Screening for Halo Organics in New York State Drinking Water

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Chloroform, carbon tetrachloride, bromodichloromethane, and other organic compounds have been detected by the Environmental Protection Agency in chlorinated drinking water (BELLAR et al. 1974, USEPA 1975a). An analytical method similar to that used in those studies and in the studies of GROB (1973) has been developed and applied to a survey of drinking water quality in New York State. This paper describes the analytical method used and the results of water analyses for halo organics determined to date.

METHOD OF ANALYSIS

Headspace analysis is the main tool in this work. Sodium chloride (5.0 g) is added to 15 ml of the water sample in a 125-ml serum bottle, which is then sealed with a Hycar septum. The sample is heated for 2.5 h by immersion in a boiling water bath. One to 3 ml of headspace vapor are removed with a closable gas-tight syringe (Precision Sampling Inc.), injected on a 6-ft Chromosorb 101 column at 150°C with argon/5% methane as a carrier gas, and measured with an electron-capture detector. Peaks are identified by retention time and quantitated by area measurement using the Hewlett-Packard 7600 Chromatograph System.

The detector was calibrated by injecting 5-µl volumes of methanol solutions of the halo organic of interest onto the column. Table 1 shows the transfer efficiency of a known mass of chloroform from water into the headspace, which was determined using spiked well water. Water derived from chlorinated tap water by distillation or by deionization or both was always contaminated with several halo organics.

TABLE 1

Efficiency of transfer to headspace

Chloroform spike (µg/l)	Recovery (%)
10	93
20	96
30	86
40	81
50	78

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Once the transfer efficiency was shown to be high, analysis was carried out by running a set of known standards with each set of samples. Typical calibration curves are shown in Fig. 1.

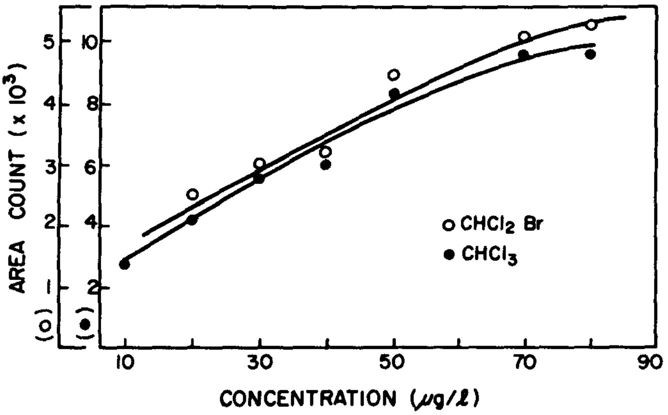

Figure 1. Calibration Curves

Chloroform, bromodichloromethane, trichloroethylene, tetrachloroethylene, and vinyl chloride were further identified by mass spectrometry using an AEI/MS30 spectrometer linked with a Fisher Victoreen 1400 chromatograph via a silicon rubber membrane separator. Two sampling methods were employed: (1) headspace vapor (20-30 ml) from a 50-ml water sample was injected directly onto a Chromosorb 101 column; or (2) nitrogen was bubbled through 100 ml of the water sample at 20°C, and the effluent was passed through an ice-cold trap and then absorbed on a 15-cm Tenax GC column at room temperature. This was used as a forecolumn to a Chromosorb 101 column in the Fisher Victoreen chromatograph, with temperature programming from 50°C to 150°C at 30°C/min.

SURVEY SCOPE

The objectives of the survey were to determine:

1. Significant seasonal variation in halo organic concentration, if any.
2. The concentration of the chemicals in highly colored chlorinated reservoir waters.
3. The relative concentrations of the compounds in chlorinated groundwater and chlorinated surface water.
4. The frequency of occurrence of halo organic compounds in chlorinated water.

To achieve this the sampling program shown in Table 2 was instituted.

TABLE 2

Chlorinated drinking water systems surveyed

Source	No. of systems	No. of samples
Groundwater wells	10	11
Lake Erie	3	13
Niagara River	3	3
Highly colored upland impoundments	2	2
Totals	18	29

RESULTS AND DISCUSSION

Figure 2 is a typical chromatogram from a Lake Erie chlorinated water supply. To date, six peaks have been quantified, but only chloroform, carbon tetrachloride, and bromodichloromethane have been identified. Other peaks were frequently observed; they have been quantitated as if they were chloroform. Other minor peaks occurred occasionally.

