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DETERMINATION OF VINYL CHLORIDE MONOMER BY GAS CHROMATOGRAPHY

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SUMMARY

A gas–liquid chromatographic method for trace amounts of vinyl chloride monomer, applicable to certain types of problems in the packaging of foods, is described. When an adequate sample can be dissolved in a suitable solvent and does not interfere, direct analysis of some materials is feasible. For other materials, food simulating solvents may be applicable. A level of vinyl chloride monomer as low as 5 ppb* can be determined in resins and plastic containers.

INTRODUCTION

Vinyl chloride (chloroethene, CH_2=CHCl) is a major industrial synthetic organic chemical whose principal use has been as a vinyl monomer, homopolymerized into polyvinyl chloride (PVC), and copolymerized into a variety of copolymers with a wide array of end uses. These polymers lend themselves easily to molding, plasticizing, sheeting, extrusion, coating, etc. As a result, PVC and vinyl chloride copolymers are present in large volume in diverse industrial and consumer products.

Vinyl chloride (VC) is a gas at ambient temperature and pressure and is a chlorinated hydrocarbon which has moderate liver toxicity[1]. Since adverse toxicological information about vinyl chloride monomer (VCM) emerged early in 1974, governments in various countries have been taking steps to lower drastically the allowable levels of VCM in the working environment and in PVC itself. Industries are fiercely striving to perfect the polymerization process in PVC production. In addition they are attempting to develop sensitive and reliable analytical techniques for the determination of VCM. Ives[2] described a method for trapping and analyzing VCM in air samples. Williams and Miles[3] reported gas–liquid chromatographic (GLC) determination of VCM in alcoholic beverages, vegetable oils, and vinegars. Ernst and Van Lierop[4] suggested use of a Hall detector for identification of VCM. Breder *et al.*[5] described GLC determination of VC in several samples. This study was motivated by the needs in our laboratory and is attempted to provide a sensitive and reliable method for VCM determination in plastic containers and food caps.

* Throughout this article the American billion (10^9) is meant.

Further information and data on VCM study will be reported when they become available from authors' laboratory.

EXPERIMENTAL

In order to achieve a clear separation and maximum sensitivity, all analyses in this study were done by GLC.

Gas chromatography

The apparatus used consisted of a Perkin-Elmer Model 900 gas chromatograph with flame ionization detector. Helium was employed as the carrier gas at a rate of 25 ml/min, air at regulator pressure (30 p.s.i.g.), hydrogen at regulator pressure (20 p.s.i.g.). The chart speed was 1 cm/min, and the amplifier range × 1.

The main column used was 25 ft. × 1/8 in. O.D. stainless steel packed with 30% SE-52 on 80–100 mesh Chromosorb W AW. The injector temperature was 200 °C, the detector temperature 240 °C; during an initial time of 6 min the oven temperature was 50 °C, then it was programmed at 16 °C/min, with a final temperature of 200 °C with final time from 6 to 48 min, depending on the particular sample injected.

In order to confirm the presence of VCM in a sample, another column of 16 ft. × 1/8 in. O.D. stainless steel was used. It was packed with 16.7% triscyanoethoxy propane on 60–80 mesh Chromosorb W AW. The instrumental conditions were as follows: injector temperature 170 °C, detector temperature 190 °C, initial time 6 min at 50 °C, then programming at 16 °C/min to 170 °C, final time 6 to 48 min depending on the particular sample injected.

Preparation of standard solutions

After screening a host of common solvents, it was found that 200 proof ethanol (Publicker Industries, Philadelphia, Pa., U.S.A.) yielded a baseline without interfering peaks in the VCM region. It was used for preparing most standard solutions and sample solutions. For determination of total VCM in plastic containers and resins, the solvent used was N,N-dimethylacetamide (DMAC, Spectro grade; Eastman-Kodak, Rochester, N.Y., U.S.A.).

A Hypo-vial (No. 12911; Pierce, Rockford, Ill., U.S.A.) was filled with solvent up to the neck level and the net weight of solvent obtained. The vial was suspended in a cooling bath of dry ice–ethanol contained in a Dewar flask. Gaseous VCM contained in a metal cylinder (Matheson Gas Products, Lyndhurst, N.J., U.S.A.) was then released through Tygon tubing with attached pipet and allowed to bubble gently below the surface of the solvent for 2–3 min. With the aid of a crimper the vial was rapidly sealed with a septum (No. 13237; Pierce) and an aluminium seal. The net weight of VCM was obtained by weighing the vial after equilibrating to room temperature. This was the stock solution.

