A field study of some swimming-pool waters with regard to bacteria, available chlorine and redox potential

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(Received 20 June 1973)

SUMMARY

The waters of one indoor bath and three outdoor baths were examined once an hour during 3 days (bath 1) or 6 days, for available chlorine, redox potential, permanganate number, ammonium, nitrate and total nitrogen, total bacterial count at 22° C., total bacterial count at 37° C. and faecal coliform bacteria. The weather, number of swimmers and the chlorine gas addition were continuously registered, and the pH was checked ^a few times at each bath. In bath 1, an indoor pool with aluminium sulphate precipitation about once a week and with sand filters back-washed every 2 days, less than 10 bacteria/ml. were found in all samples. In bath 2, an outdoor pool with aluminium sulphate precipitation twice a week and with sand filters back-washed twice a week, also few bacteria were found. In bath 3, an outdoor pool with only filtering through sand filters backwashed about every 14 days, high bacterial counts were found every day except the first, when the filters had been newly back-washed. In bath 4, an outdoor pool with only filtering through sand filters back-washed about once a week, high bacterial counts were found now and then during the first 4 days when the weather was warm, but few bacteria were found the last 2 days when the weather was cold and windy, and there were few swimmers.

Values from different analyses on the same sample showed relatively good correlation between the redox potential and the free available chlorine. In bath 3 both the redox potential and the available chlorine were weakly correlated to the bacterial count, but in bath 4 there was no such correlation. No other factors were well correlated with the bacterial count either.

The bacterial counts at 22° and 37° C. were of the same order. No faecal coliforms were ever found. Use of these bacteria as indicator organism in swimming pools is criticized.

The method of using certain minimum values of the free available chlorine as guarantee for a satisfactory bacteriological quality of the swimming pool water is also questioned. The degree of purity of the water is fundamentally connected with the disinfecting power of the available chlorine.

Use of certain minimum values of the redox potential, according to these investigations, seems to be a method of somewhat greater accuracy. Provided that the methods of precipitation are performed correctly and filters are being backwashed often enough, then an automatically registering redox potential device,

perhaps connected to the chlorine gas pump, ought to constitute a good control of the hygienic quality of a swimming-pool water. This must, however, always be completed by bacteriological examinations, preferably made at high bathing load.

INTRODUCTION

The importance of available chlorine and redox potential as indicators of the kill of Escherichia coli has previously been studied in laboratory experiments (Victorin, Hellström & Rylander, 1972). Different chlorine compounds were tested in chlorine demand free water. The reduction of bacteria within 3 min. was relatively well correlated with both available chlorine and redox potential for each pure chlorine compound, but the available chlorine needed for total kill was about 10 times higher for inorganic chloramines than for free available chlorine (hypochlorite). The organic chlorine compound chloramine T in its turn needed about 10 times the amount of available chlorine than did mono- or dichloramine. The variations in redox potential for the same degree of reduction of bacteria with different chlorine compounds were much smaller. The conclusion was drawn that in water containing unknown proportions of free, inorganic combined, and organic combined residual chlorine, the measuring of the redox potential of the water ought to be a much surer way of establishing the disinfecting properties of the water than measuring of total available chlorine.

An examination of redox potential and bacterial count in an indoor swimming pool has been made (Carlson, Haisselbarth & Mecke, 1968). They tested the water once an hour during ¹ day, and also once a day during 5 weeks. During the day test the redox potential was held on 700 mV. by controlled chlorine gas addition, whereupon a hygienically excellent water was obtained. During the 5-week test it was stated that every impairment in the water's disinfecting capacity was reflected in a lowering of the redox potential. The indoor pool had excellent water purification by continuous aluminium sulphate addition and daily back-washings of the sand filters, and the bacterial counts were always very low. In an outdoor bath the variations in the chlorine demand of the water are much greater than in an indoor bath. Systems of water purification with differing efficiencies also give different amounts of residues. It was therefore decided to test whether the conclusions from earlier laboratory experiments and from Carlson's (Carlson et al. 1968) work hold true even of outdoor baths with less efficient purification. Repeated samplings during a rather long period of time were undertaken in order to obtain variations in weather and bathing load.

THE SCOPE OF THE INVESTIGATION

Four different swimming pools were investigated, one indoor bath and three outdoor baths of different sizes. In each bath samples were taken once an hour from the water leaving the pool before entering the purification plant. The samples were analysed with regard to available residual chlorine, redox potential, permanganate number, ammonia, nitrate, total nitrogen, total bacterial count at 22° C., total bacterial count at 37° C. and faecal coliform bacteria at 44° C. The

* This includes water in the bath and in the purification plant.

