Gas-Chromatographic Determination of Vinyl Chloride in Air Samples Collected on Charcoal

R. H. Hill, Jr.,* C. S. McCammon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin

U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety & Health, 1014 Broadway, Cincinnati, Ohio 45202

Studies of over 20 different solid sorbents, particularly charcoal, revealed significant increases in breakthrough volumes with decreases in concentration or sampling flow rates. At low sampling flow rates, coconut shell charcoal had a good capacity and was selected as the most practical sorbent. Vinyl chloride was desorbed from charcoal with carbon disulfide and determined by gas chromatography. Recoveries were usually 80% or better. Samples of vinyl chloride on charcoal were found to be stable for at least three weeks when stored at ambient or sub-ambient temperatures. At ambient conditions, vinyl chloride migrated to the back section of the charcoal tubes within a few days. The overall precision of the method was indicated by a relative standard deviation of 7.5% for identical samples analyzed over a three-week period.

In January 1974, the National Institute for Occupational Safety and Health (NIOSH) was informed by the B. F. Goodrich Chemical Company of several deaths among its poly(vinyl chloride) production workers from a rare liver cancer, angiosarcoma. Shortly, thereafter, NIOSH began research on a sampling and analytical method for vinyl chloride in air. A search of the literature yielded little information on sampling techniques, but a number of analytical procedures were found which could be used for the determination of vinyl chloride in air. Gronsberg (*1*) sampled air containing vinyl chloride through two tubes containing activated charcoal and then desorbed and determined the vinyl chloride by a colorimetric procedure. Vinyl chloride has also been determined by infrared spectrophotometry (*2*) and by gas chromatography (*3–9*) with various selective detectors (*8, 10, 11*).

NIOSH has found personal sampling most valuable in evaluation of exposure to industrial chemicals. In this respect, sampling on solid sorbents has been particularly effective and convenient (*12–18*). Thus, it is not surprising that since the recognition of the carcinogenic potential of vinyl chloride several methods using solid sorbents for sampling of vinyl chloride have appeared (*19–25*).

The purpose of this work was to develop a sampling and analytical method for vinyl chloride which made use of a tube filled with a solid sorbent as a personal sampling device. The method would be used for routine analysis of large numbers of samples and would make use of commercially available and relatively inexpensive equipment. The results of the development work reported have led to a detailed procedure for sampling and analytical determination of vinyl chloride in workplace air (*19*).

EXPERIMENTAL

Apparatus. A Perkin-Elmer Model 900 Gas Chromatograph equipped with a flame ionization detector and interfaced to a Perkin-Elmer PEP-1 GC Data System was used to perform analyses. Chromatographic separations were accomplished on one of two phases, either a 10% SE-30 or a 10% FFAP, both on 80/100 mesh Chromosorb W (AW-DMCS) packed in 20-ft × ⅛-in. stainless steel columns, at column temperatures of 60 and 65 °C, respectively. The carrier gas was helium flowing at a rate of 40 ml/min. Injector and detector temperatures were 230 °C. Two-ml vials (Hewlett-Packard, Inc. No. 5080-8712) used in the desorption experiments were sealed with caps containing Teflon-lined silicone rubber septa. Sorbents used in breakthrough studies were packed in 4-mm i.d. glass tubing in beds about 1.5 cm long and were secured at either end with glass wool plugs. Sorbents used in these studies were: Chromosorbs 101, 102, 103, 104, 105, 106, and 107, all 60–80 mesh (Johns-Manville, Inc.); Carbopak A, Carbopak B, Carbosieve B, all 45–60 mesh (Supelco, Inc.); Tenax GC, 35–60 mesh (Applied Science Laboratories, Inc.); Molecular Sieve, Activated, Type 5A, 30–40 mesh and silica gel, 20–40 mesh (MCB Manufacturing Chemists, Inc.); Dow Carbon XF4175L (Dow Chemical Co.); Charcoals, 20–40 mesh (SKC-104 and SKC-105, SKC, Inc.; MSA-6, Mine Safety Appliances, Inc.; BPL and PCB, Pittsburgh Activated Carbon, Inc.) For experiments other than breakthrough studies, two-section (100-mg/50-mg) charcoal tubes (SKC, Inc. or Mine Safety Appliances, Inc.) were used.

