

VI—A method for the preparation of pure phenanthrene is shown whereby the phenanthrene is separated from the anthracene and carbazol by dissolving in crude coal-tar solvent naphtha, and further purified by boiling with boneblack and crystallizing from 95 per cent ethyl alcohol.

VII—The effect of different alkalies as agents for the removal of carbazol is tabulated.

VIII—A table is given showing the effect of different quantities of 98 per cent sulfuric acid and water as agents for the removal of anthracene from carbazol.

ACKNOWLEDGMENT

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CHLORINE ABSORPTION AND THE CHLORINATION OF WATER¹

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INTRODUCTORY

The disinfection of waters by means of various forms of chlorine has been practiced in this country and abroad for many years. During this period a general theory of chlorination has grown up, particularly on this side of the water, which has had little or no scientific basis. The general hypothesis concerning the effects of chlorination, the proper dosage, and the nature of the chemical and biological reactions have been deduced from a few well-controlled experiments on waters of certain characteristics. The results of these experiments, however, have led to the universal adoption of chlorination for waters differing materially from those upon which earlier experimental data were made available. When, therefore, a number of water supplies were treated with standardized doses of chlorine, or its compounds, failures in performance were soon recorded.

In the supervision and control of a single water supply, the problem of chlorination offers far less difficulty than in the case of a group of water supplies, all of which have distinctive and disconcertingly variable qualities. The control of disinfection of a city water supply, supported by daily chemical and bacteriological examinations, may at least approach a scientific procedure, although surprisingly few cities even at this late date actually do more than a superficial dosing at a more or less constant rate. The supervision of chlorination becomes, however, a problem of major importance where a large series of supplies are to be treated under the direction of some central authority, like a State Department of Health. With 10 or 15

water supplies—inadequately sampled, some in the raw state, some just after coagulation, some filtered, ranging through every degree of color and turbidity, now free from organic material and an hour later loaded with surface wash—what form of control should be adopted? Here a speedy, safe, easy method of antecedent control, rather than of subsequent failure, is essential. On this phase of chlorination, the preliminary routine control of widely different types of waters, scientific literature, with some few exceptions, is silent.

In the state of Maryland, as in other states, experience indicates that, in general, chlorination control has been inadequately studied. When we bear in mind that a number of supplies are under the supervision of laymen, it becomes clear that consistently good results in disinfection are hardly attainable without the use of some presumptive indicator of an efficient chlorine dose. Presumptive tests of chlorine efficiency have been discussed by various students of the problem; but their contributions, although suggestive, have been based upon such meager experimental evidence that they cannot yet be considered definitive.

The present brief discussion is the result of a study, carried on during the past 18 months, of the application of chlorinators under variable conditions. The data here set forth are fragmentary. They are reported in order to invite attention to the extreme intricacy of the whole problem rather than as the basis of a formula designed to furnish the proper doses of chlorine and its allied compounds. It may be stated, however, that observation of the conditions in this state has served to point out a wide field for further intensive experimentation and, in this respect, the material here presented may be of some little value.

ABSORPTION OF AVAILABLE CHLORINE

The importance of the absorption of so-called "active chlorine" by different waters is somewhat ill-defined in its relation to disinfection or the elimination of objectional bacterial life. Some experimenters assert that the amount of absorption discloses little concerning the destruction of bacteria, while others assume that the chlorine consumed in "oxidizing organic matter and sometimes ferrous salts or sulfides will not effect sterilization."¹ Since the latter assumption necessarily permits an increased factor of safety in the control of the chlorination, it is probably advantageous to use the hypothesis as a base until the collection of adequate data indicates what quantitative variations therefrom may be necessary.

In order to study the significance of the absorption of chlorine by waters, it is of interest for scientific and practical purposes to obtain some idea of the factors which influence or predetermine the losses of chlorine in different waters. Owing to the complexity of conditions under which the action of chlorination proceeds, such data as the above and any conclusions pertaining thereto may be ascertained in only an empirical manner. A few apparently elementary features of chlorine absorption, therefore, are described briefly in

¹ The data submitted are the results of a study of the question of chlorination control in Maryland, upon which the writers have been detailed under the general direction of Mr. R. B. Morse, Chief Engineer, Maryland State Department of Health.

