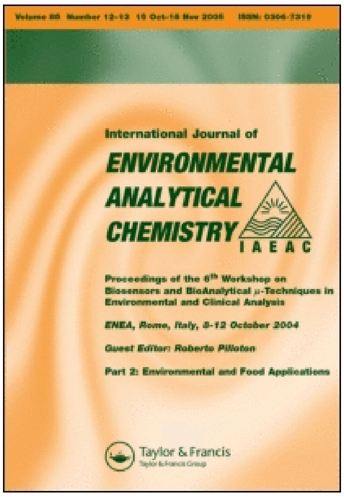

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IDENTIFICATION AND DETERMINATION OF ORGANOHALOGEN COMPOUNDS IN SWIMMING POOL WATER

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Volatile organohalogen compounds were determined in a swimming pool using three methods: determination of volatile organic halogen (VOX) after sorption on XAD-4 solid sorbent, thermal desorption and coulometric titration of the halides formed; identification and determination of the individual organohalogen compounds after sorption on XAD-4, solvent extraction and chromatographic determination; direct injection of aqueous samples to the chromatographic column. The concentration of organohalogen compounds varied from 35.9 to 99.7 $\mu g/dm^3$ for trichloromethane, 22.0 to 57.7 $\mu g/dm^3$ for dichloromethane, 2.4 to 27.4 $\mu g/dm^3$ for trichloroethylene, 2.3 to 14.7 $\mu g/dm^3$ for bromodichloromethane and 4.2 to 7.6 $\mu g/dm^3$ for tetrachloromethane. The results obtained by the three methods are consistent in principle.

KEY WORDS : Water pollution; volatile organic halogen determination; solid sorbents; trihalomethanes.

INTRODUCTION

The majority of investigations on the determination of organochlorine compounds in water concerned so far drinking water. This is quite obvious, because of the direct exposure of humans. A considerable number of investigations concerned also surface waters, i.e. rivers, lakes and seas, due to the possibility of indirect introduction of the discussed compounds to humans through the food chain, or to the impact of organohalogen compounds on the growth of living organisms[1,2]. Relatively little attention has been paid to pollution of swimming pools with organohalogen compounds, the statement concerning both water and air in equilibrium.

The problem is mainly originated by the disinfection of water, accomplished most often by chlorination. Although there are other methods of disinfection, like ozonization, UV irradiation, application of hydrogen peroxide, as well as silver or copper ions, chlorination is by far the most widely used procedure. Chlorination, on the other hand, can transform nontoxic organic compounds naturally occurring in waters into highly toxic compounds, including carcinogenic, mutagenic and teratogenic ones[1,2]. Conjunctiva irritation and ophthalmitis caused by chloramines formed in reactions of chlorine with amines from perspiration and urine, happening very often to swimmers, is a clearly noticeable example of the toxic action of water chlorination products[3]. It has also been established that trihalomethanes (THM), typical products of the reaction of humic compounds with chlorine, cause irritation of the upper respiratory tract[3].

The average concentration of trichloromethane in USA swimming pools in the seventies was equal to 150 μg/dm^3, although concentrations reaching 700 μg/dm^3 trichloromethane and 1300 μg/dm^3 total THM have been also reported[3]. Apart from trichloromethane, the following compounds have been also identified in swimming pool waters: bromodichloromethane, dibromochloromethane, tribromomethane, tetrachloromethane, tetrachloroethylene, trichloroethylene and trichloronitromethane[3-8].

Investigations have also been performed on the penetration routes of the discussed compounds to human organisms, and on their content in blood, respiration and urine of people swimming in pools or simply visiting them[3,5]. It is estimated that a six year old child, weighing 22 kg and having a body surface of 0.88 m^2, absorbs through skin, mouth, nose, orbital cavities and auricles a total of 119.9 mg THM's when swimming three hours a day in a pool, in which the THM concentration is 500 μg/dm^3 [3]. Just to compare, when drinking daily 2 dm^3 of water containing 100 μg/dm^3 THM's one introduces only 200 μg/dm^3 THM's to the organism, the figure being almost 600 times lower than during swimming three hours a day in a pool.