Atmospheres of vinyl chloride were prepared in Tedlar (E. I. du Pont de Nemours & Co., Inc.) bags or in a dynamic generation system similar to that described by Ash and Lynch (*26*).

Breakthrough studies were carried out by drawing synthetic vinyl chloride–air mixtures through the sorbent tube with a modified personal sampling pump (Sipin Model SP-1). The exit diaphragm of this pump was enclosed in a Teflon chamber so that the exit air was pushed through the sample line of a portable AID Model 521 gas chromatograph with a flame ionization detector, which monitored the vinyl chloride in the bed effluent. The void volume between the end of the sorbent bed and the detector was 0.45 ml. Samples for desorption studies were prepared in a similar manner except that the tube effluent was not monitored.

Reagents. Reagents used were vinyl chloride (Linde Division, Union Carbide Corp.) and carbon disulfide (MCB Manufacturing Chemists, Inc.).

Sample Analysis. Each charcoal tube was scored in front of the primary (100 mg) section and broken. The glass wool was removed and discarded. The charcoal in this section was transferred to a 2-ml vial containing 0.5 or 1.0 ml of carbon disulfide and the vial was immediately sealed with a septum cap. The urethane foam separating the two sections of charcoal was discarded and the second section was desorbed in a like manner. The two sections were analyzed separately. The samples were allowed to stand at room temperature for a period of 10 to 60 min before analysis. Analyses were performed by injecting 5 μl of the carbon disulfide solution with 2 μl of carbon disulfide back flush into the gas chromatograph.

Standard Preparation. Standards of vinyl chloride in solvent were prepared by the two manners described below.

(a) A stock solution of vinyl chloride was prepared by slowly bubbling vinyl chloride for 3 min into a tared 10-ml volumetric flask containing approximately 5 ml of toluene. A weight gain of 100–300 mg was usually observed. This solution was then diluted to exactly 10 ml with carbon disulfide.

(b) A 1-ml sample of vinyl chloride gas was drawn into a gas-tight syringe and the tip of the needle was inserted into a 10-ml volumetric flask containing approximately 5 ml of carbon disulfide. The plunger was withdrawn slightly to allow the solvent to enter the syringe. The action of the vinyl chloride dissolving in the carbon disulfide created a vacuum and the syringe became filled with solvent. An air bubble (~2%) in the syringe was found to be due to the head space in the needle. The solution was returned to the flask and the syringe was rinsed twice with carbon disulfide, with the washings added to the solution in the flask. Dilution to exactly 10 ml with carbon disulfide gave a stock solution.

The standards obtained by diluting aliquots from either solution gave standard curves which coincided and were linear from 0.2 ng to 1.5 μg per injection.

