FORTY YEARS OF CHLORINATION: 1910-1949*

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1. INTRODUCTION

In the preparation of this review a large number of the original papers have been consulted, but it has been quite impossible to read all of them and those to which reference is made have been selected because they contain new data or new hypotheses based on old data. The amount of work involved in reading even the abstracts will be appreciated when it is mentioned that in one section alone, that of chloramine, no fewer than 264 references had been catalogued in 1941.

Prior to 1910, the opening year of the period under consideration, various chlorine compounds had been used as disinfectants and it was but a logical step to determine their action on sewage-polluted waters.

Numerous experiments had been made in this country by Sims Woodhead, Rideal, Thresh, Moor and Hewlett and various workers in France, Germany, India and the U.S.A., but the addition of chlorine derivatives to a domestic supply was not attempted in England until 1904–1905, when the well-known trial was made at Lincoln by Sir Alexander Houston and Dr. McGowan, following a severe epidemic of water-borne typhoid caused by flood-water from a polluted river.

It is perhaps of some interest to recall that Nesfield, of the Indian Medical Service, suggested in 1903 that for military field work as much as 100 p.p.m. of chlorine might be used with a contact period of 10 minutes and later removed by an anti-chlor. He was also the first to suggest the possibilities of compressed chlorine gas in steel cylinders.

In the first decade of the 20th century the use of bleach solution in the U.S.A. for water treatment had increased rapidly and by 1912 several water authorities in England (Reading, 1910; Truro, 1911; and the West Hants Water Company, 1912) had adopted this method of treatment. Under the stimulus of war conditions its use was extended and, in 1916, Sir Alexander Houston, after extensive laboratory

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experiments, chlorinated a portion of the London supply and extended the scope in 1917 and subsequent years.

This work stamped the hall-mark of reliability on the process and its employment spread rapidly throughout the country.

In Ottawa, Canada, following two epidemics of typhoid due to an infected water supply, treatment with bleach solution was instituted pending the construction of a filter plant and in 1915 the author commenced experiments with the object of reducing the cost of treatment which had increased fivefold, owing to the rapid rise in the cost of bleach.

The germicidal efficiency of various hypochlorites was determined and of these only ammonium hypochlorite, prepared by the double decomposition of calcium hypochlorite (bleach) and ammonium oxalate, promised any measure of success. With the Ottawa river water, the only source of supply, the germicidal velocity was found to be about ten times greater than that of bleach solution, although it should be realized that this water contained about 40 degrees of colour measured by the Pt—Co scale.

An examination of the formula (NH_4OCl) suggested that the greater efficiency might be due to decomposition into NH_2Cl and H_2O and a search of the literature showed that Rideal[1] had previously noticed the increased germicidal efficiency produced by the addition of ammonia to electrolytic hypochlorite; but he also attributed the obnoxious odours produced by chlorinating sewage to the formation of chloramines.

It was obvious that, if this statement also applied to the chloramine treatment of water, the process was useless, but a series of laboratory experiments proved conclusively that the addition of dilute ammonia to dilute bleach solutions not only failed to produce malodorous compounds but actually reduced them. Other experiments showed that, unlike chlorine and hypochlorites, chloramine had no oxidizing effect on indigo and so enabled an efficient residual amount of available chlorine to be maintained in all parts of the distribution system.

After trials on a pilot plant, which were at first a failure owing to excessive concentration of the ammonia solution, satisfactory results were obtained. Later the method was applied to the main supply of 20 m.g.d. with equally good results.

Attempts to use chlorine water and ammonia were not successful, for reasons which became apparent later.

Although a few plants in the U.S.A. used the process for the suppression of "aftergrowths", in general it received little attention until the publication of the results of the work of Harold and Ward[2], supplemented by the later ones of Harold[3], which showed the possibility of using chloramines made from either hypochlorite or chlorine mixed with ammonia or ammonium salts.

After they were confirmed by Sir Alexander Houston[4] in 1926, chloramine came into more general use, although a few plants (the West Hants Water Board for instance, which used bleach and ammonia solution in 1920), had adopted the method several years before.

Harold's process was essentially an admixture of preformed chloramine with the main supply, but the Metropolitan Water Board technique improved and simplified this by adding the ammonia, as the sulphate, well ahead of the chlorine to ensure the dilution necessary to prevent loss of available chlorine.

The ammonium salt was added first because Sir Alexander had found this to be a *conditio sine qua non* for the prevention of tastes and odours. The ammonia could not destroy the malodorous substances formed by the chlorine, but if it were added first the chloramine would prevent their formation. Comparatively concentrated (200 p.p.m.) solutions of chloramines can be prepared, but experience has shown that unless great care is taken the explosive nitrogen trichloride may be produced.

In one plant, operated only during the day-time, two explosions occurred owing to the failure to ensure the complete closure of the chlorine valve.

Nitrogen trichloride has been very widely employed for many years as a bleaching and maturing agent for flour and is used as a mixture of 99 per cent of humid air with 1 per cent of nitrogen trichloride produced *in situ*.

During the latter part of the 1914-1918 war Dakin and his co-workers[5] investigated the chloramines for the Medical Research Council and were also associated with Mme. Carrel in the development of the Carrel-Dakin method for the constant irrigation of suppurating wounds at Compiègne, in which slightly alkaline hypochlorite was employed. Their work on the chloramines was directed towards the development of a stable compound that could be used in the field for the sterilization of water in bottles carried by the troops.

Of the 42 chloramines prepared, the great majority was made by the action of sodium hypochlorite on sulphonamides in accordance with the equation

$$R.SO_2NH_2 + NaOCl \rightarrow R.SO_2NaNCl + H_2O$$

If R is the benzene ring the chloramide is benzene sulpho-chloramide.

Of the numerous compounds tested, two, halazone and chloramine T, were ultimately selected on account of their solubility in water high stability, and low cost of manufacture, chloramine T being easily prepared from a by-product in the manufacture of saccharin.

Trials made by the author and by MacCrady of Montreal showed that halazone and chloramine T were inferior as germicides to the simpler chloramines.

King[6] has stated that halazone was used during World War II in tablet form for individual water bottles. Thirty minutes after the addition of the tablet, a de-tasting tablet was introduced to remove the excess of chlorine. It was found that halazone was not so stable as had been anticipated and lost a portion of the available chlorine in hot climates. Similar preparations and a stable form of bleaching powder were used by the Germans.

It may be of interest to record that the Carrel-Dakin continuous-drip treatment was used by the author, without success, for the treatment of chronic infections of the middle ear at No. 11 Stationary Hospital in Vladivostock in 1918. When a solution of monochloramine was substituted, the condition cleared up rapidly. Some years later a similar preparation was used by a team of Chicago surgeons to ensure the sterility of surgical fistulae.

The 21st Report (1926) of the Director of Water Examination of the Metropolitan Water Board contains the first reference to the large-scale use of ammonium sulphate in conjunction with hypochlorite. The New River supply was treated in this manner for several months, the Cl/NH_3 ratio being 1·6 : 1, a figure very different from that found by the author to be the optimum for the coloured Ottawa river water.

The Hampton and Staines sources were also treated experimentally with chlorine and chlorine plus ammonium sulphate, the latter being added first, on alternate days. Another supply was also treated on alternate days with chlorine and preformed chloramine, but with inconclusive results.

The M.W.B. experiments also indicated that the velocity of the germicidal activity of chloramine was somewhat less than that of hypochlorite when tap water, seeded with *B. coli*, was used, although greater total "kills" were obtained after longer contact with a smaller dose. When unseeded raw Thames water was employed, the results of both the short and long periods of contact favoured the chlorine-ammonia mixture. As regards tastes, it is stated that, in the presence of phenol, "ammonia and its salts had a remarkable power in preventing the development of taste".