Various working standard solutions were prepared when needed. Solvent (8 ml) was pipetted into a vial (No. 13028; Pierce). Using a syringe the exact volume of stock solution required was measured into the vial which was immediately closed with screw cap and PTFE–silicone septum (No. 12713; Pierce). The PTFE surface was in contact with the solution. A wide range of solutions from 100 ppm to 5 ppb of

VCM were prepared. Both stock and working standards were stored in the refrigerator, the latter discarded after a few days.

In order to analyze different levels of VCM in various containers, standard solutions of 12, 10, 8, 6 ppm VCM (1.0-μl injections) were chromatographed. Peak heights were measured. Plotting of peak heights *vs.* concentration demonstrated linearity. The following sets of standard solutions were also chromatographed for various VCM levels: a set of 2.0, 1.5, 1.0, 0.5, 0.1 ppm (2.0-μl injections) for 1 ppm level, a set of 70, 60, 50, 40, 30 (50-μl injections) for 50 ppb level, a set of 30, 20, 10, 7.5, 5 ppb (50-μl injections) for the lowest detectability. Linearity was also achieved with these standards.

Determination of VCM in lining of food caps

Several kinds of food caps used with sauce products were analyzed for possible VCM levels. This was achieved in two ways, *i.e.*, extraction via solvent simulation and by detecting total VCM present in the cap liners.

According to U.S. Code of Federal Regulations[6] aqueous products containing free oil or fat sterilized in boiling water should be tested in food simulating solvents such as heptane (120 °F at various time intervals) and water (212 °F at various time intervals). Since commercial sauce products contain water as well as oil and processed at 212 °F for various time intervals, heptane and water were then selected for simulation.

Each glass bottle was fitted with the appropriate cap which in turn was filled with 100–300 ml of *n*-heptane (No. 5177; Mallinckrodt, St. Louis, Mo., U.S.A.) or deionized water in order to maintain ample space for vapor expansion. The bottles were capped tightly and positioned upside down to maximize the contact between the coating and the extractant. Bottles containing heptane were placed in a metal tray and stored in an incubator at 120 °F for various time intervals. Bottles containing water were placed in another tray and heated in an oven at 212 °F for various time intervals. The bottles were kept in the upside down position until equilibrated to room temperature. The contents were mixed by swirling the bottles, then quickly 1 ml was taken out and delivered into a vial (No. 12911; Pierce) containing 18 ml ethanol. The vial was promptly closed with septum and aluminum seal. The remaining volume in each bottle was finally measured to obtain total actual extractant used. Under the instrumental conditions described above, 50 μl of heptane or 10 μl of water extract was injected into the chromatograph. The presence and magnitude of VCM were examined at its retention time.

In determination of total VCM content, the coatings of the cap liners were scrapped off (using a sharp metal chisel) from each cap and transferred to a vial. The vial was weighed before and afterwards to obtain net weight of the coatings analyzed. It was then dissolved in 8 ml of DMAC or tetrahydrofuran (THF) for chromatography. Later, original coating materials supplied by the manufacturer were directly utilized for analysis.

Determination of VCM in plastic containers

A host of various plastic containers supplied by different manufacturers were analyzed for possible existence of VCM. Due to limited solubility, only about 100 mg of sample from each container was used for analysis. It was necessary to cut the sample into very small units before dissolving in 8 ml of DMAC. The sample was

then chromatographed at a final temperature of 200 °C for 32 min in order to remove the high boilers.

Determination of VCM in the actual products

Several sauces were directly analyzed for any VCM contamination in the product itself. Each sauce was mixed briefly and quickly in the original jar and 1–1.5 g sample was weighed out into a vial. After the addition of 13 ml of ethanol, the vial was tightly closed with screw cap and PTFE–silicone septum. It was vigorously shaken for 10 min and centrifuged for 10 min at 1500 rpm. Then 50 μl of the clear extract was injected into the chromatograph.

RESULTS AND DISCUSSION

Gas chromatography

GLC was used throughout this study for its speed, sensitivity, and high degree of separation. Though a level of VCM as low as 5 ppb can be detected in a solvent such as heptane, it is realized that quantitation of VCM may not be feasible at this level in the wide variety of problems that may be faced by all analysts.

The retention time of VCM on the SE-52 column is only 4.7 min (Fig. 1) with ethanol and DMAC yielding a baseline without interfering peaks. There are some interfering peaks near the VCM region when using THF. Nevertheless, THF still serves as a useful solvent for many types of resin. It has been observed that a reasonably stable baseline can be achieved best when the carrier gas and hydrogen flame are left on 24 h a day during an extended analysis period with a reduced hydrogen and air flow-rate in off-times.

