

## VOCs POLLUTANTS DETERMINATION BY GC-MS

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### **Abstract**

Some important VOCs pollutants in drinking water are trihalomethanes, chlorinated by-products resulting from the reaction of chlorine with different natural organic matter in water. Different analytical methods for trihalomethanes determination in drinking water are described. VOCs as chloroform, bromodichloromethane, dibromochloromethane and bromoform were determined by four different techniques: liquid-liquid extraction-gas chromatography-mass spectrometry (LLE-GC-MS), headspace-gas chromatography-mass spectrometry (headspace-GC-MS), purge and trap-gas chromatography-mass spectrometry (purge and trap-GC-MS); and headspace extraction-gas chromatography-electron capture detection (headspace-GC-ECD). The quantitative methods were validated and applied for distribution systems control and treatment optimization studies.

**Keywords:** VOCs, GC-MS, GC-ECD.

### **1.Introduction**

Drinking water supplies has been made safer by chlorination. Unfortunately, there are several disinfection by-products (DBPs) of drinking water of possible risk, such as trihalomethanes (THMs), haloacetic acids (HAAs), bromate and chlorite. Proper chlorination kills the majority of bacteria, viruses and parasites responsible for diseases such as typhoid fever, cholera and dysentery. Alternate disinfection of drinking water are chloramine disinfection (color problems), ozone, UV light and activated carbone.

Volatile DBPs in drinking water could be determined by different analytical methods: liquid-liquid extraction gas chromatography-electron capture detection (LLE-GC-ECD), liquid-liquid extraction gas chromatography-mass spectrometry (LLE-GC-MS), purge and trap PT-GC-MS, headspace -GC-MS, headspace- GC-ECD or solid phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) [1-3]. These methods are applied for THMs (CHX<sub>3</sub>, X=halogen): chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHBrCl<sub>2</sub>), dibromochloromethane (CHBr<sub>2</sub>Cl) and bromoform (CHBr<sub>3</sub>). The maximum concentration level of 100 µl l<sup>-1</sup> set by

USEPA for total trihalomethane (TTHMs) in drinking water in 1979, was lowered to  $80 \mu\text{l l}^{-1}$ . In UE and in our country the maximum concentration level for TTHMs is still of  $100 \mu\text{l l}^{-1}$ .

THMs are by-products formed when chlorine is used to disinfect drinking water. Epidemiological studies have linked the consumption of chlorinated surface waters to an increased risk of two major causes of human mortality, colorectal and bladder cancer. Maternal exposure to THMs may be associated with fetal growth retardation, stillbirth, congenital malformations<sup>16</sup>, cancer, and more recently, with adverse reproductive outcomes. Although applications are related on the relatively high concentrations of THMs found in swimming pools. The levels are correlated with the number of people in the pool, water temperature, and TOC.

The aim of the present paper is the development and comparison of different analytical methods for THMs quantitation in drinking water. The techniques used for the determination of DBPs in drinking water include water extraction procedure as liquid-liquid extraction (LLE), purge and trap (PT) or headspace followed by gas chromatographic (GC) separation and mass spectrometric (MS) detection.

The development of most sensitive methods for THMs quantitation are useful in the kinetics studies for the optimisation of drinking water treatment, for monitoring and maintaining the lowest values of THMs into the drinking water.

## 2. Method and samples

*Material and methods.* Standard THMs, 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).