¹ Dakin and Dunham, "Handbook of Antiseptics," 1918, p. 106.

other to establish at least some salient characteristics of the phenomenon of the disappearance of the active agent in chlorination.

THE RATE OF CHLORINE ABSORPTION—A few experiments were tried to determine the velocity of absorption of available chlorine by the same water during varying time intervals. The data were collected in order to compare with similar work reported by Race.¹ The results are set forth in Table I. A comparison of

TABLE I—ABSORPTION OF CHLORINE BY WATERS AT 20° C. VARIATIONS IN K WITH TIME

SAMPLE		Values of $K = \frac{1}{t_2 - t_1} \log \frac{N_1}{N_2}$ for time intervals of		
		5 min.	30 min.	60 min.
1	Surface	0.052	0.009	0.005
2	Surface	0.069	0.012	0.006
3	Surface	0.032	0.013	0.007
4	Surface	0.041	0.013	...
5	Surface	0.082	0.018	...
6	Surface	0.066	0.017	0.003
7	Surface	0.071	0.013	0.013
8	Surface	0.082	0.023	0.015
9	Surface	0.032	0.011	0.007
10	Surface	0.099	0.026	...
11	Surface	0.036	0.015	...
12	Surface	0.017	0.007	...
13	Filtered	0.007	0.004	...
14	Well	0.014	0.005	0.003
15	Well	0.007	0.008	0.006
16	Well	0.013	0.003	0.002
17	Well	0.009	0.009	...
18	Surface	0.104	0.018	0.010
19	Surface	0.036	0.007	...
20	Surface	0.044	0.004	...
21	Surface	0.026	0.014	0.010
22	Surface	0.120	0.023	0.014

TABLE Ia—SUMMARY OF DATA IN TABLE I

Initial Chlorine Absorbed in 5 min.	Ratio K_5/K_{30}	Ratio K_5/K_{60}
0.08	1.8	1.1
0.08	1.1	...
0.10	1.0	...
0.14	4.3	6.5
0.15	2.8	3.3
0.18	2.4	...
0.26	1.8	1.3
0.31	2.5	4.6
0.31	2.9	4.6
0.34	2.8	...
0.34	5.1	...
0.38	3.2	...
0.40	11.0	...
0.45	5.9	10.4
0.53	3.9	7.3
0.55	5.6	11.5
0.56	5.5	5.5
0.61	4.6	...
0.61	3.5	5.5
0.68	3.8	...
0.70	5.8	10.4
0.75	5.2	8.6

these findings with the values reported by Race indicates that K, the velocity constant, in general, decreases with the time of contact. These values are in agreement with the conclusions noted by Race. It should be pointed out, however, that the value of K approaches a constant for different time intervals in those waters whose organic content is low. It appears, therefore, that the rate of chlorine absorption deviates from the ideal monomolecular law of chemical reaction in an increasing degree with waters of increased organic content. In other words, the monomolecular law with K constant is fairly well typified in those few waters which have only slight organic content, such as well and filtered waters, Nos. 13, 15 and 17. This is to be expected, since it is only in these latter waters that the compounds acted upon are probably of such simple chemical structure as to result in a constant reaction velocity.

COLOR AND THE RATE OF CHLORINE ABSORPTION—The use of color readings as a presumptive indicator of the

¹"Some Aspects of Chlorination," *J. Am. Water Works Assoc.*, June 1916.

