STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 4, 2009

OPTIMIZATION OF METHODS FOR THE DETERMINATION OF DISINFECTION BY-PRODUCTS IN DRINKING WATER

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ABSTRACT. Chlorination is the most widely disinfection process of drinking water in Romania. The goal of the water disinfection is to protect it in the distribution systems against microbial contamination and to prevent and control re-growth of microorganism in the distribution system. The presence of DBPs in drinking water is a matter of concern for human health and can also produce unpleasant organoleptic taste. Under Stage I of the Disinfectants/Disinfection By-products (D/DBP) Rule, USEPA sets maximum contaminant levels (MCLs) for total trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) at 80 $\mu g \cdot L^{-1}$; for a total of five haloacetic acids (monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic and dibromoacetic acids) at 60 $\mu g \cdot L^{-1}$; for bromate at 10 $\mu g \cdot L^{-1}$ and for chlorite 1.0 $mg \cdot L^{-1}$. Other DBPs have been added to the US Environmental Protection Agency's Candidate Contamination List (CCL), which is the list from which future regulated drinking water compounds will be selected. In Europe, the 98/83/CEE Directive is less restrictive than that applied in the USA. The only DBPs that must be controlled are the four trihalomethanes, and their proposed maximum level being 100 $\mu g\ l^{-1}$. Due to the fact that their identification and quantization have become extremely important to drinking water companies in order to reduce or remove their presence, other analytical methods different from those proposed by U.S. EPA have been optimized and are now commented in this article.

Keywords: disinfection by-products, gas chromatography-electron capture detector, headspace extraction.

INTRODUCTION

A particularly significant group of water pollutants consists of volatile organic compounds (VOCs). This group includes compounds, which are insoluble or sparingly soluble in water, with boiling points up to 200 °C and molecular masses between 16 and 250 Dalton [1, 2]. The compounds vary greatly in their structures and properties, e.g. hydrocarbon halogen derivatives, aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, esters, ethers, amines, phenols, etc [3]. Many of them are toxic or considered carcinogenic,

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mutagenic or teratogenic [4]. VOCs group include also some disinfection by products. They appear after the reaction of disinfectant agent with organic matter from water.

In many state, like in Romania, chlorine is the most usually disinfectant agent use for water disinfection due to its ability to kill most pathogens. However, in 1974 it was discovered that the chlorination of drinking waters resulted in the production of trihalomethanes (THMs) due to reaction of chlorine with organics in the water [1]. Since 1980's THMs raised significant concern due to evidence of their adverse human health effects, in particular cancer and reproductive disorders [5, 6]. THMs are the organohalogen compounds that are most monitored by protection agencies from treated water. Usually chloroform is the THM most commonly found in drinking water and in most of case is present in the highest concentration [7].

In choosing an appropriate analytical procedure to analyze the DBPs from water sample, it must be taken into account are not only precision, accuracy, selectivity, detectability, and reproducibility, but also limiting the time, labour and other costs involved in the procedure. The aim is also to determine a number of components of various properties in a single analytical cycle [8]. Automation of analytical procedures and making field determinations possible is also of importance. Reduction in the use of solvents in the analytical procedure and to in the amount of environment-threatening waste produced is becoming essential [9].

RESULTS AND DISCUSSION

The THMs were extracted from water sample by two different procedures, one LLE and the second HSE. In that case of HSE, the head space devices is connected directly to gas chromatography (GC) coupled with ECD.

In the analysis of THMs samples using TriPlus HS auto sampler the four peaks belonging to the four THM compounds were well separated, see figure 1.

Accuracy (%) for the four THMs compounds were in the range of 0.0003 – 0.2634 % in case of HSE and in the range of 0.52 – 4.2 % for LLE. The accuracy was determinate for every THMs compounds on 7 different samples and for the follow concentration 1 $\mu g \cdot L^{-1}$, 10 $\mu g \cdot L^{-1}$ and 100 $\mu g \cdot L^{-1}$.

The detection limit (MDLs) for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ were 0.3, 0.2, 0.3 and 0.6 $\mu g \cdot L^{-1}$ respectively (n=7). The RSD of 1 $\mu g \cdot L^{-1}$, 20 $\mu g \cdot L^{-1}$ and 80 $\mu g \cdot L^{-1}$ spiked samples were between 0.05 – 3.7 % after HSE and between 2.1 – 6.4 % after LLE.