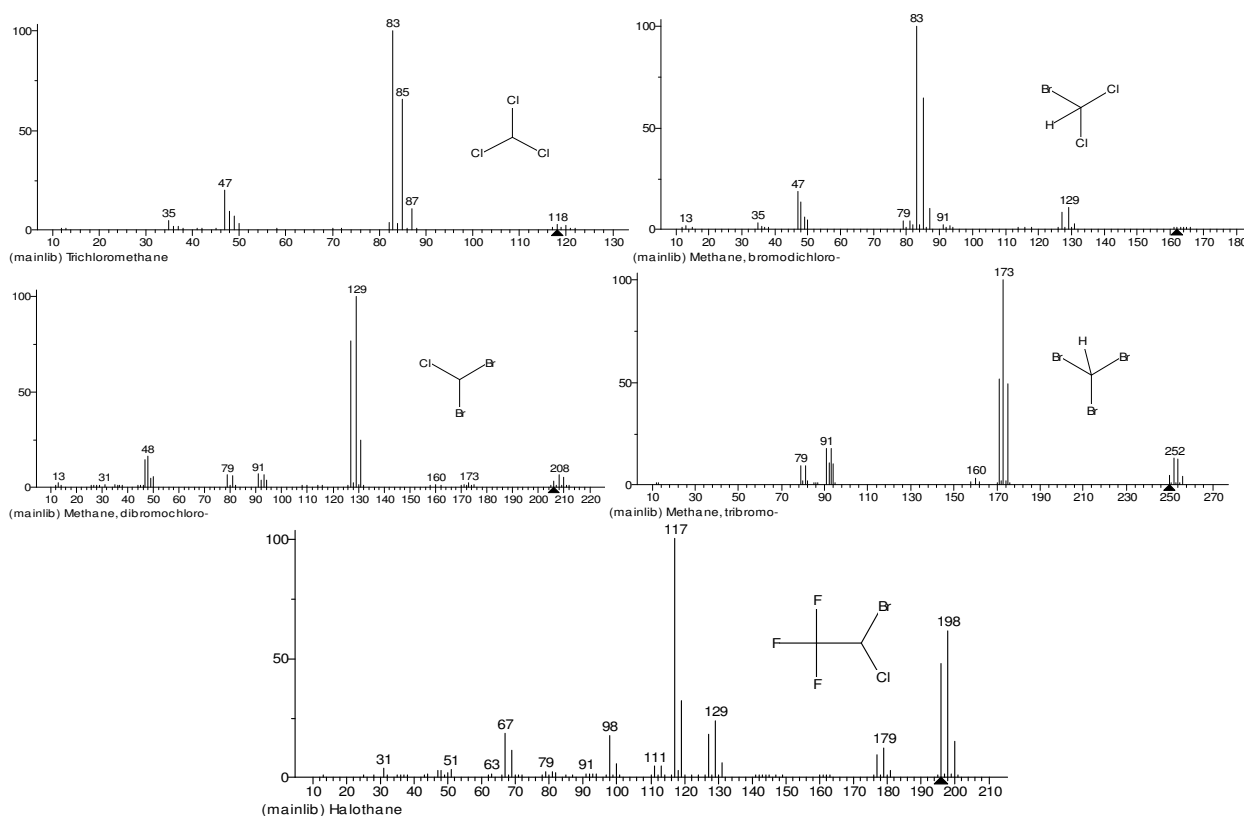
*Sample preparation. LLE-GC-MS method.* Standard solutions containing different known amounts of THMs and the same quantity of the internal standard in distilled water were prepared. Halothane was used as internal standard. 0.5 gram sodium sulphate anhydrous or NaCl and 0.5 ml methyl *tert*-butyl ether (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 centrifuged 2 min, and  $1 \mu\text{l}$  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. 100 ml standard solutions or drinking water warmed at  $30^{\circ}\text{C}$  was extracted with a 12 ml/min He, 20 min and followed by desorption at  $120^{\circ}\text{C}$  for 3 min or by mixing 1 min the

charcoal in a capped vial with 1ml methyl-*tert*-butyl ether (MTBE). 100  $\mu\text{g}$  of halothane, the internal standard, was added to each sample and 3 $\mu\text{l}$  were injected into the GC.