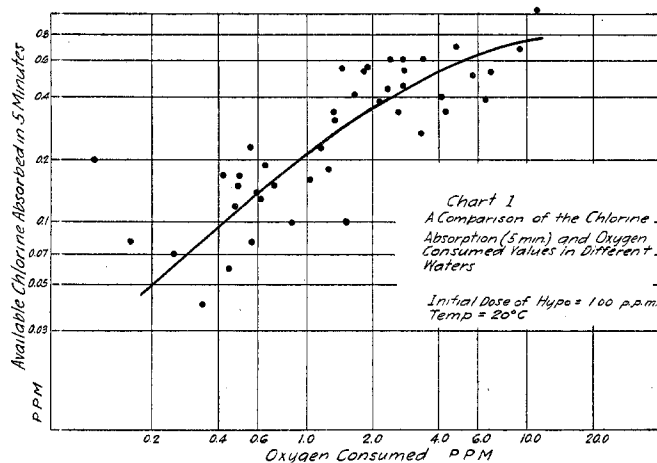
amount of chlorine which would be absorbed by a water in a given period has been suggested as a convenient procedure for routine operation of disinfectant plants. To be of any value, such readings should be the result of a long series of correlated experimental observations. Such continuous series have not been developed, it is believed, for many individual water supplies, while still less has been done in the way of comparative readings on different water supplies. Data upon this question are now being collected in this department. They are not reported in this paper on account of their insufficient number, but the evidence from the observations now available would seem to indicate that for the same water supply, changes in color are not necessarily concomitant with variations in chlorine absorption during a constant time interval, while for different water supplies the same conclusion is indicated as far as interdependent chlorine absorptions are concerned. It would appear, from the evidence now at hand, that color readings in different water supplies cannot be adapted to the prediction of chlorine absorption readings, because of the absence of any adequate conversion factor.

TURBIDITY AND THE RATE OF CHLORINE ABSORPTION

—In order to study the variation of chlorine absorption in a surface water within different ranges of turbidity, a series of 350 samples of the Potomac River water at Luke, Md., were examined during June and July 1918. A study of the turbidity readings and the chlorine absorption tests indicates practically no correlation whatever between these two phenomena, although the turbidities ranged from 0 to 90 parts per million. The Potomac River water at the above station offers an interesting illustration of the necessity for guarding against unwarranted correlations between the physical property of a water and its biochemical conduct. In the case of the above water, the chlorine absorption values (during five minutes) showed no increase whatever with increases of turbidity, but rather a slight decrease. That the absorption remained almost constant and even decreased, in a degree, with an apparent physical degradation of the water is probably explained by the fact that the Potomac River at the point under discussion contains considerable oxidizable mine wastes. Sudden rainfalls create dilutions of these wastes, but at the same time raise the turbidity readings on the river. It comes about, therefore, that the increased muddiness in the water is in reality accompanied by a reduction in oxidizable material, without a consequent increase in chlorine absorption values. The situation is somewhat analogous to the reductions in alkalinity frequently observed with rises in turbidity. It is clear from the above situation that the direct variation of dosage with increase of turbidity would have been fallacious and contrary to the demand of the water. When the attempt is made to correlate turbidities of different waters with their corresponding chlorine absorptions, even less success is experienced. This situation is to be expected in different supplies, because of the variance in character and degree of watershed pollution. It may be postulated, as a preliminary conclusion, that turbidity readings are not a

safe index of chlorine absorption for different water supplies, but may be adapted, with sufficient precautionary measures, to use for an individual supply. Even in the latter case, the conversion of turbidity to chlorine absorption is accomplished only after long studies of widely varying phases of the same supply.

OXYGEN CONSUMED AND THE RATE OF CHLORINE ABSORPTION—Inasmuch as the oxygen-consumed values of waters represent approximately the oxidizable compounds present in such supplies, it would seem that this chemical index should bear some relation to the complex action of chlorine absorption, of which some portion at least partakes of the nature of an oxidation. In order to study this phase of absorption, a series of widely varying waters, of surface and underground types and of different ranges of pollution, were examined during portions of 1917 and 1918. In all of these waters the oxygen consumed and the chlorine absorbed (5 min.) values were obtained. These readings are graphically shown on Chart 1, where the individual



and average values have been plotted, in order to permit of the construction of an empirical curve. The data there shown apparently disclose a fairly close variation of chlorine absorption with the oxygen-consumed values of different supplies. This correlation, it should be emphasized, is independent of the source or nature of the water, since the 45 waters tabulated include those from raw surface streams, deep wells, and filtered supplies.

