

The significance of some nitrogen related hygienic parameters in swimming pools

Ivan Černý, Manager /Chief of Laboratory, Ekologická laboratoř PEAL, Prague, Czech Republic

Synopsis

Excessive use of chemical parameters for water quality evaluation in swimming pools could not bring any improvements, as shown in the example from Czech Republic. Criticized parameters are ammonia (ammonium ions) and nitrates, which are strongly considered to be of doubtful significance in relation to water quality, and if omitted, no harm will be done to public health. On the other side, considerable costs will be spared. The spite of ammonia and nitrates, nitrogen trichloride in air at indoor swimming pools seems to be useful parameter.

In the first part paper deals with behaviour of urea in the presence of chlorine. There is put the stress on the slow reaction between chlorine and urea and to rapid formation of chloramines when ammonia is present, which is the reason for rare findings of ammonia in swimming pools. Also the doubtful significance of nitrates as water quality indicator is discussed.

In the second part are presented results of NCl_3 measurements in the air at several indoor swimming pools in Prague and Middle Bohemia region. The plot is created between NCl_3 in air and „specific load“ of indoor air in swimming pools. It is recommended to measure systematically NCl_3 in air at indoor pools (once or twice a year), instead of unproductive measurements of ammonium ions and nitrates in water.

In some European countries there is a tendency to the excessive use of chemical parameters, in the effort to control water quality in swimming pools. Usually are tested: Chlorine (free and bound), pH, redox potential, turbidity, chemical oxygen demand, ammonium ions (in the Czech Republic, Slovak Republic and in some Spanish provinces) and nitrates. Of these compounds, ammonium ions (further in this text only ammonia) and nitrates seem to have very poor value for water quality monitoring. When measured once a week, as it is obligatory in Czech Republic, overall costs are not negligible. In the following table are compiled limit values for ammonia and nitrates in some countries:

	Czech Rep.	Slovak Rep.	Ger	Austria	Spain	Colombia	WHO Guidelines		
ammonia	0,5	1,0	-		0,5	-	-		
nitrates	20*	-	20*	20*/30**	-	10	-		

*over the concentration in diluting water, **if ozone is used in the treatment technology

Table shows that some countries order to control either ammonia or nitrates, Czech Republic both parameters and WHO none of them. I consider WHO guidelines (3) as best solution, from many reasons.

The significance of chlorine (free and bound) is clear, as well as the pH value. Also turbidity and chemical oxygen demand is useful for the water quality maintenance. In spite of these parameters, the reasons for the ammonia determination are hard to be understood and hard to be defended as well. Probably the intention was to control in some ways the load added by the pool attendants. But most of nitrogen is added into water in the form of urea (1).

Urea is relatively stable even in the normal conditions in swimming pool water, where usually is around 0,5 – 1,0 mg/l chlorine. At these conditions, the half life time for urea is close to forty hours - see table 1, where the decomposition of urea in (static) model vessel is shown. Urea reacts with chlorine only slowly, its decomposition to ammonium is also slow, as could be followed by the slow decrease of redox potential and free and total chlorine. There were found significant differences in the time behaviour of redox potential between experimental and reference vessel, with faster decline of redox, evidently due to urea influence. Bound chlorine level was constant all the time, which probably means that when any ammonia is released as a result of urea decomposition, immediately steps into the chain of reactions with excess chlorine or its ammoniacal intermediates, leading at the end to gaseous products as nitrogen (break point chlorination) and nitrogen trichloride (4,5) or dissolved nitrates (2). Only insignificant concentrations of ammonia had been detected during the experiment.

