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Water Technology

Determination of Vinyl Chloride Migration From Polyvinyl Chloride Pipe Into Water

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Gas-chromatograph determinations of possible vinyl chloride leaching from polyvinyl chloride pipe into potable water systems alleviate fears of harmful concentrations in the systems tested.

Polyvinyl chloride (PVC) pipe has been in use to varying degrees in some water-distribution systems in the US for the past sixteen years. Recently concern has been raised that unpolymerized vinyl chloride (VC) in the pipe can migrate into the water flowing through it. To investigate this theory, existing methodology[1,2] for vinyl chloride determination was modified[1] to permit the detection and measurement of this material at very low concentrations. EPA's Water Supply Res. Div. then studied five water distribution systems that use PVC pipes. Determinations generally were made using gas chromatography with a microcoulometric titration detector (GC/MC)—the most specific detector available. The data are not unequivocal, and although results should be accepted with caution, the authors consider them to have a high degree of validity.

Experimental

Sampling. Samples were collected in serum reaction bottles, which were then sealed with PTFE-lined rubber septa held in place by crimped aluminum caps. The bottles were filled to overflowing, and the septa were slid over the top to preclude any air space at the time of sealing.

Five water-supply distribution systems (Table 1) incorporating PVC pipe were sampled. Samples were taken and analyzed in triplicate both before and after entering the pipe. Samples were shipped on ice and kept refrigerated in the laboratory until warmed to room temperature immediately before being analyzed.

Sample concentration (purging). Samples were purged in the sampling container using the procedure and apparatus described by Dressman et al.[3] Silica gel, 35/60 mesh, was used as the trap adsorbent.

Gas chromatography (GC). Qualitative accuracy was achieved through the innovative application of two types of column material, with the express aim of eliminating interference from cyanogen chloride. A 180- × 4-mm-ID glass column was packed for its first third with Chromosorb 101 and the last two thirds with Chromosorb 102. The column was operated in a program mode. The initial temperature was set at 50 C and programmed to rise 10 C/min to 160 C. Nitrogen carrier flow was 80 ml/min, and the desorb (inlet) temperature was 150 C.

A microcoulometric titration system* was used as the GC detection system. Operating parameters were: reaction furnace, 850 C; outlet furnace, 850 C; and transfer line, 240 C. The humidified oxygen-reactant gas flow rate was 40 ml/min. A range ohm setting of 600 was used to produce a 65 per cent of full-scale response for 32 ng of vinyl chloride.

Standard solutions. The standard solutions of vinyl chloride used for gas chromatographic analysis and dosing controls were dilutions of a stock solution prepared by bubbling vinyl chloride into a tared amount of acetone as described by Bellar et al.[1] The actual concentration of vinyl chloride in the stock solution was determined by gas chromatographic analysis using a reaction coulometer[4] as a quantitative GC detector.[3]

Identification and quantification. Identifications on each sample were accomplished by comparing the retention time of suspect peaks with the appropriate standard.

Quantification was accomplished by comparing the area of the sample peak with a measured amount of the vinyl chloride standard using height times width at half-height measurements. The standards were injected directly onto the GC column, which was then programmed as for sample analysis. Results obtained on the analysis of samples by the bottle-purging procedure were then divided by a factor of 0.52 to correct for incomplete recovery during purging.[3]

Five field sites were selected to determine the extent, if any, to which vinyl chloride might contaminate drinking water supplies. The sites were selected as being representative of extremes in climatic conditions and because data were available concerning the age, length, and size of the pipes used.

The results and other pertinent data are listed in Table 1. Very low concentrations of vinyl chloride were detected in four of the five water supplies studied. In all but one instance (Georgetown, Tex.) values were too low to be verified by GC—mass spectrometry. In any event at the particular time of analysis the equipment was not available. As with any gas-chromatography data, caution must be exercised in interpreting the results. Without mass-spectrometric verification the results lose a degree of confidence. The method is designed, however, to overcome all known interferences (i.e., cyanogen chloride, acetaldehyde) and to retain a high degree of validity owing to the highly specific halogen detector used.

The initial values obtained at Coolidge, Ariz., probably can be discounted because VC was detected both before and after the PVC pipe run. This suggests that an outside source had contaminated either the system or the sample itself. No VC could be detected a month later. By way of contrast, the concentration of VC (1.4 μg/l) detected in the first sampling of the Jonah water supply in Georgetown, Tex., was essentially the same (1.2 μg/l) on resample eighteen days later and

*Model S-400 equipped with T-300-S silver halide titration cell and C-200 microcoulometer, Dohrmann/Envirotech, Santa Clara, Calif.

