INTRODUCTION OF THE PARAMETER 'TOTAL ORGANIC CARBON' (TOC) AS A STANDARD FOR THE QUALITY CONTROL OF SWIMMING POOL WATER

Vitorino de Matos Beleza[1]*, Rosária Santos Costa[2], Marta Pinto Baptista[2]

[1] Osminergia, Projectos, Equipamentos e Sistemas, Lda, vmb@osminergia.pt
[2] Centro de Estudos de Águas da Fundação Instituto Politécnico do Porto

ABSTRACT

Swimmers introduce organic compounds into swimming pools due to the transferring of sweat, saliva, skin, hair, urine, feces, among other materials, to the water. Water quality control in the tank must include some chemical parameters that will quantitatively reflect the presence of these contaminants in the water. Oxidability to permanganate is included in the regulations and norms of public swimming pools in most developed countries. According to the Portuguese norm NP-731, permanganate oxidability is determined *by the oxidation of organic compounds in the water by potassium permanganate in acidic conditions when boiling for 10 minutes*. In fact, this procedure detects all reductants oxidized by the essay conditions, whether organic or inorganic. To overcome these limitations, several entities suggested the determination of Total Organic Carbon (TOC).

Isocyanuric acid, $H_3O_3C_3N_3$, is used as a stabilising agent for free chlorine. In its combustion, cyanuric acid is totally oxidised, and the products of this reaction are carbon dioxide, which contributes to the TOC value, water and nitrogen.

Analytical confirmation of the carbon:isocyanuric acid relationship was performed in the *Centro de Estudos de Águas* laboratory, achieving the value of 0.27 quite close to the theoretical relation carbon:isocyanuric acid (0.28). This relationship will help to definition of a maximum value for TOC in swimming pool water, in function of its depth.

Keywords	Materials of human origin; permanganate oxidability; total organic carbon, TOC; Swimming pool

INTRODUCTION

Swimmers are the main cause for the introduction of contaminants to swimming pools due to the transferring of sweat, saliva, skin, hair, urine, feces, among other materials, to the water. As a consequence of this contamination, nitrogenous substances and organic compounds are introduced in the water. Some of these end up reacting with halogenated disinfectants (based on chlorine or bromine).

Water quality control in the tank must include some chemical parameters that will quantitatively reflect the presence of contaminants in the water. Permanganate oxidability is included in the regulations and norms of public swimming pools in most developed countries. According to the Portuguese norm NP-731, permanganate oxidability is determined '*by the oxidation of organic compounds in the water by potassium permanganate in acidic conditions when boiling for 10 minutes*'. In fact, this procedure detects all reductants oxidized by the essay conditions, whether organic or inorganic. On top of this limitation the method suffers from some interferences, namely in the presence of high concentrations of chlorides such as in saline or brackish water.

To overcome these limitations, several entities suggested the determination of Total Organic Carbon (TOC). In this method organic compounds are fully oxidised and converted into simple molecules. The carbon present in those compounds is then converted into carbon dioxide (CO_2) which can be measured through an infra-red analyser. However, Charlier et al (2003) did not find a direct correlation between TOC and oxidability when measuring these two parameters in several pools (fig. 1). In conclusion, it is not possible to define the quality standard for TOC in the swimming pool water by the restrictions imposed to oxidability.

