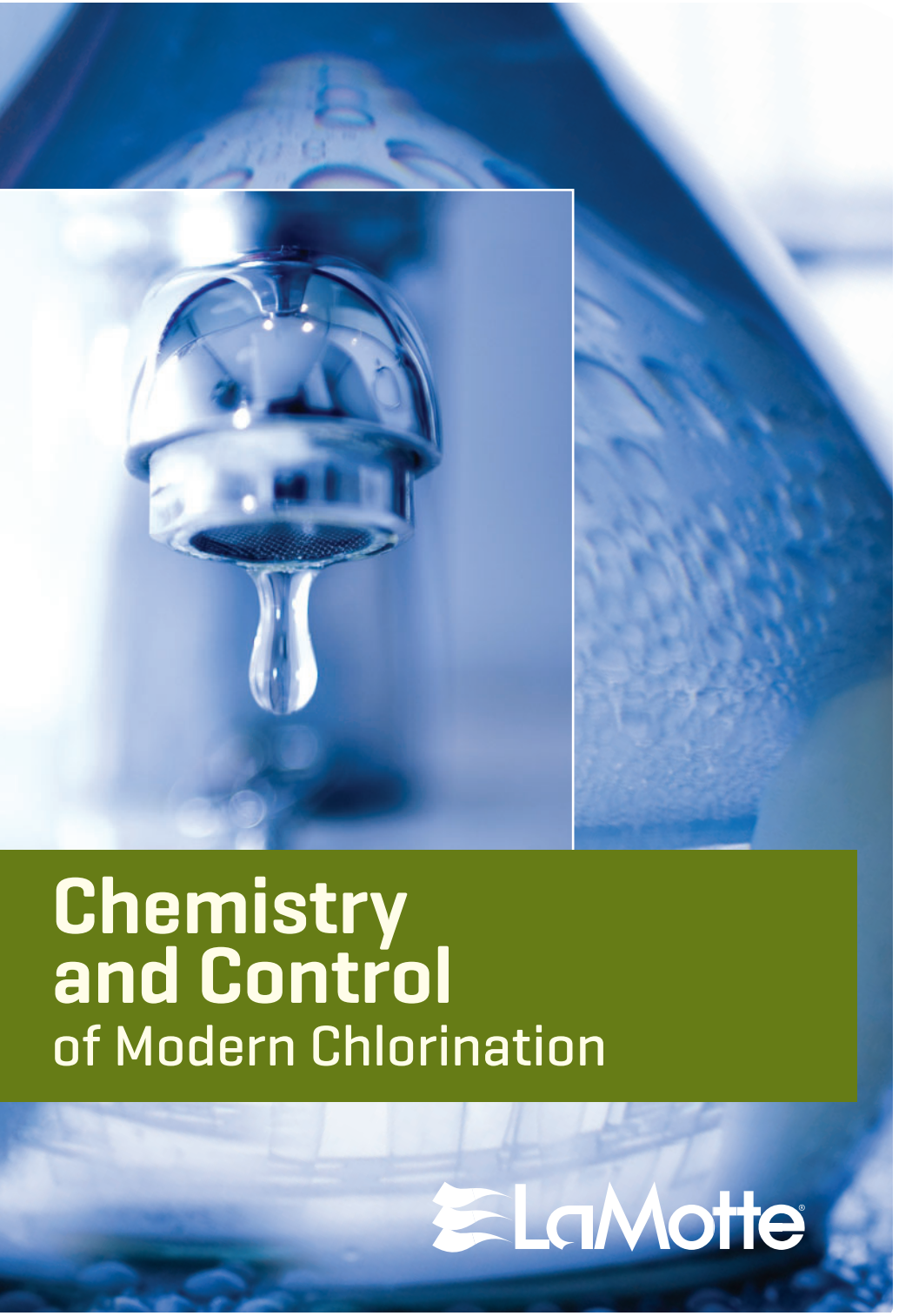

Chemistry and Control
of Modern Chlorination

LaMotte®

ABOUT THIS HANDBOOK

Test methods and specific procedures discussed in this handbook are the subject of constant research and development for the purpose of improving testing capabilities and results. These general discussions are not intended to be used as instructions for actual testing. Precise, up-to-date instructions for the various procedures described in these pages are available upon request from LaMotte.

ABOUT THE AUTHOR

In a discussion of historical developments in the Manual of British Water Engineering Practice, it is recorded as one of the "chief events" that breakpoint chlorination was first used in England at the City of Coventry in 1943. Dr. A.T. Palin, the author of this manual, was responsible for its introduction at that time. Much of his subsequent work was concerned with chlorination and other forms of water treatment, with particular attention having been directed to the development of new and improved methods of water analysis. His various procedures provided a range of simple, reliable control tests for chlorination, fluoridation, softening, and many other forms of treatment in the fields of water supply, swimming pools, wastewaters, cooling waters, boiler waters, and all types of industrial waters.

Dr. Palin was an official advisor to the Standard Methods Committee of the American Water Works Association, an active member of several of its joint task groups, and a member of the Research and Water Quality Disinfection Committees. Much of his published work first made its appearance in the journal of that association and in other American publications. Many of his other contributions to the technical literature have appeared in Canada, Japan, Spain, France, Germany, and the United Kingdom. After his service at Coventry, Dr. Palin was appointed in 1945 as the first Chief Chemist and Bacteriologist to the Newcastle and Gateshead Water Company in England. He held a Bachelor of Science Degree of the University of London, with First Class Honors, and was subsequently awarded the degree of Doctor of Philosophy for his chlorination researches. This work was also recognized by the presentation of a Gold Medal at the Public Works Congress of 1950 in London. His later work on fluoridation control methods led to his being awarded the Houston Medal of the Institution of Water Engineers for work of outstanding merit. He was a Fellow of the Royal Society of Chemistry, a past-President of the Society for Water Treatment & Examination, and a former Member of Council of the Institution of Water Engineers, the first chemist to be so honored since the establishment of the Institution in 1896. This Council, now of the Institution of the Water Engineers and Scientists, allocates each year the "Palin Award" to the author of a paper of sufficient merit.

Dr. Palin served on the Joint Working Group of the British Department of the Environment and the National Water Council responsible for the booklet, Chemical Disinfecting Agents in Water and Effluents, and Chlorine Demand 1980. This gave his DPD Titrimetric and Colorimetric procedures as the officially recommended methods. He was actively associated with the work of a similar group in the International Standards Organization. In the swimming pool field Dr. Palin acted as Honorary Consulting Chemist to the British Institute of Baths and Recreational Management.

In 1977 he retired from his position with the Newcastle and Gateshead Water Company. That year saw the inauguration by the Company of a new River Tyne Abstraction Scheme. Included in the scheme were new central laboratories which were named the Palin Laboratories, “In acknowledgement of the outstanding contribution to the Company and the Water Service made by Dr. A.T. Palin.”

Further recognition came in the Honors list of 1975, when he was appointed an Officer of the Most Excellent Order of the British Empire (O.B.E.) by Her Majesty the Queen. At the American Water Works Association Conference of 1979 he received the award of Honorary Membership “For his dedications and contributions in the water chemistry field.” Dr. Palin continued to serve as a consultant and maintained an active interest in all aspects of water treatment and examination.

INTRODUCTION

In the vast majority of cases where germ-free water is required, whether for public supply or in the swimming pool, the process of disinfection will involve the use of chlorine in one form or another. If properly applied, the chlorination process is able to provide other benefits, such as the removal of color, the correction of tastes and odors, and the suppression of unwanted biological growths. Chlorine also plays an important role in the treatment of industrial waters and wastewaters.

The purpose of this manual is to present a guide to the chemistry of modern chlorination processes and the latest developments in chlorine test procedures. Without these test methods it becomes difficult to provide effective control, and receive best results coupled with due economy in chemical costs. The most essential feature of such control resides in the regular testing for the level of chlorine in the water, that is the residual chlorine, in order that the desired antimicrobial concentration may be maintained without producing such undesirable results as chlorine tastes and odors in drinking water, or unpleasant bathing conditions in swimming pools. These unwanted side effects may arise, not only from excessive concentrations of chlorine itself, but from the presence of obnoxious chloro-compounds resulting from interactions between chlorine and ammonia compounds or nitrogenous organic matters. To utilize all the benefits now afforded by modern chlorination techniques, and to eliminate all those problems associated with incorrect control and application, the importance of a reliable, and yet simple system of testing cannot be over-estimated.

The great advances that have been made over the past three or four decades in our knowledge of water chlorination chemistry have resulted from the dedicated efforts of many research workers in the United States of America and in other countries. The results of their endeavors have provided the foundations upon which modern chlorination is based. The key that unlocked the door to many of these discoveries was found in the development of suitable analytical techniques; it was to this aspect of the work that the author paid special attention. It is now fully recognized that the apparent complexities of chlorine chemistry, as exemplified by the breakpoint phenomenon, could not have been elucidated without some means of determining the nature and the amounts of the different types of residual chlorine compounds involved in these various reactions that take place at relatively minute concentrations in water. The behavior of such compounds, especially their ability to react among themselves and with free chlorine, provide a rewarding field for continuing exploration, made possible by the analytical methods that became available. In addition to these fundamental researches, the need for simple reliable tests for practical control of the new chlorine processes was fully appreciated, with the result that the methods developed have been successfully adapted for the use in the usual test-kit form.

THE CHEMISTRY OF CHLORINATION

HISTORY

Toward the end of the nineteenth century there were several instances of the use of chlorine compounds for the disinfection of water and, with increasing experience, there came an appreciation of the effectiveness of the treatment. The introduction of water chlorination as a continuous process occurred, both in England and in America, soon after the turn of the century. The developments that have taken place since that time have been outlined1 as follows:

1905-1915

A period mainly of hypochlorite disinfection, coupled with a certain amount of skepticism and prejudice against chlorination.

1915-1925

The evolution of gaseous chlorination and continued education of the public.

1925-1935

A time of very great interest in chlorination. Bacterial and taste problems were very much to the fore, with the use of chloramine being very much advocated.

1935-1945

A period of greater flexibility in chlorination methods with increased use of semi-automatic apparatus.

1945-1955

Advances in the understanding of basic principles coupled with much fundamental research. Greatly improved methods of control of chlorination.

This last period also saw the development of chlorine dioxide treatment of water. Since 1955 attention has been concentrated on the refinement of test procedures for the more accurate determination of residual chlorine compounds, so that every requirement of treatment control could be met to ensure optimum results under all conditions. Even in situations where full laboratory facilities are not available, the modern types of test kits provide complete reliability with maximum convenience and simplicity.

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FORMS OF CHLORINE

▪ The Meaning Of Available Chlorine

The concentration of residual chlorine is always expressed in terms of "available chlorine," no matter in what chemical form it is present. It is clearly advantageous to have a common yardstick for comparing one form, say hypochlorous acid, against another form, say monochloramine. The same also applies to the chlorine compounds used in water treatment, such as sodium hypochlorite or chlorine dioxide. The available chlorine content of chlorine itself is by definition 100%.

The concept of available chlorine is to some extent an artificial one, but it remains the standard form of expression for the strengths or capacities of chlorinating chemicals, as well as for the doses in which they are applied and for the residuals which remain in the water. Any chlorine ultimately appearing as chloride, the final reduction product, represents a complete loss of available chlorine. Chlorides such as sodium chloride have zero available chlorine.

The test that determines whether or not a compound has available chlorine its ability to react with potassium iodide (KI) in an acid solution to release free iodine (I2). The percentage amount of available chlorine is obtained by comparing the amount of iodine so liberated with the amount of iodine liberated from the same weight of chlorine. When chlorine reacts with potassium iodide under these conditions, each gram liberates 3.6 grams of iodine. It is thus only necessary to calculate from the reaction that would occur between a chlorine compound and acid-iodide the amount of iodine liberated by one gram of the chlorine compound. This figure is then divided by 3.6, and multiplied by 100 to get percentage available chlorine.

While in actual analytical practice one would avoid the use of hydrochloric acid (HCl) in this determination (since it may contain traces of free chlorine as impurity), it is simpler for our theoretical exercise to use HCl rather than introduce another acid radical, such as acetate, in the equations.

In the case of hypochlorous acid the reaction shown would be:

$$\mathbf{HOCl + {}^{2}KI + HCl \leftrightarrow {}^{2}KCl + H_2O + I_2}$$

From a consideration of molecular weights we find that 52.5 parts by weight of hypochlorous acid yield 254 parts by weight of iodine. Therefore:

$$\text{1 g hypochlorous acid} = {}^{254}\!/_{52.5} = 4.84 \text{ g iodine}$$

$$\text{Percentage available chlorine} = {}^{4.84}\!/_{3.6} \times 100 = 134$$

It is apparent that some chlorine compounds can be rated as having more than 100% of available chlorine, when their capacities are compared on this basis. To take chlorine dioxide as a somewhat more complicated example, this would react as follows:

$$2ClO_2 + 10KI + 8Cl \leftrightarrow 10KCl + 4H_2O + 5I_2$$

From this it may be calculated that 1 g of chlorine dioxide produces 9.41 g of iodine. Therefore:

$$\text{Percentage available chlorine} = {}^{9.41}\!/_{3.6} \times 100 = 261$$

In these theoretical calculations it has been assumed that the chemicals in question are 100% pure. Thus taking sodium hypochlorite for example, the pure form (which being highly unstable is not commercially available) would have an available chlorine content of 95.4%. The commercial sodium hypochlorite or liquid bleach as manufactured contains 12 to 15% available chlorine, which represents a dilution of about 7 times. As is the case with many of the compounds used for chlorination purposes, there is a gradual loss of the strength on storage and this may also be gauged on the same available chlorine scale.

In assessing the costs of chlorine from different commercial products, a knowledge of their available chlorine contents is essential, as can be seen from Table 1.