TABLE II—A COMPARISON BETWEEN CHLORINE ABSORPTION INTERVALS AND EQUAL OXYGEN-CONSUMED INTERVALS

Oxygen Consumed Reading	Interval	Chlorine Absorbed Reading	Interval
0.5	...	0.117	...
1.0	0.5	0.211	0.094
1.5	0.5	0.290	0.079
2.0	0.5	0.350	0.060
2.5	0.5	0.402	0.052
3.0	0.5	0.449	0.047
3.5	0.5	0.488	0.039
4.0	0.5	0.520	0.032
4.5	0.5	0.550	0.030
5.0	0.5	0.577	0.027
5.5	0.5	0.600	0.023
6.0	0.5	0.620	0.020
6.5	0.5	0.635	0.015
7.0	0.5	0.652	0.017

The empirical curve indicates at once that the amount of chlorine absorbed in a definite time interval does not increase in direct proportion with the increase in pollution of the water (as measured by the oxygen-consumed test), but that the 5 minute rate of

chlorine absorption shows a decreasing acceleration with increases in pollution. In other words, increases in oxygen-consumed values appear to result in *relative* decreases in the intervals between successive chlorine absorption values. This phenomenon is made clearer by reference to Table II, wherein are compared certain values obtained from the empirical curve shown in Chart 1.

The apparent correlation discussed above has considerable practical importance aside from its use in the chlorination of water supplies. Its probable existence may result in the development of an extremely rapid presumptive indicator of the quality of a water, namely, its chlorine absorption in a definite time interval. It has been found comparatively simple, in this laboratory, for instance, to differentiate between an underground supply of good quality and a comparatively poor surface supply, simply by means of a chlorine absorption test made in 5 minutes. The information gained would seem to be capable of wider application to the entire field of water treatment. As a rapid diagnostic index of changes in quality of water supplies, the chlorine absorption test appears to offer a fruitful field for investigative effort.

CHLORINE ABSORPTION AND EFFECTIVE DISINFECTION DOSAGE

The practical effectiveness of any chlorine treatment is necessarily measured and conditioned by its ability to eliminate the significant bacterial life in the water. The preliminary determination of a dose which may be subsequently found to be effective has been the primary objective of past investigations in this field. In practically all of these methods of presumptive testing for effective dosage, chlorine absorption tests have played an important rôle. It is of interest, therefore, at this point to review briefly several of the methods of chlorine control now in use and to discuss the principles underlying their application.

American practice in the chlorination of water supplies has always been sharply differentiated from the foreign. In general, the foreign sanitarians have employed chlorine doses appreciably higher than those in use on this continent. This policy has been the resultant of a conservative conception of the whole question of chlorination and has therefore left its impress upon the modern systems of chlorination control. A study of the various methods of presumptive tests for the effective doses discloses the common assumption, independently promulgated, that the chlorine absorption in definite intervals bears some definite but apparently unknown relation to disinfection accomplishment. This definite relationship is, however, the subject of a wide difference of opinion among individual sanitarians, with always the sharp demarcation between the foreign and domestic viewpoints.

The principle underlying practically all of the chlorination control procedures is that of measuring the amount of available chlorine absorbed by the water to be disinfected in a given period of time. To this amount a factor of safety is usually added, giving a resultant so-called effective chlorine index. It is clear

that the important element in the above procedure is the time element. The time interval taken for the measurement of the chlorine absorption is dependent upon the consideration of the death rate of the bacteria under the particular conditions. A dose measured in the light of the above principle is a safe dose only if the time interval used in its evaluation is amply sufficient to provide for adequate bacterial destruction. The problem of measurement of chlorine dosage resolves itself, therefore, into the question, "What is the safe time interval for the chlorine absorption test?"

