

Detection and Quantification of Trihalomethanes in Drinking Water from Alexandria, Egypt

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Trihalomethanes (THMs) are one group of harmful chlorinated compounds which are known to contaminate drinking water. The total concentration of the four THMs in drinking water may vary up to 1000 µg/l but it should not exceed 100 µg/l (WHO 1984). Toxicological studies suggest that chloroform and other THMs may have detrimental effect on human health (National Cancer Institute 1976; Hogan 1979). Chloroform was reported to cause cancer in experimental animals (Bull 1981). Other THMs, based on the structural similarity to chloroform, may be also classified as health hazard compounds (WHO 1984; Parra et al. 1986). Accordingly, THMs in water supplies should be monitored closely so that measures may be taken to minimize or eliminate their presence whenever the concentration approaches levels of concern.

Little is known about the levels of THMs in drinking water of Egypt compared to other countries (Trussel et al. 1979). Few studies have been reported from Cairo (Badawy 1992; El-Dib and Ali 1992a). To our knowledge, no studies concerning the THMs levels in drinking water have been reported from Alexandria. Therefore, the aim of this study is to detect and quantitate the levels of THMs in drinking water from some main districts in Alexandria.

Solid Phase Micro Extraction (SPME) is a fast, sensitive, inexpensive, portable and solvent-free method for extracting organic compounds from aqueous samples. It is amenable to automation and can be used with any gas chromatograph (or mass spectrometer). The technique meets detection limits specified by EPA methods (Arthur et al. 1992) and was therefore used in this work.

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MATERIALS AND METHODS

Drinking water samples were collected from five different main districts from Alexandria. Three samples from each place were collected in 10 ml vials. The vials were completely filled so that no head-space was left in the bottles. Then they were capped with teflon septa faced silicone and sealed by crimping the aluminium septum retainer over the lip of the vial. The samples were then kept at 4°C until analysis.

Prepared standard mixture (EPA VOC Mix 7) was purchased from Supelco, USA in a stock concentration of 2000 µg/ml. Dilution was made using THMs free mineral water in glass bottle (Norda, Milano, Italy) to obtain the concentrations 50, 25, 10, 5, 2.5 and 1 µg/l. Norda mineral water was used as blank.

Solid Phase Micro Extraction (SPME) syringe obtained from Supelco, Bellefonte, PA, USA was used for samples analysis. Magnetic stirring was used to ensure proper mixing of the sample. All analyses were done with 10 ml vials equipped with a stir bars. Once an equilibrium is reached between the analytes concentration in the solution and the fiber coating of the needle, the plunger is drawn back up and the needle is removed from the septum. The syringe needle is then used to pierce the septum of the GC injector, where the analytes are desorbed off the coating and enter the GC column for separation and analysis (for further details, refer to Arthur et al. 1992).

For GC-MS analysis, we used Hewlett Packard HP 5890 series II gas chromatograph coupled with an HP 5971 mass-selective detector at 70 eV. The chromatographic column was 25 m, ID 0.25 mm and film thickness 1.2 µm (coating CP-Sil 8 CB) from Chrompack, Middleburg, Netherland. Chromatographic conditions were: injector temperature 190°C; oven temperature program from 40°C (for 3 min) to 150°C (7°C/min) and holding the temperature for 2 min. Carrier gas helium, head space pressure 30 kPa; source temperature 180°C. Two ions for each compound were chosen for screening analysis in SIM (Selected Ion Monitoring). Preliminary studies included also a GC/MS analysis recording all the mass spectra of the pollutants mass range has been done. THMs were found to be the most abundant among other contaminants detected.

RESULTS AND DISCUSSION

Formation of THMs and other halogenated organics is associated with use of chlorine for disinfection of drinking water (Rook 1975). THMs are suspected carcinogens and/or mutagenic compounds (Rapson et al. 1980; WHO 1984). A maximum contamination level (MCL) of 100 μl is recommended by US Environmental Protection Agency (EPA 1983) and a 30 $\mu\text{g/l}$ of chloroform as the permissible level for drinking water (WHO 1984).