REAGENT	QUANTITY EQUIVALENT TO 1 LB OF CHLORINE GAS
Chlorine gas1 lb	1 lb
High Test Hypochlorite (calcium hypochlorite) 65% - 70% available chlorine	1.5 lb
Chlorinated Lime (chloride of lime) 30% - 35% available chlorine	3.0 lb
Sodium Hypochlorite	
15% by wt. Available chlorine	0.6 gal
10% by wt. Available chlorine	1.0 gal
5% by wt. Available chlorine	2.0 gal

Table 1

▪ Gas

Chlorine gas is greenish-yellow in color. Liquid chlorine, which is obtained by compressing the gas until it liquifies, is an amber-colored, oily fluid. The gas is about 2.5 times heavier than air, thus in the event of a leak it will sink to the floor. The liquid is about 1.5 times heavier than water. Chlorine is produced commercially from sodium chloride by an electrolytic process, and is supplied under pressure in cylinders of up to 150-lb net capacity filled so that, at temperatures of about 65°C, 80% is occupied by liquid, the remainder being gas. Larger containers of up to 1-ton weight are also used, and for still larger quantities tank cars are available.

The rate of flow from a container depends upon the cylinder or tank pressure, which in turn is governed by the temperature of the contents, shown in Figure 1 (page 13).

The pressure provides no indication of the weight of the contents and will remain steady, if the temperature is steady, right to the final stages of emptying, when all liquid has been gasified. At this point the pressure drops rapidly if withdrawal of gas is continued. The amount of chlorine used over a period is determined by weighing the container at the beginning and again at the end of the withdrawal.

There is a limit to the rate at which chlorine gas may be drawn from a container, since the process of converting liquid chlorine to gas (like the boiling of water) requires a continuous flow of heat from the outside of the container to the inside. If this heat flow cannot match the rate at which the liquid chlorine is evaporated, heat will be abstracted from both the container and its contents, thus giving a cooling effect to such an extent that eventually frost will form on the outside. The guage pressure will be correspondingly reduced.

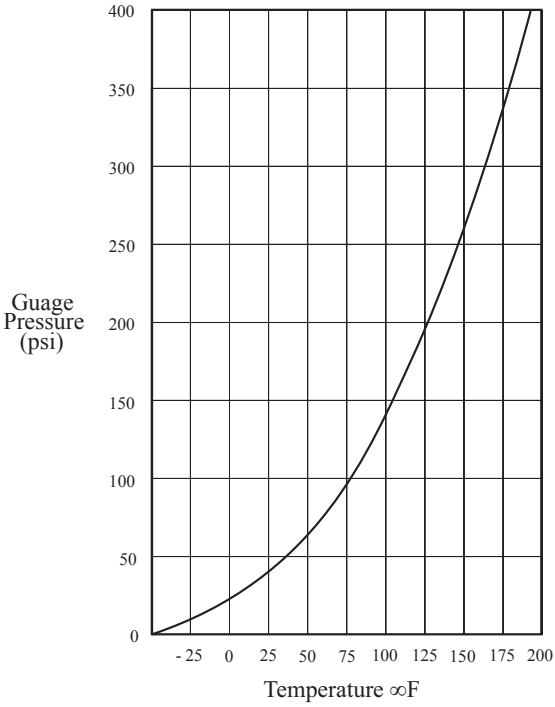

Figure 1: Temperature-Pressure Curve for Liquid Chlorine

The dependable maximum continuous rates of withdrawing gas from containers, assuming the room is at normal temperature and air circulation is reasonably good, are as follows:

100 to 150 lb cylinders	1.75 lbs. per hour
1 ton containers	15 lbs. per hour
1 ton containers (with evaporator)	400 lbs. per hour

Two or more cylinders may be connected to a manifold and discharged simultaneously to obtain an increased rate of discharge. With such an arrangement it is necessary to ensure that all cylinders are at the same temperature. Should one cylinder be much cooler than the others, as might happen when a new cylinder is added to the manifold, there would be a flow of gas from the warmer, and consequently higher pressure, container to the cooler container, where reliquification would occur, leading to the dangerous condition of being completely filled with liquid chlorine.

Chlorine cylinders normally stand upright so that only chlorine gas is drawn off. To obtain an increased discharge rate from the larger size of container, the chlorine may be delivered in liquid form to the evaporator.

Dry chlorine gas is not corrosive to most common metals, so iron cylinders and iron tubing may be used. If the gas picks up moisture, for example when a leak occurs into moist air, or when dissolved to produce a chlorine solution for application to the water, it becomes very corrosive. The solution must therefore be conveyed in such materials as glass, hard rubber, or silver. Solution-feed is the usual practice where the solution is prepared by first dissolving the gas in a supplementary flow before adding it to the main flow. This facilitates rapid distribution and uniform mixing of the chlorine in the water and avoids the risks of corrosion or undesirable side reactions resulting from high local concentrations at the point of application.

- **Solutions**

These contain chlorine in the chemical form of hypochlorite and are usually prepared from chlorine and caustic soda, thus giving sodium hypochlorite. Such solutions are alkaline and this helps preserve them. For fresh solutions the available chlorine content can be up to 15% by weight, but with storage there is a gradual loss of strength, so that within 3 or 4 months up to half the available chlorine may be lost. In practice the solution may require dilution to provide more convenient application with solution-feed dosing equipment. Sodium hypochlorite solution is sold under a variety of trade names; packing is normally in glass, earthenware, or polyethylene carboys or in rubber-lined drums. Storage should be in cool darkened areas. Care is required in handling, in view of the corrosive nature of hypochlorite solutions and the consequent risk of harmful contact with eyes and skin in the event of accidental spillage.

- **Solids**

In addition to the solutions which contains sodium hypochlorite, solid hypochlorites are available generally in the form of calcium compounds. Lithium hypochlorite (35% available chlorine) may find some application, for instance in laundries and in swimming pools, but not for potable water supplies.

One of the best known solid hypochlorites is chlorinated lime, also

known as chloride of lime or bleaching powder. The essential constituent is calcium oxychloride, which is decomposed by water to produce calcium hypochlorite. The excess lime present in chlorinated lime is insoluble; these suspended solids should therefore be allowed to settle out from the solutions before use. Alternatively, the chlorinated lime may be added directly to the water as a powder.

Fresh chlorinated lime has about 33% available chlorine content, but loses strength fairly rapidly on storage unless conditions are cool and dry, when the drop in available chlorine content may be no more than 1% a month. Containers must be made of corrosion-resistant material and kept carefully closed.

A superior form of solid hypochlorite, known as High Test Hypochlorite, is available. This is solid calcium hypochlorite produced as a free-flowing granular material or as tablets. The available chlorine content is up to 70%. Under normal storage conditions only 3 to 5% loss a year is claimed, thus giving a much more satisfactory shelf life than chlorinated lime. The calcium hypochlorite granules dissolve readily in water; the tablets dissolve more slowly, which is advantageous where a fairly steady release of chlorine is required over periods of up to 24 hours.

- **New Products**

Much attention has been paid in recent years to the development of newer types of chlorine compounds with special reference to their application to the treatment of swimming pool water.

Increasing use is now being made of the chloroisocyanurates, which arem compounds of chlorine and cyanuric acid. Their use arose from observations that cyanuric acid acts as a chlorine stabilizer, reducing the chlorine loss associated with the interaction of chlorine with ultra-violet light.

The release of residual available chlorine, in the form of hypochlorous acid, is governed by the following equilibrium:

chloroisocyanurate + water ↔ cyanuric acid + hypochlorous acid

With continued treatment the concentration of the cyanuric acid itself will gradually build up, thus causing the above reaction to proceed from right to left to maintain the chemical balance. The concentration of hypochlorous acid could, therefore, become very much reduced; to avoid this some control of the cyanuric acid level should be exercised by regular testing. The optimum level appears to be around 30 mg/L

with a recommended limit of about 200 mg/L.

The normal entry of make-up water to a pool may be adequate to keep the cyanuric acid concentration within the desired range by dilution, but should the level become unduly high, it may then be necessary to revert temporarily to hypochlorite treatment.

Chlorine dioxide is another chlorine compound which has been used in swimming pools to a limited extent, but is now more widely used for drinking water. In the water supply field, it has been available for thirty-five years or more as an improved means of controlling unpleasant tastes and odors. The compound is produced on site by mixing a strong chlorine solution, as discharged from the chlorinator, with a solution of sodium chlorite; the following reaction occurs:

$$Cl^{2} + {}^{2}NaClO^{2} \leftrightarrow {}^{2}NaCl + {}^{2}ClO^{2}$$

Alternatively in smaller installations the chlorine dioxide may be generated by mixing solutions of sulfuric acid, sodium hypochlorite, and sodium chlorite. On the basis of its available chlorine content, its oxidizing capacity is about 2.5 times that of chlorine, but it would be incorrect to claim that chlorine dioxide therefore has 2.5 times the oxidizing power or potential of chlorine. In many reactions, for example removal of color from water, it is considerably weaker than chlorine.

Chlorine dioxide treatment is generally more costly than normal chlorination. It differs chemically from chlorine in being inert towardsammonia2 and consequently does not produce chloramines and similarcombined chlorine compounds. Preparations containing so-called“stabilized chlorine dioxide” have become available for a variety of disinfection purposes, including swimming pools.

In swimming pool treatment some use has been made of a product which has the chemical name N-bromo-N-chloro-dimethylhydantoin.When added to water this compound liberates both chlorine and bromine, and gives conditions which are claimed to be more pleasant to bathers. The application of the author’s analytical methods to an examination of the active residuals produced in the water indicates that the treatment is best regarded as a bromination process since free bromine is found to predominate over free chlorine.

CHLORINE DISSOLVED IN WATER

In approaching the chemistry of chlorination it is necessary to start by considering the reactions of chlorine in pure water. In the first place the chlorine rapidly hydrolyses to form hydrochloric acid and hypochlorous acid:

$$\mathbf{Cl_2 + H^2O \leftrightarrow HCl + HOCl}$$

The hypochlorous acid then partly dissociates to give hydrogen ions and hypochlorite ions:

$$\mathbf{HOCl \leftrightarrow H^+ + OCl^-}$$

The three forms of available chlorine involved in these reactions, namely molecular chlorine Cl2, un-ionized hypochlorous acid HOCl, and the hypochlorite ion OCl–, exist together in equilibrium. Their relative proportions are determined by the pH value and temperature. Furthermore, the proportions are the same for any set of conditions whether the chlorine is introduced as chlorine gas or as a hypochlorite.

In water chlorination pH is the all important factor governing the relative proportions

as shown in Figure 2 (see next page).

It is evident that, as the pH falls below 2, the predominant form is Cl2. Between pH 2 and pH 7 the equilibrium is overwhelmingly in favor of HOCl. At pH 7.4 HOCl and OCl– are about equal, while above this increasing proportions of OCl– are present. At more than pH 9.5 all the available chlorine is present in the OCl– form.

Chlorine, which is present in water as Cl2, HOCl, or OCl–, or in any mixture of these, is defined as “free available chlorine”. Clearly, at the pH ranges encountered in water chlorination, free chlorine will consist of a mixture of HOCl and OCl–. It will be apparent from the first equation that, in adding chlorine to water, a proportion of hydrochloric acid (HCl) is produced which will reduce the alkalinity. The amounts involved are so small in practice, however, that except in very soft waters having little buffering capacity

(i.e. inbuilt resistance to pH change) or in cases where very high chlorine doses are involved, the resulting effect upon the pH of the water is inappreciable. In fact the application of chlorine to a water in a dose of 1 mg/L, will reduce the alkalinity by approximately 1 mg/L which, for example in a natural water of 100 to 200 mg/L alkalinity, would be quite insignificant.

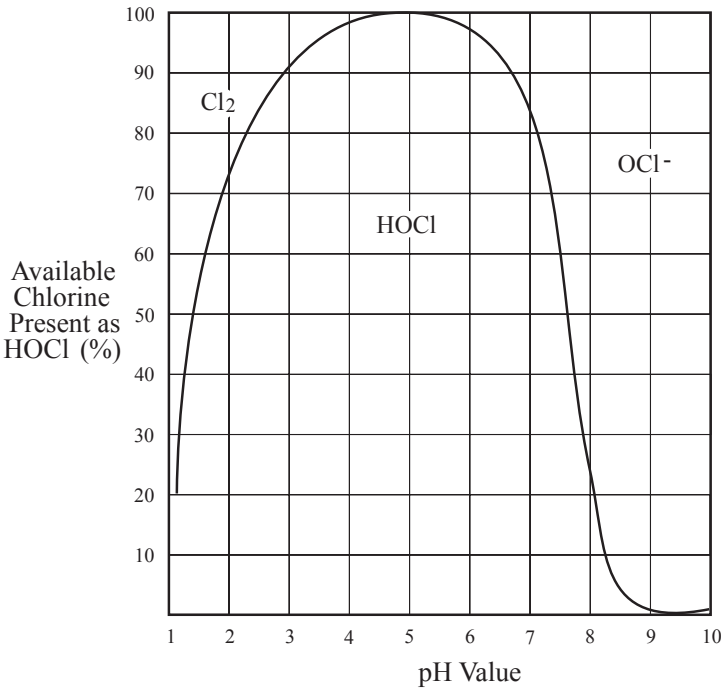

Figure 2: Effect of pH Value on form of Free Available Chlorine in Water

BREAKPOINT REACTIONS

Having considered the behavior of chlorine when dissolved in pure water, it is necessary next to examine in what way the reactions are affected by the presence of those impurities which may be encountered in the chlorination of natural and polluted waters. It is now established3 that the most profound influence upon the chemistry of water chlorination is exerted by ammonia, the presence of which is generally associated with pollutive matter. It reacts with chlorine thus:

$$\underset{\text{ammonia}}{NH_3} \longleftrightarrow \underset{\text{monochloramine}}{NH_2Cl} \longleftrightarrow \underset{\text{dichloramine}}{NHCl_2} \longleftrightarrow \underset{\text{nitrogen trichloride}}{NCl_3}$$

Generally the lower the pH and the higher the chlorine:ammonia ratio, the greater the tendency to produce the more highly chlorinated derivatives. But with an increasing chlorine:ammonia ratio secondary reactions occur, the study of which has produced results of the greatest possible significance. The rate of these reactions depends upon pH and is at its maximum in the pH range 7.0 to 8.0.