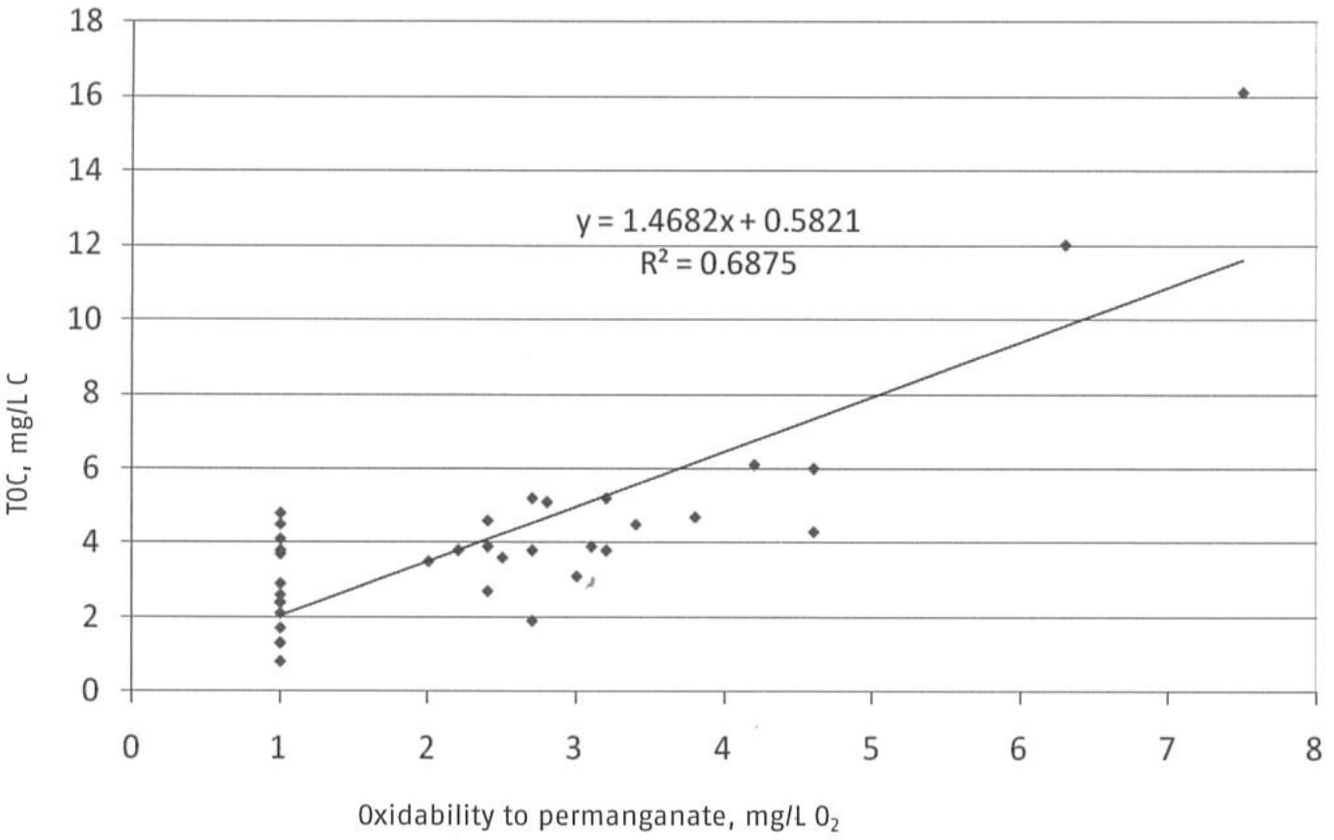

Figure 1 Correlation between TOC and oxidability to permanganate in swimming pool water, according to the values obtained by Charlier et al., 2003.

The definition of the maximum value of TOC presents two additional restrictions: a) the contribution of isocyanuric acid for the measured TOC; b) the definition of a unique value for all the different kinds of swimming pools. The aim of this study was to check how these aspects influence the definition of a TOC maximum value and to develop a correlation to introduce TOC as a parameter in water quality control of swimming pool water.

INFLUENCE OF ISOCYANURIC ACID IN THE DETERMINATION OF TOC

Isocyanuric acid, $H_3O_3C_3N_3$, is used as a stabilising agent for free chlorine (sum of hypochlorous acid and hypochlorite ion concentrations), reducing its loss in open-air tanks. It is stable to the presence of chlorine and it is not oxidised by permanganate in the essay conditions used for the determination of water oxidability.

In its combustion, isocyanuric acid is totally oxidised, and the products of this reaction are carbon dioxide, water and nitrogen, as shown in the following equation:

$$2H_3O_3C_3N_3 + \frac{9}{2}O_2 \rightarrow 6CO_2 + 3H_2O + 3N_2 \qquad (1)$$

Considering the molecular formula of isocyanuric acid, it is observed that for each 10 mg/L of isocyanuric acid there are 2.8 mg/L of carbon.

The analytical confirmation of the carbon:isocyanuric acid relationship was performed in the *Centro de Estudos de Águas* laboratory. For this purpose, different standard solutions of isocyanuric acid in the range usually used in swimming pools were prepared, and TOC and oxidability to permanganate were determined in each of these solutions. TOC was evaluated in a Shimadzu model 5000A analyser. Oxidability to permanganate was determined according to the above mentioned Portuguese norm. Results are presented in Table 1 and figure 2.

