

THE MIGRATION OF VINYL CHLORIDE MONOMER FROM PVC PIPE INTO WATER

J.D. Banzer

Diamond Shamrock Corporation
T.R. Evans Research Center
P.O. Box 348
Painesville, Ohio 44077

Introduction

Vinyl chloride monomer (VCM) has been shown to be carcinogenic by inhalation.¹ There is unpublished data by Maltoni and coworkers which indicate that, at high dietary levels, VCM is also carcinogenic by ingestion. Because of this, the Food and Drug Administration moved to revoke the prior sanctioned status of certain PVC products used in food contact applications. FDA has defined potable water as a fooditem and indicated² that it would revoke the prior sanction of PVC potable water pipe unless industry can supply data which demonstrates that "...there is little likelihood of VCM becoming a component of food."

In order to satisfy the above, FDA required an experimental study to determine the relationship between residual vinyl chloride monomer (RVCM) in potable water pipe and the amount of vinyl chloride monomer (VCM) that may be present in water in such pipe under static conditions. Laboratory experiments were conducted to relate the residual VCM to the amount of VCM extracted by water. A variety of pipe samples were prepared containing a wide range of residual VCM levels. The extraction studies were performed at several different times to determine the effect of the age of the pipe on the amount of VCM extracted. Experiments were carried out under both static and flowing conditions. The samples were analyzed using both headspace and vapor extraction techniques.

Experimental

Two procedures were developed for the analysis of VCM in water. They are referred to as the vapor extraction method and the headspace method.

Vapor Extraction Method

The analysis is based on sparging of VCM by nitrogen gas out of water onto activated charcoal. The VCM is desorbed from the charcoal with carbon disulfide and analyzed by gas chromatography. The solvent desorption technique was chosen over thermal elution since solvent desorption allows several analyses of the same sample vs. a "one shot" analysis by the thermal elution technique.

Three liters of water are placed in a 5l 3-neck flask. A nitrogen bubbler is placed in one neck with the end below the surface of the water. The second neck holds a reflux condenser with an adsorption trap containing 5g of activated charcoal at the condenser outlet. The third neck is closed with a ground glass stopper. Nitrogen is bubbled through the water at a flow of 1.4 l/min. while the water is stirred with a magnetic stirrer. After 1 hr. the charcoal is removed and prepared for analysis. The charcoal is placed in a sealed hypo vial, and the sample chilled in dry ice. 10.0 ml of carbon disulfide are added and the vial is shaken for 30 minutes.

A 2.0 μ l aliquot of the carbon disulfide is taken from the sealed hypo vial and injected into the gas chromatograph. The area counts of the VCM peak are recorded.

Samples were analyzed on a Hewlett-Packard 5830A gas chromatograph equipped with a flame ionization detector. The column was 3 feet x 1/8 inch stainless steel packed with 80/100 mesh Porapak Q.

Instrument Conditions: Column temperature 115°C for 2 minutes, program at 30°C/min. to 145°C, hold for 2 minutes; injection temperature 250°C; FID temperature 275°C; helium flowrate 36 ml/min.

Solutions for spiking water were prepared by filling 6 ml Hypo-Vials (Pierce-Chemical) liquid full with methanol and then sealing them with a Hycar septum and crimp cap. The vial was frozen in dry ice for 15 min. A known volume of pure (99+) vinyl chloride monomer (Matheson) was injected into the chilled methanol. The vial was then shaken for 30 min. and warmed to room temperature. Methanol was used for spiking since it is water soluble. GC standards were prepared in the same manner except that carbon disulfide was used as a solvent.

Solutions of distilled water were spiked at levels from 0.001 mg/kg to 0.1 mg/kg VCM. The percent recovery was determined in each case and is given in Table I. The average recovery was 94.2%. A calibration curve is given in Figure 1; demonstrating linearity over a hundredfold range in concentration. Based on the 3 σ sample, a consistent detection limit of 0.002 mg/kg is obtained.

Headspace Method

The analysis is based upon analyzing VCM in the headspace above a water solution contained in a sealed system using gas chromatography.

Samples are prepared by pipetting 15 ml of water into a 22 ml Hypo-Vial (Pierce-Chemical) which is then sealed using a Hycar septum and aluminum crimp cap. The samples are placed on a wrist action shaker for 30 minutes.

Samples are analyzed by injecting a 1.0 ml volume of air into the headspace; then a 1 ml air sample is withdrawn and injected into the gas chromatograph. The area counts of the VCM peak are recorded. Instrument conditions are identical to the vapor extraction method.