*Sample preparation. Headspace-GC-MS method.* Standard solutions or drinking water (10ml) was placed in 20 ml headspace vials and 10 $\mu\text{g}$  halothane, the internal standard, was added. The vials were placed in a sand bath at 60°C for 45 min. Then 500  $\mu\text{l}$  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 $\mu\text{m}$  film thickness, by using two different temperature programs: (1) from 31°C (1 min), then increased to 40°C at 1°C/min and then with 80°C/min to 200°C and (2) from 31°C, 1min, 1°C/min to 33°C, 100°C/min to 200°C, followed by MS detection in the selected ion monitoring (SIM) mode. In the SIM mode the following important ions will be used: m/z 83, 85, 118, 120 for chloroform, m/z 83, 85, 127, 129 for dichlorobromomethane, m/z 127, 129 for dibromochloromethane, m/z 173, 175, 252 for bromoform and m/z 117 and 198 for the internal standard (halothane).



**Fig. 1** The mass spectra of THMs: chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), bromoform ( $\text{CHBr}_3$ ) and halothane ( $\text{C}_2\text{HBrClF}_3$ ).

The method was validated in different ranges: 0 – 20  $\mu\text{l l}^{-1}$ , 0 – 80  $\mu\text{l l}^{-1}$  0 – 400  $\mu\text{l l}^{-1}$  and linearity, precision, accuracy and limit of detection parameters have been studied.

### 3. Results and Discussions

*The methods validation. LLE-GC-MS:* Aliquot samples containing 20, 40, 60, 80, 100, 200, 300 and 400  $\mu\text{g l}^{-1}$  of the four THMs were extracted by LLE as described before, and 100 $\mu\text{g}$  of halothane, the internal standard, was added at each sample.

The regression curves obtained by LLE-GC-MS method, in the range 0-80 $\mu\text{g l}^{-1}$  and respectively, 0-400 $\mu\text{g l}^{-1}$  (in brackets) were:  $y=0.0026x+0.0301$ , ( $y=0.0032x+0.0222$ ),  $r=0.991$  (0.96) for chloroform,  $y=0.0027x+0.0061$ , ( $y=0.0029x+0.0173$ ),  $r=0.97$  for dibromodichloromethane,  $y=0.0023x+0.0066$ , ( $y=0.0023x+0.0206$ ),  $r=0.96$  for dibromochloromethane and  $y=0.0014x+0.0058$ , ( $y=0.0016x+0.0122$ ),  $r=0.96$  for bromoform. In brackets are presented the regression curves for the range 0-400 $\mu\text{g l}^{-1}$ .

The regression curves were used to calculate the THMs, after adding the same quantity of internal standard to the sample and by using the methods described before.

Precision studied for the aliquot samples of 40 and 80  $\mu\text{g l}^{-1}$  showed R.S.D. values between 13.1 – 26.4 % and respectively between 10.7-21.2%. The accuracy R.S.D. calculated were between 0.9-11.3% for the sample of 40 $\mu\text{g l}^{-1}$  and between 5.8-10.6% for the sample of 80  $\mu\text{g l}^{-1}$ . Table 1 presents the results obtained for precision and accuracy. A limit of detection lower than 0.1  $\mu\text{g l}^{-1}$  was obtained for the THMs studied (0,02  $\mu\text{g l}^{-1}$  ( $\text{CHCl}_3$ ), 0,05 $\mu\text{g l}^{-1}$  ( $\text{CHCl}_2\text{Br}$ ), 0,2 $\mu\text{g l}^{-1}$  ( $\text{CHClBr}_2$ ) and 0,1  $\mu\text{g l}^{-1}$  ( $\text{CHBr}_3$ ), signal/noise 10/1. The limit of quantitation was 1  $\mu\text{g l}^{-1}$ , the RSD obtained being between 0.1-28%.