Preliminary studies have indicated that THMs (CHCl_3 , CHCl_2Br , CHClBr_2 and CHBr_3) were among the most abundant contaminants detected in water samples (Figure 1). 1,2-Dichlorobenzene was detected in only three samples in a very low concentration (39 - 78 ng/l). However, the residue levels of THMs have been detected in all water samples collected. Chloroform (CHCl_3), CHCl_2Br , CHClBr_2 and CHBr_3 were identified (Figure 2) and quantitated (Table 1) in all samples. Generally, the residue levels of THMs followed the order $\text{CHCl}_3 > \text{CHCl}_2\text{Br} > \text{CHClBr}_2 > \text{CHBr}_3$ in all samples.

Considerable variation in concentration does exist according to the sampling site. The highest concentration was found in the samples collected from El-Wardian district (67.3 $\mu\text{g/l}$). However, the lowest concentration was detected in the samples collected from El-Hadara district (18.3 $\mu\text{g/l}$). Chloroform and dichlorobromomethane constitute the major fraction of THMs (36.86% and 35.14%, respectively). Such findings are in agreement with that reported by Otson et al. (1982) and El-Dib and Ali (1992a). Chlorodibromomethane was detected in lower concentration (25.09%) while bromoform was found only in trace amounts (2.91%).

The values obtained from our study are in general within the permissible levels recommended by EPA but higher than the values recommended by European Economic Community (EEC 1980). Variable values have been recorded in different countries. Trussell et al. (1979) reported a mean value of 15.8 $\mu\text{g/l}$ for total THMs in drinking waters from several countries. In Japan (Kagino and Yagi 1980), total THMs ranged between 12.5 and 37.5 $\mu\text{g/l}$. In Thailand (Onodera et al. 1984), the mean values was 44.9 $\mu\text{g/l}$ whereas in Sweden a much lower range between 0.2 and 25 $\mu\text{g/l}$ was recorded for total THMs (Norin and Lars 1980). Such variations in THMs levels reflect the effects of different factors controlling the formation of these compounds on chlorination of drinking water (Johnson and Jensen 1986) and the performance of treatment facilities.

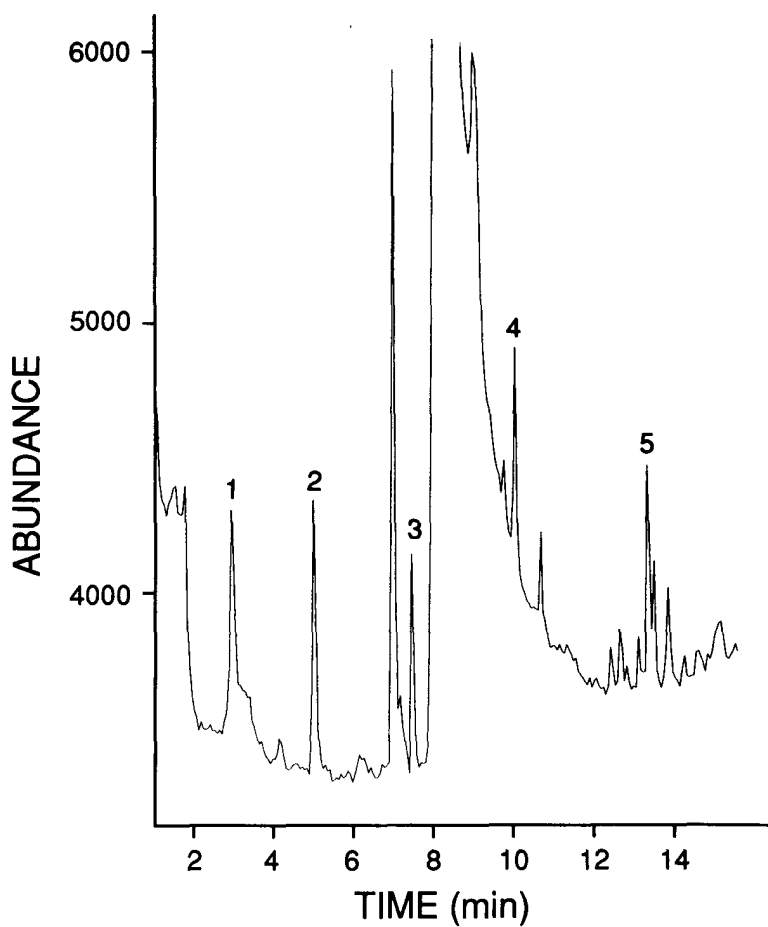


Figure 1. Reconstructed total ion chromatogram of a water sample from Alexandria. 1= chloroform, 2= dichlorobromomethane, 3= chlorodibromomethane, 4= bromoform and 5= 1,2-dichlorobenzene.