The apparently contradictory results obtained with the chloramines can be explained by the differences in the amounts of readily oxidizable matter in the water treated. Chlorine and hypochlorous acid are rapidly used up by these substances, leaving a smaller amount available for the destruction of the bacteria. Chloramine, on the other hand, has but little oxidizing potential and its function is almost entirely germicidal.

If the organisms are seeded into distilled water, the HClO should be a more potent agent and the latest results, reported by Butterfield and his associates at the Stream Pollution Station in Cincinnati, U.S.A.[7,8], indicate that either a 100-times longer exposure or a 25-fold concentration is required to get equal results from chloramines as compared with chlorine.

Butterfield also determined the effect of *p*H and temperature and, from the data so obtained, produced a graph indicating suggested minimum safe residuals.

These results appear to be startling at first sight, but the pure distilled water used in these experiments is very different from the usual potable supplies. The great majority contain amounts of organic matter that are minute in weight but quite appreciable in relation to the quantity of chlorine or chloramine used normally as a bactericide.

2. TASTES AND ODOURS

In addition to their effect on the germicidal efficiency, these small amounts of organic impurities may also determine the potentiality for the production of tastes and odours.

Creosote oil and the higher fractions obtained by the distillation of tar are particularly potent producers of odours resembling iodoform. This was noted by the author in 1918[9], but it was not until some years later that what might be described as the aesthetics of chlorination received more detailed study.

Sir Alexander Houston in his 18th Annual Report, 1923–24, stated that the iodoform taste was "apt to be associated with minor doses of chlorine", whilst larger doses produced tastes that were "frankly and solely" chlorinous. If the excess of chlorine were removed by a reducing agent, such as thiosulphate or sulphur dioxide, the water became tasteless and odourless.

Adams[10] made important contributions to this problem and showed that water exposed to air contaminated by smoke contained phenol bodies. Later, in 1929[11], he reported that salicyl compounds derived from the leaves and twigs of certain botanical species produced similar aesthetic objections.

Adams's earlier work was confirmed in this country by Thresh and Beale[12], and by various workers in North America. Howard and Thompson[13] examined a considerable number of phenol homologues and similar compounds and found that the taste- and odour-producing properties were confined to the mono substitution groups.

> "Phenol-, ortho-, meta-, and para-cresol, xylenol, and anisol (phenyl methyl ether) caused the characteristic iodoform taste in chlorinated water in varying intensity. The taste caused by phenol was more pronounced and lasting than by any other group. Of the cresol group, which produced marked odor as well as taste, ortho- produced a more marked taste than meta-. The para-cresol caused a foul iodoform odor, but the taste was less pronounced than with either of the other two and was easier to destroy with excess chlorine. Xylenol caused a strong iodoform taste and odor, whilst anisol produced marked taste and odor. Thymol retained its characteristic properties, which were not affected by small doses of chlorine but were broken down by large doses. Guiacol caused a decided taste and odor, which is distinctive from that produced by phenol and cresol."

3. SUPERCHLORINATION

Howard and Thompson, following the lead given by the M.W.B. results, experimented with larger residuals followed by dechlorination and the general trend of their results encouraged them to apply the process to the main supply (70 m.g.d.) for the City of Toronto for a short period; after minor difficulties had been overcome, very satisfactory results were obtained. With a contact period varying from 1 to 1½ hours before dechlorinating with sulphur dioxide, it was found necessary to use about 25 per cent more SO_2 than is indicated by the theoretical ratio of 32 of SO_2 to 35·5 of Cl, and in a later communication[14] they reported that a 50 per cent excess was sometimes essential.

The applied dosage of chlorine varied considerably, owing to rapid changes in the quality of the raw water. At first 1·25 p.p.m. were used but in later years the dose had to be raised to 4·5 p.p.m., which gave a residual of well under 1·0 p.p.m.

Superchlorination had been employed by Brush and Hale on the Kensico supply for New York City in 1922, but the object in this case was the destruction of *Synura*, which was causing abnormal tastes. A dose of 0·73 p.p.m. was used and was not followed by dechlorination.

4. BREAK-POINT CHLORINATION

The experimental results of both Houston and Howard suggest that zone phenomena occurred in some trials with increasing doses of chlorine. For instance, Howard found that taste developed after the addition of 0·25 p.p.m. of chlorine and became accentuated up to 0·5 p.p.m.; further increases to 0·8 p.p.m. caused a marked deterioration, followed by an amelioration at 0·9–1·0 p.p.m. No explanation for this zoning phenomenon was suggested, although Howard noted an inter-relation between chlorine and the free ammonia.

In 1927 Hale[15] reported that chlorination of sewage led to loss of nitrogen, the ratio of the lost Cl/N suggesting that the reaction proceeded largely in accordance with the equation

$$2Cl_2 + 3NH_3 \rightarrow 6HCl + N_2 \text{ (ratio Cl/N, 5·07)}$$

In 1928 Holwerda[16] investigated the chloramine process from the point of view of its suitability for use in the Dutch East Indies and devised a process for the quantitative estimation of the various forms of chlorine—HOCl, NH_2Cl, $NHCl_2$, and NCl_3. Using a solution of caporite, a stable form of bleach, and aqueous ammonia to give 1 p.p.m. as NH_3, he employed ratios of Cl/NH_3 varying from 5/1 to 12·5/1 and analysed the solutions immediately after mixing and after 15 minutes' and 30 minutes' contact. Tap water was used, but he does not record its analysis.

His results show a distinct break in the amount of the chlorine and ammonia residuals, which commenced at a ratio of 5/1 and reached a maximum at about 6·8/1 and a ratio of Cl/NH_3 lost of 6·6/1·0.

Holwerda's methods of analysis, with a Cl/NH_3 ratio over 5·7, indicated that, although $NHCl_2$ was present in appreciable amounts immediately after mixing, it practically disappeared after 30 minutes and was replaced by NCl_3. He suggested that $NHCl_2$ had but an evanescent existence.

Holwerda's results have been given in some detail because they record the first serious attempt to determine the various fractions of chlorinated ammonia and the loss of chlorine and ammonia with varying initial ratios of Cl/NH_3.

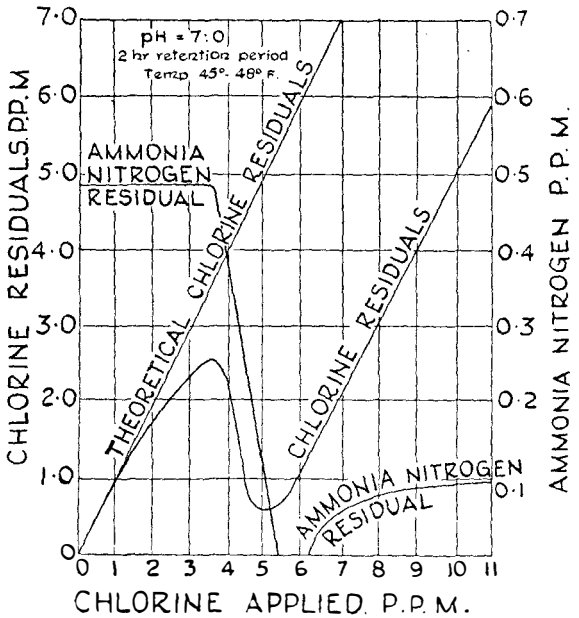
He did not, however, appear to have realized that the abnormalities observed could be made to serve a useful purpose: that was to come later.

Chapin in 1929[17] investigated the nature of the products obtained by chlorinating an excess of ammonium ions and found the result to

depend upon the *p*H of the solution. Comparatively large (0·01–0·02M) concentrations were employed and under these conditions only monochloramine was found when the *p*H was slightly over 8·5, a mixture of mono and dichloramines between *p*H 4·4 and 8·5, and nitrogen trichloride only at *p*H 4·4.

