Detecting small quantities of residual vinyl chloride monomer

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S. G. Gilbert, J. R. Giacin, J. R. Morano, & J. D. Rosen
Department of Food Science
Rutgers University
New Brunswick, New Jersey

Note - See last column for estimate of food contact hazard.

Summary: This article summarizes procedures for detecting small quantities of vinyl chloride monomer in packaging materials. The lower limit of detection by gas chromatography (flame ionization detector) was 2.2×10^{-9} gm, which is equivalent to a concentration limit of 5 ppb (w/w) in a polymer sample. Gas chromatography supplemented by a form of mass spectrometry known as mass-fragmentography was also employed, allowing detection of 8.7×10^{-12} gm VCM.

The authors point out that eliminating materials to the limits of detectability may have more serious ill effects than allowing reasonable levels of suspect material to be present.

Introduction. Attention has recently been focused on the health hazard to the general public from residual vinyl chloride monomer (VCM) in polyvinyl chloride (PVC) based polymers. The need for this scrutiny has arisen from the findings of an unusually high incidence of angiosarcoma in humans exposed to high concentrations of VCM (ca. 1000 ppm) through occupational exposure over long periods of time (1). This relationship has been strengthened greatly with direct experimental evidence of angiosarcoma in mice exposed to VCM dosages at levels as low as 50 ppm (inhalation) over an eight month period (2). The concern for the general public arises from the magnitude of the annual PVC production (about 5 billion pounds in 1973, (3)) and its use in packaging consumer products.

There are two distinguishable areas for concern. The first is that of exposure through inhalation of the highly volatile gas, either by occupational exposure through release to the atmosphere or by its use as a propellant. Present regulations by EPA ban the latter (4), while recent OSHA rulings specify a reduction to 1 ppm in the atmosphere of factories involved in PVC production and use (5). Five ppm is allowable for periods shorter than 15 minutes.

The second area of concern involves the possibility of exposure by ingestion of VCM as a result of its migration to food contacted with PVC in packaging materials. We estimate approximately 250 million pounds of PVC may be involved annually in food packaging at present levels (6).

The regulatory aspects of this type of contact are within the jurisdiction of FDA under the category of "incidental food additives." These regulations specify that: "A material used in the production of containers and packages is subject to the definition (of food additive) if it may reasonably be expected to become a component.... of food packaged in the container." The regulation further states that: "If there is no migration of packaging component from the package to the food, it does not become a component of the food and thus is not a food additive" (7). The FDA Guidelines tentatively define "no" as if computations show that no more than 0.01 ppm of a substance would be added to food assuming it all migrated. The extracts usually need not be tested for such a substance" (8).

In the absence of carcinogenesis, the 1×10^{-8} g/g level of additive (migrant) in food has been accepted as the equivalent of "no." Where carcinogens are concerned, the equivalent "no" has not been defined, except in the vague terms of the most sensitive analytical techniques available for quantification of the substance in question.

The Delaney Clause states that, "no additive shall be deemed to be safe if it is found to induce cancer when ingested by man or animal, or if it is found, after tests which are appropriate for the evaluation of the safety of food additives, to induce cancer in man or animal, ..." (9). Therefore, the concern with residual VCM in PVC packaging material is whether or not VCM migrates from PVC to the food contained in the package.

In this paper we deal with the question of VCM migration from PVC to foods. As a first step, an analytical procedure for the quantitation of vinyl chloride was developed.

For the past ten years, our laboratory has been involved with migration and desorption studies as a means of evaluating the interaction between low

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molecular weight compounds and polymers. These studies have dealt with various aspects of migration ranging from the practical problem of migrants affecting sensory properties of packaged food (10) to theoretical studies where sorption-desorption thermodynamic parameters were evaluated (11, 12). Gaseous migrants have also been used as probes for the study of macromolecular structure (13).

Studies on sensorially important residues have shown that contact of the polymer with such substances in the normal manufacturing process resulted in measurable sorption or retention, even under the extremes of commercial conditions used for their removal (14). The method developed for the determination of such residues is now an accepted American Society for Testing and Materials (ASTM) procedure (15). The apparatus is shown schematically in **Figure 1.** This method involves distillation of volatile residues from the polymers into a hermetic limited volume at sufficiently elevated time/temperature conditions so as to provide essentially complete transfer from solid to gaseous phase. Gas chromatographic analysis (GLC) of the gas phase then gives tentatively, both a qualitative identification and quantitative upper limit for the presence of the residue in question.

