Methods for analysis of trihalomethanes in water, air and exhaled breath: Applications to swimming pool and bath environments

Carolina Lourencetti[1], Joan O. Grimalt[1], Pilar Fernandez[1], Esther Marco[1], Clara Balleste[1] and Juan F. Periago[2]
[1]IDÆA-CSIC (CSIC). Jordi Girona, 18. 08034-Barcelona.
[2] National Institute of Safety and Hygiene at Work. 30120-Murcia.

Introduction

Chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$), known as trihalomethanes (THMs), are the major disinfection byproducts (DBPs) formed by reaction between aqueous organic matter and chlorine added for disinfection. Epidemiological studies have reported associations between long term THMs exposure and increased risk of cancer, mainly in bladder[1].

Besides drinking, many activities involving use of chlorinated water, e.g. household activities and swimming pool attendance, result in human exposure to THMs by inhalation, dermal absorption and ingestion. Assessment of the significance of the exposure related with these activities requires the availability of sampling and analytical procedures for the analysis of these compounds in exposure studies[2].

Objectives

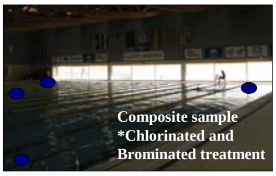
Develop and validate a sampling procedure and analytical methodology for the determination of THMs in water, indoor air and exhaled breath in order to determine **human exposure** to THMs during **showering** and **swimming** activities in two swimming pools which used different disinfection agents, chlorine (Chlorinated Swimming Pool (**Cl-SP**)) and bromine (Brominated Swimming Pool (**Br-SP**)).

Materials and Methods

Sampling and Analysis:

- Water

Water from **Shower** and **Swimming pool***



(sodium thiosulfate addition)

Trihalomethanes ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$)

SOLATek 72 Multi-Matrix Vial Autosampler coupled to a **Purge-and-Trap** Concentrator Tekmar 3100 (both by Tekmar-Dohrmann, Mason, OH, USA). **GC** coupled to a Voyager **MS** (ThermoQuest Finnigan, USA). **SIM** mode (Table 1).

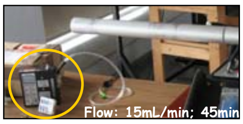
Figure 1. Water sampling and analysis.

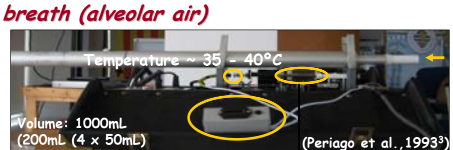
Table 1. GC-MS (SIM) parameters for identification and confirmation.

Retention window (min)	Rt (min)	Compound	MW (m/z)	Selected ions (m/z) Quantitation	Secondary	Tertiary
8.00-20.00	13.64	Chloroform	118	83	85	118
	15.96	Fluorbenzene*	96	96	70	50
	18.49	Bromodichloromethane	162	83	85	47
20.00-42.00	23.33	Dibromochloromethane	206	127	129	131
	28.05	Bromoform	250	173	171	175
	29.15	4-bromofluorobenzene*	175	174	95	176

*internal standard

- Indoor air and exhaled breath (alveolar air)





(Stainless steel cartridge (0.5cm d.;9cm): 1.8g of Tenax TA (60/80 mesh))

THMs: Automatic Thermal Desorption System (**ATD** 400, Perkin-Elmer) coupled to an Autosystem **GC-ECD** (Perkin-Elmer).

Figure 2. Indoor and exhaled breath sampling and analysis.

Study Design:

- Showering exposure:
Volunteers: 12 (6 males and 6 females);
Exposure: 10min;
Exhaled breath sampling: before and 5min after exposure;
Water sampling: 5min after beginning exposition;
Indoor air sampling: 20min before and during the whole exposure period.

- Swimming pool:
Composite water samples (at least 3 per day sampling) and indoor air samples were collected in different days. Air samples were collected every 20min during the morning or afternoon of the sampling day.

References

[1] Zwiener C. et al., Environ. Sci. Technol. 2007, 41, 363-372.
[2] Neuwenhuijsen M.J. et al., *Occup. Environ. Med.* **2000**, *57*, 73-85.
[3] Periago J. F. et al., Journal of Applied Toxicology, v 12 (2), 91-96, 1992