The percentage of VCM above the water as a function of VCM concentration in water was determined for spiked deionized water. The results are given in Table II. The results indicate the percent of VCM distributed in the headspace is 21.5. A calibration curve constructed from the data is given in Figure 2. The data indicate that good linearity is obtained over a range of .001 to 0.1 mg/kg.

Extraction Experiments

One inch schedule 40 pipe (1" ID) was selected as the pipe size used for all tests because it has the highest surface to volume ratio of any common size PVC pipe. Twenty-five foot test samples were used in order to contain a volume of 3.0 l of water. This is the minimum volume required for the vapor extraction analytical technique to permit a detection limit of 0.002 mg/kg. Shorter lengths of pipe were used for long-term sampling because of storage problems associated with 25' sections. When shorter lengths were used, only headspace analyses were performed.

Deionized water was used for all studies in order to eliminate any potential matrix effects from contaminants in tap water.

Several conversations were held with water system personnel to determine typical residence time for water systems. No absolute values were offered, but most felt that 3-3 days was a good average value. The bulk of our data was run for either 48 or 72 hrs. Additional data was collected at 24 hr. and, in some case, as long as 180 days, to provide as complete a range of time intervals as possible.

The ends of all pipe sections were terminated with 1" steel caps which were tapped to receive small ball valves. One end of

the ball valve was terminated with a 1/4" Swagelok fitting. Pipes were filled by elevating one end, drawing a vacuum on the pipe and sucking water into the other end through a piece of 1/4" Teflon tubing. Care was taken to displace all the air with water. When the pipe was liquid full, the ball valves were closed, and the pipe section was stored at room temperature for the duration of the test.

For pipe samples exposed under flowing conditions, the ends of the pipe were connected to a leak tight centrifugal pump (Cole-Parmer "Micro Pump"). Water was circulated through the pipe for the duration of the test interval at a flowrate of 0.74 l/min.

At the conclusion of the test interval, the pipe was pressurized with 4 psi prepurified nitrogen through the valve at one end. The other end was fitted with a septum. Headspace samples were withdrawn using a 20 ml glass syringe fitted with a 20 gauge needle. Three 15 ml samples were taken for headspace analysis. Each sample was transferred to a Hypo-Vial which was immediately sealed.

The remaining water was transferred under nitrogen pressure to the vapor extraction flask through 1/4" Teflon (duPont) tubing. The entire transfer system was closed to the atmosphere so that any effluent gases passed through the charcoal trap. Nitrogen for sparging the water was passed through the pipe first, then into the flask to flush out any entrapped pockets of VCM.

Blank determinations were run on 3.0 l of water to insure that the water and all reagents were free of VCM. No VCM (<0.002 mg/kg) was detected in any blank.

Results and Discussion

Comparison of Analytical Methods:

Accuracy data for the headspace method is shown in Table I and for the vapor extraction method in Table II. Both methods have been found to give comparable results on laboratory samples. A comparison of results is given in Table III.

The precision of the method was determined at both the high and low ends of the calibration range. For the headspace method, the coefficient of variation was 16.9% at the low end and 7.8% at the high end. For the vapor extraction method, the values were 2.3% and 3.0%, respectively.

Although both methods give detection limits of 0.001 mg/kg on spiked recovery samples, there was some day to day variation in sensitivity when the water from pipe samples was analyzed. Consequently, 0.002 mg/kg was adopted as the detection limit since this value could be consistently obtained on all samples.

Results of Extraction Experiments

Results of all extraction studies are given in Table IV. Residual vinyl chloride monomer (RVCM) levels were determined

using previously documented procedures.³ The age of the pipe in days at the start of the extraction period is given in addition to the VCM level in the water.

For all test results, the following two significant conclusions are drawn:

1. A decrease in the residual VCM content of the pipe reduces the VCM level in water.
2. A decrease in the extraction period reduces the VCM level in water.

The most interesting results of these studies are the VCM levels in water for the pipes containing <1.0 and 2.5 mg/kg RVCM. In all cases, the VCM levels in water are at or below 0.002 mg/kg. This is true even for fresh pipe (17 and 19 days old) and long extraction times (150 and 180 days). The low RVCM pipe currently being produced will probably result in no detectable VCM in water using currently accepted analytical methods.

