Analysis of Volatile, Halogenated Organics in Water by Direct Aqueous Injection-Gas Chromatography

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Volatile, halogenated organic compounds have been found in drinking waters by several laboratories, including THE SURVEILLANCE AND ANALYSIS DIVISION OF THE LOWER MISSISSIPPI RIVER FACILITY (1974), KLOEPFER AND FAIRLESS (1972), NOVAK (1973), GROB (1973, 1974), BELLAR (1974), DIETZ (1973), ROOK (1974). Both ROOK (1974), and BELLAR (1974) claim that chloroform, bromodichloromethane, and chlorodibromomethane are introduced during the chlorination process. Since little is known about the chronic toxicity of these compounds, a program was initiated to screen drinking waters in Ontario for the presence of volatile organohalides. Thus it was desirable to develop a convenient, fast and accurate method suitable for routine monitoring of water treatment plants and to study the formation of organohalides under water treatment conditions.

The compounds listed in Table 1, have been found in concentrations ranging between 0.5 and 100 ug/l by ROOK (1974) and BELLAR (1974). These concentrations may be significant, therefore, any new method developed must approach these sensitivity requirements. Until now, the procedures used to obtain the required sensitivity have involved some sort of extraction procedure. Gas stripping, head space analysis, solvent extraction, or adsorption on carbon or macroreticular resins have been the most popular methods for concentrating trace organics including halogenated hydrocarbons.

Although these methods all meet the sensitivity requirements, all have one drawback - they are cumbersome for the routine analysis of large numbers of samples.

Direct aqueous injection of the sample into the gas chromatograph is the simplest of the methods recommended so far, and in this procedure, the flame ionization detector is the one most commonly used. However, according to SUGAR and CONWAY (1968) its sensitivity is in the 1 mg/l range, suitable only for the analysis of industrial effluents.

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Since all of the compounds of interest are halogenated, we found the use of an EC detector more appropriate, attaining sensitivity levels suitable for drinking water analysis.

EXPERIMENTAL

Varian 2400 (instrument A) and Varian 2100 (instrument B) gas chromatographs equipped with scandium tritide electron capture detectors and 4 ft by 1/4 in. glass columns packed with Chromosorb 101 (60/80 mesh) were used for the analysis.

The conditions for operating the instruments are as follows:

Instrument A:	Injector temperature:	230°C
	Detector temperature:	230°C
	Oven temperature:	130°C
	Nitrogen Flow Rate:	50 ml/min.
Instrument B:	Injector temperature:	220°C
	Detector temperature:	225°C
	Oven temperature:	150°C
	Nitrogen Flow Rate:	60 ml/min.

Preparation of Standards

To a 1 litre volumetric flask filled to the mark with organic-free water, 1 ul of the pure compound to be determined was injected directly into the aqueous phase. The volumetric was agitated vigorously for at least five minutes. Dilutions were then made from this stock solution.

10 ul of the aqueous solutions were injected, and the calibration curves and detection limits were obtained by measuring peak heights.

RESULTS AND DISCUSSION

The detection limits for the trihalogenated compounds listed in Table 1 are all below the 10 ug/l level. Figure 1 illustrates typical calibration curves for $CHCl_3$, $CHBrCl_2$, and $CHBr_2Cl$. The percentage standard deviation of five injections was $\pm$ 1%. All measurements were made using peak heights; thus, the detection limits do not directly reflect the response of the electron capture detector for these compounds (reported by DEVAUX (1967).

The detection limit for dichloropropane by this method is only 60 ug/l, and the dichlorobenzenes cannot be detected below 500 ug/l. This analysis is, therefore, not suitable for detecting trace levels of some of the dichlorinated hydrocarbons in water.

Unexpectedly, there was little deterioration of the scandium tritide detector due to large quantities of water passing through it at high temperatures. After more than 400 injections of 10 ul of water, the standing current had decreased by less than 10%.

For the rapid analysis of volatile trihalogenated and a number of dihalogenated compounds, this method has proved to be fast, sensitive and accurate.

TABLE 1

Detection Limits of Some Halogenated Compounds.

Compound	Retention Time	Column Temperature	Detection Limit (ug/l)
Bromochloromethane	2.8	130	1
Chloroform	3.0	130	3
1,1-dichloroethane	4.0	130	90
1,2-dichloroethane	4.0	130	150
Carbon tetrachloride	4.0	130	3
Dibromomethane	6.0	130	0.6
1,2-dichloropropane	6.8	130	60
Tetrachloroethylene	13.0	130	8.0
Chlorodibromomethane	15.4	130	5
Bromoform	4.5	150	2
Tetrachloroethane	5.2	150	7
p-dichlorobenzene	9.8	150	500
o-dichlorobenzene	11.4	150	500

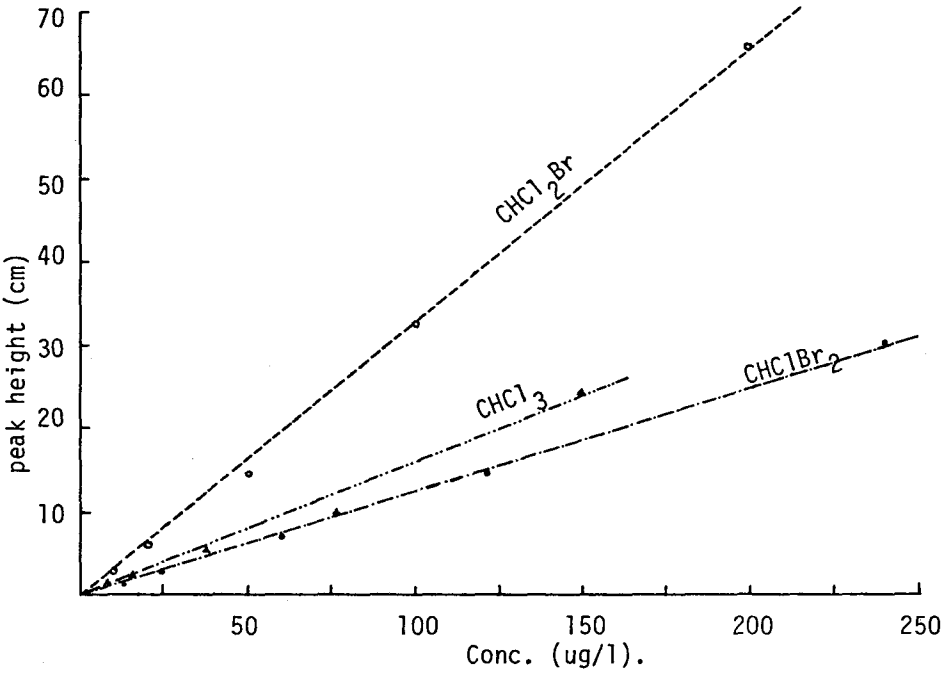

Fig. 1. - Typical Calibration Curves - o $CHCl_2Br$, Δ $CHCl_3$, • $CHCl_2Br$

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