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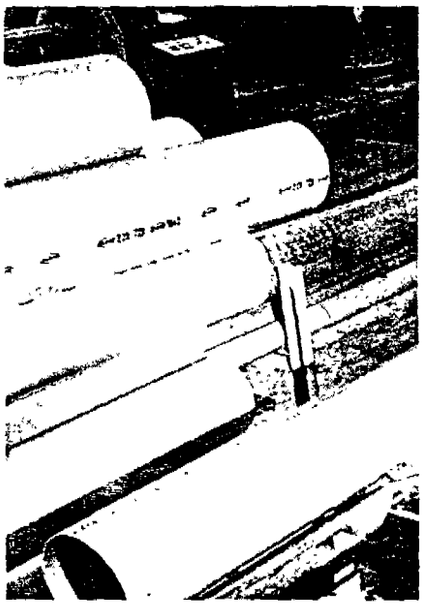
TABLE 1
PVC Pipe Systems Studied

Parameter	Water Utility				
	Coolidge, Ariz.	Georgetown, Tex.	Pioneer, Calif.	Rosenburg, Ore	Salados, Tex.
Year pipe manufactured	~1964	1975	~1966	1966–67 (1 39 km 1971)	~1968
Pipe					
Length—km	1.6 1 1	4.8 15	7.6 3 7	4 94 0 68	0 18 0 48 0.18
Length—mi	1.0 0.69	3 0 9 5	4 7 2 3	3.07 0 42	0 11 0 30 0.11
Size—in	3 2	6 & 8 4 & 5	6 4	3 2	8 6 2
Total wall area—m²	560	6 200	4 800	1 300	370
Total wall area—sq ft	6 000	66 000	52 000	14 000	4000
Water temperature—C	~20	22–25	22–24	14	21–23
Sampling point					
Source	×			×	
Well head		×			×
Treatment plant			×		
End of pipe	×	×	×	×	×
Sampling date	8/22/75	10/10/75	9/16 75	10/17/75	10/10/75
VC concentration*—μg/l	0.3† 0.3†	‡ 1.4	‡ 0.06	‡ 0 03	– ‡ ‡
Sampling date	9/22/75	10/28/75	–	–	10/28/75
VC concentration*—μg/l	‡ ‡	‡ 1.2	–	–	– ‡ ‡

*Average of triplicate analyses, corrected for recovery efficiency
†Probably spurious
‡None detected at a detection limit of 0 03 μg/l



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occurred only in water sampled at the end of the pipe.

VC was detected in three of the five systems investigated. Although all of the concentrations were far below the minimum levels that have been associated with a carcinogenic response in experimental animals,* studies are still ongoing. Because of the latency of the carcinogenic response, the results from these investigations will not be available for some time.

Interpretation of the data is difficult because the residual VC content of the pipes is not known. Within this limitation, however, the newest, longest system (Georgetown) had the highest VC concentration, and the next longest (Pioneer, Calif.) had the next highest concentration. Water temperature did not seem to influence the VC concentration. Finally, traces of VC at the microgram per liter level were still present in the Pioneer and Rosenburg, Ore., systems approximately nine years after they were installed.

The concentration of VC in the newest, longest system tested (Georgetown) was low compared with the level deemed hazardous to animals. Manufacturers claim that pipe made for water use within the past year has a lower free vinyl chloride content than pipe manufactured earlier. Large factors of safety therefore should be inherent in the use of the pipe.

*To date, experiments that have been carried out demonstrate that the minimum carcinogenic dose by chronic inhalation is 50 mg/l and by ingestion is 16 65 mg/kg/day. Additional investigations are being conducted to determine the incidence and type of liver cancer at lower dose levels by ingestion, including 3.33, 1.0, 0.3, and 0 03 mg/kg/day. The carcinogenic risk to man has been estimated by the Natl Academy of Sciences as 5 1 × 10 at a concentration of 1 μg/l, considering a consumption of 2 l/day of water

Summary

A field study of the VC concentration in the water of five distribution systems utilizing PVC pipe showed concentrations from 0.03 μg/l to 1.4 μg/l with the lowest concentration persisting in a system nine years old and the highest concentration present in the newest system. These levels are well below those that thus far have been associated with adverse effects in experimental animals, and these levels should decline as lower residual monomer pipe is put into use.

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