In a later paper[18], he confirmed his previous findings as to the relation between stability and *p*H of $NHCl_2$ and NCl_3 solutions, and in another series of experiments studied the loss of available chlorine produced by adding chlorine to comparatively weak solutions of ammonia. The maximum loss occurred with a ratio of Cl/N of 6·8/1, which produced practically complete loss of ammonia.

The ratio at which the maximum loss occurred was later termed the "break-point" and in 1939 both Faber[19] and Griffin[20] showed that the break-point phenomenon was produced, in varying degrees, by practically all waters. In 1940 Calvert[21] found evidence of the relationship of the break-point to the amount of free ammonia present and in the following year Griffin and Chamberlain[22] reported a more elaborate series of experiments in which the ammoniacal nitrogen content was fixed at 0·5 p.p.m. and the available chlorine varied from zero to 11 p.p.m. Distilled water was used, but sufficient buffer salts were added to ensure a constant *p*H value. Various *p*H values were employed and samples were analysed for residual chlorine and ammoniacal nitrogen after 20 minutes, 2 hours, and 24 hours.



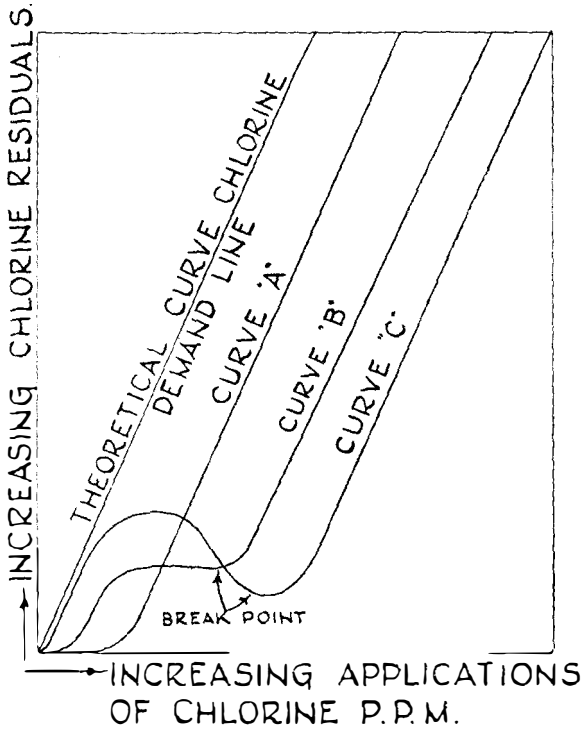
(Griffin and Chamberlain)

Fig. 1

One of their diagrams is reproduced with their permission (Fig. 1) and shows that at *p*H 7, as the Cl/N ratio increased, the residual chlorine showed very little loss until a 6/1 ratio was attained and that further additions rapidly increased the loss until it reached a maximum of about 95 per cent at a 10/1 ratio. The ammoniacal nitrogen remained constant until a 7/1 ratio was reached, after which it diminished *pro rata* to the chlorine and was entirely destroyed with a 10/1 ratio.

Other workers have been able to obtain simultaneous disappearance of both ammoniacal nitrogen and available chlorine and have found that the germicidal value of such a mixture is negligible. Larger ratios of Cl/N increased the residual ammoniacal nitrogen until there was a residue of 0·1 p.p.m. and then remained constant.

In the treatment of natural water supplies the conditions are much more complex and the residual chlorine may vary considerably even with a 10/1 ratio at about *p*H 7, which is approximately the most favourable for the decomposition of the chloramines.



(Griffin and Chamberlain)

Fig. 2

Figures 2 and 3 show a few curves obtained by Griffin and Chamberlain and one obtained by Stockwell[28] with the Ottawa river water which

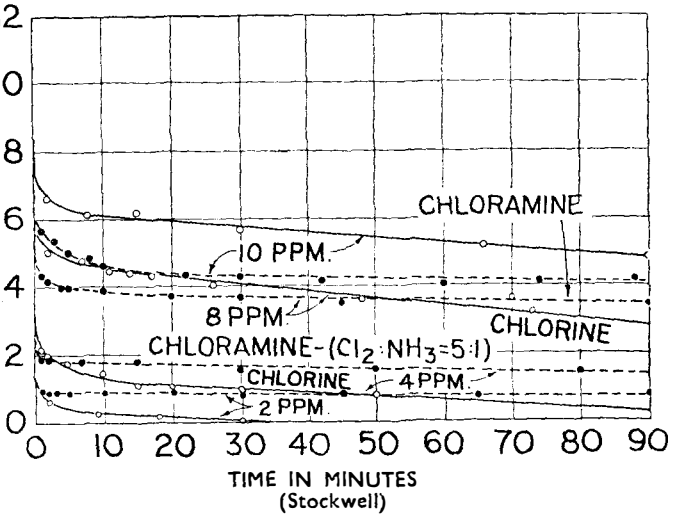


Fig. 3

shows no break-point whatever. This water has a very low ammoniacal ammonia content, but the absence of a break-point cannot be attributed to this fact as the addition of ammonia had no effect whatever.

5. CHEMISTRY OF CHLORAMINES IN RELATION TO THE BREAK-POINT

Griffin and Chamberlain considered that their results indicated that the residuals within the "hump" were due to the formation of chloramines, but recent experiments made in Buxton suggest that, with a ratio of 2·5/1 and a *p*H under 7, an almost complete absence of chloramine is indicated by the partition coefficient.

The mechanism of the chemical reactions involved is still rather obscure. The greatest loss of chlorine and ammonia occurred in Griffin and Chamberlain's experiments at a 10/1 ratio of Cl/N which corresponds to the formation of $NHCl_2$, and at *p*H about 7; but at this *p*H, according to the figures given by Chapin, the chloramines should consist of about 55 per cent of the monochlor derivative and 45 per cent of dichloramine. The equation which involves the total destruction of chloramine and ammonia is $NH_2Cl + NHCl_2 \rightarrow N_2 + 3HCl$ in which the dichloramine is 63 per cent by weight and not 45 per cent as given by Chapin for equilibrium at *p*H 7·0.

More recent work by Professor Fair and his associates at Harvard University[24] shows that the equilibrium constant for a 5/1 ratio (Cl/N) to be $\text{Req} = \dfrac{(NH_4^+)\,(NHCl_2)}{(H^+)\,(NH_2Cl)^2} = 6{\cdot}7 \times 10^5$

Professor Fair reports that the velocity of the reaction is very sensitive to changes in the *p*H and is maximal at *p*H 7·5; that the temperature coefficient is low; and that it is strongly influenced by the salt concentration. It is also suggested that one of the substances involved in the break-point reactions is dichloramine.

The nature of the mechanism involved in the simultaneous loss of Cl and NH_3 is evidently not so simple as the equation given above suggests and the table of results in the paper by Palin[25] well illustrates the diversity of results obtained by various workers.

Why mono and dichloramine should be mutually destructible under some conditions, whilst in others they may coexist for hours without appreciable loss of either chlorine or ammonia, still remains to be elucidated.

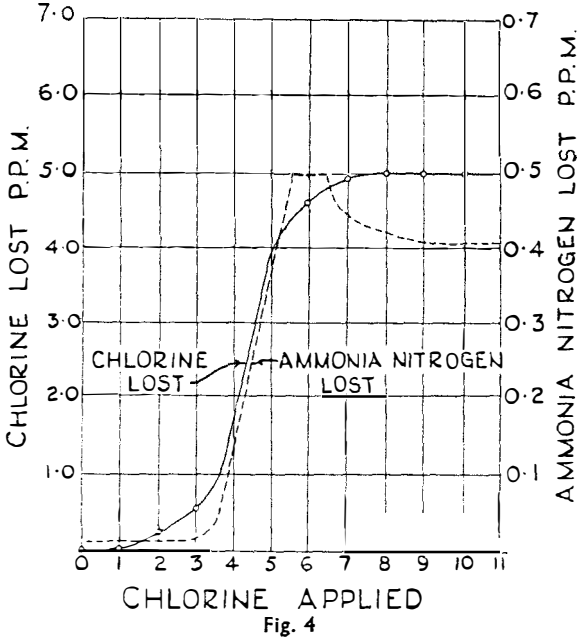


Fig. 4

In Figure 4 the results of Griffin and Chamberlain have been plotted in another way: instead of using the amounts of residual Cl and N, the points plotted represent the amounts of Cl and N lost. The so-called hump has disappeared and the general aspect is very similar to that obtained by plotting the changes in *p*H values produced by adding "strong" alkalis to "strong" acids.