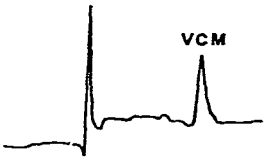

Fig. 1. VCM of 5 ppb in ethanol at 50-μl injections.

Standard solutions

Since VCM is a gas at ambient temperature and pressure, its volatility makes standard preparation difficult, particularly in low-range concentrations (ppb). When VCM is directly introduced into a solvent such as ethanol or DMAC in a cooling bath of dry ice–alcohol (—78 °C), a minimum of VCM gas escapes into the air and a stable concentration can be obtained. The head space in standard solutions was kept to a minimum by filling the solvent up to the neck in a vial. U.S. Code of Federal regulations[7] on handling VCM should be consulted before undertaking such work.

The stock solution thus prepared remains stable for more than one week, while working standards have to be replaced in one or two days. The volume of injection varies depending on the concentration of VCM (larger volumes for lower concentrations). Separate standard calibrations should be prepared for each short range of VCM concentration in order to get the best possible accuracy. In plotting

peak heights *vs.* concentration linearity was obtained in this study. Naturally, even better accuracy can be achieved when an integrator is available to determine peak areas (Figs. 2–5).

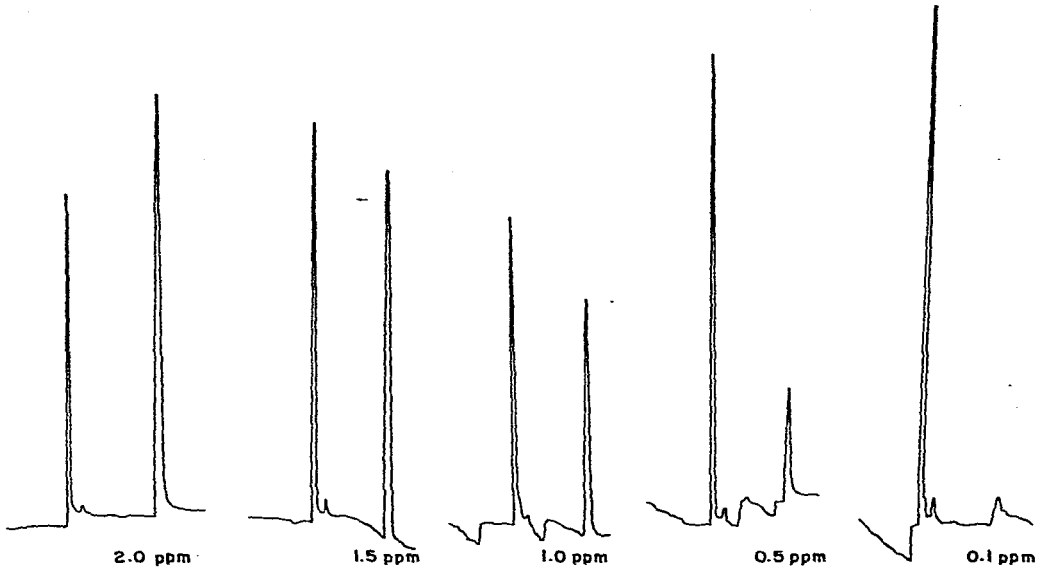

Fig. 2. VCM (ppm) in DMAC at 2-μl injections.

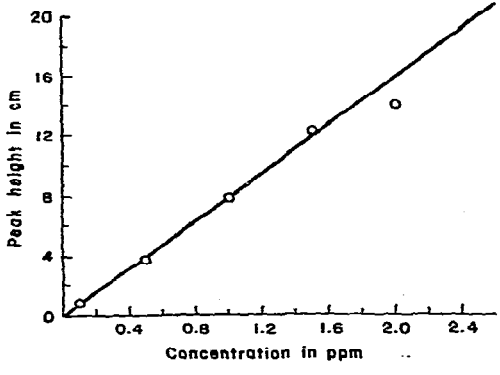

Fig. 3. Linear plot of VCM in peak heights *vs.* concentration at 2-μl injections.

VCM via solvent extraction

In the process of simulating food by solvents only 100–300 ml was used which was much less than the usual volume of sauces in regular jars. In other words, the simulants were much more concentrated in VCM than in the actual products. Although simulants were diluted in ethanol before chromatography, any presence of VCM should be easily detected since the height of the VCM peak of 50 ppb is as high as 53 mm. Only a minimum of VCM was detected in a heptane extraction for all jar closures examined. The maximum level of VCM should be less than 50 ppb.