This gas phase partition has been related to liquid phase transfer in certain cases with good agreement between methods (16).

The extension of this method to the measurement of residual VCM in PVC film and resin has been established in our laboratory. In addition, the feasibility of using mass fragmentography for the analysis of VCM in headspace gas has been determined. This method of detection was found to be immediately applicable to air sampling (17).

Materials and methods. The appratus used consisted of:

(a) Gas chromatograph. Hewlett-Packard Model 1520 gas chromatography, equipped with back flush valve. GLC conditions: 10' × ¼" i.d. stainless steel column packed with 10% SE30 on 90-100 mesh Anakrom ABS. Nitrogen flow rate 60 ml/min.; temperatures (°C)—injection port 170°, detector 220°, column maintained at ambient temperature. Vinyl chloride retention time, 2.0 min. Inject 10 ml sample with gas tight syringe, equipped with one-way metal stopcock valve.

(b) Hot jar. A 250 ml (½ pint) Mason jar fitted with stainless steel lid specially fabricated with Swagelock fittings and septum as described by Wilks and Gilbert (14).

Weigh accurately sample of PVC film or resin and transfer to Mason jar. The area and volume of PVC film, are recorded prior to analysis. The apparatus utilizing the hot jar and syringe are placed in a 90°C oven and maintained for 30 min. The GLC response obtained from three separate 10 ml on-column injections of the headspace is measured. No decomposition of the polymer to liberate VCM was detected after prolonged heating (24 hr.) at 90°C.

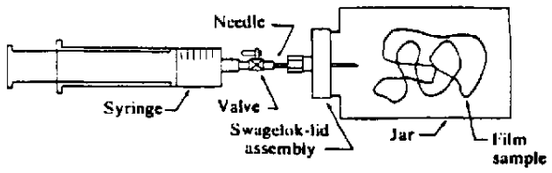


Figure 1 Apparatus used to sample gas. Method involves the distillation of volatile residues from the polymers into a hermetic limited volume under elevated time/temperature conditions.

A standard curve of response vs. VCM concentration was constructed from vinyl chloride mixtures of known concentration. A standard mixture of vinyl chloride diluted with nitrogen was prepared containing 7 ppt (v/v) vinyl chloride and was then used to prepare vinyl chloride mixtures of varying concentrations.

(c) Gas chromatography—mass spectrometer. A DuPont Model 21-490 mass spectrometer, equipped with digital mass marker and dynamic dual ion detector of the design of Pareles and Rosen (18) was interfaced to a Varian Model 2740 gas chromatograph via a single-stage jet separator. GLC conditions were similar to those used for GLC detection of vinyl chloride. Vinyl chloride retention time was 1.52 min. Detect vinyl chloride by repeatedly scanning both the m/e 62 and 64 ions. Simultaneously record on 2-pen recorder (17). Inject 10 ml sample with gas tight syringe.

Results and discussion. Table 1 represents the levels of VCM detected in freshly prepared PVC homopolymer and plasticized resin. Also listed is the retained VCM after the two resins were equilibrated in air.

As shown in **Table I,** a marked decrease in residual VCM was found in the resin following plasticizer addition. The levels being 254 and 0.59 ppm, respectively. This decrease in residual VCM may be attributed to air equilibration as well as losses during processing. In addition, the plasticizer will modify the physical properties of the polymer (e.g., Tg) and, therefore, affect the solubility of VCM in the resin.

Table I also shows that the concentration of residual VCM in the resins was markedly decreased by equilibration of the polymer samples in air. The level of VCM in the plasticized and unplasticized resins, following equilibration, was 0.02 and 2.0 ppm, respectively, which represented approximately 7.0 and 1.0% of the initial VCM concentrations. For these studies, polymer samples were transferred from a closed container to an open crystallizing dish and placed in a fume hood for 48 hrs.

This favorable partitioning of VCM between PVC and its environment may provide a method of removing residual VCM from the resin.