Table 1 TOC and oxidability to permanganate values obtained in isocyanuric acid solutions

Isocyanuric acid concentration, mg/L $H_3O_3C_3N_3$	Total Organic Carbon, mg/L C	Oxidability to permanganate, mg/L O_2
10	3.0	1.2
20	5.5	1.4
40	11	1.2
80	22	1.3

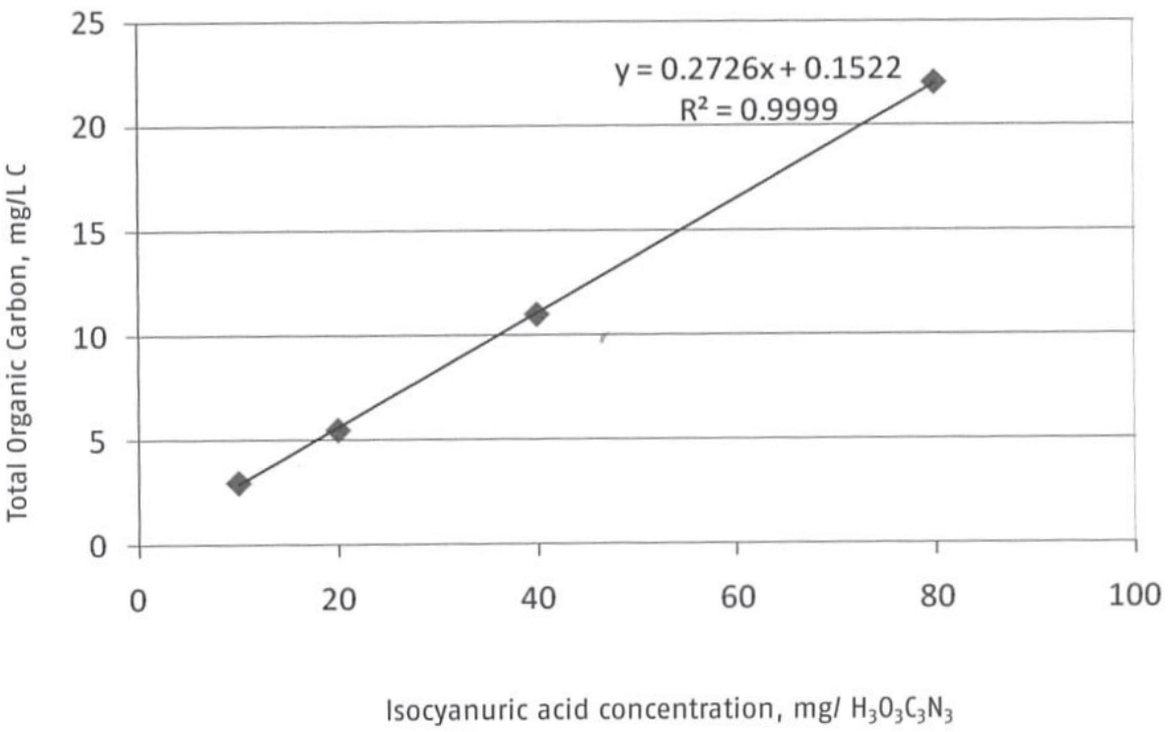

Figure 2 Correlation between TOC and isocyanuric acid concentration

The results obtained show that:

a) Isocyanuric acid is not oxidised in the essay conditions for oxidability to permanganate.
b) The correlation between the concentration of isocyanuric acid and TOC is linear with a slope of 0.27. This value is quite close to the theoretical relation carbon:isocyanuric acid (0.28).

DEFINITION OF A MAXIMUM VALUE FOR TOC IN SWIMMING POOL WATER

As mentioned above, the value of oxidability to permanganate aims to evaluate the quantity of contaminants introduced in the tank water, due mainly to the presence of swimmers. To address the issue of swimmer contamination, experimental trials related to swimming pool water (Judd & Black, 2000) have used a solution comparable to body fluid (Body Fluids Analogue, BFA). The solution contains 91.85 g/L of inorganic and organic substances dissolved and the organic carbon contained in it corresponds to 11.44 g/L. The contamination introduced in the tank water by each swimmer was estimated to be equivalent to 25 ml of BFA, that is, 286 mg of organic carbon (Judd & Black, 2000).