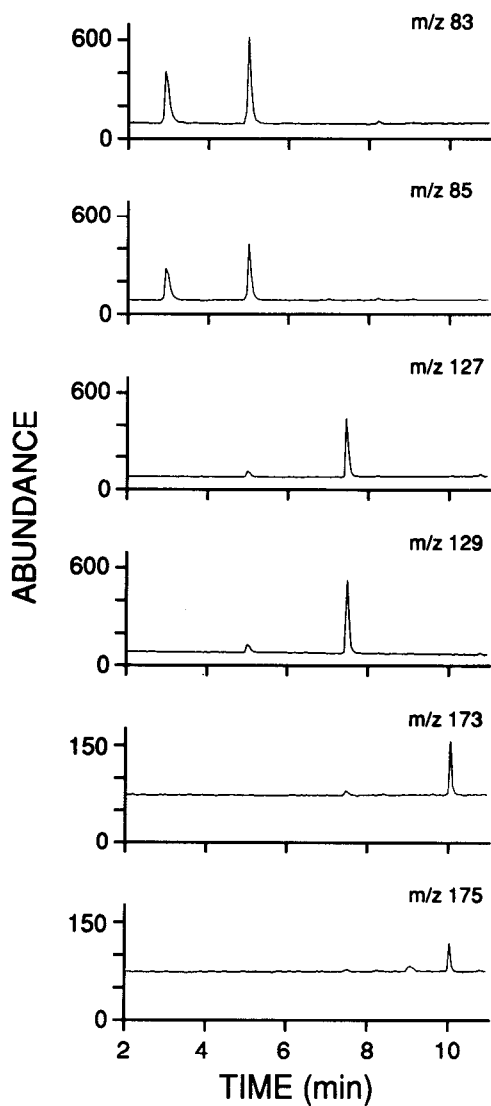


Figure 2. Selected ion chromatograms of a water sample from Alexandria. Peak retention times and identification are as in Figure 1.

Table 1. Mean values of individual and total THMs detected in drinking water samples collected from Alexandria.

| Sampling Site | No. of Samples | THMs Species ($\mu\text{g/l}$) | | | | Total THMs |
|---------------|----------------|----------------------------------|--------------------------|--------------------|-----------------|-------------|
| | | CHCl_3 | CHCl_2Br | CHCl Br_2 | CHBr_3 | |
| Moharem Bek | 3 | 16.4 | 16.7 | 12 | 1.8 | 46.9 |
| EL- Agamy | 3 | 17 | 15 | 9.8 | 1 | 42.8 |
| EL- Hadara | 3 | 6.3 | 5.2 | 6.1 | 0.7 | 18.3 |
| EL-Seyouf | 3 | 15.6 | 19.4 | 14.8 | 1.7 | 51.5 |
| EL- Wardian | 3 | 28.3 | 23.4 | 14.2 | 1.4 | 67.3 |

Conventional water treatment generally includes alum addition, flocculation, sedimentation and rapid sand filtration. Chlorine, used as disinfectant, is added to the raw water (pre-chlorination) and to the filtered water (post-chlorination). El-Dib and Ali (1992b) claimed that water pre-chlorination together with the extended contact time in the settling basins and clear well has a role in the formation of THMs. They also stated that sand filters may act as a source of THMs precursors if excessive metabolites are released by the retained microbial life.

The known carcinogenic effects of THMs other than chloroform are limited (Cantor and McCabe 1978). However, they are known to be more active than chloroform in the Ames Salmonella test for mutagenesis (WHO 1984). Based on structural similarity of dichlorobromomethane to chloroform, a MCL of 30 $\mu\text{g/l}$ will be arbitrary assumed for that THM species in this study. There is strong indication that EPA standards for THMs will be lowered (Amy et al. 1991).

We conclude from our study that the level of THMs in drinking water of Alexandria is within the permissible level allowable by EPA. Higher levels was found in the area of El-Wardian which is a district with high intensity of population. It is possible that excessive chlorination is needed there to increase water disinfection. However, further study is needed to detect the level of THMs in some water treatment plants of Alexandria before and after chlorination of water to understand more about the situation.

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