Table I. Sorbent Screening Experiments with Vinyl Chloride

Sorbent	Concentration μg/l.	Sampling rate (l./min)	Breakthrough[a] volume, l.
1. Chromosorb 101–105	500	1.00	<0.1
2. Chromosorb 106–107	500	0.20	<0.1
3. Tenax GC	500	0.20	<0.1
4. Silica Gel	130	0.20	<0.1
5. Silica Gel w/1% $AgNO_3$	130	0.20	<0.1
6. Molecular Sieve, 5A	500	0.20	2.0[b]
7. Carbopak A	500	0.20	<0.1
8. Carbopak B	500	0.20	<0.1
9. Carbosieve B	500	0.20	2.8
10. Dow Carbon, XF4175L	6.5	0.20	5.7[b]
11. Dow Carbon, XF4175L	6.5	0.15	11.1
12. Dow Carbon, XF4175L	6.5	0.10	15.0
13. Dow Carbon, XF4175L	6.5	0.05	21.2[b]
14. Petroleum Charcoal, SKC-104	6.5	0.10	7.7[c]
15. Coal Charcoal, BPL	6.5	0.10	8.2[b]
16. Coconut Shell Charcoal, MSA-6	500	1.00	0.9
17. Coconut Shell Charcoal, MSA-6	500	0.20	2.4[b]
18. Coconut Shell Charcoal, MSA-6	500	0.05	5.2
19. Coconut Shell Charcoal, MSA-6	130	0.20	3.4
20. Coconut Shell Charcoal, MSA-6	6.5	0.20	5.7
21. Coconut Shell Charcoal, MSA-6	6.5	0.10	10.3[d]
22. Coconut Shell Charcoal, MSA-6	6.5	0.05	10.7
23. Coconut Shell Charcoal, SKC-105	6.5	0.10	10.6[c]
24. Coconut Shell Charcoal, PCB	6.5	0.10	8.1[b]

[a] Values are single experiments unless otherwise indicated. [b] Average of two experiments. [c] Average of three experiments. [d] Average of four experiments.

DISCUSSION AND RESULTS

Sampling. The selection of a solid sorbent for sampling was one of the first steps in the development of a method for vinyl chloride in air. Table I lists the results of some sorbent screening experiments. Comparisons were made on the basis of capacity as indicated by breakthrough volume, which was that volume of air which had passed through the sorbent bed before 5% of the inlet concentration of vinyl chloride was detected in the bed effluent.

Of the sorbents which retained appreciable amounts of vinyl chloride, only the charcoals were further studied. Dow Carbon XF4175L demonstrated the highest capacity, but it was not commercially available. Carbosieve B has been used by Zado and Rasmuson for personal sampling to determine vinyl chloride exposure (22). However, it was eliminated from further investigation, because air sampling devices containing Carbosieve B were not commercially available whereas sampling tubes containing charcoal were and the capacity of Carbosieve B was only slightly higher than that of coconut shell charcoal.

Two interesting trends can be noted in portions of the data in Table I. The data for MSA-6 coconut charcoal and Dow Carbon XF4175L show a marked increase in the breakthrough volume with a decrease in the flow rate. The relationship appears to vary with vinyl chloride concentration and the sorbent. A second trend was that the amount of vinyl chloride adsorbed on the carbon at breakthrough was not constant, but increased with increasing concentration of vinyl chloride in air. For the MSA-6 charcoal at a flow of 0.2 l./min, the amounts of vinyl chloride trapped at breakthrough were 37 μg, 440 μg, and 1200 μg at 6.5 μg/l., 130 μg/l., and 500 μg/l., respectively. These data show a log-log linear relationship suggesting a fit on an adsorption isotherm following Freundich's equation (27).

At a flow rate of 0.05–0.10 l./min, 10-l. samples of atmospheres containing only vinyl chloride in air at a level near the OSHA standard (2.6 μg/l.) can be collected on coconut-shell charcoal without loss of the vinyl chloride from the sampling device. However, high humidity or high concentrations of other organic contaminants in the air being sampled may have an adverse effect on the breakthrough volume of vinyl chloride on the charcoal tube. Saalwaechter et al. (28), have reported a 50% reduction in the breakthrough volume of toluene on coconut-shell charcoal when the relative humidity was increased from ~0% to 80% at 1 l./min. A similar effect is expected with vinyl chloride although it may not be as drastic as that for toluene since the flow rate is significantly less. This information suggests that a maximum of 5 l. of atmosphere containing vinyl chloride may be routinely sampled at a flow rate of 0.05 l./min without breakthrough. These values incorporate a large safety factor to compensate for the possibility of interferences.