Analysis for residual VCM in several representative industrial grade PVC products was carried out and the

Table I
Residual VCM in PVC resin by hot jar technique

Sample number*	*Resin type*	*Equilibration** time (hours)*	*Average*** response*	*Total VCM (gm)*	*VCM concentration in resin (ppm)*
1	Unplasticized	0	1.85×10^{5}	6.35×10^{-4}	254.0
2	Unplasticized	48	1.78×10^{3}	5.18×10^{-7}	2.07
3	Plasticized	0	4.39×10^{2}	1.49×10^{-7}	0.597
4	Plasticized	48	1.83×10	5.33×10^{-9}	0.0213

*2.5 gm. sample of powder used
**Sample placed in hood
***Response for 10 ml injection = range × attenuation × peak height (cm) Average for two runs

results are tabulated in **Table II.** As shown in **Table II,** the detected level of VCM was between 5 ppb for PVC film to 71 ppb for PVC coated fabric.

The lower limit of detection of VCM was 2.2×10^{-9} gm by flame ionization (FID). Therefore, if a 10 gm sample of PVC film or resin is assayed by the hot jar procedure and we assume all the vinyl chloride present is released on heating, a detectable limit of 5.6 ppb (w/w) is possible.

Conventional GLC procedures for analysis of residual VCM in PVC resin require dissolution of the polymer sample in a suitable solvent (e.g., THF) and direct on-column injection of the resultant solution. While this procedure is very useful, the sensitivity of the method is limited by:

a. solubility of the polymer sample in the solvent,
b. the maximum sample size which can be injected into the gas chromatograph and
c. solvent impurities.

The sensitivity of the procedure utilizing the hot jar is limited by sample size and reactor (jar) volume and can be easily increased by varying these parameters. This technique, therefore, appears to offer some advantages over conventional methodology.

That the procedure utilizing the hot jar must be essentially quantitative is supported by the results of Berens (19), who found that above the glass transition temperature (Tg) the solubility of VCM in PVC resins was negligible. It should be reemphasized, however, that this procedure is valid only in a negative sense in that a GLC method can only establish the maximum amount of a suspected material producing a response in the detector under specified operating conditions but cannot provide positive identification.

The need for structural conformation of unknown contaminants (e.g., vinyl chloride) is difficult below the ppm level. We, therefore, employed mass fragmentography, a technique where the mass spectrometer is used as a sensitive and selective detector for GLC effluents (17).

For VCM analysis, the parent (m/e 62) and the P+2 (m/e 64) fragments were recorded simultaneously. A ratio of 3 to 1 for these peaks is obtained for vinyl chloride as a result of the natural isotopic distribution of chlorine – 37. Peak heights at these ion mass numbers and a comparison of their ratios combined with the GLC retention time afforded a specific and sensitive method for VCM determination at the 8.7×10^{-12} g level, in headspace analysis. The lower FID limit determined on our detector was 2.2×10^{-9} g. The mass fragmentography method is, therefore, almost 250 times more sensitive than flame ionization detection with the added advantage of structure confirmation.

To date, headspace analysis by this technique has been carried out on standard vinyl chloride mixtures, and the procedure is immediately applicable to air sampling. The application of the procedure using the hot jar with mass fragmentography detection for analysis of residual VCM in polymer samples is presently being investigated.

This method when applied to food simulants or to foods themselves is expected to be much more sensitive than the 10^{-8} g/g level presently considered

Table II
Residual VCM in PVC film, coated foil and coated fabric by hot jar technique

Sample number	*Film type*	*Sample wt. (gm)*	*Thickness (mil)*	*Average* response***	*Total VCM (gm)*	*VCM con. in PVC (ppb)****
1	Plasticized PVC	4.5	0.75	2.15×10^{1}	6.7×10^{-8}	15
2	PVC coated foil	8.0	1.70	1.27×10	4.0×10^{-8}	5
3	PVC coated fabric	6.0	—	1.35×10^{2}	4.25×10^{-7}	71

*Average of two injections
**Response for 10 ml injection = range × attenuation × peak height (cm)
***These analyses were preformed following major servicing of the instrument which increased the detector sensitivity tenfold to a detection level of 2.2×10^{-10} g VCM

as the "no migration" level. We consider it quite probable that this or equally advanced techniques in analytical chemistry could be developed to demonstrate the presence of VCM in any sample of PVC and by calculation infer its transfer to PVC packaged food.

Studies on desorption of low molecular weight molecules from polymers showed that two factors must be considered in relating VCM partition from polymer to food. The first concerns the equilibrium concentration of migrant in the food and the second is the time required to attain equilibrium.

