

Vinyl Chloride Tied to Workers' Skin Problems

International Medical News Service
Vinyl chloride, the industrial monomer that has been implicated in the etiology of angiosarcoma in plastics workers, can also cause skin problems including minor irritation and acro-osteolysis, Dr. Marcus Key told SKIN & ALLERGY NEWS.

Irritation can be caused by the vinyl chloride evaporating from the skin, resulting in a small local freeze.

Acro-osteolysis, which has been found mainly in workers who clean the reaction kettles in which vinyl chloride is polymerized, may be a result of both the mechanical trauma of the cleaning and exposure to vinyl chloride, said Dr. Key, former director of the National Institute of Occupational Safety and Health.

Dr. Harold Magnuson, one of the first students of the relationship between vinyl chloride and acro-osteolysis, said in an interview with this newspaper that the precise agent causing the condition is not known. Vinyl chloride is strongly implicated, but one of several other reaction products that may remain in the tank could cause acro-osteolysis.

The incidence of X-ray abnormalities caused by acro-osteolysis was almost 12% in a group of 5,011 men who worked in plants that manufacture polyvinyl chloride, while a control group of 2,407 men had an incidence of only 3.16% for such

X-ray changes, said Dr. Magnuson, of the University of Michigan School of Public Health, Ann Arbor.

A nodular thickening of the hands and the forehead and blanching of the fingers associated with Raynaud's phenomenon were the dermal manifestations found in patients with acro-osteolysis who worked at the B. F. Goodrich Company plant in Louisville, Ky., Dr. John L. Creech Jr., who has seen most of these patients, told SKIN & ALLERGY NEWS.

Dr. V. K. Rowe, of the Dow Chemical Company, Midland, Mich., told this newspaper that he feels that under present conditions workers in vinyl chloride plants do not face a very great hazard of either angiosarcoma or skin disease.

The observations that are now being made reflect the high levels of exposure

these workers were subjected to previously. Exposure levels are now much lower in most plants making polyvinyl chloride, he said.

There have been no significant vinyl chloride related health problems at the Dow plants, where operations have been maintained at relatively low levels of exposure. Apparently, the protective measures already in effect have been adequate to prevent angiosarcoma, acro-osteolysis, and scleroderma, he said.

Dr. Creech, who was the first man to recognize the association of the liver tumors in vinyl chloride workers agreed that there is probably little danger for present workers.

Both the acro-osteolysis and the angiosarcomas were found mainly in workers who cleaned out the reaction kettles, where the levels of vinyl chloride were in the range of hundreds of thousands of parts per million. Workers in the same job may now face no exposure whatsoever, because they work with a self-contained respiratory system that eliminates all atmospheric particles of vinyl chloride, he said.

None of the patients with angiosarcomas had skin diseases that could be related to their vinyl monomer exposure. Of eight cases of acro-osteolysis observed by Dr. Creech, no patients had any detectable liver abnormalities.

Because of the observed carcinogenic activity of vinyl chloride and the association between the plastic and various skin disorders, it seemed likely that an increased incidence of skin tumors might be found in exposed workers. However, no such increase was found and there were no skin tumors in any of the patients with angiosarcomas, liver changes, or splenomegaly that could be attributed to vinyl chloride, Dr. Creech said.



Dr. Rowe

INDUSTRIAL CHEMICALS

Gas-Liquid Chromatographic Determination of Vinyl Chloride in Alcoholic Beverages, Vegetable Oils, and Vinegars

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Vinyl chloride in foods is determined by gas-liquid chromatography either by direct injection of vinegars and alcoholic beverages or by headspace analysis of vegetable oils. The lower limit of detection is 10–15 ng/ml for direct injection and 5–10 ppb for headspace analysis. Confirmation by gas chromatography-mass spectrometry, single ion monitoring at m/e 62, is possible at 50 ppb for either method. The levels of vinyl chloride found in foods packaged in polyvinyl chloride bottles were 0.0–1.6 $\mu\text{g/ml}$ for alcoholic beverages, 0.0–8.1 $\mu\text{g/ml}$ for vinegars, and 0.3–3.3 ppm for peanut oil.