A comparison of the results for the static and pumped runs does not show any consistent pattern. For the 2-day data, there was a three fold increase in VCM extracted when the test mode was changed from static to pumped. However, a repeated recycling from static to pumped showed essentially consistent static data and a decrease in the VCM extracted for the pumped data. The 3-day data indicates similar results for both static and pumped test modes. Considering all the static versus pumped data, it appears that in the majority of cases, there is a negligible difference between the two modes of testing.

Acknowledgements

The author wishes to thank Neuss Griffiths for the RVCM analyses and Gil Diets, Dennis Cocco and Wes McCoy for their assistance in extruding the pipe and fabricating the test loops.

¹ P. L. Viola, A. Biogotti, A. Caputo, Cancer Research, 31, 516-522 (1971)

² 40 Federal Register 40529, September 3, 1975

³ R. R. Griffiths, "Residual Vinyl Chloride Monomer in PVC Products," MOM-1-10A-0 and MOM-1-30C-0 (Diamond Shamrock Corp. Plastics Div. Test Procedure).

TABLE I

Recovery of VCM from Water Using Vapor Extracting Method

Spike Level (mg/kg)	% Recovery*
0.001	99
0.005	100
0.010	105
0.050	72
0.100	95
Average	94.2

*Average of duplicate determinations.

23884002

TABLE II

Recovery of VCM from Spiked Samples
using Headspace Method

Spike Level (mg/kg)	% Recovered*
0.001	24.4
0.005	21.4
0.010	22.5
0.025	21.0
0.050	21.9
0.075	18.5
0.100	21.1
Average	21.5

*Average of duplicate determinations.

TABLE III

Comparison of Headspace and Vapor Extraction
Methods of Analysis for VCM in Water

Sample Number	Headspace (Concentrations in mg/kg)	Vapor Extraction
1	0.002	0.002
2	0.006	0.007
3	0.006	0.006
4	0.003	0.002
5	0.009	0.006
6	0.036	0.032

TABLE IV

Extraction of VCM from PVC Pipe by Water
Residual VCM in Pipe
(mg/kg)

Length of Extraction (days)	Static or Pumped	<1	2.5	14.8	28	34.8	179	283
1	Static		<0.002 86		<0.002 86		0.007 111	0.021 72
2	Static	<0.002 17		0.003 6		0.007 6		
2	Static	<0.002 19		0.003 8		0.004 8		
2	Pumped	<0.002 38		0.006 27		0.013 29		
2	Static			0.002 57		0.007 55		
2	Pumped			0.002 71		0.006 57		
3	Static		<0.002 99		0.002 95		0.013 127	0.041 77
3	Pumped		<0.002 93		0.002 92		0.030 124	0.038 84
150			<0.002 116		0.058 116			
180			<0.002 116		0.062 116			

Samples extracted for 1, 2, and 3 days were 25' in length.

Samples extracted for 150 and 180 days were 1' in length.

Concentration units for VCM in water, mg/kg, temperature 72°F, pipe 1" ID.

Smaller figures = age of pipe from time of manufacture to start of extraction in days.

23694004

Fig. 1 Integrator Response vs. Concentration of
VCM in Water Vapor Extraction Method

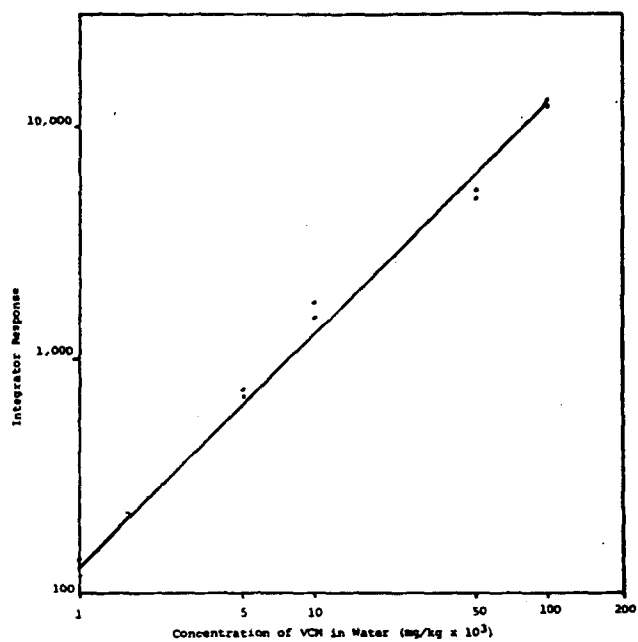


Fig. 2 Integrator Response vs. VCM Concentration
Headspace Method