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pH was checked ^a few times at every bath. The chlorine gas addition was continuously reported. The weather was noted, as was the total number of bathers every day. The indoor bath was analysed for 3 days, and the outdoor baths for 6 days. All baths were continuously filtered and chlorinated, with regular cleansing of the filters by backwashing. Water in two baths was subjected at intervals to treatment with aluminium sulphate: two baths were not so treated.

Table ¹ describes the baths and the schedules of water treatment.

METHODS

The available chlorine was analysed both with orthotolidine and with DPD ferrous titrimetric method according to Palin (Taras, Greenberg, Hoak & Rand, 1971). In this laboratory it has been shown earlier that these methods do not give equal results in waters containing inorganic and organic interfering substances, but the DPD method and amperometric titration give about the same values (K. Victorin, unpublished data). Amperometric titration is considered more accurate by the author, but as the DPD titrimetric method is faster and easier to perform in field operation, that method was used. It was shown in this investigation that the orthotolidine method gave values from 30 to 100% of the values obtained with the DPD method both for free and combined available chlorine. The values measured with DPD are shown in the figures.

The redox potential was measured on a Radiometer pH meter with a platinum electrode and against a calomel electrode as standard, which has a normal potential of $+244$ mV. at 25° C. The value was measured after the stabilization of the electrode, 5-10 min. The platinum electrode was stored overnight in ascorbic acid.

Ammonium was measured with direct nesslerization without prior treatment of the samples because analysis of ammonia in chlorinated water must be performed immediately. The values are therefore somewhat unreliable.

Total nitrogen was measured by oxidation to NO_3 ⁻ with aluminium persulphate under pressure, reduction to $NO₂^-$ through a cadmium-mercury column and spectrophotometry analysis of the nitrite.

Nitrate was measured both directly with brucine and by reduction through a cadmium-mercury column and measurement of the formed nitrite. The method of reduction by cadmium gave $30-100\%$ of the values obtained with brucine, with the greatest differences in baths 3 and 4. The cadmium reduction method was regarded as more reliable than the brucine method by the author for swimmingpool water. Analysis of total nitrogen and nitrate by the cadmium reduction method was performed 0-2 months after the collection. The samples had been treated with 5 ml. of $4 \text{ m}-\text{H}_2\text{SO}_4$ per 100 ml., but the composition of the samples stored for the longest period of time might have changed somewhat. The nitrogen analyses are thus subject to a certain degree of uncertainty, but the potential error is not so large as to prevent the use of the values obtained as background material for discussion. They are presented as means for each pool, with the range of variation included.

Table 2. Mean values and limits of variations for values of ammoniumnitrogen, nitrate-nitrogen and total nitrogen

	Bath 1	\bar{x}	Bath 2	\bar{x}	Bath 3	\bar{x}	Bath 4	\bar{x}
	NH_4 +. N 0.1–0.3 0.15 0–1.8				$0.5 \t 0-1.6$		$0.3 \t 0.8-2.2 \t 1.4$	
$NO - N$	$3 \cdot 1 - 3 \cdot 8$	3.2	$2.6 - 4.6$	3.4	$2.1 - 3.2$	2.6	$4.4 - 5.2$	4.7
$\operatorname{Tot-N}$	$2.8 - 5.0$	3.2	$2.6 - 10.6$	4.9	$2.1 - 10.6$	3.8	$4.4 - 7.8$	5.6

Fig. 1. Analytical data from bath no. ¹ during ³ days. (1) Number of swimmers during 1 day. (2) Permanganate number, mg. \ln (3) Free $(-)$ and total $(-,-)$ available chlorine, mg./l. (4) Redox potential, mV. (5) Bacteria/ml., 37° C.

Collection of the samples was made from a drain cock before the water entered the purification plant in all baths except bath number 4, where the samples were taken directly from the pool at the outflow side.

RESULTS

The nitrogen values are shown in Table 2 and other results in Figs. 1-4.

In Figs. $1-4$ the total bacterial count at 37° C. is shown. Less than 10 bacteria per ml is considered equal to 0. The standard plate count at 22° C. was about 75-125% of the standard plate count at 37 $^{\circ}$ C. No faecal coliforms at 44 $^{\circ}$ C. were ever found.