From the foregoing it is apparent that tremendous strides have been made, and will continue to be made, in the chemistry of the simple chloramines; but it must be borne in mind that the effect of a number of factors, particularly that of organic matter, has still to be investigated. This factor will be considered in more detail later.

6. PRACTICAL APPLICATION

In practice it has been found that the Cl/N ratio at the break-point may vary considerably from the 10/1 ratio found in experiments with distilled water; that the intensity may vary very considerably; and that it may not occur at all.

It might be anticipated that useful information should be obtained as to the probable effect from a consideration of the chlorine absorption and the ammonia content, but too much reliance should not be placed on these and laboratory trials should be made in every case.

One of the most important results that have accrued from the various laboratory experiments supplemented by large-scale trials is that, in the majority of cases, the nadir of the curve corresponds with the minimum of objectionable odours and tastes and that a slight increase in the chlorine dose beyond this point will, other conditions being favourable, produce the desired germicidal velocity without the production of odours and tastes.

River waters may contain very appreciable amounts of ammoniacal nitrogen due to the discharge of ammoniacal liquor from gas undertakings and which has now little or no commercial value. These liquors also contain appreciable amounts of phenol and its homologues, which are potential causes of tastes and odours.

Such waters often show a well-marked break-point and respond well to the break-point treatment but, in view of the danger that might arise from a small reduction in the chlorine dose, very careful supervision is essential. With water that shows a dip in the residual chloine curve, rather than a sharp break, the margin of safety is greater.

In many cases the addition of chlorine until a satisfactory residual is obtained results in achieving the correct post-break-point dose.

One important fact that has emerged from the plethora of experimental work on the chloramines is that the germicidal velocity of $NHCl_2$ is, in the absence of organic matter, very much lower than that of HOCl. If chloramine residues, or even free chlorine ones, are carried in the domestic supplies, all samples taken from bacteriological examination should contain a dechlorinating agent as recommended by the Ministry of Health.

7. PRACTICAL SIGNIFICANCE

The next step is to consider the practical application of the data that have emerged from the laboratory studies, and for this purpose the various classes of water may be divided into two main groups:—

(1) Lakes and upland supplies, and

(2) Rivers and wells.

1*a*. *Lakes.*

These waters in this country are generally comparatively free from colour and turbidity, contain but few salts, are bacteriologically good for the whole or the greater part of the year by reason of their storage capacity, and may be plumbo-solvent to some extent.

Chlorination adds to the safety factor and if this is effected at the source the obvious treatment is a small dose of monochloramine. If the water is chlorinated at the outlet of a service reservoir, more rapid action is desirable and chlorine in the form of HOCl is indicated; but it must be remembered that, if the *p*H exceeds 8·0, due perhaps to the addition of lime to correct excessive action on lead, the HOCl becomes changed to the relatively inactive ClO^- form. To counteract this, the concentration must be increased or, alternatively, chloramine may be employed, particularly if the available chlorine residue tends to disappear towards the periphery of the distribution system.

If the colour is sufficient to make its removal desirable, chlorination before coagulation and filtration should be considered, as it tends to reduce the amount of alum necessary to give the optimum *p*H and keeps the filters and channels in good condition. If some residual chlorine is present in the filtered water it can be converted into the monochloramine by the addition of the appropriate amount of ammonia. In this method the chlorine present (HOCl) acts at the point of minimal *p*H, i.e. when its germicidal activity is maximal.

1*b*. *Upland Waters.*

These are characterized by their low alkalinity, low *p*H, usually 6·4–6·6, which promotes action on lead, and a considerable amount of colour. Coagulation by sulphate of alumina followed by filtration is almost invariably necessary and usually results in an effluent that satisfies the standards of the Ministry of Health. Chlorination increases the safety factor and a smaller dose is necessary if it is added after filtration rather than before. The choice between HOCl and NH_2Cl should depend upon the period of contact available before the water reaches the consumer, and upon the *p*H. If the *p*H were increased to 8·0 or over to prevent action on lead, the germicidal velocity of HOCl would be retarded.

2*a*. *River Supplies.*

Because of the diversity of factors that may be encountered in river supplies, it is impossible to suggest more than a few general indications regarding the application of chlorine compounds to these supplies.

The investigations made by several River Boards during recent years have directed attention to the marked deterioration in quality which has occurred since 1939 and which still obtains. However willing local authorities might have been to tackle the problem by the extension of existing purification facilities or by the erection of new works, the difficulty of the procurement of both labour and material has prevented effective action. This situation has resulted in water authorities whose only source is river water, often highly polluted with both domestic sewage and trade wastes, being compelled by force of circumstances to rely more and more upon chlorination until extensions of their traditional methods can be made.

Thorough chemical and bacteriological examinations are necessary, followed by trials of various forms of chlorination. In many cases

the application of break-point chlorination to the raw water has proved successful but it cannot be over-emphasized that unremitting vigilance is required. The residual available chlorine should be recorded automatically and, where fluctuations in the quality of the raw water are frequent and unpredictable, automatic control of the dose is desirable. The use of chlorination after filtration must be determined by local circumstances.

The river waters appear to be a field in which the use of chlorine dioxide might be explored with advantage.

2b. Well Supplies.

These differ so widely in chemical composition and liability to pollution that each case must be considered on its own merits, bearing in mind the general bactericidal properties of the various forms of chlorine and the factors that influence them.

8. CHLORINE DIOXIDE

One of the most recent developments in chlorination is the use of chlorine dioxide (ClO_2), which from its composition might be expected to have a considerable germicidal value. Its marked instability has delayed industrial production, but in 1944 success was achieved by chlorinating a solution of sodium chlorite in accordance with the equation $2NaClO_2 + Cl_2 \rightarrow 2NaCl + 2ClO_2$. In practice the sodium chlorite solution and chlorinated water are thoroughly mixed in a separate chamber and the dilute solution of ClO_2 piped to the water main.

The solubility is low (about 3 per cent at normal temperatures) and the germicidal activity is stated by McCarthy[26] to be greater than that of chlorine in distilled water. It is such a strong oxidizing agent that in the presence of considerable organic matter it may be inferior as a germicide.

It is claimed, however, that the high oxidation potential makes it the method of choice for the treatment of river and lake waters containing much industrial wastes. At Niagara Falls, N.Y.[27,28], where none of the usual processes, including break-point chlorination, gave satisfactory results, ClO_2 is said to have been entirely successful in producing a palatable supply and similar plants have been installed elsewhere.

Macleod[29] has reported similar results from Scarborough township on Lake Ontario, where the process has been in operation for two years. With a dose of 3–4·5 lb. $NaClO_2$ per m.g. and an equal weight of chlorine, tastes and odours, which formerly persisted throughout the year with peaks in the spring and autumn, were completely removed and a palatable supply obtained.

The marked avidity of ClO_2 for organic matter may be countered by more or less satisfying the Cl demand with liquid chlorine and adding the ClO_2 at a later stage. This reduces the necessary dose of the more costly ClO_2.

The relation of the germicidal velocity to *p*H has been investigated by Ridenour and Ingols[30], who report that the lower degree of

dissociation at the higher *p*H values increases its efficacy as compared with chlorine.

Aston[31] reported that at Tonawanda, N.Y., the introduction of ClO_2 treatment caused a few complaints of tastes caused by slime growths in the mains; after these had been destroyed a uniform chlorine residual was found throughout the whole of the distribution system and complaints ceased.