Analytical. Carbon disulfide was chosen as the desorption solvent, since it gave a low response to the flame ionization detector and short retention times. Recovery of vinyl chloride from the charcoal upon desorption with carbon disulfide was not quantitative and, thus, the analytical results were corrected for desorption efficiencies. Comparison of a given air concentration determined by charcoal tube analysis with that determined by injection of gas aliquots gave the desorption efficiency (recovery). The peak shapes of the gas samples and liquid samples were found to be virtually identical as shown by Figure 1. This permitted the use of calibration curves from vinyl chloride-in-solution standards for both air and solution samples. Desorption efficiencies generally fell within the range of 80–90%. For instance, a sample weight of 13 μg (from 5 l. of air containing 2.6 μg/l. vinyl chloride) was recovered with a desorption efficiency of 85%.

A study was made of the effect of procedure, temperature, and time on the desorption efficiency. The results are summarized in Table II. The precision of each set was used as a basis for identification of the more efficient process. The results of experiments I and II indicate that addition of the charcoal to the solvent is better and that 10 min was a sufficient desorption time at sample weights around 2 μg. Later imprecise results led to Experiment III, which demonstrated that 30 min was needed for desorption of larger weights of vinyl chloride on charcoal. The results of Experiments IV–VI suggest that solvent temperature and volume have little effect on precision of the procedure.

Table II. Optimization of Desorption Procedure

Experiment	Procedure[a]	Desorption time, min	Temperature	Found, μg[b]
I	A	10	Ambient	2.13 ± 0.27
	B	10	Ambient	2.26 ± 0.09
II	A	30	Ambient	2.20 ± 0.21
	B	30	Ambient	2.23 ± 0.14
III	B	10	Ambient	113.1 ± 16.1[c]
	B	30	Ambient	112.7 ± 6.4[c]
IV	B	30	Ambient	51.9 ± 1.9
	B	30	0°	52.9 ± 1.6
V	B	30	Ambient	207.7 ± 9.2[c]
	C	30	Ambient	216.5 ± 9.2[c]
VI	B	30	Ambient	22.5 ± 1.2
	C	30	Ambient	22.5 ± 1.0

[a] Procedure: A, 0.5 ml CS_2 added to charcoal; B, Charcoal added to 0.5 ml CS_2; C, Charcoal added to 1.0 ml CS_2. [b] The means of six samples and the 95% confidence intervals are reported. The measurements are not corrected for desorption efficiency. [c] Only 3 samples were analyzed.

Table III. Comparison of Gas Samples and Charcoal Tube Samples[a]

Calculated value[b]	64 μg/l.	13 μg/l.	2.6 μg/l.
Gas injection	71.2 ± 1.7	14.5 ± 1.2	2.9 ± 0.2
Charcoal tube[c]	69.8 ± 3.6	13.6 ± 0.7	2.9 ± 0.2
Difference between gas injection and charcoal tubes	2.0%	6.4%	0%

[a] Each value represents the average of six determinations and the 95% confidence level. [b] Calculated from the amount of vinyl chloride and air used to prepare the test atmospheres. [c] Charcoal tube samples were corrected for desorption efficiency.

Stability and Storage Properties. The results of experiments to determine the stability of vinyl chloride-on-charcoal samples, shown in Figure 2, demonstrated that vinyl chloride was stable on charcoal for extended periods of time at ambient or sub-ambient temperatures. However, at ambient temperatures vinyl chloride migrated to the back section of charcoal until it achieved even distribution on the charcoal in the tube. The migration was retarded by cooling the vinyl chloride-on-charcoal samples during storage. In later experiments, it was found that sampling could be accomplished with two charcoal tubes in series with no significant drain on the working capacity of the personal sampling pump being used. The first tube could then be used as the "front" section with the second tube serving as the "backup" section. Since each section was a separate entity, the need for cooling during shipment and storage was eliminated.