The detection of 10–20 ppm vinyl chloride in alcoholic beverages led to a proposed ban, in the United States, on the use of polyvinyl chloride (PVC) materials in contact with alcoholic foods; however, this ban did not extend to other foods ((1974) *Fed. Regist.* 38(95), 12031; 38(134), 18684). In order to assess the full extent of this problem, we have developed methodology for and surveyed foods available in Canada which are packaged in PVC bottles.

Experimental

Reagents and Apparatus

Use distilled-in-glass solvents and verify absence of vinyl chloride by gas-liquid chromatography (GLC).

- Gas cylinder of vinyl chloride.
- Gas tight syringe.—2.5 or 5.0 ml.
- Reactivials®.—25 ml, equipped with screw caps and Teflon-faced septums (Pierce Chemical Co., Rockford, IL 61105).
- Constant temperature water bath.—Should maintain temperature to within $\pm 1^\circ\text{C}$.
- Gas chromatograph.—Varian-Aerograph Model 2100, with flame ionization detector and 1 mv pen recorder. Operating conditions: temperatures ($^\circ\text{C}$)—detector 270, injection port 220, column ambient until vinyl chloride peak has been recorded, then raised to ca 150 until solvent has eluted from column: $6' \times \frac{1}{4}"$ od glass columns

packed as follows: column A, 5% OV-101 on 100–120 mesh Chromosorb W (HP); column B, 5% OV-210 on 100–120 mesh Chromosorb W (HP); column C, 10% Apiezon M on 60–80 mesh Chromosorb W (acid-washed). Column D, $6' \times 2$ mm id glass column packed with 80–100 mesh Porapak Q, was operated at 130°C . In all cases carrier gas was nitrogen and flow rate was adjusted so that vinyl chloride eluted at ca 80 sec.

(f) Gas chromatograph-mass spectrometer.—Hitachi Perkin-Elmer RMU-1 mass spectrometer coupled with Perkin-Elmer Model 900 gas chromatograph fitted with flame ionization detectors. Operating conditions: temperatures ($^\circ\text{C}$)—detector 270, injection port 240, column ambient until vinyl chloride peak has been recorded, then raised to ca 150 until solvent has eluted from column; carrier gas helium 10 ml/min; $6' \times \frac{1}{4}"$ stainless steel column packed as follows: column E, 3% XE-60; column F, 3% OV-101; both on 100–120 mesh Chromosorb W (HP).

Analysis

Vinegars and alcoholic beverages.—Invert bottle several times to mix contents, remove cap, take 5 μl aliquot, and recap bottle immediately. Inject aliquot onto column A and if peak is obtained with same retention time as vinyl chloride verify by injecting another aliquot onto column B or C. Quantify by comparison of peak height or peak area with standard solutions of vinyl chloride. Confirm by GLC-mass spectrometry (MS), column E, using single ion monitoring (m/e 62).

Vegetable oils.—Invert bottle several times to mix contents, remove cap, and quickly transfer 10 ml oil to tared 25 ml Reactivial. Seal vial and bottle as quickly as possible and determine quantity of oil transferred by weighing vial and contents. Heat flask 20 min in constant temperature water bath ($75 \pm 1^\circ\text{C}$). Take 1 ml sample of headspace vapor and analyze on column A. Verify positive samples by injecting 1 ml headspace vapor onto column B, C, or D. Confirm by GLC-MS, column E or F, using single ion monitoring (m/e 62). Quantify by comparison of peak height or peak area with control peanut oil spiked with ethanol solution of vinyl chloride.

