BATHING WATER CONDITIONING

Marjana Simonič

Fakulteta za kemijo in kemijsko tehnologijo, Univerza v Mariboru, Smetanova 17, 2000 Maribor, Slovenia

Received 17-03-2003

Abstract

The aim of our article is to expose the problems around the concentration of urea and ammonium in bathing waters. The statements are based on the German DIN norms 19 643-1 from 1997. Severe requirements about bound chlorine concentrations are introduced, and it is explained why ammonium and urea determinations in chlorinated bathing waters have been crossed off the list. The comparison of the essential parameters between Slovene and German standards is given. Finally, some methods of dechloramination are presented.

Introduction

Replacing its predecessor DIN 19643 from the year 1984, the new DIN 19643 "Conditioning of swimming and pool water"[1] has been in force since April 1997. The bathing water investigations resulted in some changes, especially with regard to the improvement of the hygienic quality of bathing. Based on the new findings relating to the chemical reaction mechanisms in chlorinated waters, most of the changes were made in the field of ammonium and urea determination. The Munich scholar Dr. Eichelsdorfer, who is the leading researcher in the mentioned field, provided us with many useful pieces of relevant information.[2]

Based on the DIN 19643 norms for bathing water, new Slovene regulations for such water are in preparation. The first proposal, entitled »Rules regarding hygienic suitability of bathing water«, has already been drawn up by the »Institute of Public Health of the Republic of Slovenia «.

Discussion

The regulations for bathing waters from 1988[3] are still valid in Slovenia. These regulations require the measurement of urea $(NH_2)_2CO$, because it is shed into the water by human urination and perspiration. The DIN Standards 19643 do not require the

measurement of urea. That is because urea hydrolises into NH_4^+ after the following reactions:

$$(NH_2)_2CO + H_2O \rightarrow 2\ NH_3 + CO_2 \quad (1)$$

and

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

It means that urea is not contained in the water as $(NH_2)_2CO$, as it reacts into NH_4^+-ions and further in the presence of chlorine:

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (3)$$

NH_4^+-ions immediately react according to the following reactions:[4]

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad pH = 6\text{-}8 \quad (4)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad pH = 5\text{-}6 \quad (5)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad pH = <5 \quad (6)$$

It is evident that in chlorinated water neither urea nor NH_4^+ ions are contained. Dependent on the pH value of the water, molecular ammonium forms chloramines. If the pH value is between 6 and 8, NH_2Cl is built, if the pH value is between 5 and 6, then $NHCl_2$ is built, and if the pH value is under 5, NCl_3 is built. It means that different chloramines are formed and are contained in the water, while urea and NH_4^+ ions immediately react with chlorine to form chloramines. They cause red eyes, skin irritation, the characteristic pool smell and are claimed to be carcinogenic. All chloramines, irrespective of how they come into existence, are called bound chlorine. Free chlorine, too, is always contained in water, as presented with equation (3). Both types of chlorine are parts of total chlorine. In practice the values of total and free chlorine are measured, the value of bound chlorine is gained by counting the value of free chlorine out of the value of total chlorine. In Slovene regulations, the maximum MDL determined level for free chlorine is 0.5 mg/L. The limit of free chlorine was drastically reduced to 0.2 mg/L in DIN 19643. If the value exceeds 0.2 mg/L, the water pollution is very high due to the formation of chloramines. If the concentrations of bound chlorine are below 0.2 mg/L, none of the hygienic problems appear.

According to the rules, the MDL of free chlorine is the same in both countries' standards and it is determined with 0.3 up to 0.6 mg/L.

The major hygienic parameters are:

pH	6.5-8.5
ORP	> 700 mV
free chlorine	min 0.3 mg/L
bound chlorine	max 0.2 mg/L.

If the concentrations of bound chlorine exceed 0.2 mg/L, the water should be dechlorinated immediately. This can be done either by UV radiation with a minimum addition of the H_2O_2 solution, or by the adsorption of chloramines on powdered activated carbon PAC. The wavelength of the UV source has to be 254 nm and the intensity of UV irradiation must be at least 700 J/m^2. It is recommended to keep the flow turbulent during the irradiation. Chloramines are degraded to nitrogen. When applying PAC for dechloramination, it is recommended to use a suspension with a concentration of PAC 2 mg/L of water. With the determination of adsorption isotherms, the theoretical use of PAC can be calculated. It is necessary to use the most appropriate PAC type because of the filter fouling processes. The most applicable are the precoat filters where PAC is combined with vaculit.