The results regarding the methods performance show us good values in case of HSE than in case of LLE. Also it can be observed that the precision increase using the TriPlus HS and the incubation with agitation. That permit a better separation of the THMs compounds by the sample matrix (see table 1). The recovery in the two cases for 1 $\mu g \cdot L^{-1}$, 20 $\mu g \cdot L^{-1}$, and 80 $\mu g \cdot L^{-1}$ are

in the range 93-120 % and also the limit of detection for THMs compounds were: $CHCl_3$ is 0.3 μg/l, $CHCl_2Br$ is 0.2 $\mu g \cdot L^{-1}$, $CHClBr_2$ is 0.3 $\mu g \cdot L^{-1}$ and $CHBr_3$ is 0.6 $\mu g \cdot L^{-1}$.

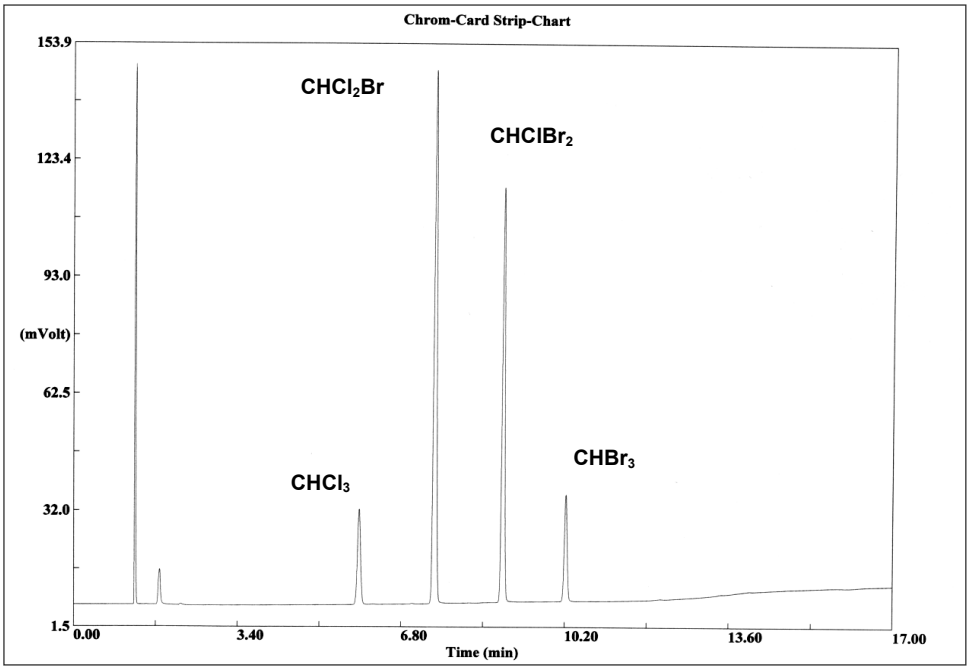

Figure 1. Chromatogram obtained after analysis of water sample – the four trihalomethanes compounds

Table 1. Relative standard deviation using the two procedures for the four THMs compounds analysis.

Compounds	TriPlus HS Autosampler		LLE Manually Injection	
	Relative standard deviation %		Relative standard deviation %	
	20 μg/l	***80 μg/l***	***20 μg/l***	***80 μg/l***
$CHCl_3$	1.43	1.17	2.05	1.91
$CHCl_2Br$	2.28	1.51	2.77	2.35
$CHClBr_2$	1.86	1.06	2.53	1.89
$CHBr_3$	2.40	1.92	3.21	2.97

CONCLUSIONS

The method of headspace extraction compared with liquid-liquid extraction has been presented in case of THMs analysis from water. HSE allows direct, trace analysis of components without disrupting the natural equilibrium established between the gas phase and the liquid phase of sample.

This method provides a better statistical accuracy. Collecting just the headspace eliminates the need to dispose of the liquid or solid sample. Present the best possible statistical accuracy. Using this method in analysis of disinfection by products on chromatography we obtain better sensitivity for THMs compounds and better statistical accuracy.

HSE sample preparation and analysis with GC-ECD can be used well for quantitative analysis of disinfection by products in environmental samples. Using it, for THMs were found good results for relative standard deviation, recovery and detection limit for each THMs compounds. Also the time necessary to perform the THMs analysis from water samples is less than in case of LLE.

