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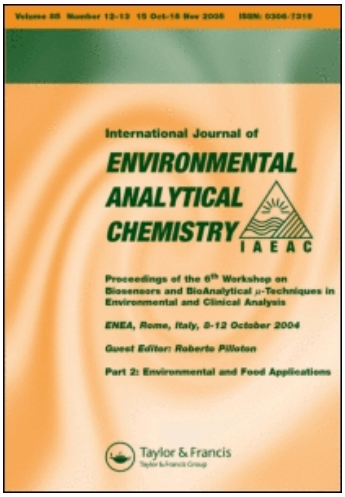

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PRESERVATION OF WATER SAMPLES CONTAINING TRIHALOMETHANES

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This work was conducted in order to emphasise the importance of using preservation methods in water samples for the analysis of volatile organohalogenated compounds, namely trihalomethanes (THM), so that representativeness of the samples analysed can be attained. Water samples, containing these compounds were analysed by CGC-ECD using the direct aqueous injection. Samples were submitted under different conditions. The influence of light, temperature, storage time and conditions, on the modification of the THM levels were studied.

Keywords: Volatile organohalogenated compounds (VOC's); trihalomethanes (THM); preservation; capillary gas chromatography (CGC); electron capture detection (ECD)

INTRODUCTION

Trihalomethanes (THM) constitute a group of compounds that can be present in drinking waters. They can originate during the water treatment, due to the reaction of chlorine used in the chlorination process, with the organic matter present in the water, especially humic and fulvic compounds[1]. In the presence of bromine, the main THM formed are chloroform ($CHCl_3$), dichlorobromomethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$).

Generally, preservation may include cold temperature (4°C), low or high pH, toxic chemicals—HgCl or pentachlorophenol, not acceptable nowadays—[2, 3] and a new preservative—sodium bissulfite[4]. The main reason for the use of this

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step in the whole analytical process, is to prevent or, at least, to delay changes in the composition of the sample compounds, which are mainly due to the volatilisation, absorption, diffusion, oxidation / reduction, photochemical and microbiological process. Not many studies are focused on this subject. Some of them are focused on different compounds, like pesticides[5-8]. Several preservation methods are described in the literature[2-4, 10-11], but a sustained knowledge of any fundamental experience concerning the transport conditions and storage time, has not been described until now for the trihalomethanes. This lack of knowledge needs more attention as it may compromise the results of the analysis.

EXPERIMENTAL

Instruments

A gas chromatograph Varian 3400 equipped with ECD (Walnut Creek, USA) and a capillary column DB-624, 30 m × 0,32 mm and 1,8 μm with a pre-column of silica with 4 m × 0,52 mm, from Varian, Sunnyvale, USA, was used. The operating conditions where: oven temperature 50°C for 10 min., 10°C/min, until 150°C, remaining at this temperature during 10 min, injector temperature 150°C, detector temperature 200°C, transport gas flow 2.5 ml/min.

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Reagents

All standard compounds (chloroform, dichlorobromomethane, dibromochloromethane and bromoform) were purchased from Fluka (Buchf, Switzerland). They were mostly of purity >98%, and used as received. Dark glass vials of 40 ml with silicone septum covered with teflon (Supelco, Bellefonte, USA), synthetic glycol packaged in plastic bags and water of HPLC quality were also used.

Analysis of the Water Samples

Preparation of the samples

The water samples were prepared with the addition of 1 μg of each one of the four THM to one litre of HPLC water grade. The preparation of all the samples was done inside a refrigerated room at 4°C. No organic solvent was added to facilitate the solubilities of the standards, in order to obtain similar conditions to the real samples. For each of the studied situations a set of 3 samples was prepared. The study was conducted for the following 6 weeks. Every week

