

DRINKING WATER POLLUTANTS ANALYSIS BY GC-MS*

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Abstract

Different extraction methods followed by gas chromatography-mass spectrometry (GC/MS) analysis were developed for qualitative and quantitative measurements of the organic compounds in water. The methods were tested for the investigation of THMs and other pollutants in drinking water. The selected ion monitoring (SIM) mode was used for the quantitative work. A capillary column Rtx 5% phenyl methylpolysiloxane, length 30 m x 0.25 mm I.D., 0.25 μm film thickness, was used with the temperature programs from 30°C (1 min), then increased to 40°C at 1 °C/min, then 80°C/min to 200°C, kept 2 min, in the selected ion monitoring mode (SIM) or from 30°C (4 min), then increased to 300°C in the SCAN mode.

Keywords: water, THMs, GC-MS

1. Introduction

Trihalomethanes (THMs) are volatile disinfection by-products (DBPs) in drinking water or recreation waters [1-3]. Halogenated disinfection by-products are formed by reaction of chlorine or other disinfectants with natural organic materials (NOM) from water. Chlorination by-products in drinking water are very toxic, human carcinogenic compounds. The 'high priority' DBPs include halomethanes, haloacetonitriles, halo ketones, haloacids, and halonitromethanes, chloral hydrates, chloropicrin. The THMs (CHX_3 , X=halogen) are: chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl) and bromoform (CHBr_3). The maximum contamination level of 100 μgL^{-1} for total trihalomethanes in drinking water, set by US Environmental Protection Agency (USEPA) in 1979 was lowered to 80 μgL^{-1} and is considered to be lowered to 40 μgL^{-1} .

The aim of the paper was to develop and compare some analytical methods for the determination of THMs.

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2. Method and samples

Standard THMs were purchased from Supelco (Switzerland), active charcoal and solvents were obtained from Merck (Darmstadt, Germany). Halothane (2-bromo-2chloro-1,1,1-trifluoroethane) was obtained from Laboratoire Belamont (Paris, France).

Sample preparation. LLE-GC-MS method: Standard solutions containing different known amounts of THMs and the same quantity of the internal standard in distilled water were prepared. Halothane was used as internal standard. 1 gram sodium chloride and 0.7 ml methyl-*tert*-butyl ether (MTBE) was added to 7 ml water (drinking water or standard solutions) in a 10 ml glass capped vial (a modified EPA Method 551.1). After mixing 1 min, the vial was left 2 min, and 1 μ l of the ether phase was injected into the GC.

Sample preparation. Purge and trap-GC-MS method: The purge and trap concentrator was active charcoal. Standard solutions or drinking water was extracted with a 12 ml/min He, 30 min and followed by desorption at 120°C for 3 min.

Sample preparation. Headspace-GC-MS method: Standard solutions or drinking water (10ml) was placed in 20 ml headspace vials. The vials were placed in a sand bath at 60 °C for 45 min. Then a 500 μ l of the gas phase was injected into the GC with a gas syringe.

Apparatus: A Trace DSQ ThermoFinnigan quadrupole mass spectrometer coupled with a Trace GC was used. A Rtx-5MS capillary column, 30 m length x 0.25 mm, 0.25 μ m film thickness, by using a temperature program from 30°C (1 min), then increased to 40 °C at 1 °C/min, then 80 °C/min to 200°C, kept 2 min, in the selected ion monitoring mode (SIM) or from 30°C (4 min), then increased to 300°C in the SCAN mode. In the SIM mode the following important ions were used: m/z 83 and 85 for chloroform, m/z 83, 85, 129 for dichlorobromomethane, m/z 127, 129 for dibromochloromethane, m/z 129, 173, 252 for bromoform and m/z 117, 198 for the internal standard (halothane). The method was validated in the range 0 – 400 μ gL⁻¹ and linearity, precision, accuracy and limit of detection parameters have been studied.

3. Results and Discussions

Fig.1. presents the mass spectra of THMs and halothane, the internal standard. Good linearity was obtained by using each extraction method. The regression curves obtained by *LLE-GC-MS method*, were: 1) $y=0.0024x+0.0267$, $r=0.98$ for chloroform, 2) $y=0.0027x+0.0061$, $r=0.97$ for dibromodichloromethane, 3) $y=0.0014x+0.0058$, $r=0.96$ for dibromochloromethane and 4) $y=0.0014x+0.0058$, $r=0.96$ for bromoform. The four THMs, 40

$\mu\text{g/L}$ each, gave for precision RSD (%): 26.5; 24.3; 14.7; 13.2 (n=4) and for 80 $\mu\text{g/L}$: 21.2; 14.4; 15.2; 10.7 (n=4). Accuracy gave RSD (%) lower than 11% for the standards of 40 and 80 $\mu\text{g/L}$.

