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Determination of Vinyl Chloride in Water by Headspace Analysis with a Photoionization Detector

Vincent B. Stein and Rajinder S. Narang

Toxicology Institute, Division of Laboratories and Research, New York State Department of Health, Albany NY 12201

The three methods most commonly used for analyzing vinyl chloride (CH_2=CHCl; VC) in water are the purge and trap technique, direct aqueous injection by gas chromatography (GC), and headspace GC analysis. DRESSMAN and McFARRAN (1977), RIVERA et. al. (1977) and NARANG and BUSH (1980) used the purge and trap technique, FUJII (1977) used direct aqueous injection by GC while STEICKEN (1976) and SQUIRRELL and THAIN (1978) utilized headspace analysis by GC. The purge and trap technique obtains high recoveries, but the glassware is expensive and the method is not suited to field sampling. For direct aqueous injection a diglycerol pre-column is used to strip water from the volatiles, and a mass spectrometer is required as a detector. This method needs further development for routine use in GC analysis of VC. SQUIRRELL and THAIN (1978) and WILLIAMS (1976) used the established procedure of headspace analysis of VC with a flame ionization detector (FID) having typical detection limits of 1-5 ng/mL. Our purpose was to develop a method which could be utilized for field sampling, did not involve transferring the sample, and had greater sensitivity (<1 ng/mL).

EXPERIMENTAL

Apparatus. The analytical system consisted of a Hewlett Packard Model 7600A gas chromatograph equipped with a Model P152-02 photoionization detector (PID) fitted with a 10.2 eV lamp (HNU Systems, Newton, MA). A 90-cm X 2-mm glass column packed with Chromosorb 104 was used. The chromatograms were recorded with a Hewlett Packard Model 3385A automation system. The GC conditions were: detector, 200°C; oven, 90°C; and carrier gas (He), 20 mL/min.

A Tracor Model 560 gas chromatograph equipped with a Hall Model 700A detector and held at 300°C was also used. For flame ionization detection and electron capture detection (at 280°C) a Hewlett Packard Model 5840 gas chromatograph equipped with a Hewlett Packard Model 5840A automation system was used. Gas chromatographic conditions were as described above for the PID.

Reagents and Standards. Only capped serum bottles with volumes of 160 ± 0.5 mL were used in the analysis. Each sample was 100 mL of water. VC gas (Union Carbide, Linde Division, Somerset, NJ) was used to prepare standards. Methanol, which contained a

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large number of interfering peaks, was distilled through heated charcoal for use with the PID. VC gas (0.72 mL) in a 1.0-mL gastight syringe was injected into 10 mL of methanol, weighed before and after the injection. This solution was used to make the appropriate standard dilutions (10, 1, or 0.1 µg/mL) for fortifications. All standards were stored in a freezer or kept on ice when not being used. Fortified solutions of 1-10 µg VC/L of water were prepared by injecting the required amounts of methanolic standards into water (100 mL) in 160-mL serum bottles, each fitted with a Hycar septum.

Equilibration and Time Study. The headspace in representative fortified 100-mL water samples was analyzed at various intervals to determine the minimum equilibration time needed for analysis. The headspace was 1 mL in samples with 10 ng VC/mL and 5 mL in samples with 1 ng VC/mL. A separate set of the 160-mL bottles were filled with 100 mL of water each and fortified to give concentrations of 1 and 10 ng/mL. These samples were analyzed daily to determine if any losses of VC had occurred.

Sample Preparation. Samples (100 mL) in septum-sealed bottles were placed in a covered water bath held at 56 ± 1°C and allowed to equilibrate for at least 2 h. Headspace (1-10 mL) was then withdrawn and injected into the GC.

Loss of VC on Transfer and Storage. Water (1 L) in a volumetric flask sealed with a rubber septum was fortified with 100 µg VC/mL methanolic standard. Then 100-mL aliquots of this solution were transferred to glass sampling bottles, sealed, and analyzed as described above.

Comparison of Detectors. The PID, FID, Hall, and electron-capture (EC) detectors were compared for their sensitivities and linearity in analysis of VC.

Calibration. Peak heights were used for quantitation, since sharp, reproducible peaks were obtained by headspace analysis. Calibration for experimental studies was performed by comparing the peak heights of headspace samples with that of a single fortification of equal concentration. For samples, a calibration curve was created from a series of at least four standards. All injections were made in duplicate.

Environmental Samples. Thirty-three wellwater samples from two wells were analyzed for VC by the above procedure. Triplicate samples were taken in septum-sealed bottles and single samples in 1-L Mason jars at three different time intervals.

RESULTS AND DISCUSSION

Choice of Detectors. Since the PID is very sensitive to unsaturated organics and the Hall detector is sensitive to chlorinated compounds, both detectors should be sensitive to VC. Comparison of linear ranges, sensitivities and precisions (Table 1) showed the PID to be the more suitable. The FID was 50 times less sensitive than the PID, and the least sensitive of the four detectors tested. With the EC detector the air peak interfered with the VC peak. The Hall detector became unstable when volumes >2 mL were injected; neither the FID or PID was affected by volumes up to 10 mL.

