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CHEMICAL ASPECTS OF SWIMMING BATH TREATMENT

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Chemical Aspects of Swimming Bath Treatment

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In recent years a considerable amount of research has been done in the field of water treatment and some aspects of this work, especially in connection with chlorine processes, have a bearing on the treatment of swimming bath water. At the same time the fact that the problems facing the baths superintendent are, in many respects, different from those involved in water purification should be given due recognition. The process of continuous circulation at once introduces a factor not found in water treatment practice, and the amount of pollutive matter that has to be dealt with is usually far in excess of anything encountered in waters used as sources of public supply.

The advantages afforded by the maintenance of free chlorine residuals in bath water have been described by Lea (1948, 1949). First and foremost there is the very much increased rate of disinfection as compared with “combined chlorine residuals” and, secondly, the general improvement in the appearance of the water. The third advantage dealt with the question of offence to bathers and, while it is true that free chlorine in water, even in relatively high concentrations, is not unduly offensive to the senses, it is necessary to consider, in this connection, the nature of the chloro-compounds which co-exist with the free chlorine. In a swimming bath, regularly used maintenance of residuals consisting entirely of free chlorine is impossible because of the continual addition of impurities the very slow rate of some of the reactions involved and the persistency of some of the chloro compounds produced

Some account will be given, in the present paper, of the fundamental chemistry of chlorination processes. Of the conclusions to be advanced, due emphasis will be placed on those which appear to relate directly to swimming pool chlorination. Reference will also be made to coagulation and filtration processes.

CHLORINATION

Methods of Analysis

The terms “free chlorine residual” and “combined chlorine residual” are by now generally recognised and understood. The development and application of analytical procedures capable of performing this simple differentiation added considerably to our knowledge of chlorination. Nevertheless the need for a closer study of the compounds produced when waters are chlorinated has been widely appreciated, although the stage had been reached where further progress was dependent upon the introduction of improved methods of analysis. To this end, therefore, the author’s researches were first directed and the procedure which eventually emerged gave, by its application, a good deal of new information about chlorine reactions. This procedure involves the use of “neutral o.tolidine” as indicator, and estimations are made by titration against standard ferrous ammonium sulphate solution or, alternatively, by comparison against standard colours. By means of this method, “residual chlorine” is divided into three fractions and where the chlorine ammonia compounds are involved these fractions are made up as follows:

Fraction 1	Cl_2 and NCl_3 (nitrogen trichloride)
Fraction 2	NH_2Cl (monochloramine)
Fraction 3	$NHCl_2$ (dichloramine)

A further procedure subdivides fraction 1.

Modification of the well-known acid o.tolidine test, either by taking an additional “flash” reading or by using the sodium arsenite technique, gives some indication of the relative amounts of free and combined chlorine in a water, and for practical purposes this may be all that is required. Precision of the test decreases with increasing temperature and, other limitations are described in A.P.H.A. Standard Methods, 1946. In addition there are indications that the o.tolidine method does not respond fully to those compounds falling in fraction 3 of the ferrous ammonium sulphate method, i.e., the dichloramine fraction. Some preliminary results are shown in Table 1.

Table 1: Determination of available chlorine in samples of distilled water, containing a small quantity of phosphate buffer, with added chlorine and ammonium chloride.

Sample		**1**	**2**	**3**	**4**	**5**	**6**
FAS Titration	NH_2Cl	1.2	1.7	0.9	0.2	-	-
	$NHCl_2$	0.1	0.7	2.6	4.1	3.7	1.9
	NCl_3	-	-	-	-	0.7	2.2
	Cl_2	-	-	-	-	0.6	1.5
	Total	1.3	2.4	3.5	4.3	5.0	5.6
Acid thio titration		1.3	2.4	3.5	4.4	5.2	5.7
Colometric Acid O.Tolidine		1.2	2.0	1.8	1.2	2.1	2.4

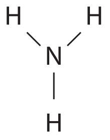
The conclusion to be drawn from these observations, and one which has received support from actual tests on swimming baths, is that the superintendent using “break point” chlorination has been carrying, in the water, higher concentrations of combined chlorine than his o.tolidine test has indicated. Whether or not this is a matter about which he should be much concerned will be discussed later.

Apart from any inherent defects of the method, however it is necessary to emphasise that where permanent colorimetric standards are used in residual chlorine tests the superintendent should satisfy himself as to their accuracy. One form of apparatus was found, in the author's experience, to give high readings and the extent of the errors was such that a superintendent using the apparatus and attempting to maintain his free chlorine residuals within the range, say, 1 to 2 ppm would in fact be working within the range 0.65 to 1.2 ppm.

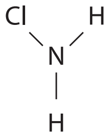
Use of the terms "free" and "combined" may be extended to the ammonia determinations. Thus one may speak of "free ammonia," that is to say in the form of ammoniums salt or ammonium ion and "combined ammonia" where combination with chlorine as in chloramines is implied. The standard distillation method is incapable of differentiating between these two forms. And again although chloramines do not immediately respond to direct Nesslerisation, the very alkaline conditions of the test result in their gradual breakdown with liberation of free ammonia. This difficulty may be overcome by allowing only one-minute contact after adding the reagent to the sample and, of course, standard colour discs must be calibrated under the same conditions. The chloramine-ammonia may be liberated by prior dechlorination of the sample using a slight excess sodium thiosulphate. In this case the normal contact period with Nessler's reagent is allowed and the figure obtained represents total ammonia, from which the free ammonia figure may be subtracted to give chloramine-ammonia. It will be necessary to consider later the practical interpretation and significance of these ammonia determinations but whatever else a swimming pool may contain, so long as free chlorine is present free ammonia will be absent, and it is easy enough to confirm this by adding Nessler's reagent to a sample of the bath water and allowing to stand for one minute, when no colour should be obtained.