In can be assumed that at any concentration of VCM in the polymer, there will be a correspondingly lower concentration in the contacting food with a maximum at equilibrium. It is quite likely that over three orders of magnitude will be found between the concentration of VCM in the polymer to that in the contacting phase. These assumptions are based on considerations of the partition coefficient and the weight ratio of packaging material to contacting phase.

The equilibrium concentration of VCM in a food resulting from contact with a PVC package may be estimated by solution of equation (1).

$$[M]_s = [M]_{p_0}[W_p/(KW_p + W_s)] \quad (1)$$

When $[M]_s$ is the concentration of VCM in the food at equilibrium, $[M]_{p_0}$ is the concentration of VCM in PVC package at zero time, K is the partition coefficient, and W_p and W_s are the weights of the PVC package and food phase, respectively.

If the following estimates for these factors are made, $[M]_{p_0} = 1 \times 10^{-6}$ g/g, K = 100, W_p = 1 gm and W_s = 100 gm; then $[M]_s$ is equal to

$$[1 \times 10^{-6}](1)/[(1)(100) + (100)] = 0.5 \times 10^{-8} \text{ g/g}$$

If we assume complete transfer of VCM from the package to food, $[M]_s = 1 \times 10^{-8}$ g/g.

In all probability, at sufficiently low levels of VCM in the polymer, the equilibrium concentration of migrant in the food will be below that estimated for $[M]_s$ by equation (1) because of nonlinear disorption of the VCM from the polymer. Berens (19) reported such a non-ideal behavior for the VCM/PVC system against VCM vapor.

While there is still considerable question as to the presence of a defined "no effect" threshold, the proposed OSHA standard of 1 ppm (v/v) will be considered as having a sufficient safety factor. The per day level of VCM inhaled by exposure to 1 ppm vinyl chloride (v/v) for 8 hrs. per day with a relative air intake of 10^3 liters/day may be estimated by solution of equation (2), after first calculating the density of VCM at STP.

$$\text{g VCM/day} = 10^3\,\ell/\text{day} \times 1 \text{ day}/24 \text{ hrs.} \times 8 \text{ hr. (work day)} \times 1 \times 10^{-6}\,\ell/\ell \times 2.54\,\text{g}/\ell = 0.85 \times 10^{-3} \text{ g VCM/day} \quad (2)$$

The total exposure to VCM from food contacting PVC packaging material may be estimated by solution of equation (3).

$$(E) = [M]_s \times (G) \times (B) \quad (3)$$

Where (E) is the effective total quantity of VCM ingested, $[M]_s$ is the concentration of VCM in food, (G) is the total weight of food contacted (ingested) in g/day, and (B) is the biological effectiveness of VCM in terms of its response at that dosage.

If the following estimates for these factors are made, $[M]_s = 1 \times 10^{-8}$ g/g, (G) = 1.814×10^3 g/day (USDA estimated daily food consumption, with the further assumption that 10% of all food consumed is packaged in PVC) and (B) = 1, then (E) is equal to 1.8×10^{-6} g VCM/day. At this ingestion level, an ingestion dosage equivalent to the yearly inhalation dosage at 1 ppm for forty hours per week for forty-six weeks would require 300 years. If $[M]_s = 1 \times 10^{-9}$ g/g (i.e. partition coefficient = 1000) an ingestion period of 3000 years would be required to equal the yearly inhalation dosage.

While a number of assumptions have been made in these calculations, we feel that the estimate of (E) is very conservative and represents an order of magnitude approximation.

The safety factors in this calculation are quite high:

1 The evidence for angiosarcoma in humans is for only a few individuals exposed (inhalation) to levels of 1000 ppm VCM for at least 10 years.

2 The biological effectiveness factor could easily be below one but is used at its maximum.

3 The partition coefficient (equation1) does not take into account the strong possibility that nonlinear desorption at low VCM concentrations will greatly affect this factor, reducing it essentially to zero at some finite VCM level in the polymer.

4 10% of all food consumed is packaged in PVC.