EXPERIMENTAL SECTION

Sampling: Several treated and untreated water were collected in the period of January – December 2008 from Gilau and Dej Water Treatment Plant in every month. The collection and the preparation of water samples make up the most important element of every analytical procedure, which directly affects the quality and accuracy of final results. The basic problem is preserving the representative character (original composition) of the collected water sample to be analyzed in the laboratory avoiding positive deviations such as contamination under operation or negative deviation like losses of the target compounds. In order to avoid any possible contamination the sample were collected in duplicate in 40 mL vials that were previously cleaned with Millipore water and dried in oven at 150 °C for 10 hour. Also in order to keep out the possibility to miss of these compounds from our water sample all vials were full filed with sample and closed with Teflon lined screw cap. Because the THMs are formed after the reaction of chlorine with the natural organic matter present in water, every sample was preserved with sodium thiosulfate ($Na_2S_2O_3$) to quench residual chlorine. Samples were stored at 4 °C for a maximum 7 days until analysis.

Methods: Tree methods of extraction were used to determine the THMs presence in the water sample. These extraction methods were performed in order to compare these methods and to establish the most exactly and easily practicable method for analysis of these compounds. After extraction THMs were carried out by Thermo Finningan U.S.S. Trace GC Ultra gas chromatography with electron capture detector (GC-ECD). In case of head space analysis was used a TriPlus HS auto sampler.

Liquid-liquid extraction: The most commune extraction method for disinfection by-products is liquid-liquid extraction (LLE). After sampling, in laboratory 2 mL of hexane (extraction solvent) was added to ten mL of water sample in a separator funnel. The partitioning is then brought to equilibrium

by shaking the separator funnel for 5 minutes vigorously and allows it to stand. Then 1 µL of aliquot of the organic layer was removed with a microsyringe for gas chromatographic analysis.

Head-space extraction: One of the most common techniques used for the isolation of THMs from water samples is extraction into the gaseous phase. Headspace analysis techniques are based on the phenomenon of partition of analytes between the liquid and the gaseous phase. The gaseous phase (headspace) is analyzed together with the volatile compounds freed from the liquid sample (see Figure 2). In this figure is presented with G the gas phase (headspace) and with S the sample phase. The gas phase is commonly referred to as the headspace and lies above the condensed sample phase. The sample phase contains the compound(s) of interest. It is usually in the form of a liquid or solid in combination with a dilution solvent or a matrix modifier.

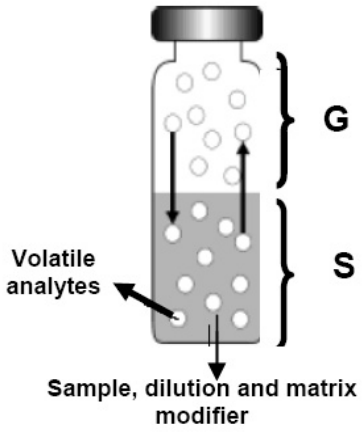

Figure 2. Schematic presentation of headspace process.

The equipment necessary for this type of analysis is very simple. The determination limit of the headspace analysis technique in a static system depends, besides the sensitivity of the detector employed, on the value of its coefficient of partition between the liquid and gaseous phase. For some compounds, the value of partition coefficient can be increased even by two orders of magnitude by varying temperature, pH, and salt effect (usually NaCl).

The analysis was made using headspace technique. 10 ml of sample was filled into 20 ml headspace vials and closed with Teflon lined screw cap. The agitator temperature was set at 60^0C, and the agitator on and the agitator off were set at 20 seconds and respectively 20 seconds. The incubation time was 30 minutes. Also the syringe was set at 80^0C. On GC the column

temperature program was 35^0C (hold time 3 minutes), 15^0C/minutes to 200^0C (hold time 3 minutes). The inlet was set at 200^0C. After this process 1 ml of the headspace was then injected into the GC (Cyanopropylphenyl Polysiloxane column, 30 m x 53 mm, 3 μm film thickness, Thermo Finnigan, USA). The column program was 35^0C (hold time 3 minutes), 15^0C/minutes to 200^0C (hold time 3 minutes). The inlet was set at 200^0C. In case of LLE extraction the same column and column program was used.

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