Precision and Accuracy. Because the vinyl chloride is not quantitatively removed from the charcoal in the analytical procedure, a measurement, m, of vinyl chloride from charcoal tube samples must be corrected for this loss. The desorption efficiency is the ratio $\bar{x}/\bar{y}$ where $\bar{x}$ is the mean concentration of a test atmosphere as determined by analysis of charcoal tube samples and $\bar{y}$ is the mean concentration of the sample atmosphere as determined directly by injection of gas aliquots. Thus, for a sample, the corrected value, z, is equal to $m\bar{y}/\bar{x}$. The precision of z, expressed as the relative standard deviation, is not simply obtained, but is best approximated by the following equation derived after Ku (29):

$$\left(\frac{S_z^2}{z^2}\right)^{1/2} \simeq \left(\frac{S_m^2}{m^2} + \frac{S_x^2}{n_x\bar{x}^2} + \frac{S_y^2}{n_y\bar{y}^2}\right)^{1/2} \quad (1)$$

where S_i is the standard deviation of n_i values and an overlying bar denotes the number is a mean.

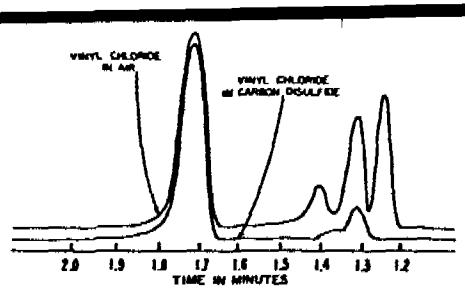

Figure 1. Comparison of peak shapes of vinyl chloride (12.6 ng) in air and in carbon disulfide

The gas chromatograms were obtained on a 20-ft, 10% SE-30 column at 60 °C at an attenuation of X16

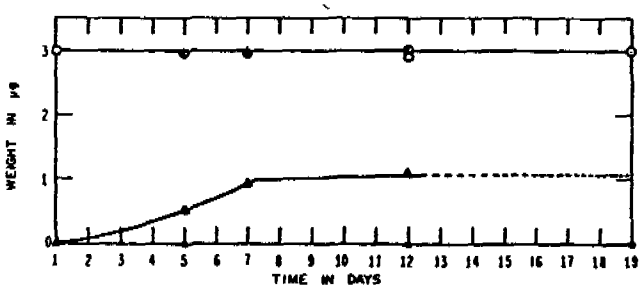

Figure 2. Stability of vinyl chloride-on-coconut-charcoal samples

(●) Back section stored at −20 °C. (△) Back section stored at ambient temperature. (⊙) Total in both sections stored at −20 °C. (⊛) Total in both sections stored at ambient temperature

A number of vinyl chloride-on-charcoal samples of two synthetic atmospheres were analyzed over 20- to 30-day periods by different analysts using different instrumentation. Using Equation 1, the relative standard deviation was determined to be 7.5% where the concentration was 7.3 μg/l. (27 samples) and 7.4% where the concentration was 71 μg/l. (29 samples).

The accuracy of the method was difficult to assess in the absence of a primary standard. In light of this fact, it was thought meaningful to compare two techniques, charcoal-tube determination and analysis by gas aliquot injection. The results of determinations of synthetic atmospheres by these techniques, shown in Table III, indicate good agreement between these methods.

ACKNOWLEDGMENT

The authors express their thanks to K. A. Busch for the statistical derivation.