The total mass of contaminants in a pool depends on the attendance. If daily frequency is represented by F_D (swimmers/day), the total daily mass (MC_D) of organic carbon introduced in the tank water will be:

$$MC_D = 286 \cdot F_D, mg\ I\ day\ ,\ \text{mg/day C} \qquad (2)$$

Part of the organic compounds introduced by contamination can be transformed, for example, by oxidation, into inorganic compounds. The remaining fraction might remain in the swimming pool water as such or originate other organic compounds like, for example, trihalomethanes. Consequently, further elimination of organic substances expressed as TOC, can only be performed by means of one of two possible pathways: a) proper physical-chemical treatment; b) replenishment of the swimming tank water. Historically, the second option has been preferred. Assuming that a given proportion α of the organic substances is removed off the tank by chemical reaction, the removed TOC in each day is calculated by:

$$(1-\alpha) \cdot M_{CD} = 286 \cdot (1-\alpha) \cdot F_D = Q_{RD} \cdot (TOC)_{AP} \qquad (3)$$

where Q_{RD} (L/day) is the flow of water renewed daily, and (TOC)AP the TOC of the swimming pool water.

Unlike most pool operation norms in other countries, the Portuguese Regulation Decree 5/97, dated from March 31st, impose daily renovations of between 2 to 5% of the total pool water volume. Let us assume an indoor swimming pool whose tank has an area of S (m^2) and an average height of H (m). If the maximum daily frequency is numerically equal to $S/2$, for a replenishment of 2% of the total tank volume, we have:

$$QRD = 0{,}02X1000 \times S \times H \qquad (4)$$

Replacing the value of Q_{RD} and F_D in (3), we have:

$$286 \times (1-\alpha) \times \frac{S}{2} = 0{,}02 \times 1000 \times S \times H \times (TOC)_{AP} \qquad (5)$$

Solving, we obtain:

$$(TOC)_{AP} = \frac{7{,}15 \times (1-\alpha)}{H} \qquad (6)$$

From equation 6, we can conclude that the limit of TOC to be established regarding the swimming pool water will depend on the tank's average height. For example, if α= 0,5 and H = 1,0m, we have $(TOC)_{AP}$ = 3,6mg/L C. In this way, considering a tolerance range of 40%, it will be acceptable that norms or regulations of swimming pool water quality control allow for a maximum value of 5.0 mg/L C for the difference between TOC in the swimming tank water and TOC in the make-up water for a swimming pool with an average height H=1 m.

CONCLUSIONS

Oxidability to permanganate has been used to measure the organic load introduced into the water of a swimming tank during daily use by swimmers. The limitations of this method have been directing some institutions towards the use of a parameter that would be more representative of the degree of water contamination by organic substances: TOC. The acceptance of this parameter in the water quality control leads to the following considerations:

- Whenever isocyanuric acid is used, either pure or combined with chlorine, the value of 2.8 mg/L C per each 10 mg/L of isocyanuric acid must be subtracted to the TOC value obtained in the laboratory;
- When defining the requirements for quality control of pool water, the difference between the TOC in the pool water and in the make-up water has to be limited to a value that depends on the average depth of the swimming pool, as dictated by equation (6).

REFERENCES

Charlier, G, Burlion, N, Schrooten, D, 2003. Harlier Convention nº 01/13240 – Étude de la Qualite de L'Air des Piscines Visant a Définir des Normes pour le Contrôle Régulier de ces Etablissements. *Institut Scientifique de Service Public*

http://environnement.wallonie.be/convent/dpa/rapport_normes_piscines.pdf. (downloaded 25/07/08)

Eaton, A, Clesceri, L, Rice, E, Greenberg, A, 2005. *Standard Methods for the Examination of Water & Wastewater*. 21st Edition, American Public Health Association, Washington

Judd, SJ, Black, SH, 2000. Disinfection By-Products Formation in Swimming Pool Waters: a Simple Mass Balance. *Water Research*, 34 (5): 1611-1619

Kim, H, Shim, J, Lee, S, 2002. Formation of Disinfection By-Products in Chlorinated Swimming Pool Water. *Chemosphere*, 46: 123-130

Macedo, J, 2003. O Estado da Arte da Relação Ácido Cianúrico e Superestabilização. *Revista Controle da Contaminação*, 6 (55): 32-38