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NOTE: $1 \mu\text{g/ml} = 1 \text{ ppm}$

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Preparation of Standard Solutions of Vinyl Chloride

(a) Weigh known volume (12 ml) of ethanol into tared septum-sealed 15 ml vial containing 2 ml mercury. Bubble vinyl chloride slowly into ethanol through syringe barrel and needle and vent vial with second syringe needle. When ca 100 mg vinyl chloride has dissolved (5-10 min) remove needles, invert vial to form mercury seal, weigh vial and contents, and determine accurate weight of added vinyl chloride. Dilute aliquots of this stock solution with ethanol to give appropriate standard solutions and confirm concentration of these standards by GLC comparison with stock solution.

(b) Prepare solutions of vinyl chloride (ca 100 mg) by bubbling vinyl chloride into known weight of ethanol (12 ml) in septum-mercury sealed vials not vented to atmosphere. (*Caution:* Avoid excess pressure buildup.) Determine accurate weight of vinyl chloride added by weight difference.

(c) Using 10 ml gas syringe, inject 20 ml (ca 55 mg) pure vinyl chloride gas into known weight of ethanol (6 ml) in septum-mercury sealed vial. Determine weight of vinyl chloride added by weight difference.

Replicate vinyl chloride stock solutions were prepared by above 3 methods. Vinyl chloride concentrations of these solutions as determined by weight difference agreed within $\pm 1\%$ with concentrations determined by GLC analysis.

Headspace volume in vials containing vinyl chloride solutions should be kept to a minimum. Ethanolic vinyl chloride solutions with headspace volume to solution volume ratio of 1:10 have ca 0.2% of the vinyl chloride in the headspace. Standard solutions of vinyl chloride must be stored in gas tight containers. Use of mercury seal coupled with septum gives both gas tight seal and ready access to solution. Ethanolic vinyl chloride solutions stored in septum-mercury sealed vials in the dark have remained stable for at least 8 weeks.

Results and Discussions

Vinegars and alcoholic beverages can be analyzed for vinyl chloride by direct injection of the sample onto the GLC column. Vinyl chloride elutes before the solvent peak (Fig. 1C, D), allowing the chromatograph to be set at maximum sensitivity and a detection limit for vinyl chloride as low as 10-15 ng/ml (3-4% full scale deflection). Positive samples are confirmed by analyses on 2 or more GLC columns of different polarity and the results on each column should agree within $\pm 10\%$. Trace interference (<25 ng/ml) was occasionally detected in blank sam-

ples when they were analyzed on the more polar column (column B), but this did not occur on the less polar columns (columns A and C). The mass spectrum of vinyl chloride (Fig. 2), as expected for a monochloro compound, shows 2 molecular ions in the ratio of ca 1:3 for the ^{37}Cl (m/e 64) and ^{35}Cl (m/e 62) vinyl chloride. GLC-MS can be used for confirmation of vinyl chloride but a full mass spectrum, distinguishable from background, could only be obtained from samples containing $>80 \mu\text{g/ml}$ vinyl chloride (ca 400 ng injected). However, with single ion monitoring at m/e 62 vinyl chloride could be confirmed at 50 ng/ml (ca 0.25 ng injected) (Fig. 3). GLC-MS, with single ion monitoring, can be used semiquantitatively and confirmation of vinyl chloride by this method should give values that agree within $\pm 10\text{--}15\%$ with the GLC determinations.

Analysis of 22 samples of the 5 types of alcoholic beverages available in Canada in PVC bottles showed levels of vinyl chloride ranging