LITERATURE CITED

(1) E. S. Gronsberg, *Khim. Prom.*, 42(7), 510–11 (1966); *Chem. Abstr.*, 65, 1759a (1966).
(2) E. D. Baretta, R. D. Stewart, and J. E. Mutchler, *Am. Ind. Hyg. Assoc. J.*, 30, 537 (1969).
(3) O. L. Hollis, *Anal. Chem.*, 38, 309 (1968).
(4) A. Foris and J. G. Lehman, *Sep. Sci.*, 4(3), 225–41 (1969).
(5) H. Koenig, *Fresenius Z. Anal. Chem.*, 232(6), 427 (1967).
(6) L. D. Hinshaw, *J. Gas Chromatogr.*, 4(8), 300 (1966).
(7) G. G. Esposito and M. H. Swann, *J. Paint Technol.*, 39, 838 (1967).
(8) E. A. Boettner and F. C. Dallos, *Am. Ind. Hyg. Assoc. J.*, 26, 289 (1965).
(9) O. L. Hollis and W. V. Hayes, *Anal. Chem.*, 34, 1223 (1962).
(10) F. W. Williams and M. E. Umstead, *Anal. Chem.*, 40, 2232 (1968).
(11) G. F. Ernst and J. B. VanLierop, *J. Chromatogr.*, 109, 439 (1975).
(12) L. D. White, D. G. Taylor, P. A. Mauer, and R. E. Kupel, *Am. Ind. Hyg. Assoc. J.*, 31, 225 (1970).
(13) W. Bertsch, A. Zlatkis, H. M. Liebich, and H. J. Schneider, *J. Chromatogr.*, 99, 673 (1974).
(14) J. Gelbicova-Ruzickova, J. Novak, and J. Janak, *J. Chromatogr.*, 64, 15, (1972).
(15) P. W. West, B. Sen, and N. A. Gibson, *Anal. Chem.*, 30, 1390 (1958).
(16) R. Herbolsheimer, L. Funk, and H. Drasche, *Staub-Reinhalt. Luft*, (English ed.), 32(10), 31 (1972).
(17) R. J. Sherwood and F. W. G. Carter, *Ann. Occup. Hyg.*, 13, 125 (1970).
(18) A. Dravnieks, B. K. Krotoszynski, J. Whitfield, A. O'Donnel, and T. Burgwald, *Environ. Sci. Technol.*, 5, 1220 (1971).

(19) "NIOSH Manual of Analytical Methods," HEW Publication No. (NIOSH) 75-121, U.S. Government Printing Office, Washington, D.C., 1974, P&CAM 178.
(20) N. F. Ives, *J. Assoc. Offic. Anal. Chem.*, 58, 457 (1975).
(21) D. H. Ahlstrom, R. J. Kolgour, and S. A. Liebman, *Anal. Chem.*, 47, 1411 (1975).
(22) F. M. Zado and J. O. Rasmuson, Presented at the Regional Technical Conference of the Society of Plastic Engineers, Inc., on "VCM, the Processors' Perspective", October 31–November 1, 1974, New York, N.Y.
(23) S. A. Myers, H. J. Quinn, and W. C. Zook, *Am. Ind. Hyg. Assoc. J.*, 36, 332 (1975).
(24) L. W. Severs and L. K. Skory, *Am. Ind. Hyg. Assoc. J.*, 36, 669 (1975).
(25) J. E. Cuddeback, W. R. Burg, and S. R. Birch, *Environ. Sci. Technol.*, 9, 1168 (1975).
(26) R. M. Ash and J. R. Lynch, *Am. Ind. Hyg. Assoc. J.*, 32, 490 (1971).
(27) M. Smisek and S. Cerny, "Active Carbon", Elsevier Publishing Company, New York, 1970, pp 91–92.
(28) A. T. Saalwaechter, C. S. McCammon, A. W. Teass, and W. J. Woodfin, "Toluene Breakthrough Studies on Activated Charcoal Sampling Tubes", Presented at the American Industrial Hygiene Conference, June 1–6, 1975, Minneapolis, Minn.
(29) H. H. Ku, in "Precision Measurement and Calibration", Volume 1, National Bureau of Standards Special Publication 300, U.S. Government Printing Office, Washington, D.C., 1969, pp 315–39.

RECEIVED for review January 19, 1976. Accepted April 29, 1976.