Table 1. Comparison of Detectors for Analysis of Vinyl Chloride.

	PID	FID	Hall[a]
Linearity	0.1-10 µg/L	1-10 µg/L	10-10 µg/L
Sensitivity	0.01 µg/L (5 mL)	0.5 µg/L (5 mL)	5.0 µg/L (0.5 µL)
Precision	17.7% (0.1 µg/L)	9.4% (20 µg/L)	6.6% (20 µg/L)

[a] Cannot be used for injection of >2-mL volumes due to instability of detector.

EC detector was not suitable for headspace analysis, due to large response of air peak, which interferes with vinyl chloride.

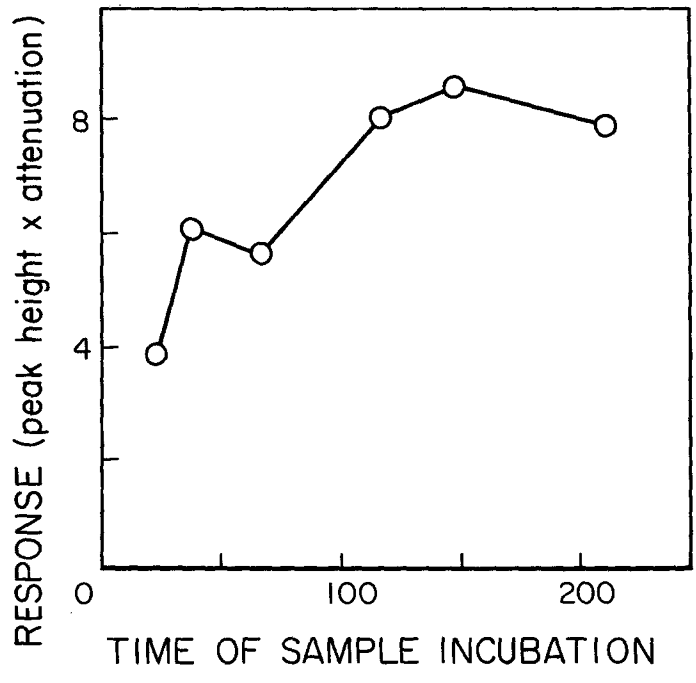

Figure 1. Response (peak height x attenuation) vs. time of sample incubation. Bottles (capacity 160 mL) containing 100 mL of vinyl chloride solution at 1 ng/mL were incubated at 56°C. At selected intervals 5-mL headspace samples were withdrawn and subjected to gas chromatographic analysis as described in the text.

Time and Equilibration Study. Under these experimental conditions approximately 2 h were required (Fig. 1) for equilibration of VC. Water samples (100 mL) fortified with VC (1 and 10 ng/mL) were stored at room temperature for up to 9 days with no losses. Standard dilutions of 10, 1 and 0.1 µg VC/mL of methanol were stored at 5°C for up to 1 month without loss.

Loss of VC on Transfer. About 30% of VC appears to be lost on transfer from a 1-L volumetric flask to glass sampling bottles. Thus, losses occur when VC solutions are exposed to the atmosphere. Such losses were demonstrated when VC concentrations in samples collected in sealed septum bottles were compared with those of samples transferred from 2-L Mason jars (Table 2).

Table 2. Effect of Storage Container on Concentrations of Vinyl Chloride in Wellwater

Well	Hours post-collection	Concentration (ng/mL) Septum-sealed serum bottles	Concentration (ng/mL) Sealed jars	% Difference
5	72	15	11	28
6	0	< 1	--	--
	0.25	1.1	< 1	--
	3	2.6	1.6	38
8	0	10	--	--
	72	10	6.7	33
14	0	81	--	--
	0.25[a]	29	10	65
	3	10	6.5	35

[a] Concentrations may be unreliable for comparison because values fell off rapidly with time.

Linear Range, Precision, and Detection Limits. For 2- or 5-mL headspace samples at VC concentrations from 0.1 to 10 ng/mL, the correlation coefficient is 0.999 ($n = 5$). Precision ($n = 10$) was determined to be 3.7% at 1 ng/mL and 17.7% at 0.1 ng/mL. By HARMAN's (1971) definition of detection limit as the amount of sample which gives a response equal to twice the background level, the detection limit of VC by GLC with a PID was 0.05 ng. For this determination triplicate 5-mL samples of aqueous solution of VC (0.01 ng/mL) were injected into the gas chromatograph.

Environmental Sample Analysis. The VC concentration in 27 of the 33 wellwater samples in septum-sealed serum bottles ranged from <1.0 to 81 ng/mL (Table 2). In well 6 the concentration of VC increased with time; in well 8, it remained constant; and in well 14 it decreased considerably.

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