The headspace method gave the following regression curves 1) $y=0.0046x-0.037$; 2) $y=0.0029x-0.019$; 3) $y=0.001x-0.007$; 4) $y=0.0003x-0.0008$, $r=0.98$ for each, precision for 40 $\mu\text{g/L}$: 14.5; 22.3; 27.9; 32 (n=7) and for 60 $\mu\text{g/L}$: 17.6; 18.6; 21.6; 25.5 (n=4). Accuracy gave lower values than 11% for the standards of 20 $\mu\text{g/L}$ and lower than 40% for the other. The LOD was 0.2 $\mu\text{g/L}$ in the two methods. The regression curves were used for the calculation of the THMs, after adding the same quantity of internal standard to the sample and by using the methods described before. The purge and trap method followed by GC-MS analysis was used for compound extraction and identification in drinking water samples. Table 1 presents the compounds separated and analysed after purge and trap extraction. The sample was analysed in scan mode for the identification of the compounds. In the SIM mode the chromatogram of THMs separation is presented in Fig. 2.

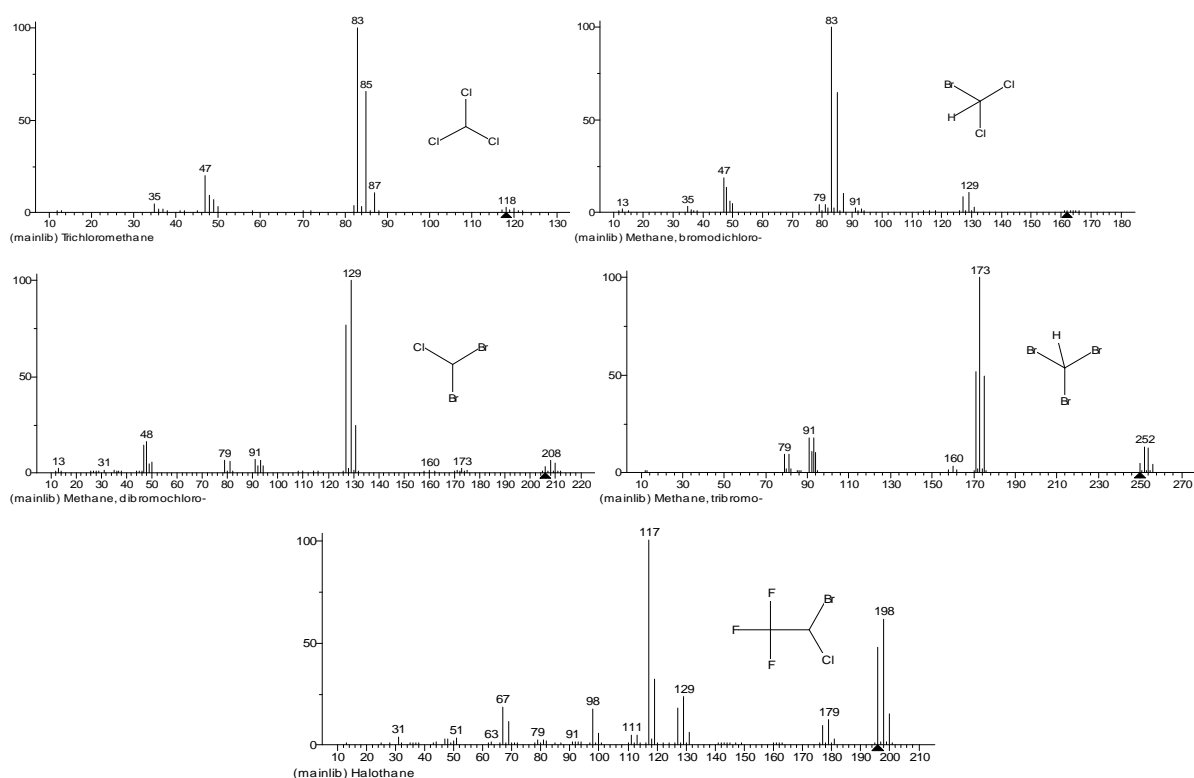


Fig. 1 The mass spectra of THMs chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl), bromoform (CHBr_3) and halothane ($\text{C}_2\text{HBrClF}_3$).