Chloro Derivatives of Ammonia, and Related Compounds

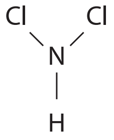
Recognition of the profound effect of ammonia on chlorine processes stimulated research on the chlorine-ammonia reactions. It will be remembered that, although we speak of "free ammonia" in water, it is normally present as ammonium salt, or, because of dissociation, as ammonium ion. For simplicity in depicting these reactions, however, it is convenient to regard the ammonia as existing in the form NH_3 when the gradual substitution of hydrogen by chlorine may be shown as follows.


Ammonia

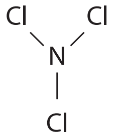
NH_3


Monochloramine

NH_2CL


Dichloramine

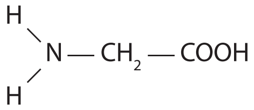
$NHCL_2$


Nitrogen
Trichloride
(Trichloramine)

NCL_3

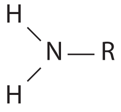
The more chlorine there is available for a fixed amount of ammonia the greater is the chance of forming the more highly substituted derivatives.

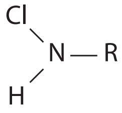
There are organic compounds, related to ammonia, for which the general formula RNH_2 may be written, where R stands for another chemical group or "radical" which has replaced one of the hydrogen atoms of NH_3. Amino-acetic acid, the simplest representative of an important class called the amino acids has the formula:

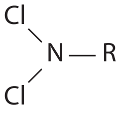


$H_2N—CH_2—COOH$

The reactions with chlorine may be shown thus:


Amino
compound


Monochloramino
compound


Dichloramino
compound

Formation of nitrogen trichloride would not be expected nor was any obtained in the author's experiments.

The anomalous results of chlorination are connected with the formation and subsequent decomposition of chloramines and similar compounds. It is known, for instance, that the presence of ammonia and, to a lesser extent, of amino compounds, in water produces the "hump and dip" type of chlorine dose-residual curve the so-called "break point" curve. Given adequate contact period, the residuals up to the minimum point of the curve, i.e., the break point, consist of combined chlorine. Chlorine in this loosely-bound form is still capable of responding to the usual tests; were it otherwise, our knowledge of the reactions would have been rather limited and it is questionable whether we should have heard of, or needed, such terms as "combined residual chlorination" and "break point chlorination".

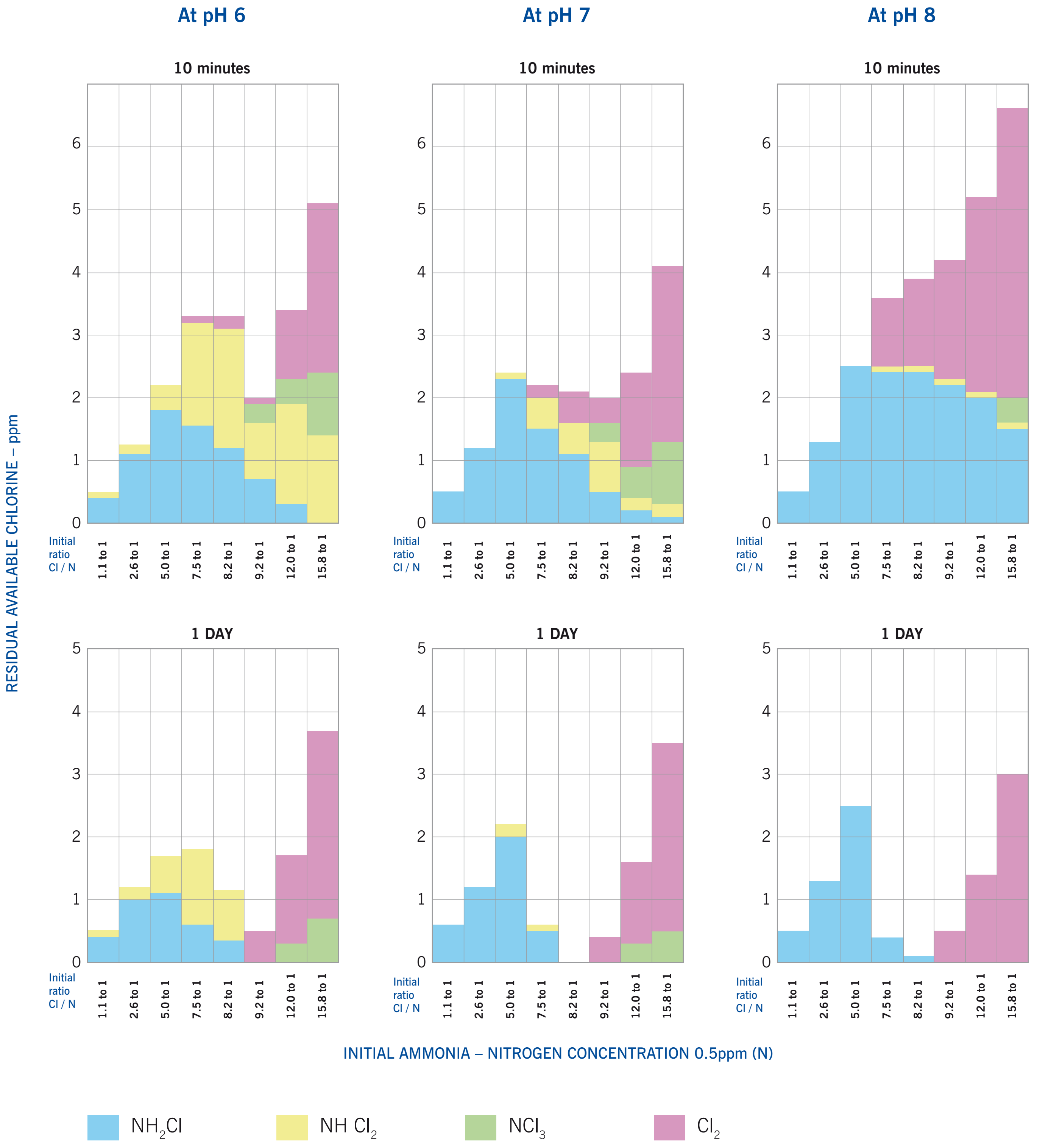
In the discussion which follows, the usual practice of referring to ammonia concentrations in terms of their nitrogen content has been adopted. The course of the chlorine-ammonia reactions is largely determined by the relative amounts of the reactants at the start and, as already noted, the higher the initial Cl/N ratio the more likelihood there is of forming $NHCl_2$ and NCl_3. Formation of these compounds is also favoured by low pH values.