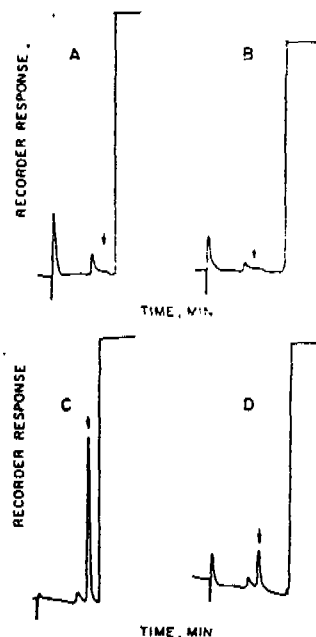


FIG. 1—Gas chromatograms (column A) of vinegars and alcoholic beverages: A, control gin; B, control apple cider vinegar; C, gin containing $0.5 \mu\text{g/ml}$ vinyl chloride, 2.5 ng vinyl chloride injected; D, apple cider vinegar containing $0.1 \mu\text{g/ml}$ vinyl chloride, 0.5 ng vinyl chloride injected. I indicates vinyl chloride peak.

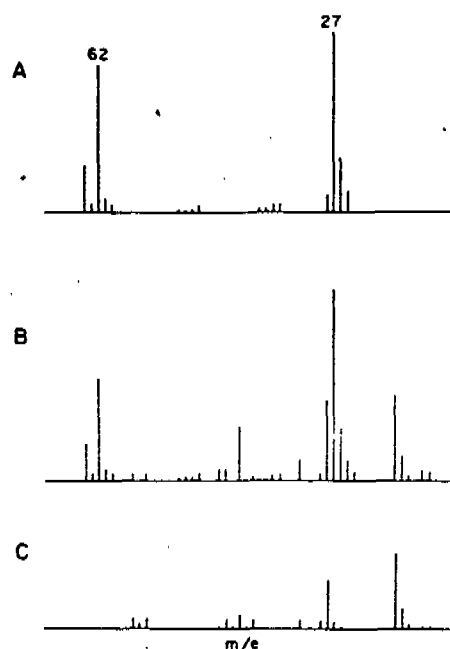


FIG. 2—GLC-MS spectra of vinyl chloride run on column E: A, vinyl chloride; B, carbon tetrachloride extract of apple cider vinegar, ca. 400 ng vinyl chloride injected; C, background spectrum immediately prior to obtaining spectrum B.

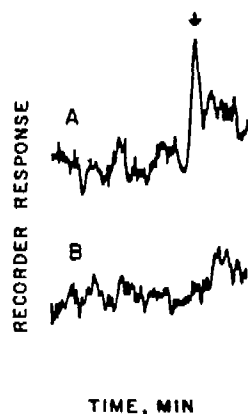


FIG. 3—GLC-MS spectra (single ion monitoring at m/e 62): A, alcoholic beverage, 0.25 ng vinyl chloride injected; B, control alcoholic beverage. $\downarrow$ indicates vinyl chloride peak.

from 0 to 1.6 $\mu\text{g}/\text{ml}$ (Table 1). Samples of similar beverages packaged in glass bottles showed no detectable vinyl chloride.

Analysis of 28 samples of vinegars packaged in PVC bottles showed levels of vinyl chloride from 0 to 8.4 $\mu\text{g}/\text{ml}$ (Table 1). Vinegars packaged in polyethylene containers showed no detectable levels of vinyl chloride. Extraction of the vinegar, in a septum-sealed bottle, with one-fortieth its volume of carbon tetrachloride gave a concentration of vinyl chloride in the carbon tetrachloride approximately 16 times that originally found in the vinegar. Those vinegars with $>5 \mu\text{g}/\text{ml}$ vinyl chloride when concentrated by this method and the carbon tetrachloride extract analyzed by GLC-MS gave mass spectra which, after subtraction of the background spectrum, were identical with that from vinyl chloride (Fig. 2).