9. GERMICIDAL ACTIVITY

(*a*) Mode of Action.

It was common knowledge 40 years ago that many of the recognized disinfectants were strong oxidizing reagents and it is perhaps natural to assume that hypochlorites, which produced nascent oxygen, derived their germicidal activity from this substance. After it was proved that the activity bore but little relation to the available oxygen and that chloramines have little or no oxidizing effect, it became necessary to abandon this hypothesis. Thermochemical considerations suggest that chlorine and hypochlorous acid should be about equally potent as oxidizing agents, but, as will be shown later, their germicidal value differs in a marked degree.

The work of Cross and Bevan[32], who found that chloramines tended to combine with nitrogenous molecules and become fixed on cellulose, led the author to suggest that the action is a cytolytic one in which the chlorine attacks and partially or wholly destroys the membranous envelope of the organisms; also that a portion of the chlorine or chlorine compound may penetrate the membrane and produce changes that result in the death of the organism[9].

The recent work of Green and Stumpf[33] at Columbia University indicates that HOCl interferes with one or more of the enzyme systems, the principal one being triosephosphate dehydrogenase which results in a sulphydryl group (—SH) being changed to the oxidized form —S : S— as in $2G.SH \rightarrow G—S : S—G + H_2$, a process that should not be confused with the antibiotic action of the sulphanilamides, which compete with the organism for a compound essential to its metabolism.

Fair *et al*[34] suggest that the penetrability of the cell wall, which determines the rate of diffusion, is a very material factor because it facilitates the passage of a small molecule of electrical neutrality such as HOCl.

(*b*) Rate of Action.

When either chlorine or a hypochlorite is added to water, hypochlorous acid results, the ionization of which is determined by the ionization constant and the *p*H. $HOCl \rightarrow OCl^- + H^+$. At *p*H 6 the available chlorine is almost entirely HOCl; at *p*H 7, 80 per cent; at *p*H 8, 30 per cent; and at *p*H 9, about 5 per cent. Fair's curve for these results shows a maximum change between *p*H 7 and 8, values

that are probably of most interest to water undertakings and particularly to those dealing with upland waters that require hardening.

They have also calculated the comparative killing power of HOCl at various *p*H values with *Esch. coli* and find that the amount required at *p*H 8 is about 30 times that at *p*H 7. These results, however, are based on the figures of Butterfield *et al*[8] for the dose required to kill within one minute. With longer contact the difference in the efficiency was much smaller.

Using *E. histolytica* as the test organism the amounts of available chlorine required to effect a 50 per cent kill in 30 mins. at 18° C. was 3·4 at *p*H 7, as compared with 23·0 at *p*H 8·0 and 28·2 at *p*H 9·1.

With the same organism they found $NHCl_2$ to have 60 per cent of the efficiency of HOCl and NH_2Cl only 22 per cent, but at *p*H values over 7·5 the chloramine gave better results than chlorine, due to the inefficient OCl^- ions at the higher *p*H.

With the sporulating organism *B. anthracis* the results were unfavourable generally, that with NH_2Cl being particularly poor.

The only results available with the enteric group of organisms were those of Butterfield[8] and showed that after 1 minute's contact $NHCl_2$ has 1 per cent of the germicidal value of HOCl, whilst NH_2Cl has even less. No data were available for longer periods of contact.

The relation between contact time and temperature, and the temperature coefficient, were also calculated for a number of various types of organisms.

These contributions of the Harvard workers towards a sound scientific understanding of the chemistry and bacteriology of chlorination are invaluable and it is to be hoped that further data will be forthcoming in the near future.

It will be appreciated that, in experiments of the nature just considered, it is essential that the factors affecting the results should be kept to a minimum although it may be possible, as in the Harvard work, to consider the effect of two variants simultaneously: the addition of such a factor as organic matter of a variable composition would add enormously to the complexity of the problem.

All organic matter is oxidizable and the amount of oxidation produced is determined by the E_h*, concentration, and temperature. If the E_h is below the critical level, a condition that usually obtains with chloramine in highly-coloured waters, practically all the NH_2Cl or $NHCl_2$ is available as a germicide and the relative killing-power of chlorine (as HOCl) and chloramines is inverted. This condition obtained in the original Ottawa experiments and the results have been confirmed by other workers.

Houston[4] reported that with raw Thames water "the addition of ammonia has a decided beneficial effect, thus allowing of considerably smaller doses being used, or alternatively increasing the certainty of sterilization with the same dose".

* E_h or E.P.D. is a measure of the intensity level and not of capacity, just as temperature and *p*H bear no relation to heat capacity and buffering power respectively.

To illustrate the variety of results that might result from the chlorination of different types of organic matter, two experiments of Mallmann and Audrey[35] may be quoted.

In one a 0·1 per cent solution of agar (*p*H 7·0) was treated with increasing doses of chlorine and the E_h and available chlorine determined at short intervals. A definite "break-point" was produced and, after the residual chlorine had reached the minimum, a further increase resulted in a solution that was more germicidal than the same amount of chlorine in distilled water at the same *p*H. This was confirmed by adding 0·3 p.p.m. of available Cl as NaOCl to a solution containing 3·0 p.p.m. of agar or a commercial hydrophilic colloid. An increased germicidal effect resulted.

In the second experiment, with a 0·1 per cent solution of peptone, no germicidal effect was found until the available Cl found by titration with KI and starch exceeded 4 p.p.m. The plotted figures showed the E_h had a much better correlation with the "kill" than the chlorine, determined by either the KI-starch process or with *o*-tolidine.

Schmelkes and Horning[36] found chloramine T superior to azochloramide as a germicide in distilled water, although azochloramide showed a greater efficiency in the presence of organic matter; and Beard and Kendall[37] have reported that, in the presence of organic matter and at *p*H 7·0, chloramines have a greater germicidal power than chlorine.

A consideration of the evidence now available suggests that, if the water contains but little organic matter, the contact period is short, or the *p*H is low, chlorine as HOCl is the superior germicide; if a coloured colloid or other organic matter is present in appreciable amounts, or the *p*H exceeds 8·0, or the contact period is long, the use of chloramines is indicated.

10. EFFECT ON CARRYING CAPACITY OF AQUEDUCTS

In view of the claims that have been made as to the beneficial effect of chlorination on friction losses, it seemed advisable to collect any data that might be available in this country. A short questionnaire was sent to the water engineers of several cities with comparatively long aqueducts and the replies, briefly summarized, are:—

Birmingham.	No data; water chlorinated at delivery end of steel pipeline concrete-lined.
Derwent Valley Water Board.	No specific data. Mr. Thompson reports: "The removal of colour from the water, the increased alkalinity and chlorination, all have a tendency to prevent further peaty deposit on the wall of the pipes and the last two measures have a positive tendency to remove the previous deposits." Residual chlorine 0·05 to 0·10 at inlet and 0·05 p.p.m. on delivery to service reservoir.

Liverpool. Chlorine-ammonia used but impossible to assess any variation in the carrying capacity.

London. Metropolitan Water Board.

Precise data is lacking as far as the Board is concerned, but for the last three years weed control has been practised in the New River by means of chlorine. This open aqueduct, chiefly clay-lined with a flow of upwards of 40 m.g.d., has had a 1–3 p.p.m. chlorine dose injected into the water at intervals during the summer months and has been instrumental in inhibiting aquatic plant growth for some distance downstream of the application point; the distance is dependent upon the type of plant, but lengths of between 1 and 2 miles downstream are, for practical purposes, kept reasonably clear, the deep-rooted plants being those least affected.

As far as larger stored water conduits are concerned it has been noted that fresh water mussels will not live downstream of a chlorination point where a dose up to 1 p.p.m. has been usual for pre-treatment purposes, but dosing such conduits to inhibit mussel growth alone has not been undertaken as yet.