**Table 1.** Precision and accuracy of the LLE-GC-MS method for THMs

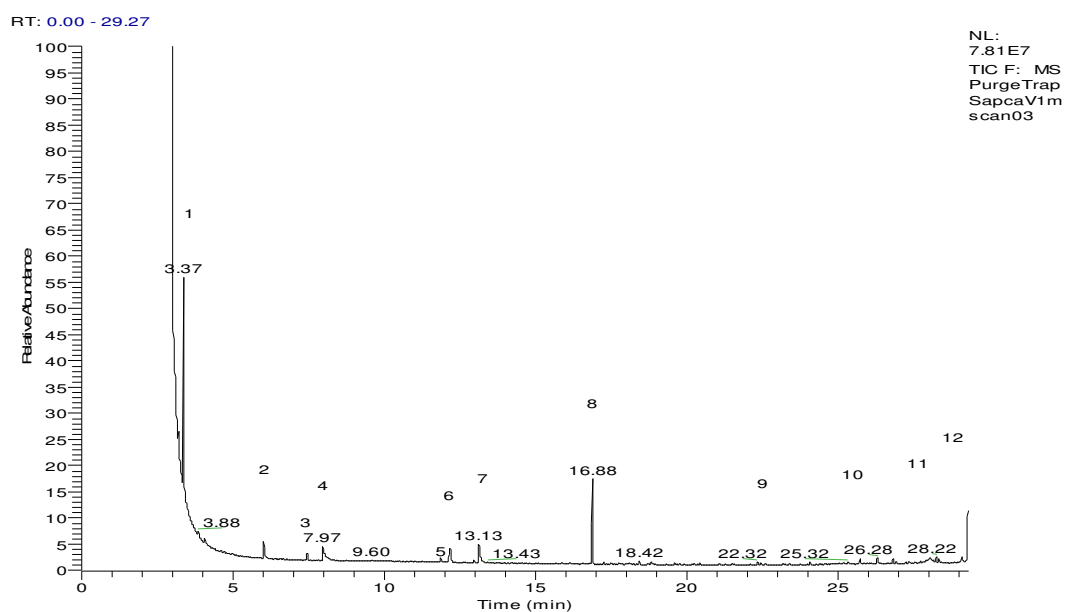
Compound	n	Concentration( $\mu\text{g l}^{-1}$ )		Comp/IS		Precision RSD(%)	Accuracy RSD(%)
		Added	Measured		SD		
$\text{CHCl}_3$	3	40	40.45	0.18	0.05	26.49	1.12
$\text{CH}_3\text{Br}$	3	40	39.65	0.15	0.04	24.26	0.87
$\text{CH}_2\text{Br}_2$	3	40	43.49	0.14	0.02	14.76	8.72
$\text{CHBr}_3$	3	40	44.50	0.09	0.01	13.12	11.25
$\text{CHCl}_3$	4	80	84.67	0.24	0.05	21.19	5.84
$\text{CH}_3\text{Br}$	4	80	88.47	0.24	0.04	14.38	10.59
$\text{CH}_2\text{Br}_2$	4	80	86.12	0.20	0.03	15.15	7.65
$\text{CHBr}_3$	4	80	87.48	0.13	0.01	10.66	9.35

The mass spectra of the four THMs and halothane, the internal standard, are presented in Fig.1.

*PT-GC-MS*: Aliquot samples containing 20, 40, 60, 80  $\mu\text{g l}^{-1}$  of the four THMs were extracted by purge and trap extraction and 100 $\mu\text{g}$  of halothane, the internal standard, was added at each sample.

The regression curves obtained by *PT-GC-MS* method, in the range 0-80 $\mu\text{g l}^{-1}$  were  $y=0.0029x+0.038$ ,  $r=0.93$  for chloroform,  $y=0.00008x+0.0003$ ,  $r=0.88$  for dibromodichloromethane,  $y=0.00004x-0.0005$ ,  $r=0.89$  for dibromochloromethane and  $y=0.00001x-0.00001$ ,  $r=0.84$  for bromoform. The regression curves were used for the calculation of the THMs, after the addition of the same quantity of internal standard to the sample.

Precision studied for the aliquot samples of 20  $\mu\text{g l}^{-1}$  showed R.S.D. values between 2.63 – 30.35 %. The limit of detection of 1  $\mu\text{g l}^{-1}$  was obtained for the THMs studied, depending of the helium flow, time and desorption procedure.