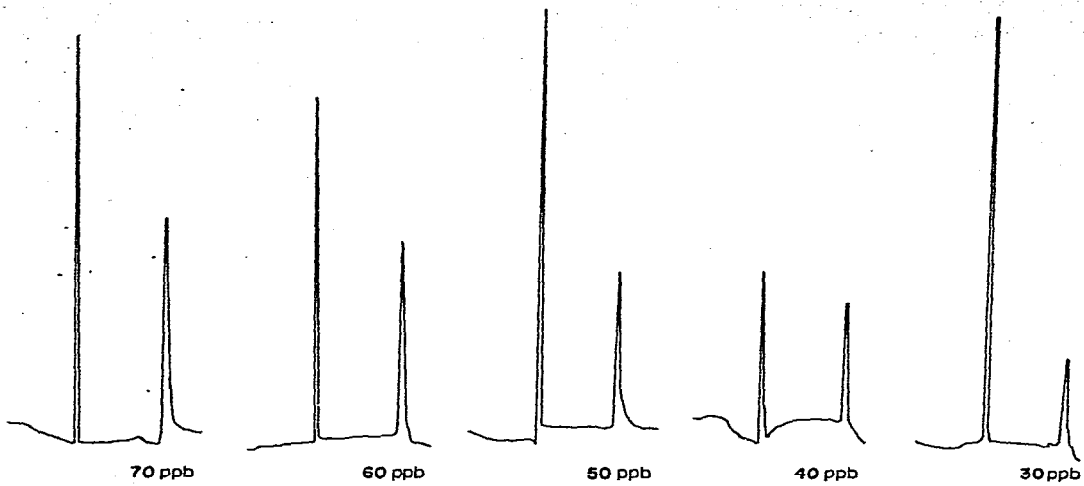

Fig. 4. VCM ppb in ethanol at 50-μl injections.

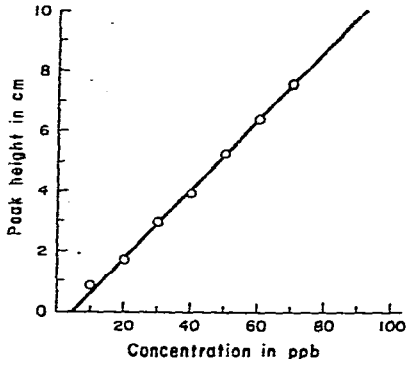

Fig. 5. Linear plot of VCM in peak heights *vs.* concentration at 50-μl injections.

When using water as an extractant, it was diluted with ethanol before chromatography. The reasons for diluting were to simulate actual product analyses and to protect the ionization detector[8]. Deionized water gives a minor peak which emerges immediately following the VCM peak. Separation between these two peaks was achieved by spiking a synthetic solution of VCM in water and ethanol. However, since the separation was unsatisfactory, water was the least useful simulant in this study.

Total VCM in plastics and resins

In the determination of total VCM in plastic and the resin materials itself, the injection volume of the sample must be bracketed in the proper range. For example, if the concentration of the VCM in the material is detected to be less than 100 ppb, it is necessary to use an injection volume of 50 μl. It is also necessary that the calibration curve be based on 50-μl injections.

Reading of peak heights against the standard calibration curve indicated that several earlier types of resins and plastics contained a few to several thousand ppb of

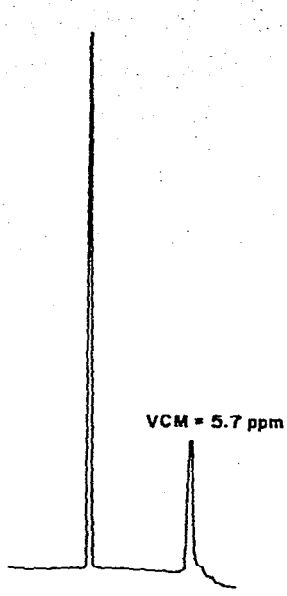

Fig. 6. Residual VCM in a PVC bottle, dissolved in DMAC.

VCM (Fig. 6). THF is a powerful solvent for some difficult dissolving resins. It is, however, unstable and gives non-reproducible patterns now and then. It can be used only as the last resort.

VCM in actual products

Many commercial products are confined in containers or wrappers which are wholly or partly made of PVC containing substances. There are possibilities that any residual VCM may migrate into the product by contact. Therefore, it is of interest to analyze for the VCM content in the product itself. In this study several sauces were directly extracted and the clear extract was chromatographed. However, these sauces are mixtures of many ingredients such as water, tomato paste, vegetable or olive oil which interfere with a clear separation of the VCM peak. Therefore, it may be more practical to use simulating solvents.

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