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Determination of Volatile Halocarbons in Water by Purge-closed Loop Gas Chromatography

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Concentrations of volatile halocarbons in water at the parts per billion level have been determined using gas chromatography in conjunction with Hall electrolytic conductivity, electron capture detection or flame ionization. These analyses have employed the following four different sample handling techniques: direct aqueous injection (Nicholson et al. 1977), solvent extraction (Hendeson et al. 1976), gas stripping (Grob 1973, Bellar and Lichtenberg 1974, Kopfler et al. 1976, and Mieure et al 1976) and static headspace sampling (Kaiser & Oliver 1976, and Dietze and Singley 1979). Each method can be effective for analysis of selected halocarbons in water. All possess advantages and disadvantages which relate to equipment needs, desired detection limits, sample matrix, and analysis speed. For this particular instance a routine method was required that would determine trichloroethylene ($CHCl = CCl_2$), 1,1-dichloroethylene ($CCl_2 = CH_2$), 1,2-dichloroethylene ($CHCl = CHCl$) and vinyl chloride ($CH_2 = CHCl$) in groundwater over a very large concentration range (0.1 ppb to 10 ppm). The method could not be adversely affected by less volatile halogenated compounds which were known to be present in many of the samples. The interference of extraneous compounds cannot be prevented when employing direct aqueous injection and solvent extraction procedures. Past experience has shown that gas stripping and headspace techniques are too time-consuming for routine application to a large number of samples. These limitations led to the laboratory development of the purge-closed loop method which combined the technique of both gas stripping and headspace methods. Many parameters were considered and tested before the present equipment and experimental procedures were adopted. Results of that work are reported here.

MATERIALS AND METHODS

A purified stream of air is bubbled through a twenty ml water sample contained in a specially designed purging chamber. The bubbler unit is equipped with an o-ring joint and injection port as shown in Figure 1. The volatile organics are rapidly purged from the aqueous phase to the gaseous phase in a ten ml or five ml sampling loop. After equilibrium is reached between the two phases, the volatile organics in the loop are injected into the gas chromatograph by a Valco six-port switch valve. The operational procedures are shown in Figures 2, 3 and 4. The detailed analytical schemes are as follows:

Before the water sample was injected into the bubbler unit, loop air was filtered through a charcoal tube for ten minutes (Figure 2) to purify the air in the system.

A twenty ml water sample was injected into the bubbler unit with a clean glass syringe via the injection port in the system. Loop air then by-passed the charcoal tube by means of a four-way switch valve as shown in Figure 3. The sample was then rapidly purged with a mini-teflon bellow pump. The volatile organic compounds in the water sample were purged, travelling through the sampling loop and back to the bubbler unit for five minutes. The concentrations of these organic compounds in the vapor phase were then at equilibrium with concentrations in the aqueous phase. The ten ml loop sample was then injected to the gas chromatograph for analysis (Figure 4) by a six-port switch valve. Sample size employed in the system could be adjusted depending upon the concentration of the sample, the organic-free distilled water being used to make up the remainder of the 20 ml sample in the bubbler. The organic-free water was prepared by purging the distilled water with an ultrapure nitrogen stream for 24 hours. Each batch of water showed no interference peaks.

After sample injection the bubbler unit was removed from the system, thoroughly cleaned with methanol and distilled water, and then heated at 200°C in the oven for five to ten minutes, or until it was ready for the next experimental run.

Without the bubbler unit in the system, the pump was on for another five to ten minutes to remove any remaining organic compounds in the apparatus. The system was then ready for the next experimental run.

