

Occurrence of Trihalomethanes, Particularly Those Containing Bromine, in Polish Drinking Waters

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Abstract

Trihalomethanes (methane derivatives containing chlorine and/or bromine) have been determined in drinking waters in Upper Silesia - the most industrious and most populated region in Poland.

Halomethane content determination is based on Capillary Gas Chromatography (CGC) with Electron Capture Detector (ECD), while these compounds' isolation from waters by Solid-Phase Microextraction (SPME) is based on optical fibres coated with poly(dimethylsiloxane) phase. In liquid phase the microextraction technique was applied to extract the halogenated compounds from the drinking water coming from consumers' taps in the Upper Silesia region.

This method showed precision in the range of 3-12% (R.S.D), depending on the compound. The volatile compounds were present in investigated water in the concentration range from a few ppb to sub ppb.

Keywords: finished drinking water, determination, solid-phase microextraction, GC-ECD, trihalomethanes.

Introduction

Besides the fact that commonly used disinfection of drinking water has been found to be one of the biggest achievements in public health in the 20th century [1], the problem of a possible human health hazard resulting from the occurrence of disinfection by-products in drinking water has been considered by scientists, consumers and producers for many years [2-4].

Trihalomethanes (THM) are the main group of compounds which are formed due to water disinfection, i.e. chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), chlorodibromomethane (CHBr_2Cl), bromoform (CHBr_3). These compounds are aromatically insensible, yet their presence in water may be physiologically hazardous. Their harmful influence on organisms is presented in Table 1. At present these compounds are known to show carcinogenic properties in bioassays carried out in ro-

dents [5-7]. Epidemiological research suggests that bladder, rectal and colon cancer are potentially associated with drinking chlorinated water [8-11]. Recent epidemiological studies have reported associations between the consumption of chlorinated drinking water and reproductive and developmental effects [12-14].

For almost half the population of Poland, and for the majority in Upper Silesia, a large industrial region in Poland, water pipes are supplied with treated surface water. Chlorination is the most common process used in water treatment. Analyses of the biggest surface water intakes in Upper Silesia have given evidence of bromine contents [15], and their presence in water during disinfection forms halomethane bromine derivatives because of their better kinetics when compared to chlorine derivatives formation [16].

Because trihalomethane occurrence in water is undesired, and because of their influence on water quality (in



Fig. 1. The region of Silesia, Poland. 1 - Slawków; 2 - Katowice; 3 - Siemianowice; 4 - Olkusz; 5 - Sosnowiec; 6 - Kozłowa Góra; 7 - Wójkowice; 8 - Zabrze; 9 - Knurów; 10 - Gliwice.

Table 1. Harmfulness of the investigated compounds [32].

Compound	Formula	Influence
Chloroform	CHCl_3	carcinogenic, easily absorbable through skin, lungs and food; accumulates in adipose tissue; may damage nervous system, liver, brain and kidneys
Bromodichloromethane	CHBrCl_2	causes liver and kidneys toxicity, possible carcinogenic influence on a man (according to IARC group 2B)
Dibromochloromethane	CHBr_2Cl	causes liver and kidneys toxicity, carcinogenic influence on a man not found (according to IARC group 3)
Bromoform	CHBr_3	genotoxic influence; causes liver and kidneys toxicity, carcinogenic influence on a man not found (according to IARC group 3)

accordance with recommendations by different organizations in many countries protecting public health), their presence in water should be determined by means of a simple and convenient analysis.

Solid-phase Microextraction is widely used at present for separation of organic compounds from matrices of various origins [17]. Theory and practice of this technique has been described by Pawliszyn and co-workers [18-22]. This technique has been also applied for determination of volatile chlorine compounds in water matrix [23-25].

The aim of the work was to determine the concentrations of trihalomethanes in drinking waters coming from consumers' taps in different towns in Upper Silesia. Halomethane content determination was based on Capillary Gas Chromatography (GC) technique with Electron Capture Detector, and these compounds' isolation from waters - on microextraction in immersion mode on optical fibres coated with polydimethylsiloxane phase (PDMS).

Materials and Methods

Sample Collection

Finished drinking water samples (100 cm³) were collected for analysis from consumers' water pipes in 10 different towns in Upper Silesia, (see the map - Fig 1.). The samples were taken in a standard way [26] after running a few litres of water from the tap. 0,1g of sodium thiosulfate (Na₂S₂O₃ • 5H₂O analytical grade POCH SA, Gliwice) was added to each sample.

The containers had teflon-lined screw caps. The water samples were kept no longer than three days at + 5°C.