The general picture for neutral and slightly alkaline waters is given below and is based on the results of experiments with an initial ammonia-nitrogen concentration of 0.5 p.p.m.

Cl/N Ratio up to 5/1
NH_2Cl is formed with traces of $NHCl_2$
Cl/N Ratio rising from 5/1 to 10/1.

Formation and Decomposition of the Chloro Derivatives of Ammonia in Water

FIG 1.



Increased quantities of $NHCl_2$ are at first obtained, NCl_3 also appears together with excess Cl_2. Further increase in NCl_3 and Cl_2 is accompanied by a decrease in NH_2Cl and $NHCl_2$. In general these mixtures are unstable and rapid decomposition takes place with a resultant loss of total available chlorine.

Cl/N Ratio rising from 10/1 to 20/1.

Considerable loss of available chlorine occurs as a result of rapid decomposition reactions after which NH Cl and $NHCl_2$ appear only as traces or not at all. NCl_3 and Cl_2 then predominate and the resultant mixtures are fairly stable. NCl_3 may persist for days in the presence of excess Cl_2.

A selection of the author's experimental results is shown in Fig. 1. These compounds evidently form a rather quarrelsome family, and when all are present they generally go into a fairly rapid decline as a result of their mutual antagonisms. No sort of stable order is maintained unless one of the constituents is present in overwhelming ascendancy. If this happens to be NH_2Cl the presence of ammonia has a further soothing and stabilising influence. The parent chlorine, however, is unable to tolerate the presence of ammonia (the other parent!) nor of any of the offspring with the exception, despite its obnoxious properties, of NCl_3 It is to these properties that attention is now directed. Nitrogen trichloride is a gas and, being volatile, may readily escape to the atmosphere. Aeration would be expected, therefore, to assist in removing any NCl_3 that might be formed in a chlorinated water. It has a pungent odour, resembling that of chlorine and the vapour attacks the eyes and mucous membrane - quite obviously the kind of compound whose presence in a swimming bath would be most undesirable.

The presence of NCl_3 in chlorinated water has hitherto been regarded as incompatible with pH values over 4.4. The important fact that, under certain conditions of chlorination, this compound may be found at much higher pH values has emerged from the present work. Except possibly at very low pH values (under 3) the NCl_3 is always associated with, and can exist only in the presence of, residual free chlorine (as HOCl) and the equilibrium may be shown thus:

$$NCl_3 + H_2O \leftrightarrow NHCl_2 + HOCl$$

The reaction may proceed in either direction so that formation of NCl_3 would be favoured by increasing the chlorine concentration. Such an increase also extends the pH range, in which NCl_3 is found, towards the alkaline end. Thus in one experiment where the initial chlorine and ammonia-nitrogen doses were, respectively 8.0 p.p.m and 0.5 p.p.m., and the contact period two hours, traces of NCl_3 were found at a pH as high as 8.2. Thus, while the virtues of free chlorine residuals are recognised it is evidently disadvantageous, from the point of view of NCl_3 formation, to maintain these residuals at unduly high levels.

So far as the final decomposition products are concerned, if the ammonia is eventually converted into nitrogen calculation shows that available chlorine and ammonia-nitrogen should disappear in a ratio of 7.6 to 1, and this, on the same basis should be in the ratio at the break point. With the low concentrations encountered in water treatment the actual ratio is invariably found to be somewhat higher than this figure. For the pH range 7 to 8 the Cl/N ratio at the break point was found to lie between 8.2 and 8.4 to 1. This precise figure is mainly of academic interest as, in practice, account must be taken of other chlorine consuming impurities contained in the water undergoing treatment. Reverting, however, to the chlorine-ammonia reactions, the discrepancies have been attributed to the production of small proportions of other nitrogen compounds such as nitrous oxide, nitrites and nitrates.