Glasgow. No data; water chlorinated immediately before delivery into the service mains; aqueducts very free from growths.

Manchester. Water treated with Cl/NH ratio of 4/1; 0·3–0·5 p.p.m.; residual Cl about 100 miles from inlet about 0·1 p.p.m. in winter but disappears in summer; slight algal growths at water level in open aqueduct at certain periods of the year. No effect on capacity noted.

These replies do not warrant any definite conclusion, although the experience of the Derwent Valley Water Board suggests that chlorination may have had some beneficial action, whilst the reply from Manchester indicates that in the open aqueducts the dose of chloramine employed is unable to prevent the development of algae.

From American sources two cases have been reported in which the results are definitely favourable. At Little Rock, Arkansas, Crisp[38] impounded water in a newly-created lake and delivered it in a reinforced concrete pipe 35 miles long and 39 in. in diameter. In 1938 the discharge was 25·3 m.g.d. (U.S.A. galls.) but by February, 1939, the capacity had fallen to 20·4 m.g.d.; on emptying, a slimy growth was found on the inner surface, the amount being greater in the sections nearer to the lake. In June, 1939, a 3/1 ratio of Cl/NH was used (dose 1·26 p.p.m., residual 0·55 p.p.m.) and after three weeks

the capacity had increased to 21·8 m.g.d. On 2nd October a section was isolated and treated with 30 p.p.m. of chlorine for two days before resuming the normal chloramine treatment. In April, 1940, the capacity had increased to 22·25 m.g.d. and Crisp suggests that "chlorine alone in high concentrations appears to remove the growth quickly and effectively, which fact suggests that superchlorination might be a more effective remedy than chloramine treatment". The conditions in this trial were not normal, as water from a newly-formed lake would be a particularly favourable medium for the growth of algae.

Hodges and Ackerman[39] found that prior to chloramine treatment the 23-in. cast iron main, 12 miles in length, at Utica, N.Y., had frequently to be cleaned and lost 20 per cent of the carrying capacity in six months. After chloramine treatment with a dosage sufficient to give a residual of 0·2 p.p.m., the capacity was unchanged after 9 months.

The present Engineer, Mr. L. J. Griswald, reports[40] that prior to chlorination the average discharge between cleanings was 13·2 m.g.d. After cleaning (1934) the rate was raised to 14·5 m.g.d. and chloramine treatment obviated further cleansing until 1941, when the flow had dropped to 13·7 m.g.d. The best results were obtained with a Cl/NH_3 ratio of 5·6/1 which carried a chlorine residual throughout the whole length of the pipe. It was also found that the growth of iron tubercles had been inhibited. Mr. Griswald adds that "discussions at various water association meetings suggest that it is not so successful with certain types of water as with our comparatively soft water".

The experience at Utica is of interest on account of the successful inhibition of the growth of iron bacteria if the development of tubercles can be attributed to this cause.

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DISCUSSION

Mr. Sherman Chase (New England Water Works Association, U.S.A.) said that, as he was not a chemist, it was a little difficult for him to discuss the technical phases of the paper without immediately showing his ignorance. Therefore, he confined his remarks to the practical application of chlorination, somewhat from the historical standpoint, to indicate what chlorination had meant in the United States with respect to the prevention of water-borne epidemics.

It was only fair to say that within the last 50 years, or perhaps a little less, the knowledge which had been acquired with respect to chlorination, the scientific aspects and its practical application, represented the most significant and most far-reaching progressive step in the water-works field from the standpoint of the prevention of disease. In 1900 the typhoid fever death rate in the United States was 35 per 100,000 of the population yearly; to-day it was probably in the neighbourhood of one. To a very large extent that tremendous reduction in the typhoid rate—the tremendous saving of life, the prevention of sickness, the economic loss and suffering that was avoided—was due to the application of the chlorination process to the water supplies. It was to men such as Mr. Race, the late Sir Alexander Houston and other pioneers in the field of chlorination that the world, and particularly the United States, owed so much. In the words of Mr. Winston Churchill, "Never did so many owe so much to so few."

One particularly valuable aspect of chlorination lay, or had lain, in its use for the emergency treatment of supplies accidentally contaminated, or for the treatment of supplies from highly-polluted

sources when such sources had had to be used in cases of emergency.

About 18 years ago he had referred to the chlorination of the Hudson River at the Watervliet arsenal at the time of the first world war. During the flood of the Ohio River in January and February, 1937, when the water supplies of Louisville, Evansville and other cities along that river were inundated and put out of service, the emergency chlorination of supplies had unquestionably prevented outbreaks of disease which would have occurred had not chlorination been used.

In contrast, in the greatest of all floods on record in the Hudson River Valley, in 1913, when the waterworks and the slow sand filters of Albany, New York State, were inundated, there was no chlorination, and for less than 24 hours raw Hudson River water was pumped into the distribution system of the city, having a population of about 100,000. After less than 12 hours of the use of that unpurified water, and in spite of the instructions issued concerning the boiling of the water, its use had resulted in approximately 250 typhoid cases and approximately 25 or 30 deaths. Yet in the Ohio River floods which he had mentioned, which were worse, for many water systems were put out of commission and emergency supplies from all sources were called upon, so far as he knew there had been no water-borne disease whatsoever. He ascribed that result to the chlorination of all emergency water supplies that were called upon during that period.

Mr. M. T. B. Whitson said that engineers were bound to use the stuff called "chlorine" or alternatives, so that they must know something about the mechanics of chlorination; and it was due to men such as Mr. Race that they knew so much. Therefore, he tendered his personal thanks to him and to workers of his kind who had given so much information and had done so much for the water supply industry.

Commenting on the statement, in the first paragraph of the paper, that no fewer than 264 references to chloramine had been catalogued in 1941, Mr. Whitson said that water engineers had some difficulty in trying to understand the position in regard to chlorine, chloramine, break-point chlorination, and so on, by reason of the plethora of information. The word "plethora" meant a superabundance; it also meant overfulness of the blood, and engineers in trying to follow the spate of information were apt to become plethoric. The author had given an excellent résumé of everything that had happened in regard to chlorine, chloramine, and so on, during the last 40 years; and yet, after studying the paper, no one could say which particular one of those substances or treatments was the best.

As a case in point arising from the paper, he said that the work done by the Harvard men in America, headed by Butterfield, in 1943, involving a long series of experiments, had rather hit chloramine on the head, for it was stated that the time required by chloramine to kill pathogenic bacteria was much longer than that required by chlorine. They had also pointed to the effect which *p*H value had on the efficiency of chlorine, and had done some very useful work. Then in 1944 another group of research workers had proved that ozone was more

effective than chlorine in killing off those pathogens. In the same year still another group of experimenters had proved that chlorine was just as good as ozone in killing the pathogens.

The result of all that information was that engineers were left high and dry, still wondering what was the best method of sterilizing water. Mr. Whitson added that he had his own private opinions, but he did not intend to propagate them on this occasion.

The paper, as he had read it, was concerned mainly with the discussion of chloramine, and engineers at the present time were being rather talked out of the use of chloramine; they were being talked into the use of break-point chlorination. Chloramine, one was told, had certain advantages over straight chlorination; it did not produce tastes and odours in the water. The break-point chlorination "fan" would say that that was correct, but that it was due to an avoiding action; it was held that chloramine avoided tackling the organic matter in the water, and therefore it did not produce tastes and odours. That was what the engineers were told by the chemists, or by certain chemists.

So the question as to whether engineers should use chloramine or chlorine or break-point chlorination had not yet been cleared up, and his purpose in speaking was to do a little of what the Americans called "barking". There was a research group of the Institution of Water Engineers dealing with the sterilization of water, the group consisting of chemists and engineers who at the present time were reviewing the plethora of information existing, trying to obtain from it something of a definitive nature. It might be impossible, but that was the aim; and it was the intention of the group to arrange a symposium on the sterilization of water early in 1950, as an effort of the Northern Section of the Institution. There would be a paper on chlorine processes from the chemist's point of view, by Dr. Palin, of Newcastle; another on chlorine processes from the bacteriologist's point of view, by Dr. Allen, of the Water Pollution Research Board; another on chlorination apparatus; and another on other processes, which would include information on the subject of ozone. After a very great amount of persuasion by the other members of the group, he had agreed to deal with that matter.