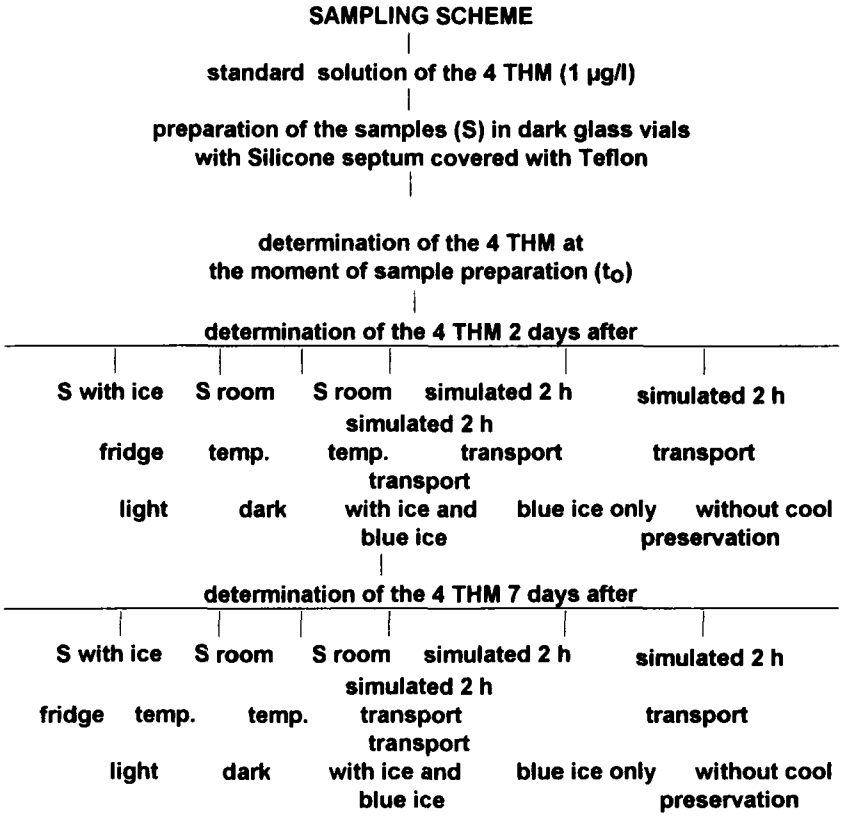

FIGURE 1 Schematic representation of the sampling program used to conduct this study during six following weeks. The different conditions to which these samples were submitted are presented.

samples were made freshly. The overall number of water samples involved in this study was 108. The four THM were analysed by GC-ECD with direct injection[12] for different times: T_0 (day of the sample preparation); T_1 (2 days after the sample preparation) and T_2 (7 days after the sample preparation). Figure 1 represents the sampling scheme used to conduct this study.

RESULTS AND DISCUSSION

Tables I, II, III and IV represent the results related to the entirety of the samples analysed. They indicate the different studied situations, as well as the mean values for the individuals and total THM and their standard deviations. The

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TABLE I Time variation of the individual and total concentration of the THM for the samples kept in ice in the refrigerator. (n = 6)

		$CHCl_3$ (μg/l)	$CHBrCl_2$ (μg/l)	$CHBr_2Cl$ (μg/l)	$CHBr_3$ (μg/l)	Σ THM (μg/l)
	x	1,16	1,05	1,09	1,12	4,42
T_0						
	s	0,20	0,13	0,14	0,14	0,56
	x	1,05	1,05	1,09	1,12	4,31
T_1						
	s	0,11	0,03	0,05	0,25	0,52
	x	1,05	1,01	1,09	1,11	4,26
T_2						
	s	0,19	0,11	0,12	0,10	0,52

T_0 - Day of sample preparation T_1 - 2 days after the sample preparation T_2 - 7 days after the sample preparation x - Mean value s - Standard deviation

TABLE II Time variation of the individual and total concentration of the THM for the samples kept at room temperature and exposed to light. (n=6)

		$CHCl_3$ (μg/l)	$CHBrCl_2$ (μg/l)	$CHBr_2Cl$ (μg/l)	$CHBr_3$ (μg/l)	Σ THM (μg/l)
	x	1,00	0,93	0,98	1,01	3,92
T_0						
	s	0,12	0,15	0,16	0,16	0,49
	x	0,81	0,74	0,79	0,84	3,18
T_1						
	s	0,33	0,25	0,26	0,31	1,11
	x	0,72	0,67	0,76	0,81	2,96
T_2						
	s	0,34	0,24	0,25	0,26	1,10