To emphasize the potential health hazards of a swimmer it should also be added that at 150 μg/dm^3 trichloromethane in water the equilibrium concentration in air is 0.7 mg/dm^3, reaching even 2.5 mg/dm^3 at the vicinity of the surface (i.e. where the swimmer's head is)[3]. This concentration significantly exceeds the TLV for workplaces. As a result, a significant increase in trichloromethane concentration is observed in swimmers' blood, respiration and urine after competitions[3].

The above data indicate that both the swimmers and the audience at swimming pools are clearly exposed to volatile organohalogen compounds. It is necessary, therefore, to develop methods for their determination in water and air of the swimming pools. Our investigations concerned the swimming pool of the Technical University of Gdańsk.

EXPERIMENTAL

Organochlorine compounds in the swimming pool water were determined using three methods:

Method A

Determination of volatile organic halogen (VOX) after sorption of the analytes on XAD-4 solid sorbent, mineralization of the liberated compounds and coulometric titration of the halides formed. This method has already been described in our previous papers[9-11]. To avoid errors that could possibly occur during transport, the preconcentration of organohalogens from water was carried out directly at the pool. After completion of the concentration step the sorbent was washed with boiled bidistilled water in order to remove residual chlorine and inorganic compounds. Organochlorine compounds were concentrated from 1 dm^3 of water at 25 cm^3/min flow rate. The desorption of the adsorbed compounds was carried out in the laboratory. The detection limit of the method was ca. 0.2 ± 0.1 μg/dm^3, in terms of VOCl and the standard deviation ranged between $\bar{s} = 3.4$–6.5%. To control the breakthrough process the concentration was carried out using two sorbent traps in series.

Method B

Identification and determination of the individual organohalogen compounds after sorption on XAD-4 solid sorbent, solvent extraction and chromatographic determination. The compounds were concentrated from 0.5 dm^3 of water at 15 cm^3/min. The concentration was carried out using sorbent tubes of 5 mm I.D., the length of the sorbent bed being 110 mm (0.8 g of 20-40 mesh sorbent). The sorbent was then washed with 50 cm^3 boiled bidistilled water, and the tubes were closed. The trapped compounds were extracted with 10 cm^3 of reagent grade pentane at 0.5 cm^3/min.

The extract was analyzed by gas chromatography using Carlo Erba (Italy) Vega 6180 gas chromatograph. The conditions were the following: 30 m × 0.32 mm fused silica capillary column, coated with bonded 5 μm apolar PS-255 phase (MEGA); 2 m × 0.32 mm fused silica precolumn; temperature program: injection at 45°C and heating up to 120°C at 15°C/min; injection system: cold on-column with secondary cooling; electron capture detector ECD 40/400, operated at 350°C with pure nitrogen (99.999%) make-up (30 cm^3/min); carrier: hydrogen at 0.4 m/s; injection volume: 1 μl. The pentane extracts were either analyzed immediately, or stored in tightly sealed ground glass flasks in a refrigerator.

Method C

Identification and determination of the individual compounds by direct injection of aqueous samples to the chromatographic column. Samples of water were drawn to glass flasks with ground glass seals in such a way that no air was left in the flasks. The analysis was performed immediately after transporting the samples to the laboratory, using the same GC equipment as above at 102°C isothermally. The injected volume was 2 μl.

The detection limits of methods B and C, dependent on the species being determined, may be estimated at ca. 0.01 μg/dm^3 on average and the standard deviation varied between $\bar{s} = 1.74$–3.02%.

RESULTS AND DISCUSSION

Figure 1 presents examples of: A - a chromatogram of a standard aqueous solution of the compounds being determined; B - the pentane extract of a sorbent, on which organohalogen