The presence of nitrite cannot be accepted as it should readily react with any excess of free chlorine. It now appears that the earlier reports arose because of the production of false colours in the standard nitrate test, an interference which, as demonstrated by the author, is caused by the presence of NCl_3 in the water under test. It may be overcome by adding the reagents in the reverse order, i.e., alpha-naphthylamine first followed, after mixing, by sulphanilic acid. When this is done nitrite is not found among the end products of the chlorine-ammonia reactions. The author has now concluded that nitrate is, in fact, the sole product in addition to nitrogen, and the amounts obtained by analysis adequately account for the observed divergence from the 7.6 to 1 ratio. An increase in the initial Cl/N ratio is followed by the production of a greater proportion of nitrate.

In the "chloramine" or "chlorine-ammonia" treatment process the principal product, in the pH range of swimming bath waters, is monochloramine, the stability of which is increased by the presence of excess ammonia. As a general rule, increased stability necessarily implies reduced bactericidal activity. Given adequate mixing, there is no risk of forming NCl_3 in the "Chloramine" process.

The new analytical technique has been applied to a study of the reactions between chlorine and amino acids. As noted earlier, there is a similarity to the chlorine-ammonia reactions; in neutral and slightly alkaline solutions monochloramino acids are obtained as main products and, furthermore in the presence of excess chlorine rapid decompositions occur. Break point curves may be obtained although the "hump and dip" is not so sharply defined as with ammonia.

The addition of urea to water containing free chlorine resulted in a gradual loss of chlorine, the rate and extent of which increased as the concentration of urea was increased.

Table 2: Addition of urea to water containing free chlorine

pH range 7.18 – 7.25
Initial Cl_2 concentration – 2.7ppm

	Available chlorine lost		
Urea added ppm (as N)	**After 10 mins.**	**After 4 hours**	**After 1 day**
0.5	0.0	0.1	0.3
1.0	0.0	0.1	0.5
1.5	0.0	0.2	0.7
2.5	0.0	0.3	1.0
3.0	0.0	0.3	1.1
4.0	0.1	0.4	1.3
6.0	0.1	0.5	1.7
10.0	0.1	0.8	2.2

In these preliminary experiments search was not made for NCl_3 and the residual which remained at any instant appeared to consist almost entirely of free chlorine. Destruction of chlorine by urea is so slow that, for short contact periods, the presence of appreciable amounts of this impurity would not seriously interfere with the disinfection process.

During these tests, however, the unpleasant odour of NCl_3 was noted and it was decided to conduct further tests and to pay special attention to NCl_3 formation.

Table 3: Formation of NCl_3 in chlorine-urea reactions

pH 7.2
Initial Cl_2 concentration – 1.75ppm

	After 4 hours	
Urea added ppm (as N)	**NCl_3**	**Cl_2**
5	0.18	1.35
10	0.14	1.21
15	0.13	1.05
20	0.11	0.96

After dechlorinating the samples, by adding sodium thiosulphate, the odour of NCl_3 disappeared.

The following mechanism is suggested to account for the slow absorption of chlorine with the accompanying formation of NCl_3. In dilute aqueous solution urea slowly breaks down into ammonia and carbon dioxide, and the rate at which ammonium ions are so produced governs the reaction with chlorine. This rate is so slow that, if appreciable quantities of free chlorine are present, the condition arises where the chlorine/ammonia ratio is high and the resultant reaction, as demonstrated earlier, leads to loss of available chlorine and also to formation of NCl_3.

At any given pH the relative amounts of Cl_2 and NCl_3 are in a state of equilibrium that, while continued formation of ammonium ion from urea would, with a fixed chlorine dose, produce more NCl_3 it would seem that hydrolysis of the NCl_3 so formed proceeds to an extent which tends to maintain the balance between it and the chlorine remaining unused. Since formation of NCl_3 from ammonia-nitrogen and chlorine is favoured by increased acidity the above hypothesis serves also to explain why production of NCl_3 from urea is similarly favoured.

Absence of free chlorine during the slow decomposition of urea permits the free ammonia, instead of having only transient existence, to build up to a concentration which, with normal chlorine doses, will give “combined chlorine”; oxidation of the ammonia now requires relatively enormous doses of chlorine. In practice, therefore, a bath which has been in use for some time on “chloramine” or “marginal” treatment will require chlorinating at a very high level before free residual chlorine becomes established in the water.

The Impurities in the Swimming Bath

Having briefly surveyed these recent researches on the chloro derivatives of ammonia and some related compounds, the next step is to consider what bearing these reactions are likely to have on the chlorination of swimming baths, bearing in mind that, in the newer processes, the aim is to maintain in the water a “residual” or “reserve of free chlorine”.

Now there cannot, to the author’s mind, be any doubt that by far the biggest source of impurity in a swimming bath is urine. In freshly passed urine the normal ratio of urea to ammonia is about 50 to 1, and something like the same ratio applies in the case of sweat. It is suggested that the chlorine-urea reactions so completely mask the chlorine-ammonia reactions as to relegate them to an insignificant position so far as break point chlorination of swimming bath water is concerned. There is no break point, as commonly understood, in the chlorine-urea reactions and the applicability of the term break point to swimming pool chlorination may well be questioned. The so called break point curve, however, has no intrinsic merit and the advantages claimed for break point chlorination are, in general, available to all waters irrespective of whether, according to present terminology they have a break point or not. Where the aim is to produce free chlorine residuals in a water one could logically regard the break point reactions as disadvantageous; inertness of chlorine to ammonia would be advantageous.