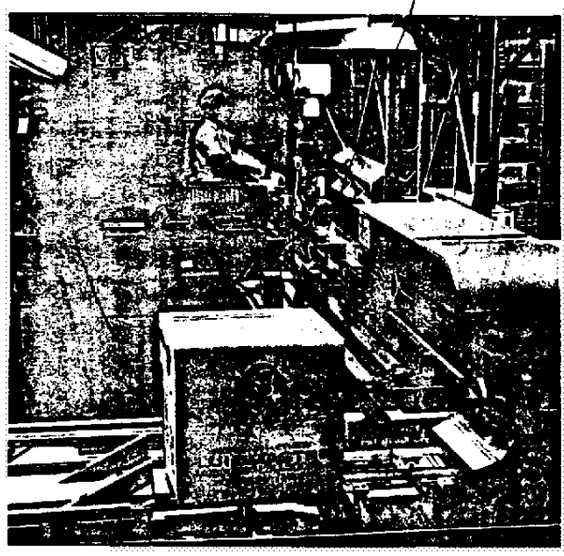
5 No provision has been made for migration of VCM from the polymer into the atmosphere. Clearly this should be taken into consideration as losses of VCM by migration from the polymer to the atmosphere have been found in recent unpublished work.

There appears, therefore, to be only a remote possibility of the demonstration of toxicity by ingestion of VCM migrating from properly controlled food grade PVC used in food packaging.

Since in such a case we would be dealing with probabilities of risk to the general public rather than with certainties, there should be some assessment of the risks occurring from disruption of thoroughly developed procedures for protection of our food supply. For example, there is the clearly defined danger from highly toxic microbial toxins, including carcinogens, which could result from improperly protected foods due to a "Delaney" ban of PVC. A list of references follows.

Switch to side-loaded carton cuts 3-man line to one worker, doubles output capacity

Fluidmaster Inc. is a leading producer of toilet waterlevel control valves sold to homeowners through home centers and hardware stores. The previous end-loaded Fluidmaster carton was high cost, both in material and in handling. Their new side-loaded carton costs substantially less . . . is much faster to form, load and close . . . and requires only 1/3 the previous labor.



Key to Fluidmaster's cost-cutting packaging operation is their automated 3-machine line. Cartons are formed and glued from blanks by Peters PG-V Former . . . loaded by worker as they pass by on conveyor . . . closed and sealed by Peters CCY-D Closer . . . and packed 5-wide by 5-deep into corrugated cases by Berney Packing & Closing Machine which also seals and ejects the cases to a holding conveyor.

Before: Three workers were required to insert the control valves into the 3" square end of 3 x 3 x 15" cartons . . . very much like stuffing items into close-fitting sleeves. Under pressure to keep the line moving, workers tore many cartons which had to be scrapped.

Now: With side-loaded cartons, a single worker literally drops the valve and fitting into the carton . . . filling as many cartons as three workers filled before.

OTHER SAVINGS

Lower carton costs: The new flat die-cut carton blanks cost $4.25 per M less than the pre-glued folded blanks used previously.

Less storage space: Delivered flat, 12,000 to a skid, the new blanks take up much less space than the previous pre-glued blanks which came packed 200 to a corrugated case.

Less handling time: Peters PG-V holds 3000 die-cut blanks. The previous machine held only 100 pre-glued blanks, which kept a worker busy unloading cases and loading the machine every few minutes.

Doubled output capacity: As Fluidmaster sales increase, it will be only a matter of machine adjustment to increase packaging line speed. Peters machines are capable of forming cartons and closing & sealing cartons at speeds of more than 100 per minute . . . double the present output.

End-opening feature retained: Although side-loaded, the cartons are formed so they can be end-opened and reclosed in the store, permitting customers to examine the contents before purchase.

For more information on the Peters machines used in the Fluidmaster operation, write to Peters Machinery Company, 4700 N. Ravenswood Avenue, Chicago, Illinois 60640 or phone 312-561-9000. ■

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package development quiz

Readers are invited to contribute questions and their answers. The answers to these questions are on page 32.

1. What is the principal advantage of fourdrinier board over cylinder board when used in the manufacture of folding cartons?
2. In view of the interest in waste disposal and recycling, what is the advantage of a cylinder board machine versus a fourdrinier board machine?
3. When manufacturing folding cartons, in which direction does the grain of the board normally run; vertically or horizontally around the carton?
4. What are the principal methods of forming rigid plastic containers?
5. What are the principal advantages claimed for ultra-violet drying inks used to print packaging materials?
6. Measurement of tinplate is by the base box. What is a base box equivalent to in terms of area?

Credit: Submitted by Dr. Harold J. Raphael, Director, Department of Packaging Science, Rochester Institute of Technology, Rochester, NY 14623