T_0 - Day of sample preparationm T_1 - 2 days after the sample preparation T_2 - 7 days after the sample preparation x - Mean value s - Standard deviation

Figure 2, Figure 3, Figure 4 and Figure 5, show with more evidence the changes attained by the THM concentrations (%) in T_0, T_1 and T_2 times, according to the different studied conditions. Probably due to its volatility chloroform is the compound which presents the highest level of losses. Following the different cases, we can observe this behaviour: for the better conditions of preservation, which are indicated in Table I, only the $CHCl_3$ undergoes losses of 10% throughout the experiment. On the contrary, the other THM - $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$ - do not suffer any change on their concentration levels. Considering the worst conditions of preservation, the loss percentage value of chloroform raises to 20% (T1) and 30% (T2). All the other compounds suffer losses of 20% (Table II). If the samples are protected from light, but at room temperature, $CHCl_3$ presents losses of 20%, as well as the other compounds

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TABLE III Time variation of the individual and total concentration of the THM for the samples kept at room temperature in dark. (n = 6)

		$CHCl_3$ (μg/l)	$CHBrCl_2$ (μg/l)	$CHBr_2Cl$ (μg/l)	$CHBr_3$ (μg/l)	Σ THM (μg/l)
T_0	x	0,92	0,95	1,00	1,03	3,90
	S	0,07	0,12	0,12	0,12	0,42
T_1	x	0,84	0,80	0,86	0,91	3,41
	S	0,39	0,17	0,20	0,24	0,94
T_2	x	0,81	0,70	0,82	0,91	3,34
	s	0,37	0,27	0,28	0,24	0,94

T_0 - Day of sample preparation T_1 - 2 days after the sample preparation T_2 - 7 days after the sample preparation x - Mean valu es - Standard deviation

TABLE IV Time variation of the individual and total concentration of the THM for the samples kept in ice and blue ice in the container. (n = 6)

		$CHCl_3$ (μg/l)	$CHBrCl_2$ (μg/l)	$CHBr_2Cl$ (μg/l)	$CHBr_3$ (μg/l)	Σ THM (μg/l)
T_0	x	1,15	1,01	1,00	1,10	4,36
	s	0,17	0,16	0,14	0,19	0,51
T_1	x	1,02	1,00	0,98	1,09	4,09
	s	0,37	0,20	0,22	0,23	0,96
T_2	x	0,99	0,98	0,97	1,09	4,07
	s	0,42	0,23	0,24	0,28	1,06

T_0 - Day of sample preparation T_1 - 2 days after the sample preparation T_2 - 7 days after the sample preparation x - Mean value s - Standard deviation

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(Table III). Finally, the results (Table IV) are very similar to the first situation represented in Table II.

Even though we have seen written evidence of several preservation methods, no study on this theme has been done up until now that has been supported by any fundamental experience. The US-EPA methods 502 and 601[7] only refer a maximum holding time of 14 days at 4°C after the collection, which is not in agreement with our results. On the other hand, is not useful to follow abstract recommendations when we have to deal with real cases.

We can conclude that there is no advantage in the use of the thermal containers with only the blue ice, because the losses verified are very close to the values found in the samples transported without cold preservation. In fact, the blue ice only is useful to maintain the ambient temperature of the thermal container, but

is unable of conducting the sample temperature to 4°C which only the ice can do. Therefore, as our study indicates, when analysing samples for volatile organohalogenated compounds, preservation by cold temperature in special conditions, should be adopted. These results alert us that it is absolutely necessary to respect all the demands of the samples that contain these compounds, if not, the analytical results will not be in agreement with the real sample composition and the data produced will be useless. This means loss of time and money and lack of accuracy which is not in accordance with the quality assurance needed to perform good laboratory practices.

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