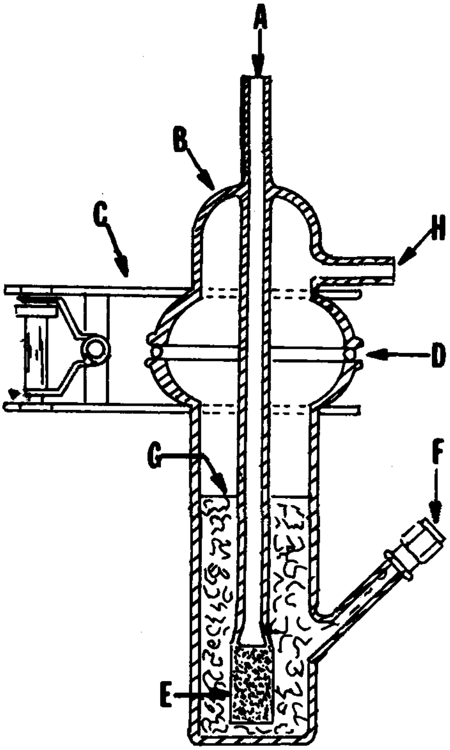

Figure 1. Water Sample Purging Device

A - Purified Air Stream

B - 30 ml Bubble Unit

C - Clamp

D - Teflon O-ring

E - Fritted Glass Stone

F - Injection Port

G - Water Sample

H - Air Stream Outlet

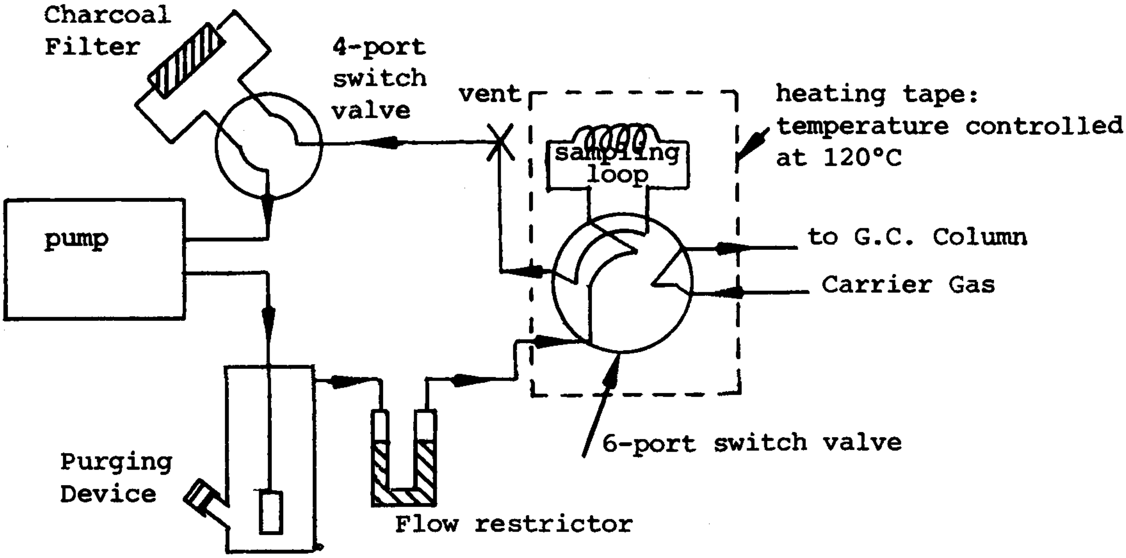

Figure 2. Loop Purification Mode

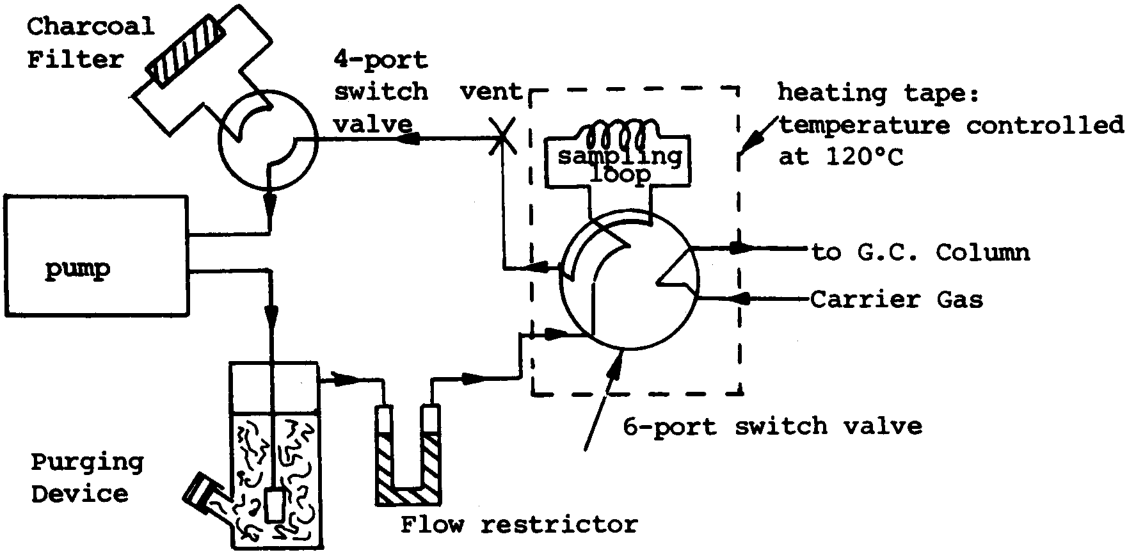

Figure 3. Sample Purging Mode

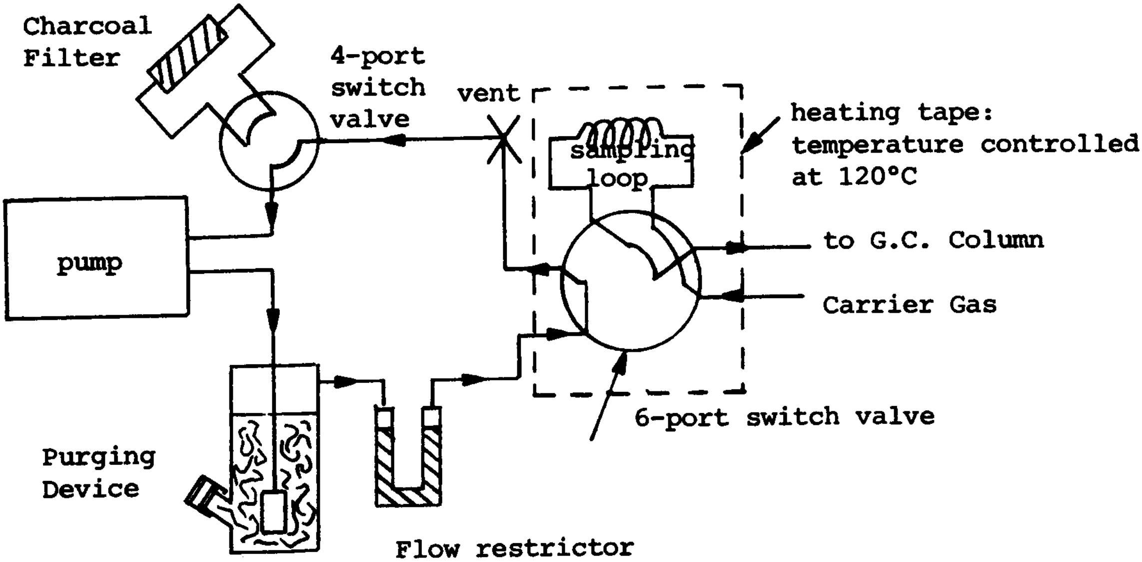

Figure 4. Sample Injection Mode

Calibration curves were prepared with three different concentrations of standard solution in the 20 ml of organic-free water in the purging unit. These samples were analyzed following the unknown sample procedure. A linear regression equation was then established to quantify the unknown samples. The gas chromatographic operating conditions are listed in Table 1.

