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Evaluation of Head Space Technique for the Determination of Trihalomethanes in Water

Mohamed Ismail Badawy

Water Pollution Department, National Research Center, Dokki, Cairo, Egypt

The occurrence of trihalomethanes has been determined in nearly every chlorinated water (Symons et al 1975; Fayad and Iqbal 1985; Ali and Riley 1989; Badawy 1991). Concern for their possible effect on human health (National Cancer Institute 1977; Hogan 1979) created a need for reliable analytical methodology.

Methods using dynamic and static headspace technique has become popular (Otson et al 1979; Japan Ministry of Health and Welfare 1981). This technique is advantageous because it is suitable for the analysis of volatile compounds which would be lost in extraction procedure. Therefore, the aim of this study is to evaluate the head space method for the determination of THMs in water.

MATERIALS AND METHODS

Appropriate concentrations of methanolic THMs were spiked (3-30 µg/L) into 500 mL double distilled water in a stoppered separatory funnels. The contents were allowed to mix for 2 hours then were distributed immediately into 20 mL headspace vials. The vials were sealed and stored overnight at 20°C before analysis.

Hewlett Packard 1939 SA Headspace Sampler was used for measuring THMs at equilibration time of 20 min. The bath and valveloop temperatures were 60°C, 65°C, respectively. Helium was used as a purge gas at a flow rate of 20 mL/min. Hewlett Packard gas chromatograph with an electrolytical conductivity detector and stainless steel column of 60/80 carbopack BSP-800, 8" x 1/8" O.D. was used. Column temperature was 60°C for 2 min, then increased to 160°C at 3°C/min and held for 10 min. The injector and detector temperatures were 200°C and 850°C, respectively.

Prepared Standard of THMs solutions (1 mL = 20 µg) were obtained from Supelco company (Gland, Switzerland). Working standard solutions were prepared by diluting 1 mL to 20 mL with methanol. Calibration standards at a minimum of five concentration levels were prepared by spiking different amounts of standard solutions to headspace vials containing 20 mL distilled water. To verify

Table 1. Effect of temperature on the recovery of THMs.

Compound	x Recovery, at				Spike range µg/L	LOD at 60 C µg/L
	40°C	50°C	60°C	70°C		
$\mathrm{CHCl_3}$	60± 3*	71±3	99±3	99±7	2-16	0.37
$\mathrm{CHBrCl_2}$	30± 3	42±2	98±3	97±2	3-18	0.40
$\mathrm{CHBr_2Cl}$	30± 2	41±7	97±4	102±5	4-24	0.70
$\mathrm{CHBr_3}$	18±16	55±5	96±1	103±4	6-30	1.00

* n = 6

Table 2. Effects of reducing agents on the recovery of THMs.

Parameter	Recovery %			
	$\mathrm{CHCl_3}$	$\mathrm{CHBrCl_2}$	$\mathrm{CHBr_2Cl}$	$\mathrm{CHBr_3}$
Sodium thiosulfate	89±3*	76±5	79±4	86±9
Sodium sulfite	87±9	37±4	29±7	40±6
Potassium ferrocyanide	98±3	102±4	98±3	95±7

* n = 6

Table 3. Effect of pH on the recovery of THMs.

Parameter	Recovery %			
	$\mathrm{CHCl_3}$	$\mathrm{CHBrCl_2}$	$\mathrm{CHBr_2Cl}$	$\mathrm{CHBr_3}$
pH 2	88±13*	91±8	89±12	90±26
pH 7	98± 3	102±2	98± 2	95± 6
pH 9	97± 4	84±4	82±12	82±12

* n = 6

Table 4. Analysis of quality control samples.

Compound	Low level, µg/L			High level, µg/L		
	Actual	$\bar{X}$ Found	%R	Actual	$\bar{X}$ Found	%R
$\mathrm{CHCl_3}$	1.19	1.06	89.1±9*	11.9	11.4	95.8±5
$\mathrm{CHBrCl_2}$	1.60	1.58	98.7±5	16.0	14.8	98.5±4
CHBrCl	1.96	2.04	104.1±6	19.6	19.3	98.5±9
$\mathrm{CHBr_3}$	2.31	2.24	97.0±8	23.1	21.1	91.3±8

* n = 6

the calibration standard curve 50 µL of THMs mixture of working standard solutions was daily injected into headspace vial containing 20 mL double distilled water and analysed. THMs free water was used for blank determination.