For our present purpose it will be unnecessary to explore the whole range of possible reactions under different conditions. We will concentrate upon the normal pH range of drinking water and swimming pool water. Here we find that the product of the reaction between chlorine and ammonia is almost entirely monochloramine. The time taken for this to form is very short, probably less than one minute, and the reaction may be shown as follows:

$$NH^3 + Cl^2 \leftrightarrow NH^2Cl + HCl$$

From this reaction it may be calculated that 1 part by weight of the ammonia-nitrogen requires 5 parts by weight of chlorine. Thus ignoring any loss of chlorine from other causes, we can say that, so long as the dose is not in excess of 5 times the ammonia-nitrogen in the water, all the chlorine will go towards producing monochloramine.

But if more chlorine has been added than is required for this rapid initial reaction, a continuing oxidation reaction occurs at a slower rate, eventually producing mainly nitrogen, as follows:

$$^2NH^2Cl + Cl^2 \leftrightarrow N^2 + {}^4HCl$$

Whenever the chlorine dose exceeds the ammonia-nitrogen in the water by more than 5:1 (again ignoring the effect of other chlorine-consuming substances), this type of reaction will occur, resulting in a loss of available chlorine. There is usually some

appearance of dichloramine and nitrogen trichloride in the zone corresponding to the chlorine dose having gone beyond the 5:1 ratio, but the net result, as chlorine is further increased, eventually corresponds to the following overall equation:

$$^2NH^3 + {}^3Cl^2 \leftrightarrow N^2 + {}^6HCl$$

From this we can calculate that the amount of chlorine required to oxidize one part by weight of ammonia-nitrogen is 7.6 parts by weight, and at this point loss of available chlorine would be at a maximum. It also happens that, because of certain side reactions leading for instance to the formation of trace amounts of nitrate, the observed ratio is a little higher at approximately 8.3:1. In practice one must allow for other substances in natural waters capable of absorbing chlorine, so that the usual ratio for this particular

point, now called the “breakpoint,” is around 10:1. Of course for grossly contaminated waters it may be 25:1 or even higher.

If a series of aliquot portions of a water sample containing ammonia is treated with progressively increasing amounts of chlorine, and the residual chlorine values after a period of contact are plotted against the corresponding chlorine doses, a “hump and dip” type of curve is produced, known as the breakpoint curve. This curve has three distinctive features which we can now relate to the chemistry so far considered:

1. An initial rise of residual chlorine in which zone the compound present is chloramine.
2. A secondary fall in residual corresponding to the unstable zone in which there has been an excess of chlorine over and above that required to give complete formation of chloramine. Here this excess has entered into mutual decomposition reactions with the initially formed chloramine.
3. A zone characterized by a final rise in the residual chlorine corresponding to complete oxidation. Here the continuing addition of chlorine to the water gives a pro-rata increase in the residual.

The minimum point between stages 2 and 3 is called the breakpoint, and the addition of sufficient chlorine to reach beyond this point provides many advantages. Stages in the development of the breakpoint in chlorine-ammonia reactions are shown in Figures 3(a), 3(b) and 3(c).

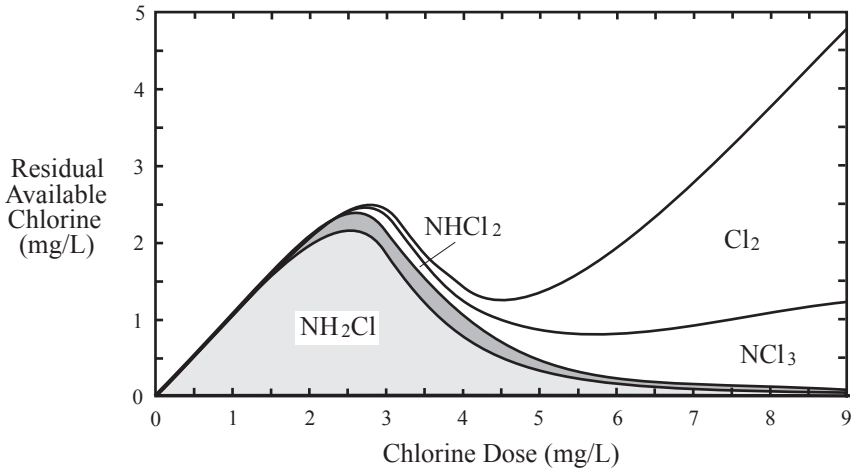

Figure 3a: Chlorine Dose-Residual Curve at pH 7.3-7.5 after ten minutes contact. Initial Ammonia- 0.5 mg/L(N).

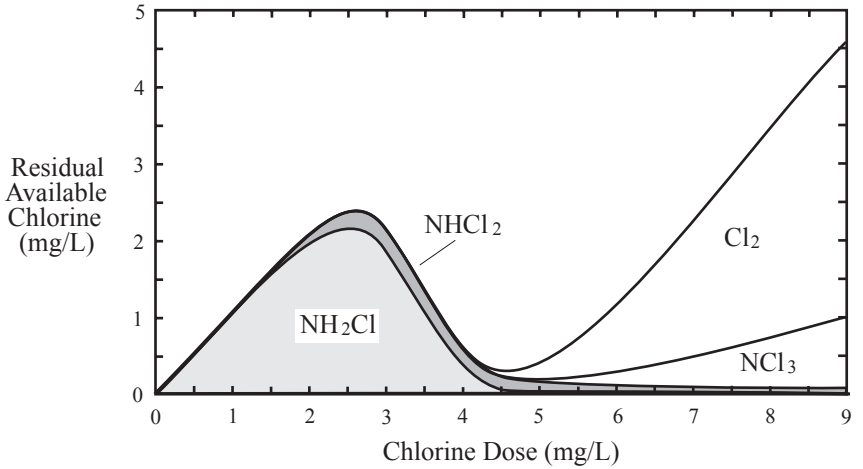

Figure3b: ChlorineDose-ResiduaCurve at pH 7.3-7.5 aftertwo hourscontact. InitialAmmonia- 0.5 mg/L(N).

The effect of pH is shown in Figures [4](a), [4](b) and [4](c).

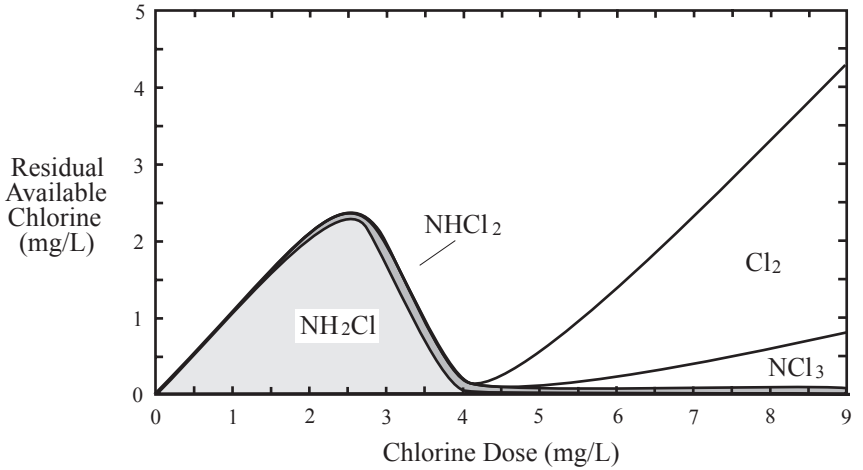

Figure3c: ChlorineDose-ResiduaCurve at pH 7.3-7.5 afterone dayíscontact. InitialAmmonia- 0.5 mg/L(N).

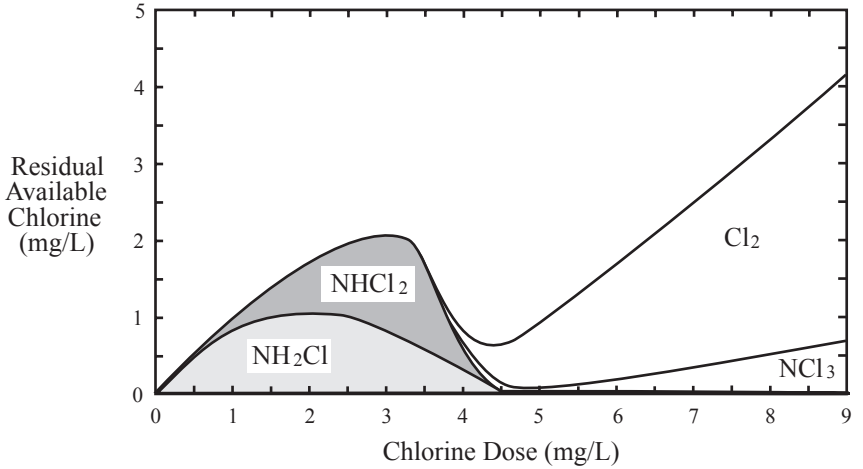

Figure4a: ChlorineDose-ResiduaCurve at pH 6.0 afteone day.
InitialAmmonia- 0.5 mg/L(N).

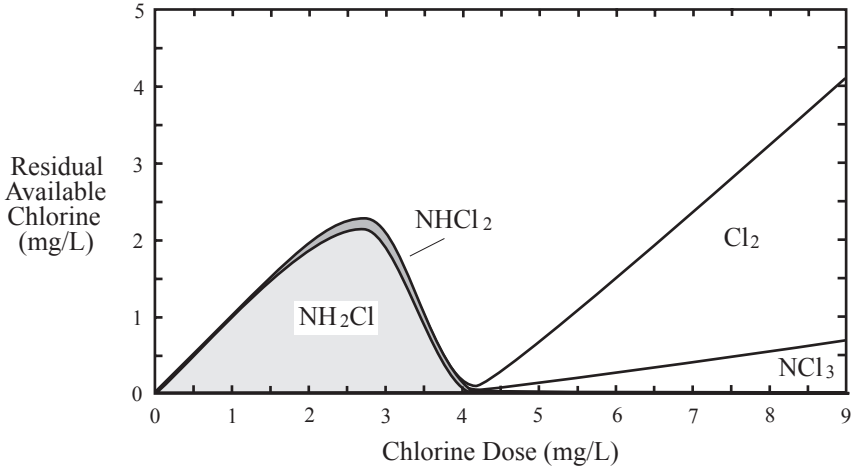

Figure4b: ChlorineDose-ResiduaCurve at pH 7.0 afteone day.
InitialAmmonia- 0.5 mg/L(N).

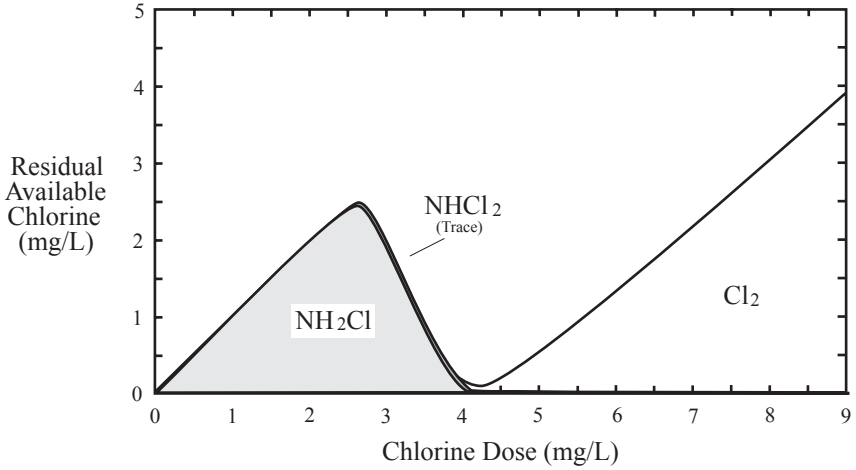

Figure 4c: Chlorine Dose-Residual Curve at pH 8.0 after one day.
Initial Ammonia- 0.5 mg/L(N).

In addition to ammonia other nitrogenous compounds can produce breakpoint curve in which the hump and dip is clearly distinguishable, although generally not so marked as in the case of chlorine and ammonia. All may be explained on the same basis.

Although free chlorine may exist temporarily in water during the early stages of the breakpoint reactions in conditions corresponding to the dip portion of the curve, the vital distinction in the breakpoint chlorination is that, prior to the breakpoint, the residual available chlorine is present in the form of chloramines and related compounds. This is termed “combined chlorine.” After the breakpoint it is present as free chlorine which, as we have seen, is a mixture at normal pH values of hypochlorous acid and hypochlorite ion.

Recognition of these two forms of residual chlorine is of the greatest importance, since the chemical, bactericidal, and virucidal properties of free chlorine are vastly superior to those of combined chlorine. Therefore, for maximum safety in the production of germ-free water, it is essential to chlorinate to the point of establishing free chlorine. Because of the presence of ammonia-type impurities, there is some initial appearance of combined residual chlorine compounds. Chlorination should be adequate to ensure that by continuing reaction with them, their concentration is reduced to a minimum – that is to say, the water must be chlorinated to beyond the breakpoint since it is here that the residuals are substantially in the form of free chlorine. That the treatment has been properly carried out can only be established by using test procedures capable of determining free chlorine separate from combined chlorine.

A disadvantage of breakpoint chlorination is that the free chlorine residuals produced in the water may vary, unless the pH is fairly high, be accompanied by traces of nitrogen trichloride. In some situations this has proved a problem4 in view of the objectionable chlorine-type odors thereby imparted to the water. It may then be necessary as a final stage to dechlorinate completely with a further stage of chlorination or ammonia-chlorine as a final treatment.

Traces of nitrogen trichloride may also be encountered in a swimming pool5, especially if the pH value is allowed to fall. In indoor pools this could cause complaints from bathers of eye irritation, since the volatile nature of NCl_3 facilitates its escape to the atmosphere. Consequently the satisfactory application of modern chlorination techniques to swimming pools requires, not only differential testing for free and combined chlorine, but a measure of pH and alkalinity control.

MODERN CHLORINATION - DEFINITIONS & CLASSIFICATION

Against this background of chemistry, we may now set down the definitions which are fundamental to modern chlorination.

Free Available Residual Chlorine is defined as that residual chlorine existing in water as hypochlorous acid and hypochlorite ion.

Combined Available Residual Chlorine is defined as that residual chlorine existing in water in chemical combination with ammonia or organic nitrogen compounds.

The chlorine demand of the water could be regarded as that portion of the applied chlorine dose which has been converted to "non-available" chlorine, that is, by definition, not able to liberate iodine from an acidified iodide solution and similarly giving no response in the usual residual chlorine tests. For a precise definition of chlorine demand, however, it is necessary to specify the chlorine dose, the time of contact, the temperature, and the nature of the residual aimed at, whether free or combined available chlorine.