Table 1. Gas chromatographic equipment and conditions

G.C. Model	Perkin Elmer Model 900	Perkin Elmer Model 900
Detector	ECD Ni^{63}	FID
Detector Temp.	250°C	
Carrier gas	95% Ar/5% methane	Nitrogen
Flow rate	45 ml/min	40 ml/min
Column packing	1% SP-100 on 60/80 Carbopack B	Porapak QS 80/100 mesh
Column dimension	6' x 1/4" glass column	5' x 1/8" glass column
Column temperature	80°C for 4 minutes initially then at, 4°C/min to 200°C	100°C isothermally
Retention time:		
Vinyl Chloride	—	5.70 minutes
1,1-Dichloroethylene	5.54 min.	—
1,2-Dichloroethylene	8.03 min.	—
Trichloroethylene	17.45 min.	—
Peak Integration and Recording Device	Sigma 10 Chromatography Station (Perkin Elmer)	Same
Switch Valve	Valco six-port switch valve	Same
Switch Valve Temperature	120°C	120°C
Sampling Loop Temperature	120°C	120°C

RESULTS AND DISCUSSION

When a water sample that contains organic compounds is placed in a closed-loop system, organics will equilibrate between the water and the headspace during the purging period. Distribution of compounds between the two phases depend on temperature, vapor pressure for each compound, sample matrix influences on compound activity coefficients, ratio of headspace to liquid volume in the entire closed system, purge time and gas purge rate.

The time and method used to equilibrate samples will affect gas chromatographic responses. Data in Figure 5 show that equilibration was rapidly attained. Equilibrium was reached within five minutes of purging for vinyl chloride, trichloroethylene, 1,1-dichloroethylene and 1,2-dichloroethylene.

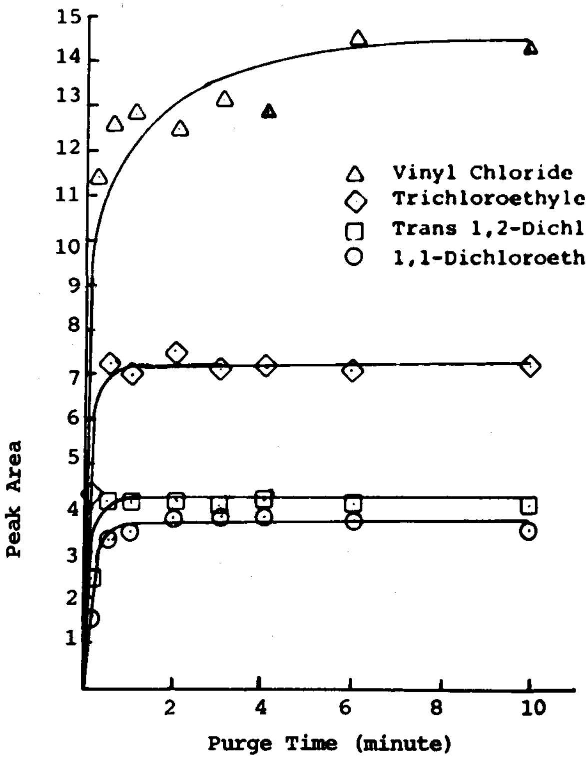

Figure 5. Gas Chromatograph Response vs. Purge Time

When carefully conducted, analytical precision of approximately 2 to 8% relative standard deviation can be achieved. The relative standard deviations and recovery efficiencies for a study in which four distilled water samples were prepared and analyzed are presented in Table 2. Minimum detectable concentrations for this method are shown in Table 3. Method validation by fortification studies has also been conducted (Table 4). A known amount of these four compounds was fortified into a fresh water canal sample, a contaminated groundwater sample, and a estuarine river water sample. The recovery efficiencies for these three samples ranged between 81% to 100% (Table 4). These results demonstrate the reliability of the method.