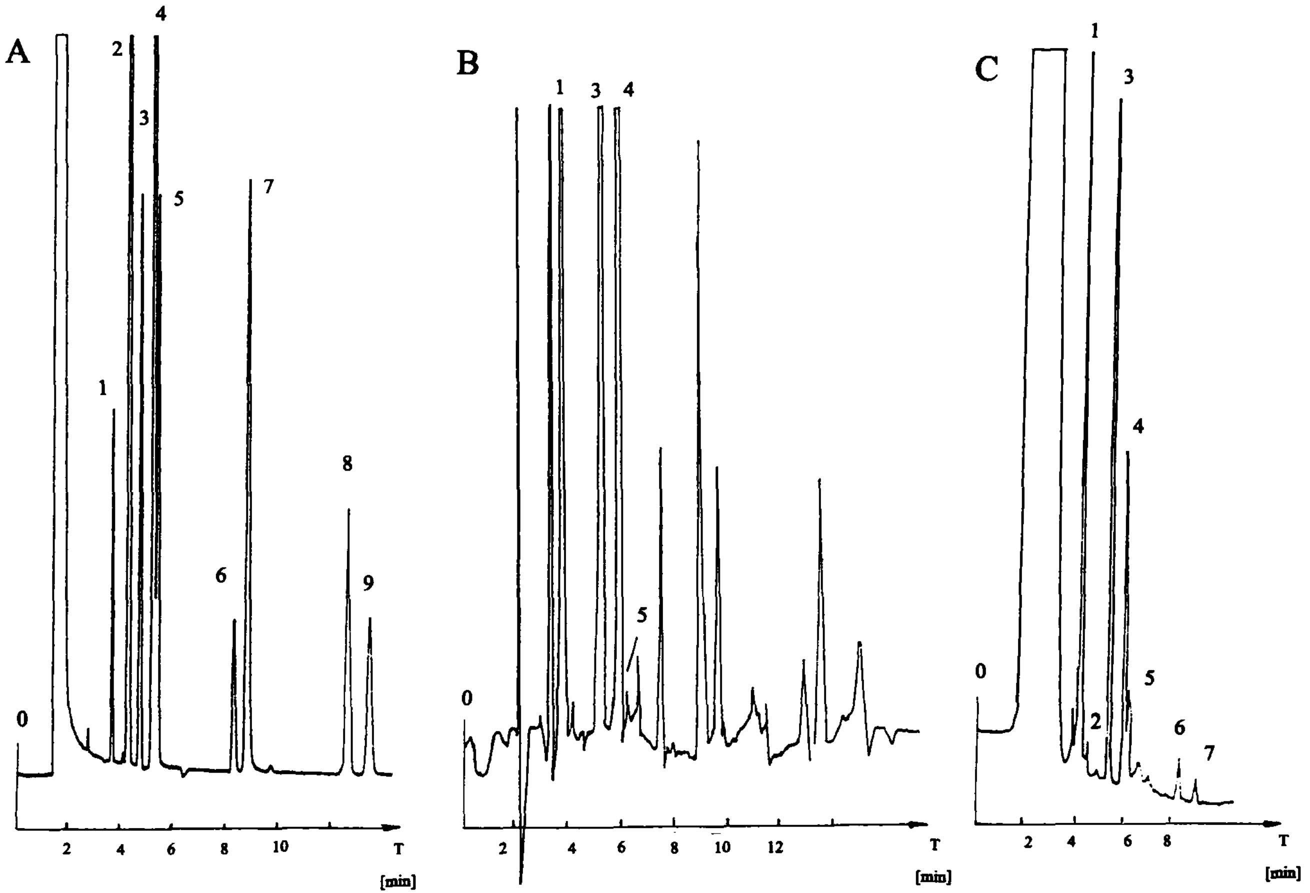

Figure 1 Chromatograms of: A - a standard aqueous solution of organohalogen compounds; B - the pentane extract of a sorbent, on which organohalogen compounds from swimming pool water were trapped; C - obtained by direct injection of swimming pool water. 1 - $CHCl_3$; 2 - CH_3Cl_3; 3 - CCl_4; 4 - $CHClCCl_2$; 5 - $CHBrCl_2$; 6 - $CHBr_2Cl$; 7 - CH_2BrCH_2Br; 8 - CCl_3CH_2OH; 9 - $CHBr_3$.

Table 1 Results of the determination of organohalogen compounds in the water from the swimming pool of the Technical University of Gdańsk [μg/dm^3]

Compound	*Sampling date*										
	20.03.90	27.03.90	03.04.90	14.03.91		25.03.91		23.09.91		19.12.91	
Method	B	B	B	B	C	B	C	B	C	B	C
CH_2Cl_2	—	—	—	22.0	27.0	51.5	57.7	—	—	—	—
$CHCl_3$	64.8	37.6	43.6	93.4	92.4	98.5	99.7	43.6	47.3	35.7	52.8
CH_3CCl_3	—	—	—	0.1	—	0.1	—	ND	2.6	2.7	13.3
CCl_4	—	0.4	0.9	7.6	6.9	6.6	7.4	4.2	6.5	5.7	5.7
$CHClCCl_2$	—	9.8	11.1	27.4	23.3	19.6	18.6	11.1	15.2	8.8	2.4
$CHBrCl_2$	—	—	—	14.6	11.5	10.9	10.9	2.3	ND	2.5	2.8
$CHBr_2Cl$	—	—	—	0.3	ND	0.2	ND	0.2	ND	ND	0.8
CCl_3CH_2OH	—	—	—	0.03	—	0.04	—	ND	—	ND	—
$CHBr_3$	—	24.3	203.2	0.05	ND	0.2	ND	ND	ND	0.1	ND

