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Analysis of Drinking Water for the Detection of Trihalomethanes

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Drinking water of the Dammam metropolitan area is a blend of raw well water and desalinated water obtained from the Al-Azizia seawater desalination plant. Chlorination is the only disinfection method applied to the blended water before the water pumped into the distribution system.

Chlorination of water containing organic compounds results in the formation of trihalomethanes (Symons et al, 1975; Stevens and Symons, 1980; Rook, 1974; Allgeier et al, 1980). Trihalomethanes (THMs) in drinking water may adversely affect the human health. Evidence of the carcinogenicity of chloroform in mammals has been confirmed by several studies. (USEPA, 1975; NCI, 1975). Other experiments showed that bromoform generated excess lung tumors in preliminary tumor induction tests with mice (Fed. Reg., 1978). In general, the known carcinogenic and physiological effects of THMs other than chloroform are limited. However, based on their structural similarity to chloroform, these compounds can be considered health hazards.

The present study was carried out in order to determine the extent of the occurrence of THMs in finished drinking water in some of the major cities of the Eastern Province of Saudi Arabia.

MATERIALS AND METHODS

Drinking water samples were collected from several locations from most of the major cities of the Eastern Province in Saudi Arabia. The geographic distribution of sampling locations in each city was designed to represent the water quality in various places in the distribution system. Water samples were collected in duplicate from each location. Glass vials (40 ml capacity) capped with Teflon faced rubber septa were used. The water samples were collected without head space in order to prevent the loss of volatile organic compounds. Sodium thiosulphate (10 mg) was added to each sampling vial in order to remove any free residual chlorine and thereby quench further formation of THMs. Sampling vials were maintained in a refrigerator at 4°C until the analysis time, at which time, they were allowed to reach room temperature. Due to the low concentration levels of THMs usually present in chlorinated drinking water, a concentration step must precede the

analysis process. Two main methods are available for the concentration of THMs in water samples, the purge and trap technique and the liquid/liquid extraction (Fed. Reg., 1978). In the present study, the liquid/liquid extraction was utilized. The method involved the extraction of 10 ml of the chlorinated drinking water sample with 2 ml of glass distilled pentane . One µl of the pentane extract was then injected into the gas chromatograph. A 30 m long fused silica capillary column, 0.25 mm I.D., coated with a thick film of the stationary phase (1 µm) DP-5 was used for chromatographic separation of the THMs components. The analysis of THMs was carried out using a Varian Vista 6000 gas chromatograph which is equipped with a Vista 401 data station and a Ni 63 Electron Capture Detector. The GC oven temperature was programmed from 50°C to 120°C at a ramp rate of 5°C/min with an initial hold time of 4 minutes. Nitrogen was used as the carrier gas with a flow rate of 2 ml/min , detector base flow at 12 ml/min and carier makeup gas at 16 ml/min. The injection technique was splitless with a split (200 ml/min) flows initiated automatically after 90 seconds and maintained for 30 seconds, the flow being then splitless throughout the analysis.

The analytical quality control scheme applied in the present study included daily analysis of standards, fortified water samples, duplicate samples, and the analyses of field blanks. Field blank samples were prepared from organic free water and were handled in the same way as the samples in order to check for any contamination during the sample collection and transportation. The accuracy and precision of the analytical procedure were evaluated at several dose levels for each of the analytes investigated in this study. Results of these analyses are shown in Table 1.

RESULTS AND DISCUSSION

The results obtained from the analyses of water samples spiked with THM standards showed that the method used in this study is very precise and accurate for the determination of these compounds. However, at very low concentration levels of chloroform and bromoform (0.5 µg /l) the recovery values were high although the precision was still good (Table 1).

Results obtained from the analyses of water samples collected from major cities in Dammam metropolitan area (Dammam, Khobar and Dhahran) and Jubail are shown in Table 2.

