

Quantifying THM by HS-GC-MS in swimming pool water

William PEYSSON

Introduction

Chloroform (CHCl_3), Bromoform (CHBr_3), BromoChloromethane (CHBrCl_2) and Dibromochloromethane (CHBr_2Cl), known as trihalomethane (THM) are present in chlorinated water. They are disinfection byproducts which are carcinogenic. In swimming pools water, the ISO 10301 standard recommends a liquid-liquid extraction with a GC-MS analysis and a sample stabilization with sodium thiosulfate. However many laboratories prefer using a static HS extraction with an incubation at 80°C because it is easier and faster. The problem of the HS-GC-MS method is an overvaluation of the measure of THMs in swimming pool water [1]. Some tests were realized in order to prevent THMs forming during the HS incubation at 80°C.

Material and methods

Parameter of HS auto sampler:

Material: COMBIPAL (static HS)
Incubation: 40 or 80°C during 30min

Parameter of MS

Perkin Elmer Turbomass Upgrade
Transfer line: 300°C
Electrons energies: 70eV
Trap emission: 75eV
Source Temperature: 300°C

Parameter of GC

Material: Perkin Elmer Auto System XL
Column: Elite-5MS; 30m*250µm*0.25µm
Gas: Helium; Flow 1mL/min; split 10mL/min
Separation: T (min)
Injection : 250 °C 0
initial column temperature 35°C 0
Ramp 1 : 5°C/ min to 130 °C 19
Ramp 2 : 35°C/ min to 200°C 23
Stage et 200°C during 4min 27

Adding sodium thiosulfate (0.3 and 3g/L), ascorbic acid and chlorhydric acid at different pH to stop the THM formation.

Results and discussion

After demonstrating that there was less THMs formation during incubation at 40°C than at 80°C, my experiments consisted in demonstrating the influence of different additives on the THMs measurement. Figure 1 shows the evolution of the 80/40 ratio in function of different additives at different pHs. If the 80/40 ratio is around one, the total THMs measurement with a 80°C incubation equals the total THMs measurement with a 40°C incubation. So there was no overvaluation of the measurement when the pH was lower than four with ascorbic acid (17g/L). To be sure the HS-GC-MS method with ascorbic acid was correct, results were compared with SPME-GC-MS method. Figure 2 demonstrates this because the various coefficients equal 30%

Figure 1 : Evolution of the 80/40 ratio in function of pH on TTHM measure with sodium thiosulfate (thio), ascorbic acid (aa) or chlorhydric acid (HCl).

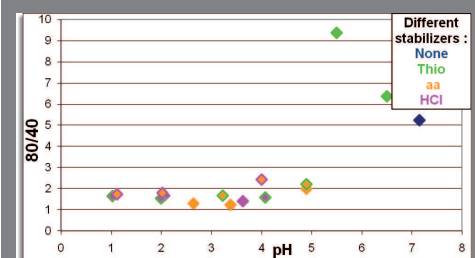


Figure 2 : Comparison of HS-GC-MS and SPME-GC-MS measure on a swimming pool water.

HS-GC-MS measure					
C	CHCl_3	CHBrCl_2	CHBr_2Cl	CHBr_3	TTHM
(ug/L)	28.93	3.94	0.72	0.00	33.60
SPME-GC-MS measure					
C	CHCl_3	CHBrCl_2	CHBr_2Cl	CHBr_3	TTHM
(ug/L)	23.08	3.21	1.01	0.05	27.35

Conclusion

With an ascorbic acid or chlorhydric acid stabilization (pH<4) the HS-GC-MS method can be used with an 80°C incubation during 30 minutes.

Now the problem is conserving the sample at 4°C because the sodium thiosulfate is insufficient. Maybe this conservation will be better with ascorbic or chlorhydric acid [2].

- [1] Journal of Health science, 49, pp1-7 (2003) "A problem in the determination of THM by headspace-Gas chromatography/Mass Spectrometry"
[2] METHOD 524.2 "Trihalomethanes ; Standard operating procedures for the collection of;"



La Drôme-Laboratoires
BP118, 37 avenue de Lautagne
26904 Valence cedex 9