The values of THMs obtained for two drinking water samples, taken in the same points but different pipe diameters are presented in Table 2. The higher values were obtained in the sample from the higher diameter pipe.

Table 1. VOCs identified in drinking water by GC-MS

<i>Tr</i>	<i>Compound</i>
3.26	Chloroform
3.37	butyl formiate (from solvent)
3.66	1,1,1trichloroethylene M=132
3.86	benzene
3.89	carbon tetrachloride M=152
4.08	butanol
5.05	dichlorobromomethane
5.50	methylcyclohexane M=98
6.03	1,1-diethoxyetane
7.46	toluene
8.03	trimethylcyclobutane?
9.07	dibromochloromethane?
9.68	tetrachloroethylene M=164
11.26	chlorobenzene
11.87	ethyl benzene M=106
12.20	p-xylene M=106
12.95	o-xylene
13.13	cyclohexanone M=98
15.72	dimethylundecane
15.86	trimethylbenzene
16.16	octanal?
16.56	tetradecane
16.81	tetradecenal?
16.88	1,2diclorbenzen
17.26	trimethyldodecane
18.07	dimethylbenzyl alcohol
18.42	nonanal
18.70	benzenethanol
18.82	tetramethyl piperidinone M=155
22.32	dibutylformamide
24.06	tetramethyldecindiol
25.71	tributylphosphate
26.28	dodecanoic acid
26.80	nonadecane
27.9	undecylbenzoate
29.07	tetradecanoic acid
29.24	dibutylphtalate

Table 2. Drinking water results for THMs in the distribution system of Cluj-Napoca

Sample	Compound	μgL^{-1}
1	CHCl_3	80
1	CHBrCl_2	3.9
1	CHBr_2Cl	1.7
1	CHBr_3	0
2	CHCl_3	130
2	CHBrCl_2	7.5
2	CHBr_2Cl	4.1
2	CHBr_3	0

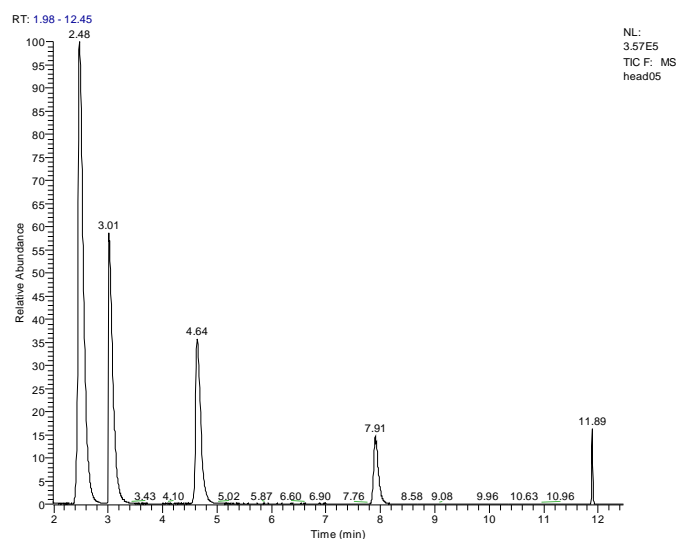


Fig. 2 SIM chromatogram of THMs for headspace extraction. Halothane, 2.48 min, chloroform, 3.01 min, dichlorobromomethane, 4.64 in, chlorodibromomethane, 7.91 min, and bromoform, 11.89 min.

4. Conclusions

The methods presented are sensitive and suitable for the determination of volatile organic compounds in different water samples. LLE-GC-MS method is more rapid but headspace-GC/MS method does not need solvent in extraction procedure, which is a good advantage in the analysis to avoid impurities from solvent, the solvent tale, but also is cheaper. The purge and trap method is useful for VOCs identification, because sensitivity could be easier improved by using more water sample and time of extraction. The development of THMs analytical methods in our country will have the impact in optimization of the current treatment practice, the improvement of drinking water treatment and quality to reduce DBPs contamination of water.

References

- [1] A. Nikolaou , T. Lekkas, S. Golfinopoulos, M. N. Kostopoulou, *Talanta* 56, (2002).717.
- [2] D.T. Williams, G.L. LeBel, F.M. Benoit, *Chemosphere* 34 (1997) 299.
- [3]. E. Martinez, S. Lacorte, I. Llobet, P. Viana, D. Barcelo, *J. Chromat., A* 990 (2002) 181.
- [4]. H. Gellard, U. Von Gunten, *Water Res* 36 (2002) 65.