 - \alpha^{(1/N_o)}] \qquad (11b)$$

$$\tilde{t} = \frac{1}{\lambda} \ell n[1 - \alpha^{(1/N_o)}]^{-1} \qquad (11c)$$

Because of the relation between $\tilde{t}$ and λ, it is also possible to express $\tilde{t}$ or t_{100} in terms of other commonly used kinetic parameters. Thus, the relation between $\tilde{t}$ and t_{90} is given by

$$\tilde{t} = t_{100} = t_{90} \log_{10}[1 - \alpha^{(1/N_o)}]^{-1} \qquad (12)$$

Define

$$\epsilon \equiv 1 - \alpha^{(1/N_o)} \qquad (13)$$

Then from equation (11b)

$$\lambda \tilde{t} = -\ell n\, \epsilon \qquad (14)$$

From equation (13)

$$\alpha^{1/N_0} = 1 - \epsilon$$

$$(1/N_0)\,\ell n\,\alpha = \ell n(1 - \epsilon) \tag{15}$$

If the Stirling approximation, $\ell n(1 - \epsilon) \cong -\epsilon$, is made, then

$$(1/N_0)\,\ell n\,\alpha \cong -\epsilon \tag{16}$$

This approximation is valid within 5% for $\epsilon \leqslant 0.1$, corresponding to $N_0 \geqslant 10$ to 100, depending on the value assigned to α. In most instances values of N_0 will be much greater in germicidal studies.

Substitution of the approximate value of ϵ from (16) into equation (14) gives

$$\bar{t} = -(1/\lambda)\,\ell n[(1/N_0)\,\ell n\,(1/\alpha)]$$

$$= (1/\lambda)\ell n[N_0(\ell n\,\alpha^{-1})^{-1}] \tag{17}$$

This equation provides a simplified relationship between $\bar{t}$ and N_0 for the selected α and established λ.

The choice of α is an arbitrary one, depending on the certainty of complete kill that is required. Three natural or simplifying choices are possibilities for an agreed-upon standard:

(a) Choice of $\alpha = 0.5$ is an instinctive one, representing a 50% chance that complete kill has been attained. For this choice of α and with the substitution $\lambda^{-1} = t_{90} \log e$, there results

$$\bar{t} = t_{100} = t_{90} \log (N_0/0.693)$$

$$= t_{90}(0.16 + \log N_0) \tag{18}$$

(b) If somewhat less certainty of complete kill than $\alpha = 0.5$ can be accepted, then a choice of $\alpha = e^{-1} \cong 0.37$ is useful, for it leads to additional simplification. With $\alpha = e^{-1}$ equation (15) simplifies to

$$t_{100} = t_{90} \log N_0 \tag{19}$$

and the total decay or reaction time is directly proportional to $\log N_0$.

(c) If considerable certainty of complete kill is wanted, then a value of α near 0.9 seems logical. This would mean that 9 out of 10 samples would give negative findings. Such a result conforms approximately to the coliform standard that permits 10% of 10-ml MPN tubes to be positive. A convenient specific choice is $\ell n\,\alpha^{-1} = 0.100$, corresponding to $\alpha = 0.903$, for then

$$t_{100} = t_{90} \log (N_0/0.100) = t_{90} \log 10\ N_0 \qquad (20)$$

The last of these possible choices provides the most advantages for use in working with disinfectants for water systems and is suggested as a standard definition of "killing time" or "complete kill."

Each of the equations (18), (19) and (20) predicts a linear variation of t_{100} with log N_0 regardless of the particular value of α. That this variation does occur can be shown, for example, from the data of Chang on the thermal destruction of cysts of *E. histolytica.*[5] In Figure 1-2, the minimum times to achieve apparent complete kill are shown plotted against the logarithms of the initial inocula of organisms, N_0. The linear relationship is clearly shown.

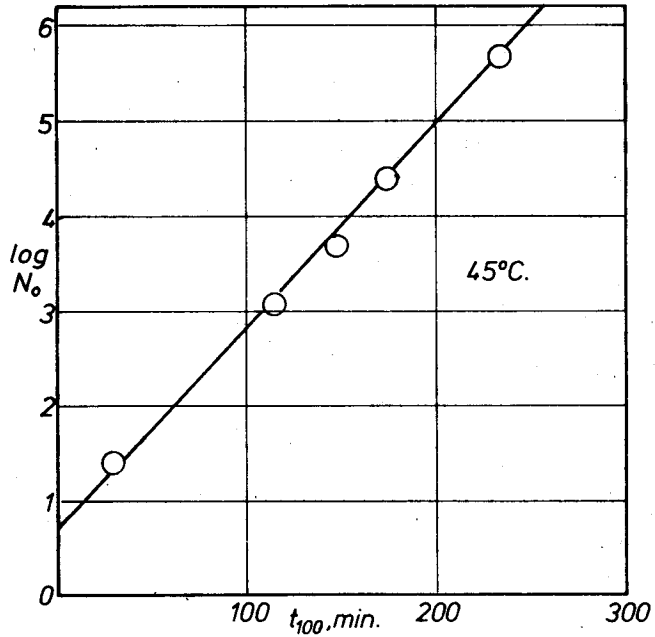

Figure 1-2. Variation in killing time with initial numbers of microorganisms. Thermal destruction of cysts of *E. histolytica* at 45°C.[5]

As pointed out by Chang, the data also suggest that he needed about six viable cysts to get a positive culture. The value of N_0 at the intercept $t_{100} = 0$ for the linear plot in Figure 1-2 may be regarded as a threshold N_0, a number of organisms required for a positive test result. It is clear that, according to the plot, values of N_0 equal to or less than the threshold

value will show complete inactivation even when no biocide is present. With an intercept of log N_o = 0.78, the corresponding threshold N_o is 6.

There remains some question about the volume of water to which N_o refers. This must be the sample size or volume in which it is expected that zero active organisms will be found. So for example if, as in the standard MPN tests, it is the portions of 10 ml in which negative results are expected 90% of the time, then N_o should be the initial population of organisms per 10 ml. The quantity, 10 N_o, is then the organisms per 100 ml, a unit already in widespread use in water and wastewater standards.

The time for complete kill is related to the specific lethality coefficient, Λ, by the relation, $\Lambda C = \ell n\ 10/t_{90}$. This yields

$$t_{100} = \frac{1}{\Lambda C} \ell n(10\ N_o) \qquad (21)$$

with equation (20). From this equation can be plotted either times required for complete kill at a given concentration(s) for complete kill in a given time, or doses for complete kill, all as a function of the initial population. Any one of these is a rational guide to disinfection practice, for it is clear that the degree of treatment needed for adequate disinfection will vary with the initial degree of contamination of the water.

REFERENCES

1. *Proc. Natl. Specialty Conf. on Disinfection* (New York: American Society of Civil Engineers, 1970).
2. Hall, E. L. "Quantitative Assessment of Disinfection Interferences," *Water Treat. Exam.* 22, 153-174 (1973).
3. Morris, J. C. "The Future of Chlorination," *J. Amer. Water Works Assoc.* 58, 1475-1482 (1967).
4. Thomas, H. A. Personal communication.
5. Chang, S. L. "Kinetics in the Thermodestruction of Cysts of *Endamoeba histolytica* in Water," *Amer. J. Hyg.* 52, 82-90 (1950).

此为试读,需要完整PDF请访问: www.ertongbook.com