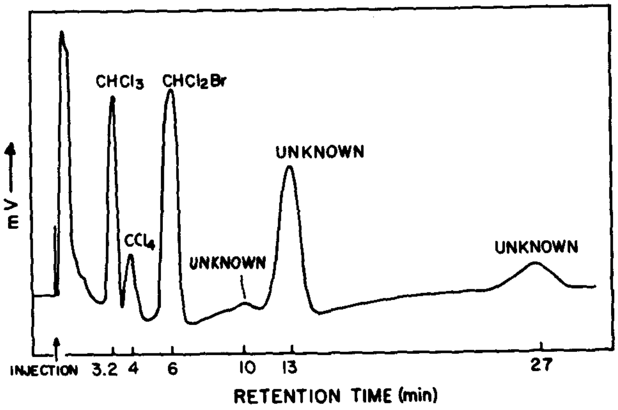

Figure 2. Chromatogram of chlorinated water from station 2 on 6/30/75

Previous studies (BELLAR et al. 1974, ROOK 1974 and USEPA 1975a, 1975b) have not reported a variation in the concentration of halo organic substances which might be associated with seasonal quality changes in surface waters. We consistently found chloroform and bromodichloromethane in Lake Erie water collected at three stations from January through August 1975 but observed no seasonal trend (Table 3A). Raw water from Stations 1-3 contained no detectable amounts of any of these substances, showing that they are definitely chlorination artifacts.

TABLE 3

Observed substances (µg/l) in chlorinated drinking water

Retention time (min) and compound

Source and Station number	Date (1975)	3.2	4	6	10	13	27
		$CHCl_3$	CCl_4	$CHCl_2Br$	Unidentified☆		
A. Lake Erie							
1	1/9	16	-	5	-	<2	4
	3/17	41	-	34	-	18	.5
2	3/17	45	-	36	-	23	4
	6/2	50	-	40	-	7	<2
	6/17	50	-	40	-	12	<2
	6/30	35	1.4	45	-	36	<2
	8/11	40	3	25	-	50	-
3	1/9	5.7	0.2	5	-	-	5
	3/24	34	-	30	-	17	-
	6/2	30	3	40	-	7	<2
	6/17	30	0.5	10	-	<2	<2
	6/30	27	4.8	26		8	-
	8/11	20	4.0	7.5	-	<2	<2
B. Niagara River (surface water)							
4	3/24	36	0.3	30	-	17	-
5	4/7	28	-	23	-	23	4
6	4/7	38	1.1	27.5	-	25	5
C. Upland reservoirs (surface water)							
7	1/9	20	-	<2	-	5	5
8	8/11	80	-	10	40	-	-
D. Ground water sources☆☆							
9	4/21	<2	<.2	<2	-	<2	<2
10	4/21	<2	<.2	<2	-	<2	<2
11	4/21	<2	<.2	<2	-	<2	<2
12	4/21	<2	<.2	<2	-	<2	<2
13	1/9	4.7	-	2.0	-	-	5
	4/28	2.0	<.2	<2	-	<2	<2
14	4/28	<2	<.2	<2	-	<2	<2
15	4/28	<2	<.2	<2	-	<2	<2
16	6/9	<2	-	2.8	-	25	-
17	6/9	<2	-	0.6	5	<2	-
18	6/9	<2	-	0.7	55	<2	-

- = Not detected (<0.1 µg/l)
☆ Quantitated as chloroform
☆☆ 9-15, Buffalo area; 16-18, Long Island

Similar water analyses were made for five other chlorinated surface water systems (Table 3B and C). Values for both chloroform and bromodichloromethane for Niagara River water are within the range of results obtained for Lake Erie water. Other substances also occur sporadically.

ROOK (1974) has indicated that chlorination of colored surface water may be associated with greater production of haloforms. Two upland reservoirs of water that consistently averages 40-60 color units were sampled after chlorination (Table 3C). Station 8 is heavily chlorinated to provide free chloride residuals in the finished water, while Station 7 produces no free residual. This may account in part for the higher values found at Station 8.

While the chloroform production is high in the highly chlorinated colored water, bromodichloromethane production remains low. This may reflect differing bromide concentrations in the upland reservoir waters and waters of Lake Erie. The source of bromine for the production of bromo derivatives is at present not clear.

The USEPA survey also indicated that chlorinated well water contains a smaller concentration of halo organics than does surface water (Table 3B-D). A comparison of the values for Stations 4-8 with those for Stations 9-18 generally confirms these findings. However, wells are susceptible to contamination by leaching. For example, at a well water supply on Long Island which is not included in this survey, vinyl chloride (50 µg/l), tetrachloroethylene (500 µg/l), and trichloroethylene (65 µg/l) were found to be leaching from a nearby air base. Leaching may also account for the bromo compound being higher at Stations 16-18 than at Stations 9-15.

A review of all values for the commonly found substances tends to confirm the findings of the USEPA survey that chloroform and bromodichloromethane occur more frequently than other halo organics in chlorinated drinking water (Table 4).

TABLE 4

Frequency of detection of halo organics in chlorinated drinking water in this survey (n=29)

Substance	Retention time (min)	Frequency of detection (%)
Chloroform	3.2	100
Bromodichloromethane	6	94
Unknown	13	72
Carbon tetrachloride	4	55
Unknown	27	39
Unknown	10	7

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