Materials

Standards chloroform (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl), bromoform (CHBr₃) (each 5000 µg/mL in MeOH, J.T. Baker) were used. The suitable solutions of the standards were prepared in methanol (Suprasolv, Merck) by dilution in volumetric flasks.

MicroExtractor for manual injection (Supelco Corp.) SPME Fibre Assembly - 100 µm film thickness of poly(dimethylsiloxane). Magnetic stirrer with a teflon stir bar.

Solid-Phase Microextraction (SPME)

The compounds were separated from the water samples by SPME technique [27]. During extraction the fibre was directly immersed in the aqueous solution. The extraction was carried out in 3 ml screw cap vials fitted with silicone/PTFE septa, (Supelco Corp.) to which the sample was being poured underneath the seal. The

microextractor fibres coated with 100 µm film of poly(dimethylsiloxane) PDMS (Supelco Corp.) phase were introduced into the vessel with the sample of water and during the fibre exposition the sample was stirred with a magnetic stirrer. Microextraction conditions were selected experimentally [27] - microextraction time: 8 min, mixing the sample: 400 turns/min; equilibrium state was achieved in the above conditions. After the set time of the microextraction the fibres were immediately inserted into the injector of GC-ECD gas chromatograph, where the desorption took place within 2 min at 170°C. The time of thermal desorption was verified by fibre purity control by blank test; moreover, the fibres were cleaned at 250°C, before each extraction. 200 extractions were performed with the PDMS fibres.

Quantitative Analysis

GC-ECD analysis was performed in the gas chromatograph of A-14 type (Shimadzu). The chromatograph was equipped with ECD (⁶³Ni) detector, Chromatopac C-R6A integrator (Shimadzu), and a column with poly(dimethylsiloxane) phase (HP-1, Hewlett Packard) of 25 m x 0.2 mm x 0.33 µm (film thickness) dimensions.

The parameters of chromatographic analysis were as follows:

Temperatures: split/splitless injector 170°C, detector 250°C; programme: 30°C (5 min), 30-120°C (9°C min), 120°C (10 min).

Carrier gas He: 20 cm s⁻¹; N₂-ECD make-up gas flow: 40 cm s⁻¹. Desorption time from the fibres: 2 min.

To make calibration curves the standard aliquots dissolved in methanol with concentration of 5000 µg/mL of all standards were applied. The solutions were kept refrigerated in amber-coloured vials. The basic aliquots were dissolved with methanol in order to prepare spiked water solutions for making calibration curves.

Calibration curves for chloroform were made for the concentration range 5-30 µg/L, for bromodichloromethane 0.25-4 µg/L, dibromochloromethane 0.5-5 µg/L, bromoform 0.05-0.1 µg/L, respectively. Calibration curves details are shown in Table 2.

Table 2. The calibration curves correlation coefficients of compounds determined by the SPME-GC/ECD method at a range of concentrations: Bromodichloromethane (CHBrCl₂) 0.25-4.0 µg/L, Dibromochloromethane (CHBr₂Cl) 0.5-5.0 µg/L, Bromoform (CHBr₃) 0.05-0.5 µg/L, Chloroform (CHCl₃) 5-30 µg/L.

Compound	b*	a*	r ²	R.S.D. [%]
CHBrCl ₂	145.7	1212.3	0.998	6-10
CHBr ₂ Cl	414.7	1220.8	1	3-5
CHBr ₃	-10.36	782.4	0.999	3-12
CHCl ₃	-22.82	308.9	0.999	3-10

*) Linear regression $y = ax + b$

n = (5-7) number of determinations

Table 3. Concentration of halomethanes in finished drinking waters of Upper Silesia (Poland) determined by SPME - GC-ECD method.

Number and City	Concentration of $\mu\text{g/L}$								
	CHCl_3	RSD %	CHBrCl_2	RSD %	CHBr_2Cl	RSD %	CHBr_3	RSD %	TTHM
1. Sławków	12.84	4.5	ND		ND		0.29	3.4	13.13
2. Katowice	19.54	4.2	2.07	3.15	0.08	5.0	0.14	5.5	21.83
3. Siemianowice	32.86	11.6	3.84	7.9	0.21	9.8	ND		36.91
4. Olkusz	10.43	14.1	ND		ND		0.097	13.4	19.53
5. Sosnowiec	5.76	9.8	3.10	9.4	0.86	7.2	< 0.05		9.72
6. Kozłowa Góra	6.93	6.5	0.82	5.4	0.19	12.4	ND		7.94
7. Wojkowice	1.35	8.9	0.84	1.5	ND		ND		2.19
8. Zabrze	2.98	4.0	2.76	1.6	1.51	1.0	0.36	5.9	7.61
9. Knurów	8.87	5.3	2.35	5.6	0.5	9.4	ND		11.72
10. Gliwice	ND		ND		ND		ND		11.72
RSD %		4.0-14.1		1.5-9.4		1.0-12.4		3.4-13.4	

n = (5-7) number of determinations

ND - non detected

TTHM - Total Trihalomethane

Results and Discussion

SPME Optimization

Microextraction is a method of equilibrium extraction, which requires determination of the process optimised parameters.