A typical chromatogram obtained for THMs found in Dammam drinking water is shown in Figure 1. From Table 2 it can be seen that, THM concentration in the distribution system of Dammam city ranged as high as 40.3 µg/l with a mean value of 14.2 µg/l. The highest values were obtained for the same sampling location at all times. Further investigations will be carried out to determine the reasons of these high values. The mean values of THMs found in Khobar city, Aramco camp, Dhahran airport and Jubail city are

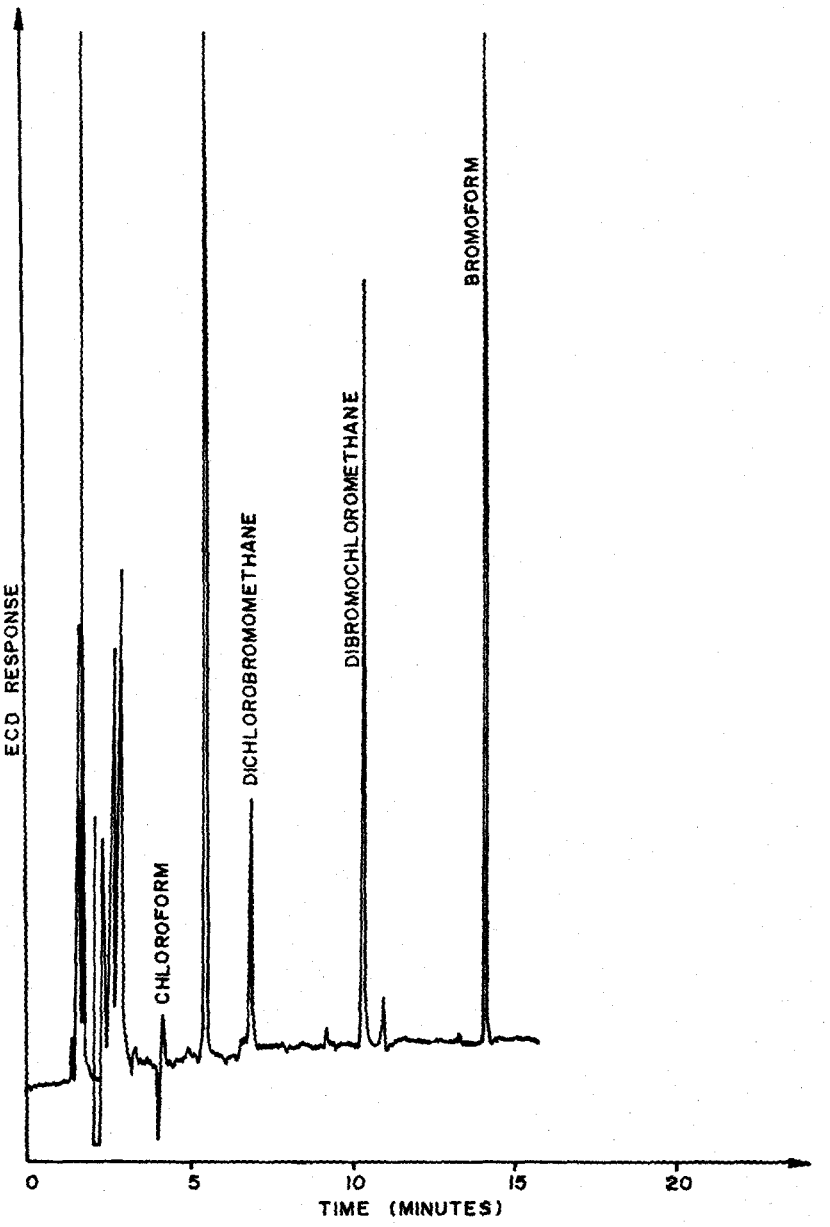

Figure 1. Typical chromatogram of THMs found in Dammam drinking water.

Table 1. Precision and accuracy of the analytical procedure.