RESULTS AND DISCUSSION

The effect of temperature on the analysis of some organics was investigated and demonstrated that the recovery of such compounds enhanced by elevating temperature because the partition of volatile compound from aqueous solution to gas phase was temperature dependent (Kopfler et al 1976). The results represented in Table 1 show that the temperature, at which the sample was equilibrated, is strongly affected on the partitioned of THMs into the head space gas. In general, as the bath temperature increases, the recovery increases until 60°C. No significant increase was noticed after 60°C. On the other hand, the analysis results were more precise at 60°C.

The effects of storage parameters on the chemical stability of the water samples containing traces of THMs were investigated. Parameters were reducing agents (sodium thiosulfate, sulfite and potassium ferrocyanide), pH (at 2,7 and 9) and holding times of 2 and 24 hrs.

Reduction in the recovery values was observed when sodium thiosulfate and sodium sulfite were added to water samples containing THMs, whereas no reduction found when potassium ferrocyanide was used as a reducing agent (Table 2). This finding due to sodium thiosulfate and sulfite can react with alkyl halides to produce S-alkylthiosulfate and sulfonic acids, respectively (March 1968; Bauman and Strenstrom 1989). In the case of chlorinated effluent unidentified compounds were formed and the concentration of spiked THMs increased when no reducing agent was added to the sample. This result indicates the value of adding a reducing agent to inhibit the chlorination reaction when collecting chlorine treated effluent for volatile organic analysis. Results available in the Table 3 show the effect of pH on the recovery of THMs from water samples. It was found the recovery and precision were affected at pH 2 and pH 9, however the optimum condition was found at pH 7. No significant change was observed when the analysis was carried out after 2 or 24 hrs.

The results represented in Figure 1 show the response (area counts) for each compound versus its respective concentration. The linear dynamic range of LECD detector for studied compounds was over 100 µg/L. Therefore, the method can be applied upto 100 LOD.

The limit of detection (LOD) for THMs was obtained by using reagent water and calculated according to the following criterion (EPA 1982).

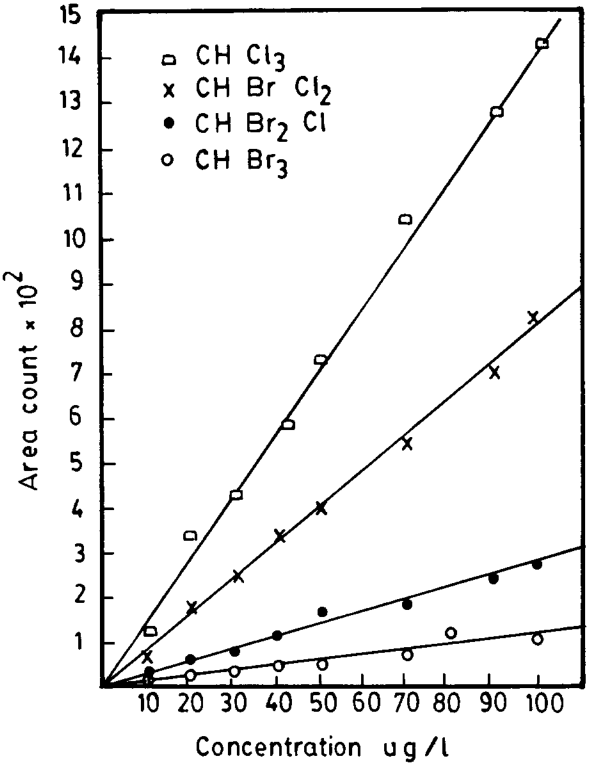

Figure 1. Linear range of LECD for detection of THMs (n = 3).

$$\text{LOD} = \frac{5\ (\text{N})\ \text{ATT1}}{\text{pH} \times \text{ATT2}} \times \text{C}$$

Where N is the noise level (< 20 area count) at the exact retention time and the attenuation (ATT1), pH is the peak height of the particular THM at attenuation (ATT2) and C is the concentration of the compound. The results listed in Table 1 show that LOD ranged between 0.34 and 1.0 µg/L. The headspace method was sensitive to recover THMs from water.

Quality control samples (used in EPA Method 601) obtained from EMSL-Cincinnati were used to check the precision and recovery by spiking reagent water with high and low concentration and analysed for THMs. The values obtained in Table 4, indicate that the headspace procedure was sensitive and simple for the determination of THMs in water because the technique provided a degree of sample clean-up without loss due to evaporation. Most of THMs (about 99%) were partitioned into head space therefore the concentration of sample was not necessary. The mean standard deviation for all samples ranged between 6% and 9%, while the recovery ranged from 89% to 104% at a population of 6.

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