The diagrams in Fig. 2 show the dependence of the absorbed standard amount on microextractor fibre in time function of fibre exposition in the water standard solution. Based on the determined dependence the following microextraction parameters were assumed: turning speed - 400 turns/min and extraction time - 8 min. For chloroform the extraction balance was achieved more quickly, probably because of higher concentration of this standard assumed for this test.

The optimised conditions for SPME and GC-ECD analysis of THMs were as follows:

SPME fibre	100 μm PDMS
Sample volume	3 mL water sample
Extraction temperature	room temperature
Extraction time	8 min
Speed turns	400 turns/min.
Desorption temperature	170°C
Desorption time	2 min.

THM Determination in Water Samples

The data presented in Table 2 show that the quantification correlations for all THMs during 8-minute extraction from water are linear, with linear correlation coefficients (r^2) are more than 0.99 for all compounds. Values of relative standard deviation of these determinations are

in the range of 3-12%, indicating good precision for the SPME-GC-ECD methods. For all determined THMs the detection limits are in the range of low concentrations 0.0015-0.020 $\mu\text{g/L}$ (ppb). Figure 3 presents a typical GC-ECD chromatogram of compounds extracted from one of the investigated tap water samples by SPME (in liquid phase). Halomethanes were found in most household water samples. Concentrations of halomethanes in finished drinking waters of Upper Silesia (Poland) determined by the SPME-GC-ECD method were presented in Table 3. In real sample determinations using this method repeatability was also acceptable (1.5-14% - see. R.S.D Tab. 3). One sample (No 10 - from Gliwice) among all the investigated samples did not contain these compounds. This sample came from a place that is supplied almost exclusively with deep-water intake.

In most water samples determined concentrations of the compounds did not exceed Polish standards and WHO standards. In all household water samples the contents of TTHM did not exceed recommended standards (the highest 37 $\mu\text{g/L}$, sample 3).

Concentrations of brominated halomethanes in waters were low, although in most water intakes in Upper Silesia bromide occurrence is found to range from 0.4 to 0.7 mg Br/L [15]. Only in one water sample (No 3) was chloroform concentration found to be higher than permissible (32 $\mu\text{g/L}$ compared to permissible 30 $\mu\text{g/L}$).

Bromodichloromethane was determined in the range of about 4 - 0.8 $\mu\text{g/L}$ in seven samples out of ten. In other samples it was absent. Dibromodichloromethane was present in the range of 1.5 to 0.08 $\mu\text{g/L}$ in six samples, while bromoform - 0.36 to 0.05 $\mu\text{g/L}$ in five water samples (Table 3).

Fig. 4 presents the percentage of particular trihalomethanes in total trihalomethane (TTHM), which illustrates a concentration distribution in tap water in Silesia region. In the samples containing halomethanes

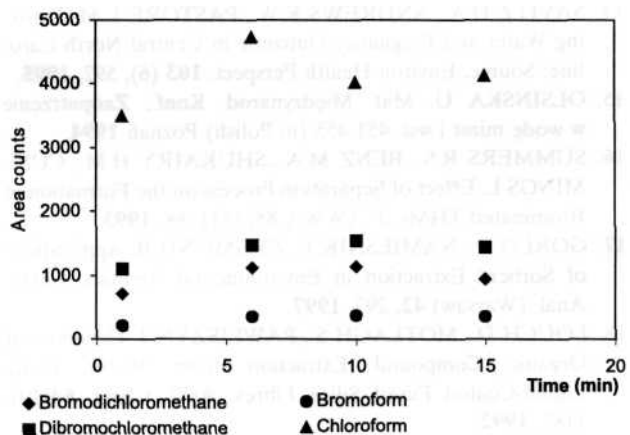


Fig. 2. The effect of extraction time for SPME. Standard concentrations: CHCl_3 (60 $\mu\text{g/L}$), CHBrCl_2 (1 $\mu\text{g/L}$), CHBr_2Cl (1 $\mu\text{g/L}$), CHBr_3 (0.5 $\mu\text{g/L}$). Turning speed: 400 turns/min.