For a pool continuously operated under these conditions of chlorination the view that ammonia, is the most important factor influencing the process is a misconception arising front a too rigid application of the principles of waterworks chlorination. The analyst’s figure for “free and saline” ammonia may be cited as proof of the presence of ammonia in the bath water although chlorinated to a free residual. In some results presented by Hoather (1949) a sample of bath water experimentally chlorinated at a dose of 35 ppm still gave, after standing 18 hours, an “ammonia” figure of 0.12 ppm. This should not be taken to mean however, that the water actually contains that amount of ammonia in the form of ammonium salt, or ammonium ion, as this would be incompatible with the presence of free chlorine These apparently anomalous results are explained by the fact that the distillation involved in the standard analytical procedure is a process sufficiently drastic to cause, some decomposition of the more complex nitrogenous organic matter contained in the sample with the liberation of ammonia during the analysis. Dechlorination of the sample may also produce ammonia by reduction of chloramines and similar compounds.

It is, of course, evident that the presence of urine in swimming bath water is a potential source of ammonia since, in addition to the small amount of ammonia naturally present, decomposition of urea is capable of producing further quantities. As mentioned earlier, the ammonia so obtained has only momentary existence in a bath on “free residual chlorination”. On the other hand, the concentration of ammonia, under conditions where a “build-up” is permitted, becomes a decidedly significant factor if a changeover to “free residual chlorination” is attempted. In addition to ammonia however, there must inevitably be an accumulation of many other impurities, all thirsting for free chlorine, and in the ensuing reactions the risk of nuisance to bathers is considerably increased; it is therefore advantageous, when adopting the new chlorine process, to start with a freshly filled bath.

Formation of Nitrogen Trichloride

The production of nitrogen trichloride, with its characteristic odour, during break point or free residual chlorination was demonstrated by the author in 1949 and this nuisance has since been recognised in America by Williams, whose conclusions regarding NCl_3 formation, although based only on odour tests, appear to be in agreement with those of the author.

So far as the swimming bath is concerned, it is now suggested that, while other chloro compounds may have contributory effects, it is the presence of NCl_3 not only in the water but in the atmosphere above it, which is the main cause of eye irritation and objectionable odours. The extent to which the reactions are capable of being controlled and the degree of control that should be applied in order to retain the many advantages of free residual chlorination without, at the same time causing offence to bathers, are matters for further consideration.

It is reasonable to suppose that eye irritation may at times, be attributable to factors unconnected with chlorination, such as the presence of soluble aluminium salts, residual alum in the water, however, would hardly account for irritation experienced in the atmosphere of the building.

Time of contact, pH and residual free chlorine appear to be important factors governing the amount of NCl_3 in a treated water and further examination of these relations will be instructive.

The following results were obtained during experiments with chlorine and ammonium salt. Monochloramine and dichloramine which were generally present in appreciable amount at the 10 min stage, probably influence the chlorine-nitrogen trichloride equilibrium but their concentrations are not shown in order that the general picture may be kept clear.

Table 4: Formation of NCl_3 from Chlorine and Ammonium Chloride in Water: The Effect of pH, Excess Chorine and Time of Contact

	Chlorine dose 7.9 ppm					
	Ammonia dose 0.5ppm (as N)					
Time	**pH 7.2**		**pH 7.5**		**pH 8.0**	
	Cl_2	NCl_3	Cl_2	NCl_3	Cl_2	NCl_3
10min	2.8	1.0	3.0	0.8	4.5	0.4
2hr	3.0	0.6	3.1	0.5	3.3	0.1
1 day	3.0	0.4	3.0	0.3	3.4	0.1
	Chlorine dose 6.0 ppm					
	Ammonia dose 0.5 ppm (as N)					
Time	**pH 6.6**		**pH 7.1**		**pH 7.7**	
	Cl_2	NCl_3	Cl_2	NCl_3	Cl_2	NCl_3
10 min	1.4	0.6	1.5	0.4	3.1	absent
2 hr	1.4	0.3	1.4	0.3	1.5	absent
1 day	1.4	0.4	1.3	0.2	1.4	absent
	Chlorine dose 4.6 ppm					
	Ammonia dose 0.5ppm (as N)					
Time	**pH 6.7**		**pH 7.1**		**pH 7.9**	
	Cl_2	NCl_3	Cl_2	NCl_3	Cl_2	NCl_3
10 min	0.3	0.3	0.5	0.3	1.9	absent
2 hr	0.4	0.1	0.4	0.2	1.1	absent
1 day	0.5	0.2	0.4	0.1	0.4	absent

It appears that, as a general rule, the maximum concentration of NCl_3 is likely to be found just after adding the chlorine so that, in practice, where conditions are suitable for NCl_3 formation, most trouble would be experienced at the inlet end of the bath. Aeration after chlorination would therefore be advantageous; NCl_3 is a Volatile gas whereas chlorine, existing as hypochlorous acid and/or hypochlorite should suffer no significant loss.

The importance of maintaining a reasonably high pH in the bath water in order that the irritation to eyes and mucous membranes caused by NCl_3 may be avoided, is apparent from the above figures, as also is the generally increased risk of finding this objectionable compound as the residual free chlorine content is increased.

Formation of Other Chloro Compounds

Other pollutive matter in addition to urea, gaining access to the swimming bath must, by reason of its complex nature, produce a variety of compounds, possibly with odoriferous properties, when chlorinated. Some of the rather indefinite odours, often of a sweetish-chlorinous type, are believed to arise in this way and it may well be that, with free residual chlorination their formation cannot be entirely avoided at all times.