The literature of chlorination suggests various answers to this question. Adams,¹ in his discussion of the chlorination of the water for Toronto, Canada, seems to assume that 3 minutes (plus a factor of safety) is a sufficient time interval for such a test. The basis for his criterion is not apparent. He states, however, that "by conducting a series of tests it was determined that Color No. 2 represented a surplus of chlorine in the finished water that would guarantee efficiency in bacterial destruction at all times, and in the great majority of cases would not give taste or odor, and under no circumstances a bad taste or odor." Color No. 2 was equivalent to the intensity of color existing with a definite excess of available chlorine.

That such a short time interval as the above is not universally applicable is evidenced by a survey of the data reported by Race.² It would appear from a number of the experiments there cited that effective sterilization or even approximately fair destruction is frequently not obtained even after a 60 minute interval. The application of a 3 minute absorption test to such a condition would demand, of course, an auxiliary factor of safety of high proportions in order to eliminate the danger of ineffective dosage.

Dienert,³ of the city of Paris, France, approaches this problem in the conservative manner suggested in the preceding statement. He not only stipulates factors of safety abnormally high in comparison with American practice, but uses in addition a chlorine absorption time interval of 15 minutes. His procedure of presumptive testing is of sufficient interest to quote at length in this discussion. His statements follow:

For the treatment of water we use always a quantity of available chlorine equal to that absorbed in a quarter of an hour increased by 0.5 p. p. m. We estimate that to sterilize a clear water with a quantity of chlorine determined as we have just said, 3 hours contact are necessary. If, for certain reasons, we are obliged to distribute water before this delay, we must increase the quantity of chlorine and bring it up to 1.00 instead of 0.5 p. p. m.

Thus, let us take a water whose absorption of available chlorine in a quarter of an hour is equal to 0.2 p. p. m. If the water must be distributed in a very short time we would add 1.2 p. p. m. in order to sterilize it. If we should store the water longer than 3 hours, we would use only $0.2 + 0.5 = 0.7$ p. p. m. of available chlorine.

We have established, in following the bacterial content of river or turbid waters treated with doses of free chlorine of from

¹ "Water Chlorination Experiences at Toronto, Canada," *Am. J. Pub. Health*, August 1916.

² "Some Aspects of Chlorination," *J. Am. Water Works Assoc.*, June 1916; "Chlorination and Chloramine," *Ibid.*, March 1918.

³ "New Perfections in the Chlorination of Waters," *La Technique Sanitaire et Municipale*, February 1917.

1.00 to 1.5 p. p. m., that at certain moments *B. coli* was not destroyed. Safety in treatment demands the use of a dose of free chlorine a little higher than the doses given above.

Professor Santoliquido,¹ of Italy, adds to the general theory by stating that "the bactericidal action of chlorine is not instantaneous for any particular bacterium; in order that the action should result, there is always necessary a contact period, which, at a minimum, must be from 10 to 20 minutes."

Costa and Pecker² modify somewhat the system of presumptive test for chlorine dosage by eliminating the factor of safety and using their so-called "chlorine index." The index appears to differ but slightly, in its evaluation, from the usual chlorine absorption tests reported by other authors and in our own discussion. They establish as a principle or hypothesis that the useful dose for the purification of water is determined by the total quantity of chlorine fixed by the water in a given time and under definite conditions. They have determined, as a result of experience, that the initial dose of chlorine to be used in evaluating their index should be 5 p. p. m. As to the period of contact for the test, the authors have taken the figure of 30 minutes, which they state "is generally adopted for the purification of water by chemical substances."