In view of the general acceptance of the superiority of free residual chlorine compared with combined residual chlorine, it is evident that the preferred definition applicable to the majority of cases is as follows:

Chlorine Demand is defined as the difference between the amount of chlorine added to water and the amount of free available chlorine remaining at the end of a specified contact period.

This definition may thus be related to the breakpoint curve, and corresponds to the chlorine required to reach the breakpoint plus such further amount as may be required to produce the desired level of free residual chlorine beyond the breakpoint.

It will be appreciated, however, that many waters may have a chlorine demand due to non-nitrogen organic matter or oxidizable inorganic substances with relatively insignificant amounts of ammonia or nitrogen impurity. In such cases the chlorine dose-residual curve will not exhibit the typical "hump and dip" of the breakpoint curve, but will remain at a low level during the stage of satisfying the demand, after which free available residual chlorine will appear and show the pro-rata increase with increasing dose. The common feature is that sufficient chlorine is applied to produce free, as opposed to combined, available residual chlorine.

The modern approach to the classification of chlorination processes is based upon this important distinction between free and combined chlorine, thus giving two main types of process. These are termed Free Residual Chlorination and Combined Residual Chlorination. In applying free residual chlorination to some water supplies, it may be desirable, either because contact time is very short or pollution loads are variable, to operate at levels of free chlorine so high that dechlorination is subsequently required before delivery to the consumer. This process, which is known as superchlorination and dechlorination, may then be applied without particular reference to a breakpoint, the aim being to ensure that ample free chlorine is produced.

In other circumstances, where there is adequate time for disinfection to be achieved, there may be some advantage, for example lessened risk of producing some types of taste and odor, in working with combined chlorine residuals produced by reaction between chlorine and nitrogenous constituents naturally present in the water ("simple" or "marginal" chlorination). Alternatively, ammonia may be deliberately applied, usually before the chlorine, as part of the process (chloramine or ammonia-chlorine treatment).

Thus the system of classification may be set down as in Table 2.

CHLORINATION			
Free Residual		**Combined Residual**	
Breakpoint Chlorination	Super-chlorination & Dechlorination	Simple (or Marginal) Chlorination	Ammonia-Chlorine Treatment

Table 2

It is possible, of course, to introduce variations to suit particular requirements; for instance an operator may apply free residual chlorination through his plant with final conversion to combined residual (by applying ammonia) to maintain chloramine-type residuals rather than free chlorine in the distribution network. Another novel use of the breakpoint reactions is to employ ammonia as a dechlorinating agent.

Whatever modification of chlorine treatment is used, however, the results obtained under any given conditions must always depend upon the nature and amount of the residual chlorine produced in the water. The production of residuals of known composition by suitable control of chlorination has been made possible by the methods of chlorine residual differentiation now available.

DISINFECTION BY CHLORINE

THE EFFECT OF PH

While the present manual is primarily concerned with the chemistry rather than the bacteriological aspects of water chlorination, it is necessary to have regard for those physical and chemical factors which influence the bactericidal and virucidal power of chlorine.

From Figure 2 (on page 18), it may be seen that within the range pH 6.0 to pH 9.0 free available chlorine comprises a mixture in varying proportions of hypochlorous acid and hypochlorite ion. With pH rising over 6.0 the proportion as HOCl declines from virtually 100% down to almost zero at pH 9.0. The activity of HOCl as a bactericide is greatly superior to that of the OCl^- ion, being something like 80 times more powerful. Consequently it may be concluded, and practical experience bears this out, that in free residual chlorination the higher the pH value the less active is the residual, because of its lower proportion of HOCl. Apart from the desirability of distinguishing free chlorine from combined chlorine in the residual chlorine test, there would seem, therefore, also to be a need to differentiate between these two forms of free chlorine, HOCl and OCl^-. This has not, however, been considered necessary in practice, and usually the recommendation has simply been to work to a higher free chlorine residual at the higher pH values. Some have taken this further by specifying the level of free chlorine residual for different pH values to ensure that at all times the same amount, say 1 mg/L, of HOCl is present. Table 3 shows the levels of free chlorine required to achieve this result.

The extensive work that has been carried out on the bactericidal efficiency of free available chlorine has provided ample confirmation of the retarding influence of high pH. Possibly the most comprehensive studies were those conducted by the Public Health Service[6, 7] from 1943 to 1948, which also demonstrated that the killing power of chloramines diminishes with increasing pH.

pH Value	Total Free Residual Chlorine to Give 1 mg/L HOCI	
	Temp. 0°C	Temp. 20°C
6.0	1.0	1.0
6.5	1.0	1.1
7.0	1.1	1.4
7.5	1.5	1.8
8.0	2.5	3.6
8.5	5.7	9.3
9.0	15.9	27.1

Table 3

EFFECT OF TEMPERATURE & TIME OF CONTACT

The bactericidal power of both free chlorine and chloramines decreases with falling temperature. In any situation where the effects of lowered temperature and high pH are combined, the reduction in the efficiency of free chlorine and chloramines is very marked.

These factors have an important bearing, therefore, on the time of exposure necessary to achieve satisfactory disinfection. Under favorable conditions the contact time required with free available chlorine may be only a few minutes; combined available chlorine under the same conditions might require one or two hours. Whatever the conditions, however, the final test of disinfection resides in bacteriological examination to ensure that the treated water complies with recognized standards such as, for example, the USEPA National Primary Drinking Water Regulations, 1975.[8]

NATURE OF RESIDUAL CHLORINE & MINIMUM SAFE LEVELS

In the studies by the Public Health Service, a comparison was made between the bactericidal activities of free chlorine and chloramine. The experiments were conducted so that the chloramine would be preformed in the water before the addition of the bacterial suspension, which is not truly representative of actual water treatment practice.

Nevertheless the conclusions were highly significant in showing that to obtain complete destruction of bacteria;

(a) with the same exposure period – about 25 times as much chloramine as free chlorine was required and;

(b) with the same amounts of residual – about 100 times the exposure period was required with chloramines as with free chlorine.

Data secured in these studies using 10 minutes contact with free available chlorine and 60 minutes contact with combined available chlorine provided the basis for recommended minimum safe residuals. In 1956 the National Research Council9 reanalyzed the Public Health Service data and submitted revised recommendations based on a 30 minute exposure period. At the same time additional recommendations were made in connection with minimum cysticidal chlorine residuals. These later recommendations form the basis of Table 4.

Minimum Cysticidal and Bactericidal Residuals (After 30 Minute Contact)

pH	Free Chlorine			Combined Chlorine
	Bactericidal 0 - 25°C	Cysticidal 22° - 25°C	Cysticidal 2° - 5°C	Bactericidal 0 - 25°C
6.0	0.2	2.0	7.5	2.0
7.0	0.2	2.5	10.0	2.5
8.0	0.2	5.0	20.0	3.0
9.0	0.6	20.0	70.0	3.5

Table 4

It may be assumed that the performance of ammonia-chlorine treatment in practice, where chloramine formation occurs in the water itself rather than being preformed, will be considerably better than is suggested by the figures in Table 4. This is explained by the fact that the reaction between chlorine and ammonia is not instantaneous but requires up to 1 minute, or thereabouts, for completion, the actual time being dependent upon pH and temperature. During this period the proportion of unreacted chlorine, although decreasing quite rapidly, nevertheless retains the bactericidal power of free available chlorine. As a result there is a short initial period in ammonia-chlorine treatment during which an enhanced rate of bacterial kill may be expected. Upon completion of the reaction between chlorine and ammonia the rate falls to the very much lower level characteristic of combined chlorine. Thus, even if full allowance is made for the initial period of rapid action in ammonia-chlorine treatment, the differences in the bactericidal and other properties of free chlorine and combined chlorine remain so marked that modern trends can only be more and more towards free residual chlorination.

CHLORINATION OF WASTEWATERS & INDUSTRIAL WATERS

INTRODUCTION

Various tests have been devised for the practical assessment of the pollution that results from the discharge of sewage effluents and similar wastewaters to streams and rivers. Of these, one of the most important is the test for Biochemical Oxygen Demand, that is the BOD test, designed to provide an indication of the amount of oxygen required for biological stabilization of the river water after it has received the polluting discharge. This test involves the measurement of the amount of dissolved oxygen absorbed by the sample under controlled conditions, normally after 5 days in the dark at 20°C, and simulates the process of aerobic degradation that occurs in the receiving water. The BOD test is applied to sewage, sewage effluents, and river waters, and provides a reasonably good indication of the load of impurity represented by oxidizable constituents.

The information afforded by the BOD test is supplemented by the results of other physical and chemical determinations covering a wide range, including pH, suspended solids, ammonia, nitrite and nitrate, permanganate value, chemical oxygen demand (or dichromate value), surface active agents, and constituents such as cyanides and phenols known to be toxic to fish. It is generally appreciated that, no matter how satisfactory a sewage effluent may be, as gaged by such analysis, it remains bacteriologically impure with possibly a high proportion of pathogenic organisms. The risks to public health associated with the disposal of such wastewaters makes it imperative that adequate protection be provided to water supplies, bathing beaches and shell fish growing areas. Recognition of the need for disinfection has led to the use of chlorine as the most practical and efficient means available for this purpose. Although originally introduced principally for odor control, for which it remains an effective remedial measure, the present position is that chlorination finds its primary use as a disinfectant, in which capacity it has become established as an integral part of

wastewater treatment processes.

In addition to disinfection and odor control, the chlorination of wastewater serves a number of other useful functions, of which the following may be mentioned – prevention of septicity, control of slime and insect life on trickling filters, control of activated sludge bulking, and restriction of bacterial slimes and fungal growths in effluent channels and pipes.

In once-through systems the water used is drawn, in many cases, from surface sources. Such natural supplies contain a variety of living organisms which can cause trouble from biological slimes, algae, and growths of iron bacteria. The most economical control method is to apply chlorine intermittently as a "shock" dose of short duration. Difficulties due to slime and algal growths are also to be expected in open circulating systems, and here again chlorination provides the control measure in widest use.

Other important applications of chlorination are to be found in the food industry and papermaking. In general the uses of water in industry are so varied that treatment methods must be geared to suit particular application. However, in any situation where problems arise from unwanted biological growths such as slimes or bacteria, it is frequently found that chlorination is relied on to provide the desired control.

The effluents from sewage treatment plants serving industrialized communities contain, in varying quantities, the host of chemicals that modern industry either uses in its various processes or discards as the unwanted end products of its activities. Treatment of such effluents may pose special problems, especially where discharge is to rivers subsequently used as sources of public water supply. Chlorination often assists in the breakdown of these harmful pollutants or their conversion to less toxic products.

CHEMISTRY OF WASTEWATER CHLORINATION

While chlorine reactions in wastewaters are influenced by factors not usually encountered in the potable water field, there is a fundamental similarity, especially where nitrogenous compounds are concerned. The organic nitrogen compounds encountered are, however, more complex and upon chlorination yield to a variety of organic chloramine residuals of doubtful germicidal value. To some extent the various reactions with proteins and protein degradation products may be accounted for by a consideration of the reactions between chlorine and amino acids, in which it has been shown that mono- and dichloramino derivatives are obtained.3 Such compounds are capable of responding to the residual chlorine tests, and to that extent they are to be regarded as a form of combined available chlorine, although uncertainty as to their germicidal value has led to their being relegated to the class of nuisance residuals.

These chloramino compounds are of varying stability in the absence of free chlorine. Decomposition is enhanced by excess chlorine, so that a breakpoint effect is obtained. However, because of the more complex nature of the impurities present, the chlorine dose-residual curve does not display quite so markedly the "hump and dip" feature of the simple ammonia-chlorine breakpoint curve. In the chlorination of sewage an increase in applied dose generally leads to a further stage in the progressive chlorination and oxidation of the organic impurities, so that there is no clearly defined saturation point.

The presence of impurities such as hydrogen sulfide, cyanides, phenols, ferrous salts, and other pollutive matters of industrial origin, adds to the chlorine demand,

making it difficult to predict with any certainty the relation between the composition and strength of the waste to be treated and the probable chlorine requirements. It is considered that the BOD value is probably the most useful parameter as a guide to chlorine consumption.

The odor problem is associated with the putrefaction of proteins and other organic matters in wastewaters through the activities of micro-organisms, resulting in a variety of unpleasant products. The worst offender by far is hydrogen sulfide. Chlorine reacts instantaneously with sulfide to form colloidal sulfur or sulfates depending upon conditions.

$$H_2S + HOCl \rightarrow S + HCl + H_2^0$$

$$H_2S + {}^4HOCl \rightarrow H_2SO_4 + {}^4HCl$$

The theoretical requirements for these reactions are 2.1 mg/L and 8.4 mg/L of chlorine respectively for each mg/L of sulfide (as H2S), but in practice the chemistry is probably much more complex. The contribution by sulfide to chlorine demand must therefore be judged by actual operating results, bearing in mind that complete oxidation to sulfates may not be required if elimination of H2S by the first reaction suffices to overcome the odor problem.

In addition to odoriferous compounds wastewaters may contain toxic substances, such as cyanide residues from case hardening of steel, electroplating of metals, and similar industrial processes. Industrial wastes contaminated with cyanide may be successfully treated by chlorination, whereby the cyanides are converted to relatively non-toxic cyanates.

In these reactions cyanogen chloride (CNCl) may form as an intermediate product, giving rise to extremely toxic vapors unless the pH is maintained at a fairly high level, under which conditions thecyanogen chloride becomes hydrolyzed to relatively harmless cyanate. The reactions may be shown as follows:

$$HCN + HOCl \rightarrow CNCl + H_2O$$

$$CNCl + {}^2NaOH \rightarrow NaCNO + NaCl + H_2O$$

The theoretical requirement for the overall conversion of cyanide to cyanate is 2.7 mg/L of chlorine for each mg/L of cyanide (as CN).

Continued chlorination at pH 8.5 - 10.00 decomposes the cyanate to give nitrogen and carbonates as the principal end products, for which reactions the theoretical chlorine requirement is 6.8 mg/L for each mg/L of cyanide (as CN). Chlorination of cyanide wastes thus provides a relatively cheap and easily controlled method capable of giving virtually complete removal of the cyanide.