Although these odours are much less offensive than NCl_3 type odours, the extent to which the process may be controlled in order to keep them at a minimum is a matter for further study. There may, for instance, be some relation between such odours and the amount of “residual combined chlorine" in the water. In one case a bath water giving, in the author's test, a high proportion of fraction 3 compounds (i.e. dichloramine-type) had a decided odour. If this relation could be substantiated generally and placed on some sort of quantitative basis, the combined chlorine figure, instead of being, as at present, of doubtful value to the operator, would become of real significance. Whatever interpretation is to be placed on the "combined chlorine figure," however, there still remains the point that with the usual o.tolidine test much of the combined chlorine produced under these conditions of chlorination appears, in any case, to have been missed.

There have been indications that in the free residual chlorination of swimming baths the fraction 3 compounds tend to build up to a figure which presumably depends on such factors as rate of chlorination, bathing load and proportion of make-up water added. These dichloramine type compounds seem to be fairly stable and if their presence, at unduly high concentrations, is to be regarded as undesirable, either because they are suspected of being responsible for odour or are indicative of incomplete oxidation generally, then it is by no means certain that increased chlorination is going to effect their destruction.On the contrary, it seems just as likely that their concentration may increase if, by the addition of more chlorine, the reactions responsible for their formation are accelerated.

The extent to which the baths superintendent should attempt to oxidise organic matter in the water is debatable. Bleaching of organic colouring matter is obviously desirable, but removal of colour does not necessarily imply any diminution of total organic content. There is no reason to believe that the presence of organic matter in solution in the swimming bath water has any more significance, from the bather's point of view, than the presence of such things as chlorides or nitrates, nor would it be of any more concern to the superintendent if, apart from the bleaching effect, such organic matter were completely inert to chlorine. That it does require to have its chlorine demand satisfied and may, in other ways, affect the chlorine process must, however, be taken into account, but over-chlorination in a problematical attempt at its complete oxidation would seem to involve the risk of generating compounds which, by having odoriferous or irritant properties, are much more of a nuisance than the organic matter from which they derive.

This danger was recognised by Lea and Mills (1949), who stated that "the complete oxidation and therefore destruction of urea by chlorine at the extreme dilutions concerned in bath water is thought to be a relatively slow process which cannot easily be accelerated by increasing the dose and concentration of chlorine. This merely leads to the formation of undesirable compounds."

Some of the opinions expressed above require, for their substantiation, a good deal of additional information, much of which can be acquired only by those engaged on the day-to-day control of swimming bath treatment.

The results of the following experiment, although only of a preliminary nature, indicated that:

(a) loss of free chlorine from water containing small amounts of urea or urine is relatively slow, but being continuous may cause the free chlorine to disappear completely over a long period, e.g. overnight,

(b) the gradual accumulation of fraction 3 compounds (dichloramine-type) appears to be associated with the constituents of urine other than urea,

(c) once established this dichloramine fraction appears fairly stable and not readily affected by increased chlorination,

(d) when NCl_3 was present the characteristic odour was usually detectable.

The experiment was conducted by taking two 20-litre portions of tap water to which chlorine and polluting agent were added at intervals, as indicated in Table 5, in order to reproduce, so far as possible, conditions in the swimming bath. The volumes withdrawn for the purpose of available chlorine estimations were replaced by fresh tap water, which would, in effect, correspond to the make-up water added to the bath. The samples were adjusted initially to pH 8 with alkalinity approximately 200 p.p.m. (as $CaCO_3$) and there was, during the test, no appreciable drop in pH.

Table 5: Chlorination of tap water with added (a) Urea and (b) Urine

a) Urea

Chlorine dose ppm	**Urea dose ppm**	**Contact period**	**Available chlorine as**			
			M	D	N	C
2.0	1	15 min	0.2	0.1	0.1	0.8
		overnight	0.1	0.1	absent	absent
2.0	1	15 min	0.1	0.1	absent	1.7
		2 hr	0.1	0.1	absent	1.4
	1	15min	0.1	0.1	0.1	1.2
		overnight	0.2	0.1	absent	0.4
5.0		30 min	0.1	0.1	0.1	3.5
		4 hr	0.1	0.1	0.1	3.2
		overnight	0.1	0.1	0.1	1.9
3.0		30 min	0.1	0.1	0.3	4.6
	5	30 min	0.1	0.1	0.3	4.5
		overnight	0.1	0.1	0.1	2.7
		1 day further	0.1	0.2	absent	1.3

b) Urine

Chlorine dose ppm	Urine dose ppm	Contact period	Available chlorine as			
			M	D	N	C
2.0	50	15 min	0.1	0.1	absent	0.6
		overnight	0.1	0.1	absent	absent
2.0	50	15 min	0.2	0.2	0.1	1.0
		2 hr	0.2	0.2	absent	0.6
	50	15min	0.3	0.3	absent	0.1
1.0		overnight	0.1	0.3	absent	absent
5.0		30 min	0.1	0.4	0.2	2.9
		4 hr	0.2	0.3	0.1	2.4
		overnight	0.1	0.3	0.1	1.1
3.0		30 min	0.1	0.3	0.2	3.6
	250	30 min	0.2	0.4	0.1	3.0
		overnight	0.2	0.4	0.2	1.6
		1 day further	0.2	0.4	absent	0.8

M = monocholoramine fraction
D = dicholramine fraction
N = nitrogen trichloride
C = free chlorine

Control of Chlorination

The main purpose of the tests prescribed for the routine control of swimming bath treatment is to provide information enabling the amounts of applied chemicals to be adjusted to suit all conditions of the water. The two determinations which are most frequently made are those of pH and residual chlorine.