**Fig. 2.** VOCs extracted by purge and trap, separated and identified by GC-MS (tap water extracted during three day)

In Fig. 2 and Table 2 presents the compounds separated and identified in a drinking water sample (tap water) analysed by purge and trap GC-MS. 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. 5 (drinking water without internal standard).

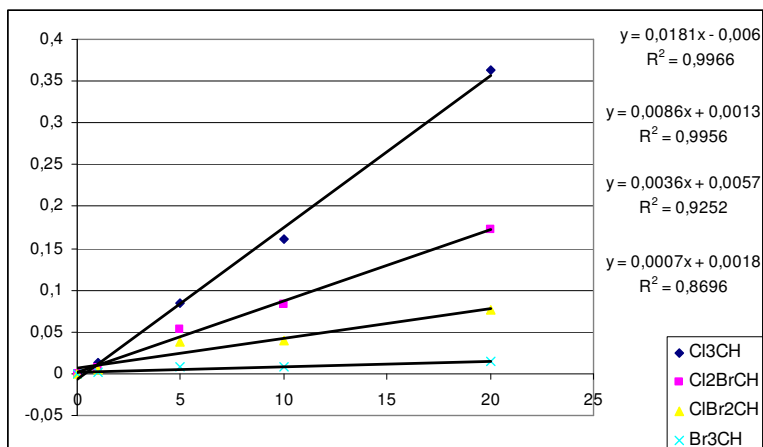
**Table 2.** VOCs identified in drinking water by PT-GC-MS

Nr.crt	Tr	Compound
	<b>3.26</b>	<b>Chloroform</b>
1	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
	<b>5.05</b>	<b>dichlorobromomethane</b>
	5.50	methylcyclohexane M=98
2	6.03	1,1-diethoxyetane
3.	7.46	toluene
4.	8.03	trimethylcyclobutane?
	<b>9.07</b>	<b>dibromochloromethane?</b>
	9.68	tetrachloroethylene M=164
	11.26	chlorobenzene
5.	11.87	ethyl benzene M=106
6.	12.20	p-xylene M=106
	12.95	o-xylene
7.	13.13	cyclohexanone M=98
	15.72	dimethylundecane
	15.86	trimethylbenzene
	16.16	octanal?
	16.56	tetradecane
	16.81	tetradecenal?
8.	16.88	1,2diclorbenzen
	17.26	trimethyldodecane
	18.07	dimethylbenzyl alcohol
	18.42	nonanal
	18.70	benzenethanol
	18.82	tetramethyl piperidinone M=155
9.	22.32	dibutylformamide
	24.06	tetramethyldecindiol
	25.71	tributylphosphate
10.	26.28	dodecanoic acid
	26.80	nonadecane
11	27.9	undecylbenzoate
	29.07	tetradecanoic acid
12	29.24	dibutylphtalate

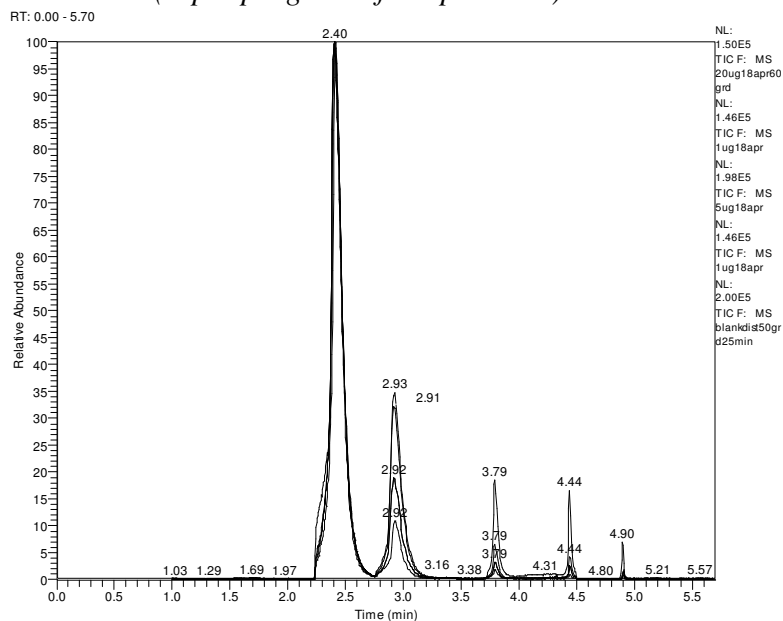
*Headspace-GC-MS:* Aliquot samples containing 20, 40, 60, 80,100, 200, 300  $\mu\text{g l}^{-1}$  of the four THMs were extracted by headspace extraction described before, and 100 $\mu\text{g}$  of halothane, the internal standard, was added at each sample.