Industrial wastes from chemical plants frequently contain phenols. The need for destruction of such phenolic substances in effluents before they are discharged arises because of their toxic effect on aquatic life and also because the presence of even trace amounts in rivers used as sources of water supply may lead to the development of obnoxious taste and odor problems in the finished water. Under suitable conditions phenols are susceptible to biological oxidation, but if that is impracticable, a process of chemical oxidation by chlorine may be used, although phenolic wastes generally have a very high chlorine demand and in consequence require excessively high chlorine doses.

In other industrial applications use is made of the very effective bleaching properties of chlorine, as a means of removing color from certain types of wastewaters and for bleaching textile wastes. The chlorine requirement may in some cases be very high, possibly several hundred mg/L. The effectiveness of bleaching may also be related to the pH of the waste.

As a general rule for all wastes and industrial waters the final confirmation of chlorine requirement must come from laboratory or plant trials. This term is preferred to chlorine demand where wastewaters are concerned; it is defined simply as the chlorine dose required to produce the desired result under stated conditions.

RESIDUAL CHLORINE CONTROL

In view of the fact that chlorine can be exceedingly toxic to fish, it is essential to guard against too high a residual in chlorinated effluents. The lethal concentration depends to some extent upon the species, but in general a risk of fish mortality is to be expected where the discharge leads to levels of about 0.1 mg/L in a stream. In some circumstances, therefore, it may become necessary to dechlorinate effluents before discharge, a process best accomplished by the addition of sulfur dioxide using dosing equipment similar to that used for chlorine. The reactions leading to destruction of free and combined residual chlorine may be represented as follows:

$$\mathbf{SO_2 + H_2O \leftrightarrow H_2\,SO_3\ (sulfurous\ acid)}$$

$$\mathbf{H_2SO_3 + HOCl \leftrightarrow H_2SO_4 + HCl}$$

$$\mathbf{H_2SO_3 + NH_2Cl + H_2O \leftrightarrow NH_4HSO_4 + HCl}$$

Chlorination of sewage effluents and similar wastewaters high in organic content is rarely, if ever, carried to the stage of producing free available chlorine. Because of the considerable amounts of nitrogenous matter usually present, the residuals will be in the form of combined chlorine; in practice, differential analytical procedures for separation of free from combined chlorine are not required. On the other hand, for water used in some industrial precesses, for example cooling water in canneries, the maintenance of free chlorine residuals is very desirable, and here free available chlorine test procedures must be used.

All methods for the determination of available chlorine in wastewaters that contain appreciable quantities of organic and other impurities are subject to increased interference as compared with potable waters. For best results the iodometric method and the amperometric titration require modifications, so that a reverse end point or back-titration procedure is used.10 An excess of the standard titrant is added to the test sample; the unused fraction is then determined by titration with standard iodine or iodate solution. Of colorimetric methods it has been stated that only the DPD method is worthy of consideration.[11]

The control of disinfection is based essentially on operating at that level of residual chlorine concentration which may be expected to give, on the basis of plant or laboratory trials, the required degree of bacterial improvement. Once a correlation between bacteriological results and residual chlorine has been established, it will suffice to base operational control on the residual chlorine test with the occasional bacteriological check to verify the correlation.10 Similar considerations apply where chlorine is used for other purposes, such as odor control or BOD reduction. The

chlorine requirement is that quanitity of chlorine needed to produce the desired result. The suitability of residual chlorine tests for control in a particular application will have been indicated by previous plant or laboratory results. In the chlorination of industrial wastes for a specific purpose, the chlorine requirement is similarly based upon the objective for which the chlorine is applied.

GENERAL GUIDE TO CHLORINE REQUIREMENTS

In the chlorination of potable water the normal procedure is to ensure that, in any given circumstances, the applied doses are adequate to produce at least the minimum safe residuals as officially recommended. On the other hand the range of application of chlorine in treating wastewaters and industrial waters can be so much wider that it is often helpful in the selection of chlorination sizes and capacities to consult a planning guide, such as Table 5.

Rule of Thumb Guide to Chlorine Requirements	
Application	**Probable Chlorine Requirement mg/L**
Algae Control	3 - 5
Bacterial Slime Prevention	3 - 5
BOD Reduction	10 - 20
Color Removal	5 - 100 or more depending upon type of wastewater
Cyanide Oxidation to Cyanate Complete Destruction	 2.7 times Cyanide content as CN 6.8 times Cyanide content as CN
Hydrogen Sulfide Odor Control Oxidation to Sulfide	 2.7 times H_2S content 8.4 times H_2S content
Iron Bacteria Control	2 - 10 depending upon extent of growth
Iron Precipitation	0.63 times Fe content
Manganese Precipitation	1.3 times Mn content
Sewage: Raw (including Odor Control) Primary Sedimentation Effluent Trickling Filter Effluent Activated Sludge Effluent Sand Filtered Effluent Septic Tank Effluent	 10 - 30 8 - 15 3 - 10 2 - 8 2 - 5 30 - 45
Water: Cooling (once through) (open recirculation) Chilling Washdown Disinfection of Mains and Tanks	 5 - 15 intermittent 3 - 5 20 50 10 - 50

Table [5]

DISINFECTION BY-PRODUCTS

The discovery in 1974 that traces of trihalomethanes (THM's) such as chloroform, bromodichloromethane, dibromochloromethane, and bromoform, could be formed during the disinfection of water by free chlorine has led to a review of the entire subject of water disinfection. Chloroform and the other THM's are suspected of being human carcinogens, and this presumed health hazard has necessitated regulating their concentration in drinking water under the Safe Drinking Water Act provisions.

Information on measurement techniques, mechanism of formation, and techniques for treatment evaluation, is presented in the EPA's "Treatment Techniques for Controlling Trihalomethanes in Drinking Water,"25 along with three approaches for controlling THM's. These comprise THM removal, THM precursor removal, and the use of other disinfectants in conjunction with chlorine or possibly as alternatives.

It is accepted that chloramine, chlorine dioxide, and ozone do not produce significant amounts of THM's when used alone as disinfectants, although each may have inherent disadvantages. Chloramine is a weaker disinfectant than free chlorine; chlorine dioxide produces chlorite and chlorate as by-products, the health effects of which are currently unknown; and ozone does not produce a residual in the distributed water. Nevertheless, increased consideration is being given to their use. Mixed treatments, such as chlorine plus chlorine dioxide and ozone plus chlorine, are also receiving attention. For control purposes a suitable differential test capable of the separate determination of mixed residuals is essential. Only the DPD method, officially adopted as standard in the U.S.A. and in many other countries, can meet these further analytical requirements.

THE DETERMINATION OF FREE CHLORINE & OTHER RESIDUALS

INTRODUCTION

The following general discussion is mainly concerned with those methods that appeared in the 1971 edition of *Standard Methods, for the Examination of Water and Wastewater* (hereafter refered to as Standard Methods) published jointly by American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Since that time all methods using acid or neutral orthotolodine have been withdrawn and therefore do not appear in the current edition of *Standard Methods* (1980).[10]

Iodometric: This is essentially a laboratory procedure in which a standard solution of sodium thiosulfate is used to titrate the iodine liberated from potassium iodide by the chlorine, usually in acid solution, although neutral solution is preferred when interfering substances are present. Starch, which gives a blue color with iodine, is used as the indicator. For high chlorine residuals the method is more precise than colorimetric procedures, but lower down the range it becomes inaccurate. The method gives total residual available chlorine. If performed in neutral solution there are indications that chloramines tend not to respond, so that by carrying out two titrations, one in acid and the other in neutral solution, an approximate free-combined residual separation may be obtained. For this purpose, however, superior methods are available.

Amperometric Titration: This is not a practical method for field use, since it requires a source of 110-V current. It does provide, however, an accurate titration method for laboratory use and permits the separate determination of free and combined chlorine. The principle of the method is based upon the fact that a suitable bi-metallic cell immersed in a solution containing an oxidizing agent produces a current flow which is indicated on a microammeter. If a reducing agent is now added to decrease the concentration of the oxidizing agent, the current will fall. With continuing addition an end point is eventually reached where the current is reduced to a minimum beyond which any further addition of reducing agent causes no change. For accurate results considerable operator skill is required and certain essential precautions, as discussed later, must be observed. The presence of oxidized manganese gives false readings, but otherwise, for potable water, the method is substantially free from interference.

Orthotolidine Methods: Four versions of the orthotolidine method are given. The first dates back to 1913 and, with the various modifications introduced from time to time, has been in wide use for many years for the routine measurement of residual chlorine. The simple test utilizes the reaction between chlorine and orthotolidine in acid solution to give a yellow color. For correct color development it is necessary that (a) the solution should be acidified to give a pH of 1.3 or lower, (b) the ratio by weight of o-tolidine to chlorine must be at least 3:1, and (c) the chlorine concentration must not exceed 10 mg/L. The addition of the reagent to the water sample must be carried out in the prescribed manner, that is, sample to o-tolidine in tube followed by rapid mixing.

To remedy the deficiencies of the original test, a modified reagent was introduced in the 9th Edition of APHA Standard Methods (1946), and this remained a standard reagent up to the 13th Edition (1971). It was unfortunate, however, that in correcting some of the deficiencies of the original reagent the value of the test for the differential determination of free and combined chlorine, the need for which had already become apparent, was adversely affected. Because of the increased proportion of o-tolidine in the color mixture, coupled with the lower pH, the rate of color development with combined chlorine became so speeded up as to make the test inadequate for this purpose.

The temperature specified for maximum response of combined chlorine, while minimizing loss of color by fading or increase of color from interfering substances, was 20°C. Standard Methods required that samples be brought to that temperature quickly after mixing with the o-tolidine. Under these conditions maximum color from free chlorine appears almost instantly and begins to fade, whereas the color from combined chlorine is at a maximum after about 3 minutes. In the standard procedure it was laid down, therefore, that the color matching against standards should be carried out at the time of maximum color development.

Attempts have been made to improve the o-tolidine test in order to provide reasonable accuracy in the determination of free chlorine separate from combined chlorine. The introduction of arsenite in the form of a solution of sodium arsenite formed the basis of the OTA (Ortho-Tolidine Arsenite) test.

The purpose of the arsenite is to destroy the combined chlorine immediately (i.e. within 5 seconds) after the free chlorine has reacted with the o-tolidine. In a second test arsenite is not used, so that the resulting color corresponds to total available chorine. By comparison of the two readings, an estimate of both free and combined chlorine can be made.

Further, it is possible to allow the effect of any interfering substances that might give false colors by adding the arsenite before the o-tolidine. This destroys all forms of available chlorine, leaves the interference, and enables the previous readings to be suitably corrected.

Because the range of these o-tolidine methods is limited to available chlorine concentrations not greater than 10 mg/L, a “Drop Dilution Method” is provided for field use. This consists essentially in bringing the chlorine concentration within the prescribed range by diluting the sample with distilled water. The procedure uses a calibrated pipet to deliver a sufficient number of drops of the water sample to a prepared tube containing the o-tolidine reagent and distilled water. Serial addition of drops is not permitted. If an increased number of drops is required to produce an easily readable color, the procedure must be repeated using a fresh tube of o-tolidine plus distilled water. The method is not recommended for use where accuracy is desired.

The neutral o-tolidine method was developed by the author during the course of his studies of the formation and decomposition of the chloro substituents of ammonia and related compounds.12 This new method subsequently appeared in the 10th Edition of Standard Methods (1955). The normal yellow color produced in the acid o-tolidine test is due to the formation of a holoquinone, a compound resulting from complete oxidation of the o-tolidine. In neutral solution only partial oxidation is obtained, giving products known as meriquinones. The resulting colors are generally greenish, but in the presence of stabilizers, such as hexametaphosphate, only the pure blue meriquinone color is formed.

In the titration version of this method, the author introduced ferrous ammonium sulfate as a standard solution. The strength was adjusted so that the volume required to destroy the blue color indicated mg/L chlorine directly . For the free-combined chlorine differentiation, use was made of potassium iodide as an activating agent for the development of color from the combined chlorine. This method of inducing a response from combined available chlorine in colorimetric testing was discovered by the author in his previous work using the indicator p-aminodimethylaniline (dimethyl-p-phenylene diamine).[13]

In further studies, using the iodometric method as a standard comparison procedure, it became evident that with some waters, usually rather acid in character, a full response from combined chlorine was not being obtained. This elusive fraction was found to be due to dichloramine. A modified procedure with a third stage involving acidification and subsequent neutralization was therefore introduced, thus permitting, for the first time, differentiation of monochloramine from dichloramine. Coupled with this, a supplementary procedure was devised to permit determination of nitrogen trichloride, since it had by then become apparent that, contrary to previous assumptions, this compound could under some conditions form and co-exist with free chlorine in waters treated by breakpoint chlorination.

Stabilization of the colors in the neutral o-tolidine test by hexametaphosphate, while adequate for a titration procedure, was found hardly good enough for a colorimetric method, since in such procedures judgement of the color match against standards can often take a little time. For this purpose, therefore, an improved stabilizer was introduced consisting of an anionic surface active agent.14

Following this discovery of the stabilizing influence of such anionic surfactants, a similar procedure for free and combined chlorine was developed at the School of Public Health, University of North Carolina, using Aerosol OT as the stabilizer. This has become known as the “SNORT” method (i.e. Stabilized Neutral Ortho-Tolidine Method). Provision is made for the separate determination of monochloramine by reaction with iodide in neutral solution, and of dichloramine by reaction with iodide in acid solution, as in the original neutral o-tolidine method. The author’s finding that the action of iodide is catalytic in nature was confirmed by the workers at the University of North Carolina. It is stated in *Standard Methods* (1971) that, because of this catalytic effect, lesser amounts of iodide are required compared to amperometric titration, thus improving the separation of the monochloramine and dichloramine fractions.

Leuco Crystal Violet: Another colorimetric method that receives mention in *Standard Methods* (1971) utilizes leuco crystal violet. The procedure is capable of measuring separately the free and the total available chlorine, thus giving combined available chlorine by difference. The colors produced in the two stages of the differential test are dissimilar, so that two different sets of standards are required. Correct color development is dependent upon a number of factors, and conditions that must be carefully observed. Dilution is required for samples containing more than 2 mg/L available chlorine. Preparation of the buffer and indicator solutions is a complicated procedure, and extreme care is essential in handling ingredients such as mercuric chloride. Reagent stability is questionable; for instance, it is not good practice to incorporate potassium iodide in a buffer solution of pH 4.0, since iodides in an acid medium become more susceptible to oxidation by exposure, with liberation of traces of free iodine, consequently giving high readings in the test for total available chlorine.