Since the purge and trap technique (Bellar and Lichtenberg 1974) is currently popular, a brief comparison was conducted between this method and the purge-closed loop method (Table 5). The two samples used represented two different levels of contaminated groundwater. The results were not significantly different and both methods delivered a relative standard deviation of less than 10%. The purge-closed loop method provided better quality chromatograms, exhibiting no peak tailing or detector baseline noise which were observed when using the purge-trap method. Eight to ten samples per day (8 hr) can be analyzed using the purge-trap method vs. twenty five to thirty samples using the purge-closed loop method. When a sample contains a high concentration of organics, the purge-trap system can present difficulties in removing residuals from the trap whereas the purge-closed loop method is easily cleaned. It can also be used for a series of successive purges on a sample. The ratio of the area of a peak to its area on the previous purge, purge ratio (PR), can be used to confirm the identity of a peak by comparison to the PR of a standard. Furthermore, a constant PR of a series of purges can be used to demonstrate the absence of underlying peaks. Successive peaks can also reveal the correct retention time of a less volatile component. For these reasons, it is felt the purge-closed loop method can be an effective, reliable technique for routine sample analyses of volatile organics.

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Table 2. Reproducibility study and recovery efficiency

Compounds	Prepared Distilled Water (ug/1)				Mean ± Standard Deviation	Relative Standard Deviation (%)	Theoretical Concentration (ug/1)	Recovery Efficiency (%)
	I	II	III	IV				
1,1-Dichloroethylene	4.65	4.96	4.49	4.07	4.52 ± 0.37	8.1	5.77	79
Trans 1,2-Dichloroethylene	61.5	56.4	56.3	54.0	57.0 ± 3.21	5.6	69.8	82
Trichloroethylene	1.10	0.90	0.98	0.96	0.99 ± .08	8.0	0.952	104
Vinyl Chloride	79.1	79.1	78.9	81.7	79.6 ± 1.36	1.7	76.2	104

Table 3. Minimum detectable concentration

Compound	Purge and Closed Loop (ug/1) (20 ml sample)
Trichloroethylene	0.2
1,1-Dichloroethylene	0.2
Trans 1,2-Dichloroethylene	4.0
Vinyl Chloride	1.0

Table 4. Fortification study

Compounds	Concentration (ug/1) Fresh Canal Water	Concentration (ug/1) Contaminated Ground Water	Concentration (ug/1) Estuarine River Water	Fortification Level (ng)	Recovery Efficiency (%) Fresh Canal Water	Recovery Efficiency (%) Contaminated Ground Water	Recovery Efficiency (%) Estuarine River Water
Trichloroethylene	45.8 ± 0.6	8091 ± 235	5.04 ± 0.11	8.8	905 ± 53	82 ± 5.4	87 ± 8.2
1,1-Dichloroethylene	0.88 ± 0.04	56 ± 5	< 0.2	60	81 ± 2.4	96 ± 2.6	96 ± 2.9
Trans 1,2-Dichloroethylene	23.7 ± 0.97	2646 ± 123	< 4.0	742	89 ± 5.4	106 ± 9.1	103 ± 7.1
Vinyl Chloride	< 1.0	525 ± 23	< 1.0	1524	94 ± 7.5	84 ± 5.3	92 ± 4.5

Table 5. Comparison of purge-closed loop and purge-trap methods

Sample Number	Method	Concentration (ug/1) Trichloroethylene	Concentration (ug/1) 1,1-Dichloroethylene	Concentration (ug/1) 1,2-Dichloroethylene	Concentration (ug/1) Vinyl Chloride
WELL #15	Purge-Closed Loop	304 ± 41	2080 ± 80	98.6 ± 1.4	128 ± 0.0
	Purge-trap	325 ± 6	2280 ± 250	115 ± 8	145 ± 40
Contaminated Well Site	Purge-Closed Loop	6090 ± 70	1760 ± 40	48.2 ± 3.3	725 ± 0.0
	Purge-trap	6540 ± 30	1740 ± 100	48.8 ± 6.1	766 ± 39

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