Table 1 shows the comparison between the German DIN 19 643 and the valid regulations for bathing waters chemical analyses in Slovenia. The chlorinated hydrocarbons (THM) determination has been developed. The sum is expressed as mg/L of a typical representative in this case, chloroform, which is claimed to be carcinogenic. The limit value for such materials in the bathing water is 20 µg/L. Direct inhalation of such evaporable materials might represent a problem in indoor swimming pools, though in open-air swimming pools this effect plays no role because of the air shipping (wind).

The organic water pollution is determined as COD value. It is determined as Potassium permanganate consumption and is expressed in mg/L of oxygen. The maximum allowed value is 3.0 mg/L of oxygen. In Slovene regulations, COD must be determined as Potassium dichromate consumption and the maximum allowed value is 20 mg/L of oxygen. The values in the Slovenian standards differ entirely from those in the German standards.

Table 2 shows the comparison between the German DIN 19 643 and the valid regulations for bathing waters in Slovenia with regard to the microbiological analyses. It is recommended to control the microbiological water quality systematically and

continuously. The bathers' health is strongly dependent on the microbiological quality of the bathing water.[5] Standard microbiological analyses are presented in Table 2. The novelty is the Legionella pneumophila measurement in the waters with a temperature higher than 23 °C. Other parameters remained practically the same.

Table 1. The comparison between the German DIN 19 643 and the valid regulations for bathing waters in Slovenia (SI).

Parameters	units	filling water (DIN)	bathing water (DIN)	bathing water (SI)
color at 436 nm	1/m	max 0.4	max 0.5	–
ammonium as N	mg/L	–	–	<0.1
urea as N	mg/L	–	–	<1
turbidity	NTU	max 0.2	max 0.5	–
transparency	–	–	pool bottom must be visible	–
pH	–	max 7.6	max 7.6	max 8.5
NO_3	mg/L	–	max 20 (above filling water)	max 20
ORP	mV	>770	–	500
free chlorine	mg/L	min 0.3	min 0.3	min 0.3
bound chlorine	mg/L	max 0.2	max 0.2	max 0.5
COD ($KMnO_4$)	mg/L O_2	–	3 (above filling water)	< 20 mg/L*
THM	mg/L	–	<0.02	–
chloride	mg/L	–	–	< 200
TOC	mg/L C	–	–	< 10

* $K_2Cr_2O_7$ method.

Table 2. The comparison between the German DIN 19 643 and the valid regulations for bathing waters in Slovenia with regard to microbiological analyses.

Name	unit	bathing water according to DIN	bathing water according to SI
Colony number at 22 C	1/mL	100	100
Colony number at 37 C	1/mL	100	100
Coliforme of germs	1/100 mL	0	0
Pseudomonas aeruginosa	1/100	0	0
E.coli	1/100 mL	0	–
Legionella pneumophila (temperatures above 23 °C)	1/mL	0	–

Conclusion

We tried to point out the urgency to change the Slovene regulations for bathing waters. The improvement has to be made soon, because the extant regulations have become obsolete. Recent investigations have proven changes, especially in the chemistry of ammonium.

Beside our government, the Slovene health and safety inspectorate and project organisations also considered the problems shown in this paper. I truly hope that we shall find our own way to solve these problems successfully.

References

1. DIN 19643, *Deutsche Norm "Aufbereitung von Schwimm-und Badebeckenwasser*, Teil 1, 2 und 3. DIN Deutsches Institut für Normung e.V., Beuth-Verlag, Berlin 1997.
2. D. Eichelsdorfer, *Personal Message*, München, 1994.
3. *"Rules regarding hygienic suitability of bathing water"*, UL. No9, 1988.
4. V. Ozim, *Novi vidiki vrednotenja amonija in sečnine v kopaliških vodah*; Posvet Dezinfekcija kopaliških voda, Zbornik referatov, ZTI, Radenci **1997**, 1–6.
5. N. Klun, *Sanitarno mikrobiološki vidiki kopalnih voda*; Posvet Priprava in kondicioniranje kopalnih voda, Zbornik referatov, ZTI, Ljubljana **1995**, 7–13.

Povzetek

V prispevku obravnavamo problematiko vsebnosti amonija ob prisotnosti aktivnega klora v kopalniških vodah. Pri tem se opiramo na nemške norme DIN 19643-1 iz aprila 1997, ki uvaja strožja merila za vsebnost vezanega klora v teh vodah, obenem pa opušča določevanje sečnine in amonijaka v kloriranih kopaliških vodah. Prikazane so možnosti za dekloraminiranja kopaliških vod in primerjava med bistvenimi fizikalno-kemijskimi parametri po slovenskih in nemških predpisih.