The importance of maintaining a reasonably high pH has already been emphasised, and it is suggested that, for best results, the amount of alkali added to counteract the acidifying influence of chlorine and coagulating chemicals should be so regulated as to ensure, at all times, a pH within the range 7.0 to 8.

With the new chlorine process the aim is to maintain residual free chlorine throughout the bath in an amount sufficient to give rapid disinfection, an adequate margin for load variation and, by bleaching organic colouring matter and discouraging algal growths, a water of good appearance. On the other hand, the amount of free chlorine should not be so high as to permit the formation of compounds with undesirable properties.

The limits between which the free chlorine residual should be maintained in order to meet these various requirements are influenced also by the turnover period and their fixation is largely a matter of experience. It is considered, however, that as a general rule this residual should range between 0.5 and 1.5 ppm. The higher values will, of course, be found at the inlet points.

The extent to which the residual free chlorine concentration should be raised towards the end of the day in order to allow for the continuing loss overnight is again a matter to be determined by experience; possibly an increase to 2 ppm would suffice.

Having established, by regular testing under all conditions, the most suitable range of residual free chlorine for a given bath, it may well be found in practice that the information afforded by the residual free chlorine and pH determinations is adequate for all control purposes.

The determination of residual combined chlorine although undoubtedly giving further information regarding the state of the water appears at present to be of questionable value so far as control of the new treatment is concerned.

If a swimming bath is continuously on free residual chlorination, routine tests for “free ammonia” by direct Nesslerisation appear to be of no value to the operator.

The importance of frequent determination of “alkalinity,” a sufficient reserve of which is desirable in order to minimise the risk of a pH drop, has been emphasised by Lea and Mills (1949), who gave details of this useful supplementary test. The advantages of using sodium bicarbonate as an alkalifying agent were also given by these authors.

Before leaving the question of control, a further aspect which merits serious consideration, and to which much of the work described in the present paper adds point, is that mentioned by W. J. Jones, who suggested, in his contribution to the discussion on Lea’s (1948) paper, that by “creating physical conditions designed to make our bathers involuntarily urinate before entering the water, much of our troubles in connection with break point chlorination would be obviated.”

COAGULATION AND FILTRATION

The superintendent making a study of water coagulation will usually find it necessary to wade through a whole lot of chemical formulae purporting to show how the coagulants aluminium sulphate and sodium aluminate react with the various constituents of natural waters. It is suggested, however, that there is a much simpler approach to these problems, and one which, although ignoring other possible factors, serves as a general guide to the results likely to be obtained in practice.

Briefly, then, two conditions which require to be satisfied before coagulation may take place are:

1. the amount of aluminium ion must be sufficient,
2. the pH must be suitable.

Furthermore, these two factors are interdependent. There will be one pH, the optimum pH, in the region of which coagulation proceeds most readily and where minimal amounts of Al ion are required. The further the pH is removed from this optimum the greater will be the concentration of Al ion required to coagulate the water. In the limit the pH may be so far from the optimum - above or below it - that coagulation becomes impossible no matter how much Al ion is added; aluminium compounds remain in true solution both in extremely acid and alkaline conditions.

In order to achieve coagulation it may be necessary therefore to vary one or both of the above factors. It is easy enough to vary the amount of Al ion added and consideration of the problem is made simpler by assuming, for the moment, that such variation may be made without in any way altering the pH of the water. Variation of pH if required, would then be effected by the addition of an alkali, e.g. lime, sodium hydroxide, to raise it, or an acid, e.g. sulphuric acid, to lower it.

If we now consider the salts normally used as sources of Al ion we find that one, aluminium sulphate ("aluminoferric"), provides both Al ion and acid, and the other, sodium aluminate, provides both Al ion and alkali. It can readily be seen therefore that by suitable choice of coagulant it is possible, in one operation, to apply sufficient Al ion and to move the pH in the right direction, i.e. towards the optimum pH.

Most natural waters have a pH well above this optimum, other waters such as those derived from moorland sources, may have a pH below the optimum, and there is an intermediate class where the pH is already within the region of the optimum value. Waters may, accordingly, be divided into three groups:

(a) where depression of pH favours coagulation and the use of aluminium sulphate is therefore indicated,
(b) where elevation of pH favours coagulation and the use of sodium aluminate is therefore indicated, and
(c) where a change of pH is unfavourable to coagulation and the combined use of aluminium sulphate and sodium aluminate, in suitable proportions, is indicated.

In the case of swimming bath water, which normally falls into class (a), improved coagulation would be obtained by working at pH values lower than those customarily found in practice, a fact already pointed out by Lea (1948). It would appear therefore that no advantage is to be gained by replacing a proportion of the aluminoferric dose by an equivalent amount (in terms of Al content) of sodium aluminate.

A further point arising from this discussion is that maintenance of a pH between 7.5 and 8, now regarded as advisable for the chlorination process, will not be conducive to good coagulation. This unfortunate state of affairs may be overcome, to some extent, by applying the chlorine with the alum (i.e., before filtration) so that the acidifying influence of both reagents is brought to bear at the point where it is most needed, and by delaying the addition of alkali until after filtration.