The regression curves obtained by LLE-GC-MS method, in the range 0-80 $\mu\text{g l}^{-1}$  (0-300 $\mu\text{g l}^{-1}$ ) were  $y=0.0037x+0.0031$ , ( $y=0.0046x+0.036$ ),  $r=0.98(0.997)$  for chloroform,  $y=0.0024x-0.0015$ ,

( $y=0.0029x-0.019$ ),  $r=0.99$ ( $r=0.98$ ) for dibromodichloromethane,  $y=0.0008x+0.0021$ , ( $y=0.001x-0.007$ ),  $r=0.97$ ( $r=0.98$ ) for dibromochloromethane and  $y=0.0003x+0.001$ , ( $y=0.0003x-0.0008$ ),  $r=0.98$ ( $r=0.97$ ) for bromoform. In brackets are presented the regression curves for the range 0-300 $\mu\text{g l}^{-1}$ . For the range 0-20 $\mu\text{g l}^{-1}$  the obtained regression curves and coefficients of regression are presented in fig. 3. These curves were obtained in the fast program of temperature mentioned before, from 31°C,1min, 10°C/min to 70°,80°C/min to 150°C, used for kinetic studies and low value measurements, as shown in fig. 4.



**Fig.3** Regression curves and regression coefficients obtained for THMs in the range 0-20 $\mu\text{g l}^{-1}$  (rapid program of temperature)



**Fig.4** SIM-GC-MS chromatograms of standard samples

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.

Precision studied for the aliquot samples of 40 and 60  $\mu\text{g l}^{-1}$  showed R.S.D. values between 14.97 – 31.95 % and respectively between 17.93-25.49%. The accuracy R.S.D. calculated were between 5.07-10.36% for the sample of 40 $\mu\text{g l}^{-1}$  and between 6.00-32.78% for the sample of 60  $\mu\text{g l}^{-1}$ . Table 3 presents the results obtained for precision and accuracy. A limit of detection for signal/noise ratio 10 was lower of 0.1  $\mu\text{g l}^{-1}$  for the THMs studied. The limit of detection gave RSD between 1-18%.

**Table 3** Precision and accuracy of the headspace-GC-MS method for THMs

Compound	Concentration( $\mu\text{g l}^{-1}$ )			Comp/IS	SD	Precision	Accuracy
	N	Added	Measured			RSD(%)	RSD(%)
$\text{CHCl}_3$	3	40	39.06	0.14	0.02	14.97	2.28
$\text{CH}_3\text{Br}$	3	40	35.86	0.08	0.02	22.29	10.36
$\text{CH}_2\text{Br}_2$	3	40	37.97	0.03	0.01	27.87	5.07
$\text{CHBr}_3$	3	40	36.17	0.01	0.003	31.95	9.56
$\text{CHCl}_3$	4	60	63.60	0.26	0.05	17.93	6.00
$\text{CH}_3\text{Br}$	4	60	68.48	0.18	0.03	18.59	14.13
$\text{CH}_2\text{Br}_2$	4	60	79.67	0.07	0.02	21.55	32.78
$\text{CHBr}_3$	4	60	76.02	0.02	0.01	25.49	26.69

The values of THMs obtained for four months in the drinking water samples, taken in the same points of the distribution system (the tap of laboratory), are presented in Table 2.