Thanking Mr. Race again for his paper, he said he hoped the discussion would justify the trouble taken to prepare it; discussion was the finest means of conveying thanks to the author of a paper.

Mr. A. H. Waddington said that, as a raw and inexperienced waterworks chemist, translated straight from the University to a large waterworks in the Midlands, and at a time when far less was known of the physical and chemical aspects of chlorination than was known to-day, he had, when in any trouble, automatically turned to a small maroon-covered volume of some 150 pages entitled "The Chlorination of Water," by Joseph Race, F.I.C., published in 1918. In that book, if one did not find the exact answer to any question one was dealing with, one did find some clue to the steps one ought to take in order to

overcome one's troubles. It was with some trepidation that Mr. Waddington ventured to take part in the discussion of the present paper, albeit with pleasure.

The author had endeavoured to abstract, from the growing volume of literature on the physical and chemical aspects of chlorination and chloramination, important facts which had a direct bearing on the practical application of those processes. Unfortunately, a considerable amount of work still needed to be done, despite several recent papers on two aspects of the problem, namely, the determination of residual chlorine in waters which had been subjected to controlled superchlorination (or, as it was more commonly called, break-point chlorination) and the determination and recognition of the compounds of nitrogen and chlorine formed after such treatment.

In the latter respect one had to agree with Mr. Race's observation that, whilst useful information could be obtained as to the probable effect of those modern chlorination processes from a consideration of the chlorine absorption and the ammonia content of a water, those gave only part of the story; it was on laboratory trials that the final decision should be made as to the dosages required and their ultimate effect upon the water. Even such laboratory trials, however, presented their problems, and the utmost care must be exercised in controlling the conditions of experiment, such as the *p*H value of the water before and after treatment, the temperature and the time interval between the commencement of the test and the actual determination of the residual chlorine compounds. Again, whereas direct Nesslerization of a water which had been subjected to controlled superchlorination gave in most cases a negative result for ammonia, it would be found that, if the distillation method for ammonia estimation were used, there appeared to be a continuous evolution of free ammonia; such a test was at the present time valueless, or perhaps he should say it could not be interpreted correctly, for waters treated by break-point chlorination. That phenomenon was very marked in waters which contained both ammoniacal nitrogen and albuminoid nitrogen. The colour formed with Nessler solution was also of a different tint from that obtained with inorganic salts of ammonia.

There was one other observation on the effect of controlled superchlorination upon coagulation by alum; and whilst it was true that in certain cases such chlorination of itself, given sufficient time for reaction, would reduce the colour of a water, it did not always follow that such treatment would necessarily help coagulation either by reducing the dose of alum or by giving an ultimately better filtrate. In numerous cases it had been found that the application of heavy doses of chlorine to a water of moderate hardness, colour and turbidity appeared to prevent the formation of the desired dense granular quick-settling floc which was so helpful in water treatment plants having sedimentation. In such cases floc formation was inhibited and the floc formed appeared to be stabilized and of a colloidal nature.

Finally, he said that a lot of interest had been aroused recently in various fluorine compounds, and chemists would doubtless be aware

that there were certain combinations of chlorine and fluorine. He asked whether the author had had any experience of such compounds.

Mr. N. J. Pugh regarded the paper as very valuable for reference; when in difficulty in regard to a special problem one might readily turn to it and obtain a lead to the literature which might be helpful. In compiling such a bibliography, the author had rendered very great service to water engineers.

Mr. Pugh said that many less informed persons had to consider the possible applications of chlorine, particularly in an emergency. Then there was not much time in which to discuss matters; it was a question of "do" or "don't", and, if one did something, of how far one should go.

In Section 1 of the paper there was a reference to the much greater rapidity of "kill" of bacteria by straight chlorine than by any of the chloramine group. But in Section 9 (*b*) there was a reference to the addition of ammonia giving a better kill with a smaller quantity of chlorine. Those two statements appeared to be opposed. Then the last paragraph of Section 9 underlined that one could not lay down rules as to whether a method of treatment was the right or the wrong one. There were *p*H considerations, the presence of colour, organic matter, and so on. These might vary from day to day or from hour to hour, and in Mr. Pugh's opinion, if one became too deeply involved in technical considerations and purely chemical arguments, there was the danger that one might fail to see the wood for the trees and might not take the common-sense action in an emergency. He did not think engineers were failing in that way, but he urged the importance of viewing the matter from the point of view of their day-to-day problems.

Mr. Pugh put forward a simple working rule for chlorination: "If in doubt, do not underdo it". If one were going to make a mistake at all, it was better to overdo the job when sterilizing with chlorine or any other of our known agents.

Another possible source of confusion was the spate of terms used—"superchlorination", "break-point chlorination", "chloramination" and so on. After all, they were all chlorination, but certain other things were brought into the picture to meet special circumstances. One might try to remove some of the superabundant terms and bring the matter down to the use of chlorine in the sterilization of water, avoiding the use of the "super" and "break-point" terms; if one added to chlorine another agent, it was just a variation of the use of chlorine for sterilization of water. He asked how Mr. Race felt about trying to simplify the approach by talking simply of chlorination and avoiding some of the extraneous terms which had been brought in to designate phenomenona which were not understood at the time.

Mr. A. B. Baldwin said that on the first page of the paper reference was made to some of the early attempts at chlorination. In the interest of the completeness of the record, and also because of the kudos it meant to the Institution, it was right that he should recall an experience which had occurred as far back as 1909. Mr. Race had recalled the

well-known typhoid epidemic at Lincoln in 1904–5, when a polluted river water was pumped directly into the supply. At that time conditions in Shrewsbury were exactly the same, and in 1909 Mr. W. Arnold Hewitt, a member of the Institution, had introduced pressure filters and chlorination there. After consulting Dr. S. Rideal he had decided on a fixed dose of $\frac{1}{2}$ p.p.m. of chlorine, using "Chloros", supplied by the United Alkali Company in 10-gallon carboys. He had used the standard pressure filter chemical pump, such as was supplied with all standard pressure filters, and the plant was actually operating in the summer of 1909.

The figures relating to the reduction of typhoid cases in those years were perhaps even more illuminating than those given by Mr. Sherman Chase. The average number of typhoid cases, in a population less than 30,000, in the 15 years prior to 1909, was 24 per annum—a very high rate. Following the introduction of chlorination in 1909, the typhoid rate dropped immediately to an average of 1 per year. The local Medical Officer of Health was very interested in the matter, for the town had been a very black spot as far as typhoid was concerned, and he had been able to show that each of the cases arising after 1909 were "imported" into the town, i.e. the disease had been contracted before the person concerned had come there.

In the face of such striking evidence, continued Mr. Baldwin, it was somewhat difficult to criticize the paper, and indeed, he hesitated to do so. But he felt he ought to recall what was perhaps a parallel case. When Lord Lister had discovered antiseptics he had used carbolic and had experienced immediate and striking success. But before very long he had found that it had also disadvantages and he had abandoned it altogether. With regard to the use of chlorine for the sterilization of water, Mr. Baldwin felt it was at least permissible to hope that one day we might follow much the same course, by leaving it a place of honour in the archives of water engineering and never using it again. He looked forward to the finding of a sterilizing agent having all the advantages of chlorine and none of its disadvantages.

Referring to the author's remarks, in Sections 7 and 8 of the paper, on the chlorination of river supplies, Mr. Baldwin endorsed his opinion that each case should be treated as unique. That applied particularly to the application of break-point chlorination; whilst he agreed with the author that that treatment had proved successful in some instances, he added a warning that indiscriminate changing over from marginal to break-point treatment by the over-enthusiastic might result in so many disappointments as to bring break-point treatment into disrepute. Probably it did not deserve that.