Table 1 – Decomposition of urea in the presence of chlorine (hypochlorite)

Time	Exp. vessel (tap water with urea and Cl)					Reference vessel (tap w. with Cl only)			
	redox	Cl (F)	Cl (B)	urea	ammonia	redox	Cl (F)	Cl (B)	ammonia
0	722	1,83	0,07	2,29	0,076	722	1,80	0,09	0,042
2	739					739			
5	712			2,15	0,035	713			0,039
7	721	0,54	0,21			721	0,67	0,21	
8	716	0,42	0,26	1,94		716	0,54	0,24	
10	421	0,28	0,20			714	0,35	0,30	
11	378					673			
12	362					650			
23	308	0,05	0,15			329	0,06	0,14	
25	Addition of hypochlorite								
26	406	0,74	0,29			657	0,70	0,19	
27	642					643			
30	658	0,30	0,21	1,52	0,080	665	0,28	0,23	
31	Addition of hypochlorite								
37	725			1,13	0,026	725			

Time is in hours from beginning of the run. Conditions in both vessels were the same, except

of urea, which was added only to experimental vessel. Redox potential is expressed in mV, all concentrations in mg/l. Cl (F)=free chlorine, Cl (B)= bound chlorine.

In contrast to urea, ammonia reacts with chlorine immediately and creates chloramines. These reactions are followed by dramatical changes in redox potential, namely at the break point.

With the knowledge of the behaviour of ammonia and urea, it is not a great surprise, that the findings of ammonia in swimming pool water are very rare, even in the not well maintained and crowded pools, where other parameters, as bound chlorine, turbidity, chemical oxygen demand and also bacteriological ones far exceed the limits. In the Czech Republic, all public swimming pools and spa pools are controlled frequently, and ammonia has to be measured once a week. From more than three thousand of analyses performed in our PEAL Ecological laboratory every year only less than ten exceeded the limit value for ammonia (0,5 mg/l). When calculated this limit to the content of monochloramine, that has least percentage of chlorine from the chloramines, the result is about 1,5 mg/m bound chlorine, value which exceeded the limit value for bound chlorine five times. From this point of view, the unpracticality of frequent ammonia measurement is given.

Many national guidelines for swimming pool water quality only regulate, with accordance to WHO Guidelines for safe recreational water environments (2006), the important parameters - which are turbidity, free and bound chlorine, pH, redox potential and microbiological criteria. This approach seems to be more effective, than frequent examination of broad scale parameters, without any response towards water quality improvements. If there is somewhere a demand for more detailed investigation, the necessary reasons for that should be given, to avoid costly, excessive and inefficient demands in regional or national guidelines or regulations.

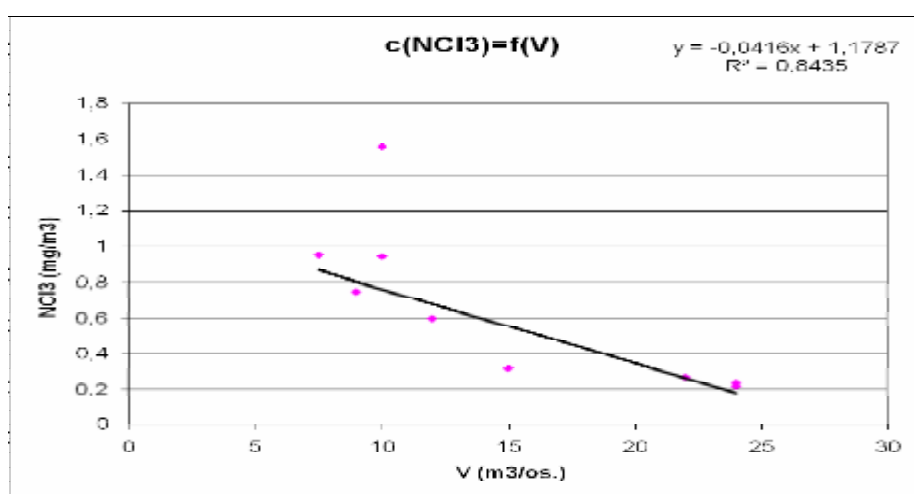
This remark aims mainly to ammonium, but concerns also the nitrate determination. Certainly it is true, that nitrates content grows when addition of free water is not sufficient(2). Limit value, 20 mg/l over the nitrate concentration in fresh diluting water, is exceeded only rarely, in a way similar to ammonia. It is also known, that nitrates formation is promoted by the influence of ozone (6), which can lead to false conclusions. Even if elevated limit 30 mg/l is adopted, the doubts about usefulness of this criteria remain. If there is any need to follow the water "age", better markers should be found, maybe potassium (7).