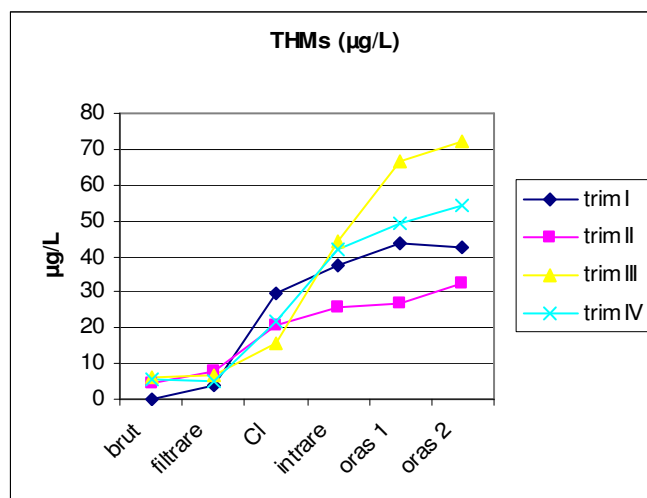
**Table 4.** Drinking water results for THMs in the distribution sistem of Cluj-Napoca

Sample	Compound	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$
1	$\text{CHCl}_3$	45.3	45	34.19	15.56
1	$\text{CHBrCl}_2$	0.54	0.53	1.57	2.62
1	$\text{CHBr}_2\text{Cl}$	0	0	0	0
1	$\text{CHBr}_3$	0	0	0	0
2	$\text{CHCl}_3$	34	34.26	31.25	10.01
2	$\text{CHBrCl}_2$	2.3	0	1.56	1.58
2	$\text{CHBr}_2\text{Cl}$	0	0	0	0
2	$\text{CHBr}_3$	0	0	0	0

The low temperature of start (31°C) was needed especially for halothane and chloroform separation.



The total trihalomethanes (TTHMs) determination in the distribution system of our town as seasonal mean values of the year 2006 are presented in Fig. 5. Lower values than the maximum concentration level were obtained.



*Fig.5 Seasonal mean values of THMs*

The comparison of the presented analytical methods show probably preference for headspace extraction method because of the possibilities to be used in automatic extraction (autosamplers, robot injectors). PT-GC-MS could be improved by optimizing analytical parameters as high helium flow, time of sampling, thermal desorption and is good also for automatic extraction<sup>8</sup> and especially for the trace level pollutant identification, when longer extraction time is used. The LLE-GC-MS is simple and rapid, but the use of methyl *tert*-butyl ether solvent is an disadvantage when this solvent is of interest in some waters<sup>4,5</sup>. Recovery was found between 70-90% in the method studied. The selection of a proper internal standard, not found in the drinking water, is important also because recovery become not very important and the extraction duration could be rapid.

#### 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 rapid but headspace-GC/MS method does not need solvent for the extraction procedure, a good advantage in the analysis to avoid impurities from solvent and solvent tale. The purge and trap method proved to be useful for VOCs identification, because

sensitivity could be easier improved by using higher quantity of water sample and time of extraction.

Linearity study in the different ranges of interest for the THMs gave good regression curves and correlation coefficients. Precision, accuracy, recovery, the limit of detection and the limit of quantitation showed good values.

The development of THMs analytical methods will have an impact in optimization of the current treatment practice, the improvement of drinking water treatment and quality to reduce DBPs contamination of water.

The optimization of chlorine or ozone doses for disinfection processes correlated with frequent bacterial analysis of drinking water will permit the assessment of the risks caused by THM contamination of drinking water in our country.

The major impact will be the improvement of the quality of drinking water and of the health of the consumers, by the reduction of THM concentrations in drinking water. Some alternative disinfectants as coagulation, sedimentation, use of nanomembranes, or ultrafiltration membranes or alternative water supply will contribute to the removal of THM precursors prior to disinfection.

### **References**

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