Vinyl chloride is best determined in vegetable oils by headspace analysis. Heating the vegetable oil to 75°C gave about 18% of the vinyl chloride in the headspace; a change of $\pm 1^\circ\text{C}$ at this temperature gave a variation of $\pm 0.3\%$ in the concentration of the vinyl chloride in the

RECORD RESPONSE

FIG. 4—Gas chromatograph headspace analysis of vegetable oil containing 0.32 $\mu\text{g}/\text{ml}$ vinyl chloride injected.

headspace. Equilibrium was reached and maintained in the headspace at periods from 50 ppb of vinyl chloride for the headspace (5–50 μl) decrease of vinyl chloride with the same alcoholic beverage. Porapak column the 1 ml in somewhat better headspace sample vinyl chloride comparable vine

Table 1. Levels of vinyl chloride in alcoholic beverages, peanut oil, and vinegars contained in PVC bottles

Sample	Type of PVC bottle	No. of samples	Range, $\mu\text{g}/\text{ml}^a$	Av., $\mu\text{g}/\text{ml}$
Alcoholic beverages				
Gin	A	4	0.21–0.65	0.44
Martini	A	4	0.86–1.60	1.37
Beaujolais	B	4	0.15–0.84	0.60
Cognac	C	4	<0.025	—
Sherry	D	6	0.38–0.98	0.66
Vegetable oil				
Peanut	H	10	0.3–3.29 ^b	2.16 ^b
Vinegars				
Apple cider	E	13	0.56–8.40	3.49
Malt	E	4	0.16–2.28	1.86
Malt	F	7	0.1–1.5 ^d	—
Malt	G	1	0 ^c	—
Salad	G	2	0 ^c	—
Red wine	G	1	0 ^c	—

^a Analyzed on column A, average of duplicate injections.

^b Values expressed as ppm.

^c No vinyl chloride detected, detection limit 0.01 $\mu\text{g}/\text{ml}$.

^d Single positive, 6 negative.

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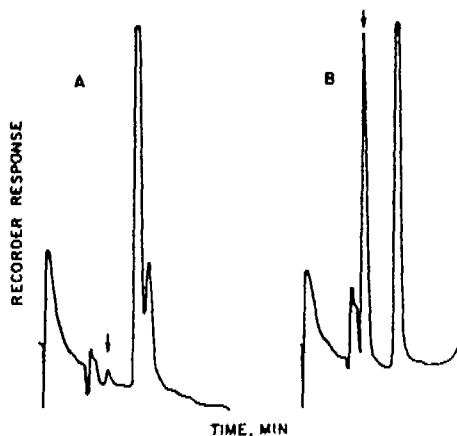


FIG. 4—Gas chromatograms (column A) obtained from headspace analysis of peanut oil: A, control; B, peanut oil containing 0.32 ppm vinyl chloride, ca 23 ng vinyl chloride injected. ↑ indicates vinyl chloride peak.

headspace. Equilibration of the system is rapidly reached and the concentration of vinyl chloride in the headspace remains constant when analyzed at periods from 5 min to 2 hr. Peanut oil spiked from 50 ppb to 20 ppm with ethanol solutions of vinyl chloride give a linear calibration graph for the headspace analysis. The ethanol added (5–50 μl) does not detectably affect the percentage of vinyl chloride in the headspace. GLC determination and confirmation are carried out with the same columns used in the vinegar and alcoholic beverage analysis and, in addition, a Porapak column can also be used. Because of the 1 ml injection volume the GLC peak is somewhat broader (Fig. 4B) but since the 1 ml headspace sample contains about 14 times more vinyl chloride than a 5 μl sample from a comparable vinegar the actual limit of detection is

slightly better (5–10 ppb). GLC-MS (single ion monitoring m/e 62) can be used down to the 50 ppb level (about 3.5 ng injected) but GLC-MS (full spectrum) is not very useful since the air present in the headspace sample tails into the vinyl chloride peak and interferes with the mass spectrum below m/e 40. A scan over the range m/e 50 to m/e 70 can be used but is at least an order of magnitude less sensitive than single ion monitoring.