Compound	Dose Level (µg/l)	No.of Samples	Mean ± SD (µg/l)	Recovery (%)
$CHCl_3$	0.5	5	0.9 ± 0.11	170
	2.1	7	2.1 ± 0.16	100
	10.5	5	9.1 ± 0.40	87
$CHCl_2Br$	0.4	5	0.4 ± 0.04	95
	1.7	7	1.7 ± 0.13	100
	8.6	5	9.1 ± 0.33	105
$CHClBr_2$	0.5	5	0.5 ± 0.05	100
	2.0	7	2.0 ± 0.08	100
	10.0	5	11.1 ± 0.34	111
$CHBr_3$	0.5	5	0.7 ± 0.10	140
	3.1	7	3.0 ± 0.17	97
	15.4	5	16.2 ± 0.49	105

Table 2. Total trihalomethanes in drinking water

Location	No. of Samples	Mean (µg/l)	Median (µg/l)	Range (µg/l)
Dammam City	14	14.2	12.4	1.6 - 40.3
Khobar City	16	11.4	11.7	4.4 - 20.6
Dhahran area				
Univ. of Petr. & Minerals	11	0.5	0.3	0.0 - 2.2
Aramco Camp	4	7.5	8.5	3.3 - 9.6
Airport & Dhahran Village	4	4.2	3.4	0.17- 9.9
Jubail City	5	6.4	7.3	0.31- 10.0

11.4 µg/l, 7.5 µg/l, 4.2 µg/l and 6.4 µg/l respectively. Drinking water samples collected from various locations in the campus of the University of Petroleum and Minerals showed the lowest concentrations of THMs, the mean value of THMs being 0.3 µg/l. Residual chlorine concentrations of 0.2 mg/l and o.1 mg/l were

found in the UPM drinking water at the outlet of the reverse osmosis desalination plants. However, it was absent in drinking water samples collected from all locations of the water distribution system. Several studies have shown that the concentration of THMs in chlorinated water depends on the chlorine dose (Stevens and Symons, 1980; Kajino and Yagi, 1980). The absence of chlorine in the water distribution system could be the reason for the low concentrations of THMs found in UPM drinking water. A range of 0.0 to 1.5 mg/l of residual chlorine was found in drinking water collected from Khobar city.

A considerable variation in water temperature was noticed at different locations of the water distribution systems. For example a temperature range of 22°C to 35°C was noticed in Dammam city. However, in the present study, no correlation was found between the water temperature and the THMs contents of the water. Other studies have shown that THMs formation in chlorinated drinking water is temperature dependent (Allgeier et al, 1980).

The United States Environmental Protection Agency has proposed a concentration level of 100 µg/l as the interim maximum allowable limit for total trihalomethanes in water. That concentration level was suggested to be as a starting point which will, over time, lowered progressively as technology, economic and practical constraints permit (Fed. Reg., 1978). The mean values obtained for THMs at the survey locations are generally low as compared with the US EPA maximum allowable concentration. Trussell et al (1979) have surveyed drinking water in twelve countries for their THMs and other volatile organic contents. The results of their study have indicated a mean value of 15.8 µg/l for THMs in international drinking water. This value compares favourably with values obtained for these compounds in drinking water of Dammam metropolitan area.

Table 3. Trihalomethanes in drinking water

Location	Mean Concentration (µg/l)			
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
Dammam City	0.36	1.07	2.6	10.0
Khobar City	0.26	0.38	1.26	9.5
Dhahran Area				
UPM	0.03	0.02	0.06	0.41
Aramco camp	0.34	0.25	1.16	5.76
Dhahran village	0.36	0.23	0.83	2.76
Jubail City	0.66	1.27	2.31	3.77

Usually, chlorinated drinking water contains relatively high concentrations of chloroform as compared to other THMs. In the present study, considerably higher concentrations of bromoform were found in most water samples as it is shown in Table 3. This phenomenon can be explained by the fact that chlorinated drinking water in the study area is prepared by blending of ground well water and desalinated water obtained from the Gulf. The Gulf water contains about 85 mg/l of bromide ions (MacLaren and Sabek, 1979). Stevens and Symons, (1980) have shown that bromide ions are oxidized by aqueous chlorine to species capable of producing brominated halomethanes. They also indicated that bromine substitution is favoured over chlorine even at high concentration levels of chlorine, compared to bromide ions. Trussell et al (1979) also attributed the high levels of bromoform found in China drinking water to the water sources which they expect to contain high concentrations of bromide ions.

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