The variations in the number of swimmers are not shown in the figures. In sunny weather the number was greatest between about ¹ and ² p.m. When the weather was cloudy and not so many people came to the pool, the number was usually highest in the morning and in the late afternoon.

The correlation between some variables analysed is shown in Table 3, in which it can be seen that the redox potential is relatively well correlated to the free available chlorine except in bath 1, where the variations were small. The redox potential and the free available chlorine were weakly correlated to the bacterial count in bath 3, but not at all in bath 4. The total nitrogen was weakly correlated to the bacterial count, but the permanganate number was not. Total nitrogen and permanganate number were not correlated to each other within each bath, but calculated for the values from all baths, a weak correlation was achieved.

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Fig. 2. Analytical data from bath no. 2 during 6 days. (1) Number of swimmers during one day. (2) Weather. (3) Permanganate number, mg./l. (4) Chlorine gas addition, g./hr. (5) Free $(-)$ and total $(- -)$ available chlorine, mg./l. (6) Redox potential, mV. (7) Bacteria/ml., 37° C.

DISCUSSION

Probably in most countries the hygienic quality of public swimming-pool water is controlled by bacteriological examinations performed by health authorities. These can be made very infrequently, however. The amount of disinfectant in the water is checked by the pool manager every day. When using chlorine as ^a disinfectant effort is made to attain certain minimum values of the free available chlorine. In Sweden it is professed that the hygienic control of so called break-point chlorinated water can be made exclusively with continuous measurement of the free available chlorine. This should then be ≥ 0.4 mg./l. at pH 6.5-7.5, ≥ 0.8 at pH 7.5-8.5 and ≥ 1.5 at pH > 8.5 . Whether any of the four swimming-pool waters examined can be called break-point chlorinated is however doubtful. The water in bath number 3 is closest to this theoretical designation, but whether water is really break-point chlorinated or not ought not to be very interesting from a theoretical hygienic point of view, as long as the free available part of the total available chlorine can be measured. In bath number ¹ the free available chlorine was ≥ 0.4 mg./l. in 91% of the samples, and no bacteria were found. In bath number 2 the free available chlorine was less than 0.4 mg./l. in 53% of the samples, but still no bacteria were found. In bath number 3 the free available chlorine was higher than 0.8 mg./l. in 82% of the samples, but more than 100 bacteria/ml., 37° C. were still found in 55% of the samples. (In Sweden a swimming-pool water with more than 100 bacteria/ml., 35° C. is not desirable.) In bath number 4 the

Fig. 3. Analytical data from bath no. 3 during 6 days. (1) Number of swimmers during one day. (2) Weather. (3) Permanganate number, mg. (1, (4) Chlorine gas addition, g./hr. (5) Free $($ ——) and total $($ - \cdot - \cdot $)$ available chlorine, mg./l. (6) Redox potential, mV. (7) Bacteria/ml. 37° C.

free available chlorine was lower than 0.8 mg . (i. in 95% of the samples, and in 16% of the samples more than 100 bacteria/ml., 37 $^{\circ}$ C. were found.

Thus according to these examinations the free available chlorine gives a poor estimation of the number of bacteria in the water. The minimum values of the free available chlorine practised in Sweden are not satisfactory for all baths.

In Germany there are now official recommendations that a swimming-pool water should have a redox potential of ≥ 700 mV. at pH < 7.5 and ≥ 730 mV. at pH $>$ 7.5. The same values have been proposed in Sweden. In the present investigation in bath 1, 97% of the samples had a redox potential of ≥ 700 mV. and no bacteria were found. In bath, 2, 60% of the samples were ≥ 700 mV., and no bacteria were found. In bath 3, 24% of the samples were ≥ 730 mV, and, of these 16 samples, 8 contained ≥ 100 bacteria/ml., 37° C. In bath 4 the redox potential was never as high as 730 mV.

In short, it cannot be claimed that a high redox potential could function as an absolutely sure yardstick of the disinfecting power of swimming-pool water. But according to the results of this investigation, the error is less than that experienced when using free available chlorine as a standard.