Peanut oil is the only vegetable oil packaged in PVC bottles in Canada and analysis of 10 samples showed levels of 0.3–3.3 ppm vinyl chloride (Table 1). Analysis of a control sample of peanut oil showed a trace peak (about 15 ppb) with a retention time similar to vinyl chloride (Fig. 4A). Other vegetable oils (corn, soybean, rapeseed, olive), packaged in glass bottles, contained no detectable levels of vinyl chloride except for samples in glass bottles with caps containing a PVC liner. These samples showed trace peaks (about 5–10 ppb) with the same retention time as vinyl chloride but the levels were too low to confirm by GLC-MS.

The problem of vinyl chloride contamination is complicated by the use of a different type of PVC resin by each bottle manufacturer. Eight types of PVC bottles, varying in shape, source of resin, and/or formulation were encountered in this survey but in no case were 2 different foodstuffs packaged in the same type of bottle (Table 1). It is, therefore, not possible to assess which of the foodstuffs is most susceptible to vinyl chloride contamination. However, it can be seen that the problem is not restricted to alcoholic foodstuffs packaged in PVC containers.

Acknowledgment

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**Plastics Engineers
To Hear FDA Director**

Dr. Charles P. Jellinek, director of the U. S. Food and Drug Administration's Division of Chemical Technology, will be a feature speaker at a special session dealing with vinyl chloride monomer (VCM) at the Society of Plastics Engineers' Annual Technical Conference (ANTEC). The ANTEC will be held at the Atlanta Marriott Hotel in Atlanta, May 5-8, 1975. Dr. Jellinek will speak during a 3 p.m. panel discussion on Tuesday, May 6.

At the ANTEC, representatives from the industry will also be on the panel with Dr. Jellinek and will discuss the effects of the regulations on present and future PVC markets.

Stringent monomer-exposure levels, promulgated by

the Department of Labor's Occupational Safety and Health Administration (OSHA), went into effect on April 1. The low worker-exposure levels affect companies manufacturing VCM or processing it into polyvinyl chloride (PVC), and those who further process PVC into products.

The controversy over the regulations was recently fueled by Dr. Herbert E. Stockinger, chief of the toxicology branch of the National Institute for Occupational Safety and Health (NIOSH) and the agency that establishes industrial exposure levels for OSHA. Dr. Stockinger has described the government's regulation that workers be exposed to virtually no vinyl chloride as "an irrational decision," and that he was "consternated" at NIOSH's "essentially zero-tolerance" recommendations to OSHA.

**OCCUPATIONAL SAFETY +
HEALTH REPORTER**

4/17/75

California

**CAL/OSHA APPEALS BOARD OVERTURNS
VC HAZARD CITATION FOR LACK OF PROOF**

SAN FRANCISCO — (By an OSHR staff correspondent) — In what is believed to be the first contested case in California involving alleged vinyl chloride exposure, the state Occupational Safety and Health Appeals Board overturned a citation because of lack of proof that harmful exposure actually existed.

The case involved Safeway Stores, Inc., Store #240, Sacramento (Docket No. 886), and the board unanimously adopted the proposed decision of presiding hearing officer Paul F. Dauer in the matter.

Safeway was cited for an alleged nonserious violation of 8 CAC 5142 (c) for failure to provide ventilation adequate to disperse vinyl chloride fumes generated by a meat wrapping operation. The Division of Industrial Safety engineer who made the inspection testified that he observed fumes rising through a meat wrapper's breathing zone. He said the fumes arose when the wrapper severed the wrap with heat wire. However, no measurements were taken to determine the concentration of the fumes or even that they were, in fact, vinyl chloride fumes.

Safeway told Dauer that an exhaust fan did exist four to five feet above the meat wrapping machine. The firm also noted that there have been no complaints received from the meat wrapping workers of any discomfort experienced at the work station.

Dauer noted that the division failed to provide any competent, objective, or scientific evidence of any harmful exposure to the fumes. Not only does the division's case fail to establish the presence of harmful quantities of fumes, it fails to establish that any fumes that were present were harmful, he said.

The violation was set aside. No penalty was proposed by the division.

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