Modified Solution Approach for the Gas Chromatographic Determination of Residual Monomers by Head-Space Analysis

Richard J. Stelchen

The Goodyear Tire & Rubber Company, Research Division, Akron, Ohio 44316

Head-space analytical methods are described for the determination of residual vinyl chloride monomer (VCM), butadiene, acrylonitrile, styrene, and 2-ethylhexyl acrylate (2-EHA) in their associated polymers at the ppm level and below. The more volatile monomers (VCM, butadiene, and acrylonitrile) are determined by dissolution of the polymer and analysis of the equilibrated head space above the polymer solution. It was possible to determine VCM and butadiene at the 0.05-ppm level and acrylonitrile down to 0.5 ppm. The injection of water into polymer solutions containing styrene and 2-EHA monomers prior to head-space analysis greatly enhanced the detection capability for these monomers making it possible to determine styrene down to 1 ppm and 2-EHA at 5 ppm. Incorporation of polymer into the calibration standards compensates for the effect which the polymer matrix has upon the equilibrium partitioning of the monomer between the solution and head space. The relative precision and error in the determination of these monomers near the quantitation limit was less than 7%.

The disclosure of evidence (*1*) linking the inhalation of vinyl chloride monomer (VCM) to the occurrence of angiosarcoma (cancer) of the liver has made it necessary to determine trace levels of residual monomer in poly(vinyl chloride) (PVC) products. This concern for VCM-based polymers has promoted an interest in monitoring more closely the levels of residual monomers in other types of polymers, such as styrene, acrylonitrile, butadiene, and 2-ethylhexyl acrylate (2-EHA). The allowed level of residual monomer in polymers used in food-contact applications is regulated by the Food and Drug Administration (FDA). In nonfood applications or in the absence of a definitive FDA ruling, good manufacturing practices dictate that the level of residual monomer should be minimized and within generally accepted health standards.

Sensitive analytical techniques are required to measure residual monomers in the polymer matrix when present at the part-per-million level and below. Gas chromatography (GC) has been the method of choice because of its resolution, versatility, and ease of manipulation. The monomers styrene, acrylonitrile, butadiene, and vinyl chloride have been determined (2) by dissolving the polymer in an appropriate solvent and chromatographing an aliquot of the polymer solution. To prevent polymer build-up in the GC injection port, water or methanol (*3, 4*) was used to precipitate the polymer and the supernatant liquid was injected. The detection limits for these methods were about 10 ppm. The ether extraction of residual acrylonitrile from the polymer, followed by the GC analysis of the extract gave a sensitivity of 100 ppm (*5*).

Several authors have described head-space gas chromatographic methods for the determination of volatile components in polymeric materials (*5–10*). These techniques offer distinct advantages over the direct-injection GC techniques. The most important are the prevention of column contamination, the reduction of interference arising from the injection of large amounts of solvent, and enhanced sensitivity.

Two approaches to the head-space analysis of residual monomers in polymers have been used—the solid and solution approaches. The solid approach (*10, 11*) involves the equilibration of a solid polymer sample in a sealed system. The residual monomer is partitioned between the headspace and the polymer phase. The monomer concentration in the head space is determined and the original concentration in the polymer is calculated. Since polymer standards of known monomer content are not readily available, the head-space monomer concentration must be related to the original concentration in the polymer either by assuming 100% diffusion of the constituent into the head space or through equilibrium calculations utilizing Henry's law and the appropriate partition coefficient. Berens (*11, 12*) determined this coefficient for the vinyl chloride–PVC system and applied this to the determination of VCM in PVC resin powder. Rapid equilibration of residual VCM with the head space (<1 h) occurred when PVC powder was heated to 90 °C. The validity of this approach was confirmed in the laboratory by the author.

The solution approach to head-space analysis involves equilibration of a sample solution in a sealed system followed by the analysis of the head-space gas. Calibration is readily accomplished by using internal or external standard techniques. Quantitative methods utilizing solution head-space analysis have been reported for determinations of blood alcohol (*13–15*), organics in aqueous solution (*16, 17*), and residual styrene in polystyrene (6).

Although the solid head-space method provides about 10-fold more sensitivity than the solution head-space method (10% sample solution), the solid method may be applied only to sample systems where equilibration with the head space is rapid and complete. For example, residual styrene monomer in polystyrene does not reach equilibrium with the head space