Fig. 4. Analytical data from bath no. 4 during ⁶ days. (1) Number of swimmers during 1 day. (2) Weather. (3) Permanganate number, mg. β . (4) Chlorine gas addition, g. β hr. (5) Free $($ ----) and total $($ - $\cdots)$ available chlorine, mg./l. (6) Redox potential, mV. (7) Bacteria/ml. $(37° \text{ C.})$

Table 3. Coefficient of correlation (r) for some values simultaneously analysed

			Free	Tot.				
			Cl ₂	Cl ₂		Redox, KMnO ₄ , Tot. N		
	Free	Tot.	tot.	tot.	tot.	tot.	tot.	
	Cl ₂	Cl ₂	bact.	bact.	bact.	bact.	bact.	KMnO ₄
	redox	redox	22° C.	22° C.	22° C.	22° C.	22° C.	tot N
Bath 1	-0.28	-0.16						$+0.01$
Bath 2	$+0.49$	$+0.47$						-0.58
Bath 3	$+0.49$	$+0.47$	-0.39	-0.45	-0.32	-0.31	$+0.20$	-0.19
Bath 4, days $1-4$			$+0.09$	$+0.08$	$+0.11$	$+0.01$	$+0.39$	
Bath 4. days $1-6$	$+0.54$	$+0.52$						$+0.09$
Baths 3-4, day ₄			-0.08	-0.13	$+0.12$	-0.13	$+0.15$	
All baths	$+0.39$	$+0.26$						$+0.24$

The values from days ¹ and 2 in bath 2 are interesting. The free available chlorine was less than 0.4 mg./l. in 19 samples out of 22, and the redox potential less than 700 mV. in 15 samples out of 22. The number of swimmers was very high, and the weather sunny and warm. During the night between days ¹ and 2 the chlorine tube ran out of gas and the available chlorine and the redox potential of the water were not normal again until 10 o'clock on day 2. Despite this, less than 5 bacteria/ml. were found in the water. This can be compared with bath 3, where relatively few bacteria were found on day 1, but high bacterial counts were found on the other days, although the available chlorine was considerably higher than in the other baths. In bath 4 no bacteria were found the 2 last days when the weather was cloudy and the number of swimmers low.

No definite conclusions can be drawn from an investigation of this restricted volume, but there seems to be a difference between those baths (1 and 2) using aluminium sulphate precipitations + sand filter and those (3 and 4) using only sand filters. In both baths 3 and 4 the filters had been back-washed on the day before the investigation, and the bacterial count was lower on day ¹ than on the following days. This indicates that the efficiency of the water purification system is of as great an importance for the bacteriological state of the water as is the mere disinfection process. The nitrogen values did not increase significantly during the week in any baths. The permanganate number did not increase either during the week in baths 1, 2 or 3, but it increased in bath 4, where the permanganate number from the start was already significantly higher than in the other baths. This probably depends on a more efficient water purification in baths ¹ and 2, and an oxidative destruction of organic compounds by the high available chlorine in bath 3.

If the efficiency of the water purification is of such importance as the present investigation indicates, the high bacterial counts probably can be explained by the formation of particle clusters containing bacteria surrounded by a protective coat, so that the chlorine cannot reach the bacteria.

No classification of the bacteria was made. It is interesting though that the bacterial count at 22° C. was about the same as that at 37° C. This contradicts the possibility that 'normal flora' exist in the swimming pools.

It is further noted that faecal coliforms were not found in baths 3 and 4 even when high counts of bacteria growing at 37°C. occurred. This suggests that faecal contamination was effectively controlled, but reinforces the criticisms raised by various experts that faecal coliform organisms may not be the best indicators of the numbers of all organisms derived from the human body during swimming.

The main reason for performing this investigation was to test whether the redox potential could be used instead of measurement of the available chlorine to estimate the bacteriological quality of swimming-pool water. Available chlorine is obviously not reliable in all waters, and in some cases not even a high amount of free available chlorine necessarily guarantees a germ-free water (bath 3). Considering that in most swimming pools probably only the total available chlorine is being measured (Black et al. 1970), the reliability may be very low if repeated bacteriological examinations are not performed. The proposed method of using

certain minimum values of the redox potential of the water as guarantee for hygienic safety, however, seems to involve a lesser degree of uncertainty than the available chlorine does. Neither does a high redox potential necessarily mean a germ-free water in all cases, however, according to the present investigation. The efficiency of the water purification system is probably decisive for the disinfective effect of the available chlorine. If filters are back-washed often enough and coagulants are dosed correctly, then an automatic, continuously registering redox potential device, perhaps connected to the chlorine dosing pump, ought to constitute a good control of the hygienic quality of the water. Even so, bacteriological examinations of the water must be performed. These should preferably be made at high bathing load.

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