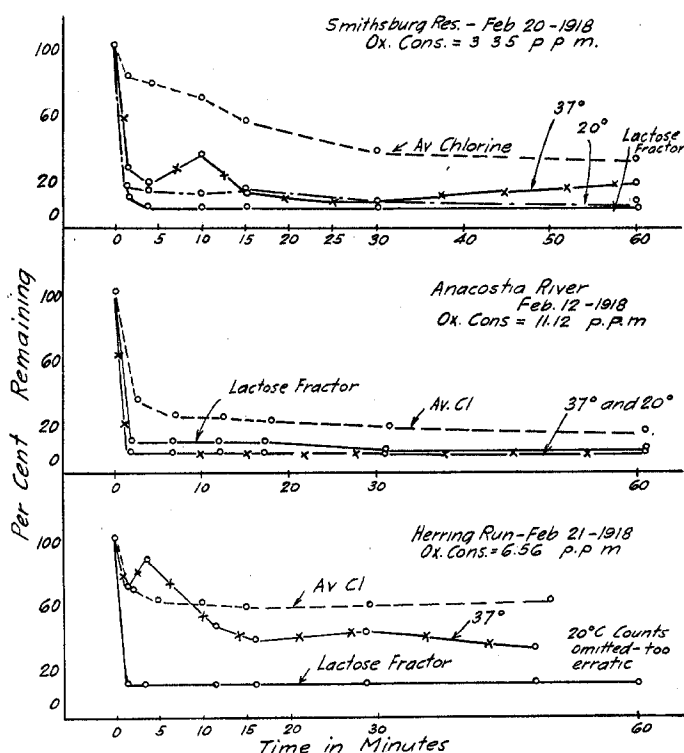


CHART 2—A COMPARISON OF THE RATES OF CHLORINE ABSORPTION AND BACTERIAL DESTRUCTION

These authors declare further, that they have been able to decide after more than 2 years' experimental work that the sterilization of water is not very often obtained if the quantity of chlorine used does not reach the figure fixed by the index, and that these latter figures give quantities sufficient for purification.

¹ "Note on the Purification of Potable Water by Calcium Hypochlorite," *Office International D'Hygiene Publique*, May 1918.

² "The Determination of the Useful Dose of Chlorine for the Purification of Water: The Chlorine Index," *Compt. rend.*, February 1918.

The foregoing discussion seems to indicate the absence of any general agreement either as to the necessary time interval for the chlorine absorption test or the relative scale of factor of safety. The evidence as to the velocity of bacterial destruction under widely varying conditions is far from complete. If the rates of disinfection on Chart 2 (experimental data) are approximately as shown, it would seem that a 30 minute absorption plus a high factor of safety is hardly necessary. It is doubtful, too, whether such factors of safety as 0.5 to 1.00 can be universally employed under such conditions as exist in Maryland, where frequently the period of contact before consumption is so brief as to preclude a dose which would result in such excessive amounts of free chlorine at the tap.

A general survey of this phase of chlorination discloses a need for additional data regarding the velocities of disinfection under actual operating conditions. That the conceptions of this phase are inadequately developed is evidenced by the wide discrepancy in the phenol coefficients of chlorine, for example, quoted in current literature.¹

FIVE OR THIRTY MINUTE ABSORPTION TEST?

For practical purposes, any rapid method of presumptive indication of efficient dosage is particularly valuable. It remains to be determined, however, whether the substitution of a rapid 5 for a safer 30 minute test will result in any practical diminution of a necessary safety factor. The demonstration of such an effect either in the positive or negative direction would demand manifestly far more experimental proof than the present writers are in a position to adduce.

TABLE III—SHOWING THE ADDITIONAL PERCENTAGES OF AVAILABLE CHLORINE ABSORBED BY DIFFERENT WATERS IN INCREASED TIME INTERVALS