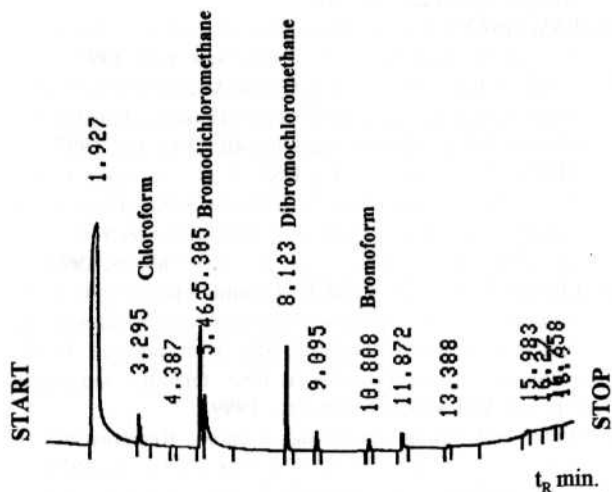


Fig. 3. GC-ECD chromatogram of tap water.

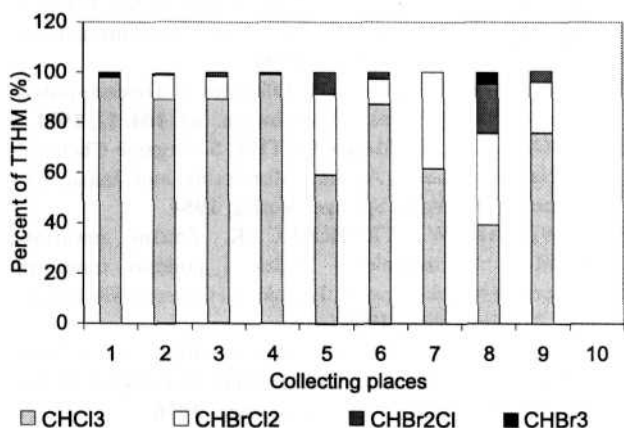


Fig. 4. Trihalomethanes contents (%) in TTHM. (Numbers of collecting places: 1 - Stawkow, 2 - Katowice, 3 - Siemianowice, 4 - Olkusz, 5 - Sosnowiec, 6 - Koztowa Gora, 7 - Wojkowice, 8 - Zabrze, 9 - Knurow, 10 - Gliwice (see also Fig. 1).

chloroform was the biggest fraction, then - bromodichloromethane (samples No 2,3,5,6,7,8, and 9), and dibromochloromethane and bromoform. Such a distribution is representative for household water in the investigated region and thus provides us with information about the realistic range of environmental concentrations.

The occurrence of volatile organic halogen compounds, particularly THMs can be found in all kinds of waters, i.e. drinking water, surface water, deep water, rain water, seawater and even in polar ice and water [28].

Half-life values ($t_{1/2}$) of these compounds in many cases can be estimated up to several thousands years, e.g. for bromoform - 686 years [29, 30].

Total emission of these compounds is high, estimated to be approximately $1 \cdot 10^6$ ton/year, including chloroform - about $0.2 \cdot 10^6$ ton/year [29, 30].

From water and soil the pollutants may transfer into living organisms, either directly or via the food chain. It is particularly hazardous for organisms at the end of the food chain, e.g. humans, who can take a big portion of concentrated pollutants through food. Volatile organic halogen compounds were determined in such materials as mother's milk, urine, and blood [30].

THM concentration contents in drinking waters are considerably influenced by technological systems in water treatment station, i.e. which medium is applied: chlorine, chlorine dioxide, or ozone. Sawiniak and Trybulec [31] have found out that in the case of ozone or chlorine dioxide application THM contents are lower, although chlorine is used in final disinfection. Moreover, when ozone or chlorine dioxide is applied, bromoorganic compounds have better kinetics, even if too much chlorine in relation to Br^- is added in the final chlorination.

Investigations have also proved that THM contents are getting lower in winter due to lower average temperature of water and air, and the contents of THM precursors and micro organisms are getting lower, too.

Our investigations were carried out on water samples collected in the second half of November. Thus, it can be expected that average contents of THMs per year will be higher.

Conclusions

The applied analytical procedure including SPME for sampling halomethanes from water and determination by GC-ECD enabled us to determine selectively and relatively quickly (approx. during 20 minutes) the main compounds of the disinfections by-products in finished tap water. This method showed precision in the range of 3-12% (R.S.D), depending on the compound. The volatile compounds which were present in water in the concentration range from a few ppb to sub-ppb such as: chloroform, bromodichloromethane, dibromochloromethane, bromoform can be efficiently isolated by this method. In the investigated drinking water samples the contents of the most dangerous for health compounds did not exceed the maximum permissible concentrations obligatory in Poland.

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