Probably much more important parameter than ammonia and nitrates in water, also closely related to ammonium nitrogen, is the nitrogen trichloride in air (4,5,9,10). This volatile compound, practically undissolvable in water (8) and easy to escape by air stripping (9), which typically smell as chlorine, is linked to respiratory problems, both occupational (5) and the prevalence for asthma in children (10). Its concentration in air at indoor swimming pools should not exceed the limit of 0,5 mg/m³, by the WHO Guidelines 2006 (3). We can find nitrogen trichloride in air in the indoor swimming pools, often in rather high concentrations, when ventilation is not sufficient and the pool is heavily visited. We have been investigating some indoor swimming pools in Prague and the Middle Bohemian region, and found nitrogen trichloride in the air up to 1,56 mg/m³, which even led to corrosion of air ducts. From our measurements results a plot between "specific air load" and nitrogen trichloride in the air. Specific air load is defined as air space volume belonging to one visitor (swimmer), when count in the day of air investigation. Following table and figure show the results.

Table 2 – trichloramine concentrations, indoor swimming pools in Prague

POOL	day	NCl₃, mg/m³	V m³/person
B	4.4.06	0,24	24
B	5.4.06	0,22	24
C	12.4.06	0,32	15
D	12.4.06	0,95	7,5
E	26.6.06 (10-12 A.M.)	1,56	10
E*	26.6.06 (1-3 P.M.)	0,94	10
F	26.1.07	0,75	9
F	31.1.07	0,60	12
B	8.2.07	0,27	22
Background, outdoor	6.4.06	0,006	

Figure 1 – Plot between NCl₃ in air and the specific load (data from table 1)



The higher value for pool E, which relates to conditions of insufficient ventilation, had been omitted from calculation.

Correlation could be calculated in the linear form

$$c(\text{NCl}_3) = a - b \cdot v$$

where v means specific load (space volume to one pool attendant)

$c(\text{NCl}_3)$ means NCl₃ concentration i air, mg/m³

as a = constant (intercept 1,2) and b (slope 0,04) - according to our measurements - and equation could be written as follows

$$c(\text{NCl}_3) = 1,18 - 0,04 \cdot v \text{with } R^2 = 0,84.$$

In other words, when v is less than 15 m³/swimmer, problems with odour could be expected.

Such a characteristic relates for example to indoor pool with air space of about 3000 m³ and more than 200 swimmers a day. The number of measurements in this plot is of course very limited and many important aspects have been omitted in this calculation, which not necessary have to be linear. The principal factor omitted was the intensity of ventilation, which has crucial effect, as shows results from pool E, where concentration of NCl₃ dropped immediately to half, when more fresh air was added.

Determination of NCl₃ in air had been made by the method according to Hery (5), with the only difference at the final chloride determination after leaching exposed filters, when using photometric method instead of ion chromatography. Photometric method uses solid mercuric thiocyanate which reacts with chloride to liberate thiocyanate ions, appropriate for photometric determination (11). Such determination of chloride does not demand expensive equipment and its limit of detection at 0,5 mg/l chloride in filter leachate enable sensitivity of 0,05 mg NCl₃/m³ by air sample volume about 0,1 m³.

I wanted to stress in this lecture, that for the obligatory health controls of the swimming pool environment, the scope according to WHO Guidelines 2006 is quite sufficient. Frequent investigation of parameters like ammonia and nitrates in water could not lessen the health risks. In the other side, regular control of air quality could be better used for good swimming pool maintenance.

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