But the main problem in using the leuco crystal violet method is the near impossibility of preventing, without such frequent cleaning as to be practically unacceptable, the glass or plastic cells of test kits from being stained by the crystal violet dye. In chlorination control little, if any, use is made of this method.

Methyl Orange: The indicator methyl orange has been adapted to the colorimetric testing for free chlorine and chloramines, and several different procedures have emerged since 1928. The principle of the test is that free chlorine bleaches an acid solution of methyl orange quantitatively; chloramines can then be made to react by adding excess bromide. The optimum pH of the color mixture is 2.0. A higher pH results in incomplete color development, and a lower pH increases interference by chloramines in the free chlorine test. The latest modification of the methyl orange method appeared in 1965 and forms the basis for the procedure given in *Standard Methods* (1971). There are certain inherent disadvantages in any type of method based upon a bleaching action. Care is required in mixing sample and reagent. Furthermore the observed result is dependent upon the amount of indicator added, thus accurate measurement is required. If the amount of indicator is selected to give reasonable sensitivity at low chlorine levels, it will be bleached completely at high levels. Conversely, if the amount of indicator is increased to provide the necessary excess when testing for high chlorine levels, the test becomes too insensitive for low levels. In addition to the methyl orange reagent, the test requires an acid reagent to give the desired pH, and sodium bromide solution for chloramine activation. For these reasons it has received little or no general acceptance by water analysts.

Syringaldazine Procedures (tentative): A test for estimating free chlorine in water has been reported,[15] using a mixed indicator consisting of syringaldazine and vanillinazine in conjunction with a pH 6.0 buffer. The role of the vanillinazine is not fully understood. The solutions are used to impregnate strips of paper which, after drying, may be used during field testing as a simple means of detecting free chlorine. The test conditions would appear to preclude any reasonable approach to the accuracy of normal colorimetric techniques.

Further work has resulted in the development of a syringaldazine procedure referred to as the FACTS method,[26] now classified as tentative in *Standard Methods* (1980).[10] This uses two reagents, first a

saturated solution of syringaldazine in 2-propanol and second a buffer solution of pH 6.6. Variability of reagent preparations limits the quantitative use of this test, in its present form, to the laboratory.[27] Accuracy and precision are claimed to be comparable to that of the DPD method. The limit of detection of FACTS at 0.1 to 0.2 mg/L Cl2 is relatively high, and the results for free chlorine are subject to strong positive interference by any nitrogen trichloride present.[28] Attempts have been made to adapt the method to the determination of combined chlorine and ozone, but efforts at differentiating between monochloramine and dichloramine were unsuccessful.[29] Its particular merit lies in the ability to determine free chlorine without interference from high levels of monochloramine. For the specific determination of free chlorine in such conditions it is comparable to the DPD-Steadifac procedure,[30] although the latter has the advantage, as confirmed by workers at Johns Hopkins University, U.S.A.,[27] of being able to selectively decolorize any breakthrough of monochloramine-developed color that might otherwise interfere in the free chlorine test. The FACTS methods has not received extensive testing and up to now very little use has been made of it in practice.

DPD Methods and Their Development: The development of the DPD methods, both titrimetric and colorimetric, for the determination of residual chlorine compounds in water figured prominently in theauthor's researches on chlorine chemistry from about 1940 onwards.

This work received its initial inspiration and impetus from the enthusiastic accounts, presented in the American Waterworks literature of that period, of the remarkable benefits to be obtained from the practice of breakpoint chlorination, a process already established at a practical level but not too well understood so far as the chemical mechanisms were concerned.

In the search for the ideal residual chlorine method, attention was first paid to the use of p-aminodimethylaniline. Further work convinced the author that the use of neutral o-tolidine had more to offer. At this stage the use of ferrous ammonium sulfate was introduced as a standard solution to provide a titration method, in addition to a colorimetric procedure, for the separate determination of free chlorine, monochloramine, dichloramine, and nitrogen trichloride. Independent comparative trials in England in 1949 against the amperometric titrator of that time revealed that the latter did not in fact respond to dichloramine, contrary to what had originally been claimed in 1942.

To correct this deficiency the amperometric titration was subsequently modified by the introduction of an acidifying stage to induce a response from dichloramine, and at the same time a change was made from sodium arsenite to phenylarsine oxide as the titrant.[16]

However, methods of testing for chlorine in water that require acidification at one stage or another cannot be viewed as completely acceptable, because of the possibility that the pH shift might conceivably change the conditions of chlorine equilibria existing in the water as sampled, either between the different components of the chlorine-chloramine system or between the chlorine and the

chlorine-consuming constituents present in the water. Ideally the reagent used in the residual chlorine test should not alter to any appreciable extent the pH value of the water being tested.

In the test for free available chlorine the following methods do not meet this requirement; orthotolidine, OTA, leuco crystal violet and methyl orange. It follows, therefore, that none of those methods meets this requirement in testing for total available chlorine; to them must be added neutral orthotolidine, SNORT, the amperometric titration, and FACTS.

This possible disadvantage of his neutral o-tolidine method was recognized by the author, as was the desirability of further simplicity in differential chlorine-chloramine testing through a reduction in the number of different reagents. The behavior of the phenylenediamine group of indicators was therefore reexamined. The dimethyl derivative (dimethyl-p-phenylene diamine or p-aminodimethylaniline) had been the first indicator used, and a return to this earlier work revealed that by switching to the corresponding dimethyl compound (dimethyl-phenylene diamine) the goal of the ideal residual chlorine test could be achieved.[17]

Following extensive trials by many independent workers and particularly by the Analytical Reference Service of the Environmental Protection Agency,[18] the new method, to be called the DPD method, subsequently appeared in *Standard Methods* (1971), thus providing both titrimetric and colorimetric procedures adequate to meet all laboratory and field requirements for chlorination control and investigation. Its status as a Standard Method has been maintained since that time.

Selection of Procedure

The iodometric method is regarded as the standar against which other methods are judged, but is rarely used as a practical method for water chlorination control. Interference by nitrites, ferric iron, and oxidized manganese can be quite considerable, as well as other disadvantages, such as the uncertain end point and the necessity for rather large sample volumes, have contributed to its unpopularity. The iodometric method retains a place for special purposes, including the standardization of chlorine water used in the preparation of temporary colorimetric standards and in laboratory studies of chlorine demand. It also provides the means of determining available chlorine strengths of chemicals used for chlorination purposes.

As a titrimetric method for general use, the amperometric titration has been widely accepted in America in preference to the iodometric method, although acceptance in the U.K. and other European countries is minimal. The Water Research Association in England reported adversely on it, following an investigation of methods for determining free chlorine in water.19 The agitation caused by the stirrer was found to result in chlorine loss, thus giving low results. Doubt was also expressed as t whether or not the reaction with phenylarsine oxide proceeded to completion in a reasonably short time. IN these comparative studies the performance of the DPD titrimetric method was judged superior to that of the amperometric titration.

In a later report by the Medical Enviromental Engineering Research Unit of the U.S.A. Army Medical Research & Development Command20 precautions taken in using the amperometric titration included:

(a) exposing the samples to as little light as possible.

(b) adding ahout 90% of the titrating solution before turning on the cell stirrer.

(c) completeing the titration as quickly as possible.

When an amperometric analysis for combined chlorine, which entails addition of potassium iodide, was followed by an amperometric analysis for free available chlorine, residues of iodide were found to cause erratic results. As a further precaution, therefor, it was changes of chlorine-demand-free water and the stirrer being operated for 30 seconds with each change of water. Attention was drawn to the desirablilty of circumventing this source of error by using two titrators, one for combined chlorine and one for free chlorine.

The work carried out by the Water Research Association was subsequently extended to cover combined chlorine as well as free chlorine. It was eventually concluded that the DPD methods, both titrimetric and colorimetric , were tehe best of all those examined.19 Research supported by the U.S. Army Medical Research & Development Command at Syracuse University N.Y., confirmed that the DPD method was applicable for the determination of free residual chlorine, and accurate results could be obtained by a relatively simple procedure.21 The more recent U.S. Army studies of field test kits led to the conclusion that DPD was more accurate and precise over temperstire and pH variation than were the other test kit procedures studied.20

Finally it may be noted that the DPD method has been adopted by the Ministry of the Environment of Ontario, Canada, for inclusion in its Basic Gas Chlorination Workshop Manual.22

Of other colorimetric methods only those using ortho-tolidine can claim to be sufficiently well tried to warrant further discussion at this time. In general, the various limitations of the others have precluded any serious consideration for acceptance as practical residual chlorine tests. Even the well established ortho-tolidine procedures are now recognized as having serious deficiencies, and in consequence have been the subject of much adverse criticism, particularly where free-combined differentiation is concerned. This separation can only be achieved with any approach to accuracy by chilling the sample to 1°C. In the OTA version the reaction between arsenite and chloramine is relatively slow, resulting in higher readings for free chlorine than are actually present. Additionally there are reports that other interfering substances continue to give erroneous results.

Besides this growing widespread dissatisfaction with o-tolidine methods, another no less important factor responsible for the swing to DPD lay in the discovery that o-tolidine could be a potential cause of tumors in the urinary tract. Consequently this chemical has been placed on the list of carcinogenic agents, and its use should therefore be discouraged.23 In some countries it has been virtually banned, and in its place the DPD method has been recommended by the governmental authorities. For instance, in the recommended methods for water analysis published by the U.K. Department of the Environment24 only the DPD method is now given for the colorimetric determination of free and combined residual chlorine. In America the method has similarly received a substantial measure of official support by its maintained status in the current Standard Methods.10 Other countries in which DPD is now the officially recommended method include West Germany31 and Japan.32

Possibly the most searching investigations of methods for determining chlorine in water were those carried out by the Analytical Reference Service of the U.S. Environmental Protection Agency.18 It is on their findings that we may safely rely for the final word in deciding the selection the best procedure. In their first report, published in 1969, it was concluded that:

"The best overall accuracy and precision was shown by the DPD titrimetric method. The lack of accuracy of the old ortho-tolidine methods makes them the least acceptable."

In continuing investigations all o-tolidine methods, except OTA, were deleted and the DPD colorimetric procedure was added to those selected for further study. Conclusions of the second report, published in 1971, included the following statements:

"The two DPD procedures, colorimetric and titrimetric, were nearly equal in overall performance. The overall performance of the amperometric titration ranked below the DPD methods. The poorest results were obtained with the orthotolidine arsenite (OTA) procedure. The data show the method to be the least in precision, next to last in accuracy and unacceptable for all determinations."

It may be concluded that the general consensus of authoritative opinion is overwhelmingly in favor of DPD, the EPA-approved method for both titrimetric and colorimetric procedures. Therefore only these methods will be considered in detail, together with the amperometric titration which, being based on a different analytical technique, retains considerable value for comparative purposes, although it should be noted that EPA has reported that differences in results can be caused by variations in the quality of the phenylarsine oxide (PAO) used.37

Where the indirect idiometric method is used, that is involving a back titration with either an amperometric or starch-iodide end point, limited EPA approval is granted. This extends only to use where National Pollution Discharge Elimination System permits involve total residual chlorine, and then only for wastewater.

AMPEROMETRIC TITRATION

▪ Principle

Phenylarsine oxide reacts with free available chlorine at pH 7.0. The subsequent addition of 50 mg/L potassium iodide causes monochloramine to respond. To obtain dichloramine it is necessary to lower the pH to 4.0 and increase the iodide concentration by adding 250 mg/L potassium iodide. The behavior of nitrogen trichloride in this procedure is uncertain; it appears that part may appear in the first fraction as free chlorine and part in the third fraction as dichloramine.

The amperometric titrator consists of a two-electrode cell connected to a microammeter with an adjustable potentiometer, and serves the purpose of an end point detector, thus permitting the titration of each of the above fractions with the standard phenylarsine oxide solution. If only free-combined chlorine is required the intermediate step may be omitted.

▪ Reagents

Standard phenylarsine oxide solution (0.00564N) 1 mL = 0.200 mg available chlorine
Phosphate buffer solution (pH 7.0)
Acetate buffer solution (pH 4.0)
Potassium iodide solution (5% w/v)

(AWWA Standard Methods, 15th Edition, should be consulted for details of preparation of solutions)

▪ Procedure for Free Available Chlorine

Add 1 mL of pH 7.0 buffer to 200 mL of sample and titrate in the amperometric apparatus with the standard phenylarsine oxide solution (Reading 1).

▪ Procedure for Combined Available Chlorine Compounds

Add 2.0 mL potassium iodide solution and continue titration to second end point (Reading 2). Add 1 mL of pH 4.0 buffer and 1 mL potassium iodide solution and continue titration to third end point (Reading 3).

▪ Calculations

For 200 mL sample 1 mL PAO solution = 1 mg/L available chlorine.

In the absence of nitrogen trichloride:

Free Available Chlorine	=	Reading 1
Monochloramine	=	Reading 2 - Reading 1
Dichloramine	=	Reading 3 - Reading 2

If the step for Reading B is omitted, then:

Free Available Chlorine	=	Reading 1
Combined Available Chlorine	=	Reading 3 - Reading 1

DPD TITRIMETRIC

▪ Principle

Dimethyl-p-phenylene diamine is now used in preference to neutral o-tolidine to provide a superior ferrous titrimetric method for available chlorine. The colors produced are more stable, fewer reagents are required for complete differential analysis of residual chlorine compounds, and a full response is obtained from dichloramine without the need for acidification. In the titration with standard ferrous ammonium sulfate (FAS) solution, decolorization is instantaneous and permits each step to be performed rapidly.

In the absence of iodide, free available chlorine reacts instantly with DPD to produce a red color. The subsequent addition of a small amount of potassium iodide acts catalytically to cause monochloramine to produce an immediate color. Further addition of potassium iodide to excess evokes a rapid response from dichloramine. The color at each stage is titrated to a colorless end point.