Consideration of the various factors involved, however, leads to the belief that the answer will be found in intermittent coagulation, a process which was developed by the author several years ago and, combined with pre-chlorination is in regular use at one water filtration plant. It must of course, be recognised that, so far as coagulation itself is concerned, intermittent treatment cannot possibly achieve as good a result as continuous treatment. At the same time, however, unless chemical doses are under constant check, there would seem to be a risk, in swimming pool operation of a condition arising where the continuous dose is a chronic underdose and where several turnovers are required before the Al concentration in the water builds up to the critical value for coagulation, by which time precipitation in the bath, resulting in cloudy water, may be just as likely as deposition in the filter. Intermittent treatment for short periods, during which it is feasible to maintain constant watch over the rate of dosage, would be advantageous therefore from this point of view in addition to the other aspects which have to be considered in relation to the chlorination process.

Many of the results obtained by sand filtration of an alum-dosed water are best explained by regarding the process, not as simple mechanical straining with the formation of a surface mat but as a gradual accumulation of film on the sand grains in the bed of the filter. For instance, the application of water containing alum to a zeolite softener would result in a general impairment of the whole bed; the stifling of reactions due to the formation of film on the grains would not be confined to the surface layers. With a sand filter a limit will eventually be reached when, due to the gradual decrease of the free space, the water velocity past the grains increases to an extent which prevents further deposition. If the water velocity, at this stage, is very considerably increased, as in washing, the deposit is removed. Now it is generally accepted that a clean sand filter is less efficient than one in which some deposition has already occurred; the film acquired by the sand grains has certain adsorptive properties. When the application of alum is stopped the adsorption of impurities continues although, admittedly, with gradually decreasing efficiency. Nevertheless, it is considered that the degree of clarification achieved would still be adequate for swimming pool purposes. It is clear that if alum is to be used in this way as a "filter-conditioner" the period of application should be at the start of the filter run, i.e. immediately after washing.

The extent to which the precipitated alum floc tends to re-dissolve when after stopping the alum treatment, the applied water is of a higher pH has been investigated. For floc deposited at about pH 7 the subsequent pick-up when water of pH 8 is applied is negligible; "aged" floc shows no great tendency to re-dissolve.

If the alum dosing is to be thus restricted to a short period, say of two hours' duration, after washing, it is essential that the dose should be adequate for complete precipitation. This will consequently entail a temporary reduction in pH, possibly to a figure as low as 7, so that the alkali dose, which in the process now envisaged follows filtration, will need temporarily increasing. Thereafter the amount of alkali added will be only that needed to counteract the acidifying influence of the chlorine.

BIBLIOGRAPHY

American Public Health Association, Standard Methods for the Examination of Water and Sewage. 9th Edn. 1946.
Hoather, Jour. Royal Sanitary Institute, 1949, 69, 219.
Lea, Paper presented at Annual Conference, Nat. Assn. of Bath Superintendents, 1948.
Lea & Mills, Paper presented at Annual Conference, Nat. Assn. of Bath Superintendents, 1949.
Palin, Journal Institute Water Engineers, 1949, 3,100.
Ph.D. Thesis, University of London, March 1949.
Williams Jour. Amer Wat. Wks. Assn. 1949, 41, 441.

APPENDIX
Method for the Estimation of Free Chlorine in Water

Reagents

1. Hexametaphosphate-Phosphate Solution.
   28 gm. anhydrous NA_2HPO_4, Analytic reagent (AR)
   88 gm. KH_2PO_4, AR
   40 gm. sodium hexametaphosphate, B.D.H.

   Dissolve all in distilled water and make up to 1 litre. Mould growths may be prevented by the addition of 20 p.p.m. mercuric chloride.

2. Neutral Ortho-Tolidine Solution.

   Place 1 gm. extra-pure o-tolidine, B.D.H, in a mortar with 5 ml. 20% (by vol.) HCI and grind to a thin paste. Dissolve in chlorine-free distilled water and make up to 1 litre.

3. Standard Ferrous Ammonium Sulphate Solution (1 ml=0.1 mg. Cl)

   Dissolve, 1.106 gm. A.R. salt in distilled water containing 1 mil. of 25% (by vol.) H_2SO_4 and make up to 1 litre. Use freshly boiled and cooled distilled water.

Procedure

1. Place 2 ml. each of reagents (1) and (2) in a titration flask and mix
2. Add 100 ml of sample and mix.
3. Titrate with standard ferrous solution until the blue colour is discharged. For 100 ml. sample, 1 ml. Fe solution = 1 ppm Cl

Notes

(a) The quantities of reagents given above are suitable for concentrations of free chlorine up to 3 p.p.m.

(b) The titrations are definite but the later stages must be conducted slowly allowing approximately 15 seconds between additions of the standard solution. Instead of performing titrations the same procedure may be used in colorimeters with permanent glass standards.

(c) If the presence of nitrogen trichloride is suspected proceed as follows:
   1. Extract the NCl_3 by shaking a portion of the sample (say, 120 ml) with 1/10th as much A.R. carbon tetrachloride.
   2. Pour off 100 ml. of the aqueous layer and add to the titration flask containing reagents (1) and (2).
   3. Titrate with standard Fe solution as before. This reading gives free chlorine. To obtain the nitrogen trichloride figure subtract this reading from that obtained by the normal procedure and multiply by 1.5.

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