At the end of Section 7 (*2a*), dealing with river supplies, the author had pointed out that river waters appeared to provide a field in which the use of chlorine dioxide might be explored with advantage. But in Section 8 he had pointed out that chlorine dioxide was such a strong oxidizing agent that in the presence of considerable organic matter it might be inferior as a germicide. Mr. Baldwin felt that, on the face of things, those two statements were somewhat contradictory; but

probably the operative word was "considerable". When he thought of river supplies he had in mind rivers in their middle reaches, where normally one could expect at least fairly heavy loadings of organic matter, and as he had a rather special interest in such waters he would be glad if the author would enlarge on the point.

AUTHOR'S REPLY

The author said that Mr. Sherman Chase had rightly drawn attention to what could only be described as an enormous fall in typhoid rates in the period under review. Over 30 years ago this effect was already apparent and the author wrote: "It may justifiably be said that no other sanitary measure has accomplished so much at so small a cost. . . ."

It could not be over-emphasized, however, that both men and machines were fallible and that chlorination should be employed as the only line of defence in exceptional circumstances.

The point raised by Mr. Whitson as to the relative bactericidal value of chlorine and chloramines could be conveniently discussed in conjunction with the apparently paradoxical statements referred to by Mr. Pugh.

The work of Butterfield *et al*, which had been carried out several years before the initiation of the Harvard experiments, and had had no connexion with that University, demonstrated beyond doubt that in a medium of very pure distilled water the bactericidal velocity of chlorine (HOCl) was very much greater than that of any of the chloramines. Several years later (references 24 and 34) Professor Gordon Fair, Dean of the Harvard Graduate School of Engineering, and his associates had studied the dynamics of the destruction of various test organisms and for the mathematical analysis of the viability of *Esch. coli* had utilized the results previously reported by Butterfield *et al*. These were based on a 50 per cent "kill" with a one-minute contact period, a condition that bore no relation to those obtaining in actual practice except in very unusual circumstances.

As pointed out in the paper, the relative germicidal effect of HOCl and the chloramines depended upon a number of factors of which the most important were (1) *p*H, (2) contact period, (3) the organic content of the water and its nature, (4) temperature, (5) the quantity of so-called free ammonia and (6) the amount and nature of the mineral matter. Some quantitative assessment of the effect of some of these factors was available from the publications of the Harvard team and elsewhere, but much still remained to be done regarding the effect of organic matter. The apparently contradictory statements referred to by Mr. Pugh abundantly illustrated the effect of varying experimental conditions on the results obtained.

It should also be remembered that *Esch. coli*, usually regarded as the criterion of purity of water supplies, had been mainly used in the determination of killing rates of chlorine and its compounds and that

experiments with *Eber. typhosa* had been comparatively few and different strains had given variable results.

Mr. Race said that the contradictory results reported as to the relative efficiency of chlorine compounds and ozone might be due to variations in the experimental conditions. The chemistry of ozone treatment was rather vague and it was still controversial whether the bactericidal effect was due to the ozone *per se* or to the oxides of nitrogen concomitantly produced.

It was very gratifying to hear that a symposium on water chlorination had been arranged to be held in the early part of 1950 and he felt it might be suggested that the programme should also include a consideration of the various methods of determining chlorine and chloramines. The recent process suggested by Dr. Palin* apparently gave good results, but in view of the possible alteration of the equilibrium by the reagents added it was desirable that it should be checked by a purely physical method. Absorption spectrographic methods had been used at Harvard and, according to Dr. Morris, the physicist in the team, all three chloramines showed strong absorption below 220 mμ (2,200 Angstrom units), but gave well-defined absorption bands at longer wave lengths, the maximum for NH_2Cl, being at 245 mμ, 295 mμ for $NHCl_2$, and 340 mμ for NCl_3.† The ultra-violet light used in this method probably affected the stability of the solutions, but the time of exposure was so small as to cause but a negligible error. For checking the purity of solutions of the various chloramines, particularly the mono- and di-derivatives, the author said that a variation of the partition technique was very useful. It was simple and required no special apparatus as it merely necessitated a repetition of the partition coefficient (P.C.) with chloroform, using either the epiphase or the hypophase left over from the determination of the P.C. With NH_2Cl it was preferable to use the epiphase and with $NHCl_2$ the hypophase. If the chlorine was pure (homogeneous) the second extraction would give the same P.C. as the primary extraction.

Mr. Waddington had very properly stressed the importance of extensive and intensive laboratory trials before making a decision as to the method to be employed. With a river water it was advantageous to instal and operate a small experimental plant for a period that would include the normal variations of composition, temperature, *p*H, etc.

The question of the use of fluorine or its compounds was a most interesting one, although it might lead to no useful purpose at the present time. Its position in the chemical periodic table as the halogen with the smallest atomic weight at once suggested that the order of the bactericidal coefficients would be F>Cl>Br>I and, in view of the marked advances that had comparatively recently occurred in the technology of fluorine and its derivatives, enquiries had been made from the I.C.I. as to the possibilities of their utilization in water purification.

* *Jour. I.W.E.* (1949), **3**, 100.

† Private communication from Professor G. M. Fair.

The most likely compound was chlorine trifluoride (ClF_3), which was gaseous at normal temperature and pressure, but boiled at 11° C. and could probably be stored in the liquid condition.

It had been rather disappointing to hear from Mr. Lea, of the I.C.I., that ClF_3 reacted explosively with water and that the only oxy-acids formed were derived from the chlorine component. Mr. Lea had added, "Prior to receiving your letter I had looked also at ClF_3, since it might have offered a useful comparison with NCl_3. The fact is, however, that there is no analogy chemically between these compounds."

A disadvantage shown by fluorine, as compared with chlorine, was its tendency to produce a characteristic calcification of the bones known as fluorosis when its compounds were absorbed in excessive amount over a course of years. A deficiency of fluorine in domestic water supplies might lead to dental caries, but an excess tended to the development of fluorosis.

Some of the points raised by Mr. Pugh had been dealt with in the reply to Mr. Whitson.

Regarding the choice between underdosing and overdosing, Mr. Pugh had very rightly plumped for the latter. In an emergency this was the only safe practice, but in ordinary circumstances overdosage might make the water so unpalatable as to drive consumers to the use of other waters, if available, that might be palatable but dangerous.

The author agreed with Mr. Pugh as to the desirability of reducing the nomenclature attached to chlorination to a minimum, but this minimum must be consistent with a concise and accurate description of the nature of the process involved.

For the purpose of historical accuracy, the statement of Mr. Baldwin as to the employment of Chloros at the Shrewsbury plant in 1909 by Mr. W. A. Hewitt was of considerable interest and the author felt indebted to him for directing attention to it.

As to the use of chlorine dioxide the author's intention had been to emphasize that this substance was such a strong oxidizing reagent that there was a danger of the ClO_2 being diverted from its bactericidal function. In Section 8, paragraph 5, it had been suggested that the oxidizing function might with advantage and economy be performed by chlorine and the ClO_2 added later. This had been found to be satisfactory by Wallace Johnson, of Huron, South Dakota.*

The author was entirely in agreement with Mr. Baldwin as to the desirability of producing a sterilizing agent of the nature described by him and was convinced that science would go a long way towards the development of a germicide having the desiderata mentioned. In this opinion he was fortified by the dictum of Willis R. Whitney made in 1917:—

"Through all I see the same interesting fact. It is the desired unforeseen which frequently eventuates, and our constant need is for faith that it will occur again. The regularity with which we conclude that further advances in a particular field are improbable seems equalled only by the regularity with which future events prove that we are of too limited vision. . . ."

* *Water and Sewage*, Toronto, Canada, February, 1949, p. 24.