In the DPD method, unlike other methods, nitrogen trichloride does not appear in the free chlorine fraction, but is included with dichloramine and may in general be left in that fraction without further differentiation. However, if iodide is added before the DPD, a proportion of any nitrogen trichloride present is caused to appear with free chlorine. A supplementary procedure based upon altering the order of adding the reagents permits the estimation of nitrogen trichloride, if required separate from other residual chlorine compounds.

▪ Reagents

Standard ferrous ammonium sulfate (FAS) solution 1 mL = 0.100 mg available chlorine
DPD No. 1 powder
Potassium iodide crystals
Thioacetamide (Steadifac) solution (0.25% w/v)

(AWWA Standard Methods, 15th Edition, should be consulted for details of preparation of FAS solution, phosphate buffer solution, and dimethyl-p-phenylene diamine solution. The above DPD No. 1 powder is a combined buffer-indicator reagent in stable powder form and is now available commercially.)

▪ Procedure for Free Available Chlorine

To 100 mL sample add approx. 0.5 g DPD No. 1 powder. Mix rapidly to dissolve and titrate immediately with FAS solution (Reading A).

- **Procedure for Combined Available Chlorine Compounds**

Add to the above, one very small crystal of potassium iodide (approx. 0.5 mg). Mix and continue titration immediately (Reading B). Add several crystals of potassium iodide (approx. 0.5 g). Mix to dissolve, let stand about two minutes, and then continue titration (Reading C). If this fraction is fairly high, use double the quantity of potassium iodide (i.e., approx. 1.0 g).

- **Calculations**

For 100 mL sample 1 mL FAS solution = 1 mg/L available chlorine.

Free Available Chlorine	=	Reading A
Monochloramine	=	Reading B - A
Dichloramine	=	Reading C - B

If the step for Reading B is omitted, then:

Free Available Chlorine	=	Reading A
Combined Available Chlorine	=	Reading C- A

Total Available Chlorine may be obtained in one step by adding the DPD No. 1 powder and the full quantity of potassium iodide to the sample at the start and letting stand for about 2 minutes. A combined DPD and potassium iodide reagent known as DPD No. 4 powder is available, thus providing a single reagent for total available chlorine. For 100 mL sample use about 0.5 g of this powder or, if high concentrations of available chlorine are present, use about 1.0 g. After letting stand the required 2 minutes or so, titrate with the FAS solution to obtain total available chlorine (Reading D).

To obtain the Hypochlorous Acid concentration multiply the above Reading A by the appropriate factor in Table 6.

pH Value	Multiplying Factor to Obtain Hypochlorous Acid From Reading A	
	at 10°C	at 25°C
6.6	0.93	0.90
7.0	0.83	0.78
7.2	0.76	0.69
7.4	0.66	0.58
7.6	0.54	0.46
7.8	0.44	0.35
8.0	0.33	0.26
8.4	0.16	0.12
9.0	0.05	0.03

Table 6

- **Supplementary Procedure for Nitrogen Trichloride**

It may be accepted under normal conditions that absence of color in the above free available chlorine fraction also indicates absence of nitrogen trichloride. Otherwise, proceed as follows:

To 100 mL sample add one small crystal of potassium iodide (approx. 0.5 mg).Mix, then add approximately 0.5 g DPD No. 1 powder. Titrate immediately with FAS solution (Reading N).

- **Supplementary Calculation**

Nitrogen Trichloride	=	2 (Reading N - Reading A)

In the presence of nitrogen trichloride the dichloramine result requires correction as follows:

Dichloramine	=	Reading C - Reading N

[Note: In the unlikely event that monochloramine is present with nitrogen trichloride, it will be included in Reading N, in which case obtain NCl_3 from 2(Reading N - Reading B).]

- **Very High Monochloramine Levels**

Where very high levels of monochloramine are produced, as may happen during the chlorination of heavily polluted waters, there can be an intrusion of this monochloramine into the free chlorine fraction of the DPD and other differential methods, especially at high temperatures. To ensure that the DPD fraction remains specific for free chlorine under such extreme conditions, use is made of the thioacetamide reagent. Added to the sample after the free chlorine color has developed, this immediately dechlorinates any remaining chlorine compounds, without affecting the previously developed free available chlorine color. In other words, a steady FAC reading is obtained, hence the name “Steadifac” for this reagent. Should any delay occur in performing the test, so that some color intrusion from the high monochloramine occurs, the Steadifac is able to selectively decolorize and thus maintain the specificity of the test for free chlorine.

In Procedure D(3) add 0.5 mL Steadifac reagent immediately after mixing and dissolving the DPD powder. Again mix and titrate with the FAS solution (Reading A). In carrying out Procedure D(4) a fresh portion of sample must now be used, to which is added DPD No. 1 powder as in D(3), followed by the potassium iodide, to obtain Readings B and C, as prescribed in D(4).

- **Interferences**

The only interfering substance likely to be encountered in chlorinated water is oxidized manganese. To correct for this, add a few drops (about 0.5 mL.) of 0.25% w/v thioacetamide (Steadifac) solution to 100 mL sample. Mix and then add approximately 0.5 g DPD No. 1 powder. After further mixing, titrate immediately with FAS solution. The reading obtained is subtracted from the free chlorine result of the normal procedure or from the total available chlorine result, when this is performed in one step.

The presence of chromate in industrial waters and wastewaters may give rise to positive errors in chlorine determinations. Although chromate itself responds very slowly to the indicator, the reaction is catalyzed by the addition of the standard FAS solution in the DPD Titrimetric procedure. The resulting color development then seriously interferes with the end point determinations. The interference may be completely overcome by first adding (and mixing to dissolve) barium chloride, BaCl2.2H2O, in the proportion of approximately 0.2 g to 100 mL sample, thus removing the chromate by precipitation. If the sulfate content of the sample is greatly in excess of 500 mg/L SO4=, use double the quantity of barium chloride.38

DPD COLORIMETRIC

▪ Test and Calibration Procedures

Instead of titrating with standard FAS solution, measure the developed colors by using either the specified liquid reagents or, preferably, the solid DPD No. 1 powder in which the buffer and indicator are combined. To calibrate colorimeters, prepare a standard potassium permanganate solution containing 0.891 g KMnO4 per liter. Dilute 10 times for use, whereupon 1 mL made up to 100 mL with distilled water is equivalent to 1 mg/L available chlorine. Prepare the standard calibration colors by adding the calculated volumes of potassium permanganate solution, thus diluted with distilled water, to approximately 0.5 g of DPD No. 1 powder, with mixing to dissolve. Check for any loss resulting from permanganate absorption by the distilled water with a titration of the calibration colors against standard FAS titrant. Make the necessary correction in the chlorine equivalent of the standard colors. Permanent color standards are commercially available.

▪ Interferences

In the colorimetric procedure chromate interference is insignificant for Cr+6 levels below about 2 mg/L, except at elevated temperatures. Correction, when required, is performed quite simply by using thioacetamide (Steadifac) to selectively destroy the residual chlorine in the same manner as for the oxidized manganese correction in D(9) above.

Because the chromate-produced color develops slowly, it is necessary to take the correction readings at the specified times for the normal DPD readings. The rate of color development from chromate is reduced by about one half when chlorine also is present.

This continues to apply even when the chlorine originally present has been destroyed by the added thioacetamide.

When comparators with permanent color standards are used, the thioacetamide-treated sample may be used as a blank to compensate for any color interference, so long as the DPD reagents are added at the same time to both the blank and sample cells.

DPD METHOD FOR CHLORINE DIOXIDE & CHLORITE

▪ Principle

This method is an extension of the standard DPD method for determining free chlorine and chloramines in water. Chlorine dioxide appears in the first step of this procedure, but only to the extent of one-fifth of its total available content, corresponding to reduction of chlorine dioxide to chlorite ion. If the sample is first acidified in the presence of iodide, however, chlorite also is caused to react. When neutralized by the subsequent addition of bicarbonate, the color thus produced corresponds to the total available chlorine content of the chlorine dioxide. If chlorite is present in the original sample, this will be included in the step involving acidification and neutralization. In evaluating mixtures of these various chloro-compounds, it may be necessary to suppress free chlorine before reacting the sample with the DPD reagent. Glycine is used for this purpose.10, 24, 34, 36

▪ Reagents

The reagents are the same as the DPD free-combined chlorine methods, with the addition of:

Sulfuric acid solution (5% v/v)
Sodium bicarbonate solution (5.5% w/v)
Glycine solution (10% w/v)
Disodium EDTA solution (4% w/v)

(Note: EDTA solution is not required for the colorimetric procedures.)

▪ Procedure for Chlorine Dioxide

To 100 mL sample add 2 mL glycine solution and mix. Then add approximately 0.5 g DPD No. 1 powder and 5 mL EDTA solution. Mix and titrate immediately with standard FAS solution (Reading G).

▪ Procedure for Free Available Chlorine

To a second 100 mL sample add approximately 0.5 g DPD No. 1 powder and 5 mL EDTA solution. Mix and titrate immediately (Reading A).

▪ Procedure for Combined Available Chlorine Compounds

Add to this second 100 mL portion one very small crystal of potassium iodide (approx. 0.5 mg). Mix and continue titration immediately (Reading B). Then add several crystals of potassium iodide (0.5 - 1.0 g). Mix to dissolve, let stand about 2 minutes, and then continue titration (Reading C).

▪ Procedure for Total Available Chlorine Including Chlorite

After obtaining Reading C, add 1 mL sulfuric acid solution to the same portion, mix, and let stand for 2 minutes. Then add 5 mL sodium bicarbonate solution, mix, and continue titration (Reading D).

High concentrations of chlorite may interfere by causing color driftback at end points. A procedure to overcome such interference has been developed33 and may be found in the approved methods of the U.K. Department of Environment24 and the U.S. Environmental Protection Agency.34

▪ Colorimetric Procedures

Instead of titrating with standard FAS solution, the readings at each stage may be obtained by colorimetric procedures. Calibration of colorimeters is by standard potassium permanganate solution, as given under DPD Colorimetric [VI.E(1)].

▪ Calculations

For a 100 mL sample, 1 mL FAS solution = 1 mg/L available chlorine.

In the absence of chlorite:

Chlorine Dioxide	=	5 Reading G
Free Available Chlorine	=	Reading A - Reading G
Monochloramine	=	Reading B - Reading A
Dichloramine	=	Reading C - Reading B
Total Available Chlorine	=	Reading C + 4 Reading G

If the step for Reading B is omitted, then monochloramine and dichloramine are obtained together as:

Combined Available Chlorine	=	Reading C - Reading A

In the presence of chlorite:

Chlorine Dioxide	=	5 Reading G
Chlorite	=	Reading D - Reading C - 4G
Free Available Chlorine	=	Reading A - Reading G
Monochloramine	=	Reading B - Reading A
Dichloramine	=	Reading C - Reading B

Alternative calculations for chlorine dioxide and chlorite may be carried out as follows:

Chlorine Dioxide as ClO2	=	Reading 1.9G
Chlorite as ClO2	=	Reading 0.48 (Reading D - Reading C - 4 Reading G)

In the absence of chlorine and chloramines the glycine procedure is not required, since Reading A now corresponds only to $^1/_5$ chlorine dioxide and Readings B and C are omitted. The calculations then become:

Chlorine Dioxide	=	5A or 1.9A as $C1O_2$
Chlorite	=	Reading D - 5 Reading A or 0.48 (Reading D - 5 Reading A) as $C1O_2$

DPD METHODS FOR BROMINE, IODINE, OZONE & CHLOROISOCYANURATES

These methods are modifications of the standard DPD method for determining free chlorine and chloramines in water.

▪ Bromine

Residual bromine may consist of free bromine, bromamines or a mixture of these. These forms are chemically similar in giving flash readings with the usual residual chlorine indicators. In the DPD method, therefore, the result obtained in the first step, after elimination of free chlorine, if present, corresponds to free bromine plus bromamines. The term "residual bromine" is to be taken as meaning this total figure. As there are not the same differences in chemical and bacteriological behavior between free bromine and bromamines, as between free chlorine and chloramines, the need for their separate determination is not important. For the determination of mixtures of residual bromine, free chlorine, and chloramines by the DPD method, a supplementary procedure is introduced to eliminate free chlorine from the first step by addition of glycine.[24, 36]

If only residual bromine is present the procedure consists of performing the standard DPD method according to the same procedure as for free available chlorine. Call this Reading BR. The result thus obtained is in terms of available chlorine. Multiply by 2.25 to convert to bromine.

If free chlorine and chloramines are also present the further Glycine procedure is required. To a second 100 mL sample add 2 mL glycine solution and mix. Then add approximately 0.5 g DPD No. 1 powder, mix, and titrate with the standard FAS solution (Reading BR).

In this differential procedure Readings A, B, and C are obtained as in the DPD chlorine method. The calculations are as follows.

For a 100 mL sample, 1 mL FAS solution = 1mg/L available chlorine.

Residual Bromine	=	Reading BR
Free Available Chlorine	=	Reading A - Reading BR
Monochloramine	=	Reading B - Reading A
Dichloramine	=	Reading C - Reading B
(or Combined Chlorine	=	Reading C - Reading A, as before)

If it is desired to report the residual bromine in terms of bromine, this particular result is multiplied by 2.25.

Should the need arise for the separate determination of free bromine from bromamines, use is made of sodium nitrite which selectively destroys the free bromine.[24, 35] This is carried out by adding 0.5 mL of sodium nitrite solution (10% w/v) to 100 mL sample, mixing, then repeating the above step as used for Reading BR. After the nitrite addition the result now corresponds to bromamines (Reading BRA) thus:

Free Bromine	=	Reading BR - Reading BRA
Bromamines	=	Reading BRA

Where liquid bromine or bromochlorodimethyl hydantoin (DiHalo) is used in swimming pool treatment, little or no free chlorine co-exists with the residual bromine. Some combined chlorine compounds may persist together with traces of complex organo-bromo compounds and by-products from treatment by solid bromine donors. In the above procedure these residuals would appear in Reading C.

- **Iodine**

Iodine reacts with DPD in the same manner as free available chlorine, so that it is necessary only to perform the same procedure as laid down for free available chlorine. DPD methods of differentiating free iodine from free chlorine and chloramines are available using a technique similar to that for free bromine. In the case of chlorine-iodine differentiation, it is necessary to use about ten drops (0.5 mL.) of 0.5% mercuric chloride solution with the glycine.