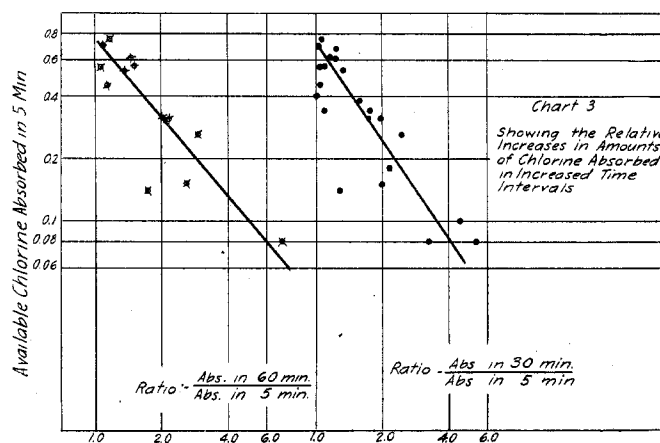
SAMPLE	Initial Dose of Chlorine = 1.00 p. p. m.			Temperature 20° C.	
	Per cent of Initial Chlorine Absorbed in			Ratio of Per cent Chlorine Absorbed	
	5 min.	30 min.	60 min.	30 min. to 5 min.	60 min. to 5 min.
1 Surface	45	47	50	1.04	1.12
2 Surface	55	57	58	1.04	1.06
3 Surface	31	60	62	1.95	2.00
4 Surface	38	60	..	1.59	..
5 Surface	61	71	..	1.17	..
6 Surface	53	70	72	1.32	1.36
7 Surface	56	61	84	1.09	1.50
8 Surface	61	79	88	1.21	1.44
9 Surface	31	53	63	1.71	2.02
10 Surface	68	84	..	1.24	..
11 Surface	34	59	..	1.74	..
12 Surface	18	39	..	2.15	..
13 Filtered	08	25	..	3.22	..
14 Well	15	30	38	2.00	2.53
15 Well	08	42	56	5.25	7.00
16 Well	14	18	24	1.29	1.71
17 Well	10	45	..	4.50	..
18 Surface	70	72	75	1.03	1.08
19 Surface	34	37	..	1.09	..
20 Surface	40	40	..	1.00	..
21 Surface	26	64	75	2.48	2.90
22 Surface	75	80	85	1.07	1.14

It is of interest, however, in connection with this problem, to refer to the experimental data shown in Table III and Chart 3. These experiments² were de-

¹ Rideal, *J. Roy. San. Inst.*, 31 (1910), 33-45, gives 2.2, while Schneider, "Bacteriological Methods—Food and Drugs," p. 260, gives 12.5.

² The determinations were all made according to the 1917 A. P. H. A. Standard Method of Water Analysis. The oxygen-consumed readings were obtained in acid digestion, with a period of digestion of 30 minutes at a boiling temperature. No corrections for oxidizable mineral substances were applied to the oxygen-consumed values, since these latter were to be used to represent the total oxygen demand of the water supply. In the measurement of available chlorine in the different experiments the temperature used was 20° C.

signed to answer in a preliminary manner the question as to the effect of increased time intervals upon the total amounts of available chlorine absorbed by different waters. In other words, what additional information is gained by extending absorption tests from 5 to 30 or 60 minutes? Chart 3, with its few empirical values, seems to suggest that the importance of increasing the period of test decreases materially with the increased values of the initial 5 minute absorptions. The evidence in Table III would appear to point to the conclusions that increased safety in dosage is occasioned by the 30 minute test in those waters where the factor of safety is least essential, whereas little additional safety is gained in waters of higher initial absorption or in those where it is most necessary.



If the 5 minute chlorine absorption test is at all indicative of the pollute content of a water, then the evaluation of a 30 minute test seems to add but little necessary information as to effective dosage. It would hardly be advantageous to use a 30 minute test, in preference to a 5, when the former increases greatly the dosages for good waters and affects but little those of poorer waters. The addition of a constant factor of safety as, for instance, 0.2 to the 5 minute absorption value would apparently accomplish the same result in the routine control of chlorination as the use of a longer absorption time interval.

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ACCURATE DETERMINATION OF SOIL NITRATES BY PHENOL DISULFONIC ACID METHOD

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Nitrates play such an important rôle in plant nutrition and the amounts present in the soil are so dependent on bacterial activities that frequent determinations of soil nitrates are important in soil fertility investigations. The two general methods used for the determination of nitrates are the reduction and the colorimetric methods. Both methods have been criticized by various investigators. The present paper is a report of work to determine how and to what extent the different errors in the colorimetric (phenol disulfonic acid) method can be overcome in soil work.