compounds from the water from the swimming pool were trapped; C - a chromatogram obtained by direct injection of swimming pool water.

The results of the determination of individual compounds according to methods B and C are listed in Table 1. Table 2 presents a comparison of the values of VOX determined by the three methods, expressed in terms of VOCl.

The concentration of organohalogen compounds in the swimming pool water was found to be much higher than in drinking water, e.g. from the Gdańsk region[9,10,13]. The spectrum of the compounds was also different. Although trichloromethane prevailed (from 35.9 to 99.7 μg/dm^3), still high concentrations of other compounds, viz. dichloromethane (22.0 to 57.7 μg/dm^3), trichloroethylene (2.4 to 27.4 μg/dm^3), bromodichloromethane (2.3 to 14.7 μg/dm^3 and tetrachloromethane (4.2 to 7.6 μg/dm^3), were also encountered. The high concentrations of organohalogen compounds result from the very intensive chlorination of water for sanitary purposes.

The occurrence of organobromine compounds is due to the fact that raw water contains small amounts of bromides, which are oxidized to free bromine during chlorination. The bromine formed takes part in the haloform reaction similarly to chlorine. As the organobromine compounds are less volatile, they can concentrate in the swimming pool water.

Table 2 Comparison of the VOX concentrations in the water from the swimming pool of the Technical University of Gdańsk determined by the three methods (expressed in terms of VOCl - μg VOCl/dm^3)

Sampling date	*method A*	*method B*	*method C*
20.03.90	98.6	57.7	—
27.03.90	114.6	52.0	—
03.04.90	181.6	134.1	—
14.03.91	—	140.6	137.7
25.03.91	—	160.9	161.3
23.09.91	98.6	53.3	61.6
19.12.91	80.7	48.0	67.1

According to the expectations, the results obtained by method A are the highest, since this method allows the determination of the sum of all volatile organohalogen compounds contained in the sample. The variability of the results obtained on various days can be explained by the time elapsed between partial changing of the water in the pool and the day of sampling. Chlorination is made permanently. The results obtained by methods B and C are consistent in principle, thus showing the good accuracy of both methods.

Higher results obtained in some cases for volatile compounds (di- and trichloromethane) in method C can be explained by further chlorination of the sample during transport. Removal of free chlorine by addition of non-volatile reducing agents was not possible due to the direct sample introduction onto the GC column. Chromatograms obtained by direct injection of swimming pool water samples, illustrated in Figure 1C, prove that no other organohalogen compounds occur in the water analyzed in significant amounts.

At low concentrations better results were obtained by method B (utilizing preconcentration of the analytes on a solid sorbent), since it offered much lower detection limits (ca. 100-fold concentration of the analytes). Additional advantages of this method are the possibility of easy transportation and storage of the samples prior to the analysis. This is particularly important for analysis of natural waters. Method B can be utilized for the determination of both volatile and non-volatile compounds, and enables the analysis to be performed using various columns and separation conditions.

The results obtained in the present case are close to those reported for a swimming pool in Schwerin[4], but lower than average results reported for USA swimming pools[3].

The noxious character of the organohalogen compounds determined, their high concentration in pools, and the ease with which they penetrate the bodies of the swimming pool users, indicate that a much closer attention should be paid to this problem. New methods of water treatment should be developed, ventilation systems of the swimming pools should be improved, but first of all it is necessary to introduce threshold limit values both for individual compounds and for total organic chlorine in water and air of swimming pools.

The results obtained confirmed the suitability of XAD-4 for the concentration of organohalogen compounds from water. The method is very suitable for field investigations and determination of organic compounds in natural water samples. However, the matrix effect related to the occurrence of other organic and inorganic compounds in the analyzed samples should be taken into account.

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