For 100 mL sample 1 mL FAS solution = 1 mg/L available chlorine. If it is desired to report in terms of iodine, multiply the result by 3.6.

- **Ozone**

In the absence of iodide, residual ozone gives a color with DPD which corresponds to only a fraction of its total equivalent available chlorine concentration. On the other hand, if the titration is carried out with the iodide being added before or with the DPD, the full content is obtained. The latter is therefore the preferred procedure and is carried out as follows:

To 100 mL. sample add several crystals of potassium iodide (approximately 0.5 g) followed by approximately 0.5 g of DPD No. 1 powder. (Alternatively the combined reagent DPD No. 4 powder may be used.) Mix and titrate with standard FAS solution.

Should the need arise for the separate determination of ozone and residual chlorine in a mixture, this may be accomplished by introducing another step in the procedure in which the sample is first reacted with glycine (aminoacetic acid). With the optimum amount of 0.2 g glycine per 100 mL of sample, the ozone is destroyed instantaneously, whereas there is no loss of total available chlorine. Any free chlorine present reacts with the glycine to give chloraminoacetic acid which, together with any combined chlorine originally present, responds fully to DPD in the presence of iodide, with the result that the reading corresponding to the total available chlorine content of the ozone-chlorine mixture remains unchanged.

In the standard DPD procedure carried out as above in the presence of iodide, the result obtained now equals residual ozone plus total available chlorine residual. The normal standing period of about 2 minutes is omitted from the differential procedures because of a slight tendency for the developed colors to change.[24, 36]

The following supplementary procedure is now required:

To 100 mL sample add 2 mL glycine solution (10% w/v). Mix and then immediately add approximately 0.5 g potassium iodide and approximately 0.5 g of DPD No. 1 powder (alternatively the combined reagent DPD No. 4 powder may be used). Mix and titrate with standard FAS solution to obtain total available chlorine only.

Normal Procedure gives...
Total Available Chlorine plus Ozone

Procedure after adding Glycine gives...
Total Available Chlorine

Difference between above two readings equals...
Residual Ozone

For 100 mL sample 1 mL FAS solution = 1 mg/L available chlorine. To express the ozone readings in terms of ozone instead of available chlorine multiply by $^{48}/_{71}$ (say 0.7). Further separation of mixed residuals into free chlorine, combined chlorine, and ozone is possible.[24, 36]

- **Chloroisocyanurates**

Chloroisocyanurates dissociate in water to give an equilibrium mixture with free chlorine and cyanuric acid. Because this equilibrium is a dynamic one, the DPD A reading for free chlorine also includes the reserve chlorine. As fast as the free chlorine reacts with the DPD indicator, more chloro-compound is decomposed, thus releasing all the bound chlorine.

It is possible to analyze mixtures of chloroisocyanurates with free chlorine and chloramines by the normal DPD method, the difference being that the A reading will also include the free chlorine available as reserve in the chloroisocyanurates.

- **Colorimetric Procedures**

Instead of titrating with standard FAS solution, the reading at each stage may be obtained by colorimetric procedures. Calibration of colorimeters is by standard potassium permanganate solution as given under DPD Colorimetric [VI. E (1)].

CONCENTRATION RANGE OF DPD PROCEDURES

The quantities of reagents given are suitable for concentrations of total available chlorine up to 5 mg/L. Where the total chlorine exceeds this figure, use a smaller sample and dilute to a total volume of 100 mL. Mix the usual 0.5 g quantity of DPD powder with the volume of distilled water required for the dilution before adding the sample up to 100 mL. Alternatively an increased amount of DPD powder may be used with the normal volume of sample without dilution, but for very high chlorine concentrations the dilution procedure is preferred.

SIMPLIFIED DPD METHODS FOR FIELD TESTING

The various methods presented so far are essentially laboratory procedures. By appropriate modification of the basic techniques suitable tests have become available to cover all requirements of works control and field testing, ranging from the simple determination of free available chlorine to the differential analysis of complex mixtures.

In test kits for such purposes convenience in dispensing reagents is very desirable. The use of standardized tabletted reagents is therefore to be preferred, with the added advantage of much enhanced stability compared with liquid reagents. In the modern type of foil pack a virtually indefinite shelf life may be expected. The red colors produced in applying the DPD test are matched against permanent color standards, for which purpose suitable comparators are available in most, if not all countries.

The principal tablets of the DPD system are numbered 1 to 4 as follows:

Tablet	Contents
DPD number 1	DPD indicator plus buffer
DPD number 2	Stabilized KI for monochloramine activation
DPD number 3	Stabilized KI for dichloramine activation
DPD number 4	All reagents in a single tablet

Depending upon the information required, the appropriate procedure is selected in the following manner:

To Determine:	Use Tablet(s):
Free Available Chlorine	DPD number 1
Free & Combined Chlorine	DPD Nos. 1 & 3
Complete Differentiation	DPD Nos. 1, 2 & 3
Total Available Chlorine	DPD number 4

The comprehensive studies by the Water Research Association[19] included an examination of the above DPD tablets. They were found, as in the case of the DPD solution, to give the most reproducible results of all reagents examined. The results indicated further that the red colors were more easily discriminated by the eye than the yellow colors of the orthotolidine test.

Additional tablets used in more specialized procedures are given below:

DPD Acidifying

DPD Neutralizing

DPD Glycine

DPD Nitrite

Other tablets recently developed are:

DPD Chlordiox No. 1

DPD Chlordiox No. 2

These provide a simplified field test for control of swimming pool treatment by "stabilized" chlorine dioxide preparations. The control methods used depend essentially upon determining total available chlorine, since a full response from these stabilized compounds is obtained only from reactions incorporating iodide in acid solution.

For swimming pools where normal chlorination methods are used, control testing will reside in the simple determination of free available chlorine using the DPD No. 1 tablet with the additional determination, if required, of combined chlorine using the DPD No. 3 tablet. Other tests which are essential for satisfactory swimming pool operation include pH, Alkalinity, Calcium Hardness, and where choroisocyanurates are used, Cyanuric Acid. Standardized reagents in tablet form are available for all these tests.

The DPD range of tablet tests, which forms part of this comprehensive system, relates specifically to the measurement of free available chlorine, combined available chlorine compounds, and other residuals likely to be encountered in the treatment of water by chlorine and related chemicals. An outline of these tablet test procedures is given in Table 7. When incorporated in test kits for use with color comparators, the appropriate detailed instructions are provided.

Outline of Palin-DPD Tablet Tests for Free Chlorine and Other Residuals in Treated Water		
Test	**Tablets Required**	**Notes**
1. Free Chlorine	No. 1	
2. Free Chlorine Combined Chlorine	No. 1 No. 3	
3. Free Chlorine Monochloramine Dichloramine	No. 1 No. 2 No. 3	Half of any nitrogen trichloride present will be included with dichloramine. If separation is required, combine with Test 4.
4. Nitrogen Trichloride	No. 2 No. 1	Results give free chlorine plus $^1/_2$ nitrogen trichloride. Deduct free chlorine, multiply by 2.
5. Total Available Chlorine	No. 4	Can use No. 1 and No. 3, added together in place of No. 4.
6. Chlorine Dioxide	Glycine No. 1	Result gives $^1/_5$ chlorine dioxide (as $C1_2$). Multiply by 5.
7. Chlorine Dioxide plus Free Chlorine & Combined Chlorine	No. 1 No. 3	To obatin free chlorine from No. 1 reading, deduct the $^1/_5$ chlorine dioxide of Test 6.
8. Chlorite (continuation of Test 7)	Acidifying Neutralizing	To obtain chlorite (as $C1_2$) from this further reading (i.e., Test 8 - Test 7), deduct 4 times the $^1/_5$ chlorine dioxide of Test 6.
9. Total Available Chlorine (including Chlorite)	No. 4 Acidifying Neutralizing	Can use No. 1 and No. 3 added together in place of No. 4.
10.“Stabilized” Chlorine Dioxide	Chordiox No.1 Chordiox No. 2	Simplified test for control of treatment.
11.Free Bromine plus Bromamines	No. 1	Differentiation generally unnecessary, since bactericidal efficiencies are similar.
12.Free Bromine plus Bromamines	Nitrate No.1	To separate any free chlorine from Test 11 or 12 result, first use Glycine tablet. For further differentiation, combine with Test 1 or 3 as required.
13. Iodine	No. 1	

Outline of Palin-DPD Tablet Tests for Free Chlorine and Other Residuals in Treated Water (continued)		
Test	**Tablets Required**	**Notes**
14.Ozone	No. 4	Can use No. 1 and No. 3, added together in place of No. 4
15. Total Chlorine plus ozone Total Chlorine only	No. 4 Glycine No. 4	Provides for srparate determination. Supplementary procedure for separation of free and combined chlorine requires No. 1 and No. 3 tablets
16.Chloroisocyanurates	No. 1	Gives free chlorine plus reserve chlorine
17.Chloroisocyanurates Combined Chlorine	No. 1 No. 3	As for Test 16 plus combined chlorine

Where two or more tablets are required per test, they are listed above ɪn the order of use.

Table 7

REFERENCES

1. Waddington A.H., *Proc. Soc. Water Treat. & Exam.*, 4:71 (1955).
2. Palin A.T., *Jour. Inst. Water Engrs.*, 2:61 (1948).
3. Palin A.T., *Water & Water Engng.*, 54:151 189, 248 (1950).
4. Williams D.B., *Jour. AWWA*, 41:441 (1949).
5. Palin A.T., *Proc. Nat. Assoc. Baths Superintendents*, 20:78 (1950).
6. Butterfield C.T. and Elsie Wattie, *U.S. Public Health Rep.* 58:1837 (1943), 61:157 (1946).
7. Butterfield C.T., *U.S. Public Health Rep.*, 63:934 (1948).
8. U.S. Environmental Protection Agency, National Primary Drinking Water Regulations, 1975.
9. Snow W.B., *Jour. AWWA*, 48:1510 (1956).
10. *APHS, AWWA, and WPCF Standard Methods for the Examination of Water & Wastewater, 15th Edn.*, Washington, D.C., 1980.
11. White G.W., *Handbook of Chlorination*, New York, 1972, p. 436.
12. Palin A.T., *Jour. Inst. Water Engrs.*, 3:100 (1949).
13. Palin A.T., *Analyst*, 70:203 (1945)
14. Aitken R.W. and Mercer D., *Jour. Inst. Water Engrs.*, 5:321 (1957).
15. Bauer R., Phillips B.F., and Rupe C.O., *Jour. AWWA*, 64:787 (1972).
16. Marks H.C., Williams D.B., and Glasgow G.U., *Jour. AWWA*, 43:201 (1951).
17. Palin A.T., *Jour. AWWA*, 49:873 (1957).
18. Analytical Reference Service, U.S. Environmental Protection Agency, Study No. 35 (1969), Study No. 40 (1971).
19. Nicolson N.J., Water Research Assoc. England, Technical Reps. 29 (1963), 47 (1965), and 53 (1966).
20. Guter K.J. and Cooper W.J., U.S. Army Medical Environmental Eng. Res. Unit, Medical Research & Development Command, Oct. 1972.
21. Bjorklund J.G. and Rand M.C., *Jour AWWA*, 60:608 (1968).
22. Ministry of the Environment of Ontario, *Basic Gas Chlorination Workshop Manual*, 3rd Edn., June 1972.
23. Chester Beatty Research Institute, Royal Cancer Hospital, London, April 1966.
24. U.K. Department of the Environment, *Chemical Disinfection Agents in Water and Effluents, and Chlorine Demand*, London, 1980.
25. U.S. Environmental Protection Agency, *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*, Sept. 1981.
26. Cooper W.J. and Meier E.P., *Jour. AWWA*, 67:34 (1975).
27. Snead M.C. and Olivieri V.P., Division of Environmental Health Engineering, Johns Hopkins University, Baltimore, MD, U.S.A., March 1980.

28. Strupler N., Proc. *6th Water Quality Technology Conference*, AWWA, Dec. 1978.

29. Lieberman J., Meier E.P., Cooper W.J., and Rosher N.M., Am. Chem. Soc. Symposium on Disinfection, March 1978.

30. Palin A.T., *Jour. AWWA*, 72:121 (1980).

31. Mitteilungen aus dem Bundesgesundheitsamt (29.4.77) No. 92, Mitteilung Part 2.4, *Bestimmung der Chlorzehrung*.

32. Notification of Ministry of Health & Welfare, Japan, Effective from April 1st, 1979.

33. Palin A.T. and Darrall K.G., *Jour. Inst. Water Engrs. and Scientists*, 33:467 (1979).

34. U.S. Environmental Protection Agency, Method 330.6 (Titrimetric, DPD-FAS), Method 330.7 (Colorimetric, DPD). Issued Oct. 1980.

35. Palin A.T., *Jour. Inst. Water Engrs. and Scientists*, 34:383 (1980).

36. Palin A.T., *Jour. Inst. Water Engrs.*, 28:139 (1974).

37. Environmental Monitoring and Support Laboratory, Cincinnati, OH, U.S.A., EPA News Letter, 3, 1980.

38. Palin A.T., *Jour. Inst. Water Engrs. and Scientists*, 36:351 (1982).

LaMotte Company is proud to publish this handbook as a source of valuable information for anyone involved in the management and control of chlorine-treated waters. We welcome your comments about the handbook.

Working in close cooperation with Dr. A.T. Palin, LaMotte Company has developed a line of portable test kits employing the reagents and procedures discussed in these pages. The DPD tablet reagents and color comparators with permanent color standards are available in test kits covering various ranges of concentration for free chlorine only, free and combined chlorine, total chlorine only, or for differentiation of the separate chlorine fractions. LaMotte tablet reagent test kits are also offered for alkalinity, bromine, chlorine dioxide, cyanuric acid, hydrogen peroxide, iodine, nitrite, and other factors. Test kit specifications, prices, and ordering information may be obtained by contacting **LaMotte Company, P.O. Box 329, Chestertown, Maryland 21620, phone 800-344-3100 or 410-778-3100, fax 410-778-6394, or visit our website at www.lamotte.com.**

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