Quality Control and Quality Assurance

- The sampling pump was calibrated in situ by a Dry-Cal DC-Lite (BIOS, UK) prior to and following the end of sampling day.
- Breakthrough of THMs during air sampling was assessed by sampling with two cartridges in series; less than 5% for each THMs was observed for back-up tubes;
- Detector linearity was tested by injecting 1µL of standard solutions directly onto different Tenax TA tubes to obtain calibrations curves. Good linearity was obtained for all THMs with correlation coefficient > 0.999.
- Analytical precision was determined by the analysis of replicate airborne and water samples. Mean relative standard deviations of the replicates were 3.2% and 5.5% for $CHCl_3$, 5 % and 5.3% for BDCM, 4.8% and 5.8% for DBCM and 36.7% and 8.2% for $CHBr_3$, for air and water samples, respectively.
- The limit of detection (LOD) and quantification (LOQ) were calculated from blanks by averaging the signal of all blanks plus 3 or 10 times the standard deviation, respectively. In air samples, the LOD were 0.235ng for $CHCl_3$, 0.037ng for BDCM, 0.013ng for DBCM and 0.043ng for $CHBr_3$ whereas in water samples they were 0.012, 0.005, 0.006 and 0.004mg/L, respectively. For exhaled breath, blank levels of the sampler determined at the beginning and the end of each sampling day were used as LOD. Limits for $CHCl_3$, BDCM, DBCM and $CHBr_3$ were 0.461, 0.044, 0.053 and 0.097mg/m^3, respectively.

Results and Discussion

Swimming Pools

Chloroform and bromoform were the most abundant compounds detected both in water and air of the Cl-SP and Br-SP, respectively (Figures 3 and 4 and Table 2).
Good correlation has been detected between the THMs levels in water and indoor air for both Cl-SP and Br-SP (Table 2).

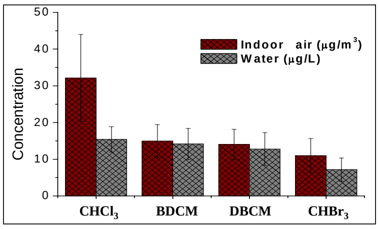


Figure 3. THMs distribution in air and in water (Cl-SP).

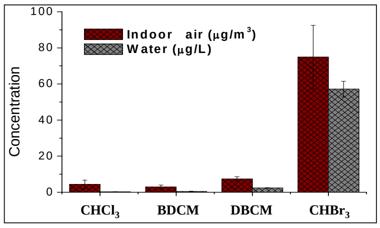


Figure 4. THMs distribution in air and water in Br-SP.

Table 2. Spearman's Rank correlation coefficient for THMs distribution in indoor air and water

	Chlorinated Swimming Pool			Brominated Swimming Pool		
Indoor air x water	n	r	p	n	r	p
$CHCl_3$-$CHCl_3$	68	0.569(**)	0.000	12	0.867(**)	0.000
BDCM-BDCM	68	0.326(**)	0.007	12	0.930(**)	0.000
DBCM-DBCM	68	0.448(**)	0.000	12	0.937(**)	0.000
$CHBr_3$-$CHBr_3$	68	0.387(**)	0.001	12	0.727(**)	0.007
TTHM-TTHM	68	0.089	0.468	12	0.657(*)	0.020

Air (µg m^{-3}); water (µ L^{-1}); * p <0,05; ** p <0,01

Showering exposure

Showering resulted in a significant increase ($p<0.05$) of all THMs in indoor and exhaled breath (Tables 3 and 4).

The average concentrations of THMs **in water** do not exceed the corresponded Spanish and European Commission standards (RD 140/2003; Directive 98/83/CE).

Table 3. THMs concentration in water, indoor air and breath exhaled prior and post shower exposition.

Total THMs	Water (µg/l) [a]		Airborne bathroom (µg/m³) [b]		Exhaled breath (µg/m³)[c]	
	Prior showering (N=5)	During showering (N=12)	Prior showering (N=9)	During showering (N=12)	Pre exposition (N=12)	Post exposition (N=12)
Mean ± SD	67.69 ± 33.33	49.38 ± 20.29	3.79 ± 1.85	34.94 ± 22.41	0.77 ± 0.32	7.15 ± 3.91
Median	57.36	46.57	2.76	31.20	0.68	7.31
Min-Max	33.84 -120.9	21.69 -78.17	1.84 -6.95	14.20-88.57	0.48 -1.64	1.55 -12.74

a. Not statistically significant difference between prior and during showering samples for all THMs.using Wilcoson Rank-Sum Test (sig <0.05).
b. Statistically significant difference between set data prior and during showering samples for CHCl3, BDCM and DBCM using (sig <0.05).
c. Statistically significant difference between set data pre and post showering samples for CHCl3, BDCM and DBCM using Wilcoson Rank-Sum Test (sig <0.05).

Table 4. Spearman rank correlations among water and indoor air measurements and exhaled breath.

	N	Chloroform	BDCM	DBCM	Bromoform
Water vs. Airborne	9	0,3	0,166	0,700(*)	0,817(**)
Water vs. Exhaled breath	12	0,489	0,454	0,741(**)	0,077
Exhaled breath vs. Airborne	9	0,817(**)	0,800(**)	0,783(*)	0,750(*)

Conclusions

-The observed correlations between individual THMs airborne and exhaled breath concentrations after a shower exposure are consistent with showering being a source of THMs exposure;

- Examination of air and water in swimming pools showed a good correspondence between the disinfection method, e.g. chlorination or bromination, and the THM distributions in both media;

- Overall, the method developed in the presented study is feasible for the assessment of THM in different environmental compartments and human samples.