a week in the lower troposphere and weeks in the upper troposphere (14, 15), any cloud seeding with AgI at some distant location and previous time could have enhanced the Ag aerosol concentrations. Because Cd is the most volatile element under study, its behavioral pattern may result from fossil fuel combustion at some distant time and place.

Seasonal differences, with associated causes, are most pronounced with Al and Mn. The increase in aerosol Pb appears to be related to the return of 2000 students (and associated autos) for the fall semester. Less explainable though are the reasons for the reduced Cd, Co, Tl, and Zn concentrations during the drier and dustier 1974 summer season, unless these elements, too, are at times from anthropogenic sources. Their sources may be difficult to document.

Acknowledgment

The author is grateful to Michele Daniels, Michael Diechart, Kermit Kinsley, Marie Smith, and John W. Winchester for technical assistance and advice.

Literature Cited

(1) Struempler, A. W., "Adsorption Characteristics of Silver, Lead, Cadmium, Zinc and Nickel on Borosilicate Glass, Polyethylene and Polypropylene Container Surface," *Anal. Chem.*, 45, 2251–4 (1973).
(2) NOAA, EDS-NCC, "Annual Climatological Summary for Chadron, Nebraska, 1973," Federal Building, Asheville, N.C. 28801.
(3) *Ibid.*, 1974.
(4) Nat. Air Pollut. Control Admin. Pub. No. AP-49, "Air Quality Criteria for Particulate Matter," 1969.
(5) Adams, R., Goodbins, J. W., Winchester, J. W., Brar, S. S., Nelson, D. M., "Areawide Trace Metal Concentrations Measured by Multielement Neutron Activation Analysis: A One Day Study in Northwest Indiana," *J. Air Pollut. Control Assoc.*, 21, 363–70 (1971).
(6) Kay, M. A., McKown, D. M., Gray, D. H., Eichor, M. E., Vogt, J. R., "Neutron Activation Analysis in Environmental Chemistry," *Am. Lab.*, July, 1973.
(7) John, W., Kaifer, R., Rahn, K., Wesolowski, J. J., "Trace Element Concentrations in Aerosols from the San Francisco Bay Area," *Atmos. Environ.*, 7, 107–18 (1973).
(8) Shum, Y. S., Loveland, W. D., "Atmospheric Trace Element Concentrations Associated with Agricultural Field Burning in the Williamette Valley of Oregon," *ibid.*, 8, 645–55 (1974).
(9) Hoffman, G. L., Duce, R. A., Zoller, W. H., "Vanadium, Copper, and Aluminum in the Lower Atmosphere between California and Hawaii," *Environ. Sci. Technol.*, 3, 1207–10 (1969).
(10) Duce, R. A., Hoffman, G. L., Zoller, W. H., "Atmospheric Trace Metals at Remote Northern and Southern Sites: Pollution or Natural?," *Science*, 187, 59–61 (1975).
(11) Zoller, W. H., Gladney, E. S., Duce, R. A., "Atmospheric Concentrations and Sources of Trace Metals at the South Pole," *ibid.*, 183, 198–200 (1974).
(12) Mason, B., "Principles of Geology," 3rd ed., Wiley & Sons, New York, N.Y., 1966.
(13) Nat. Acad. of Sci., "Lead, Airborne Lead in Perspective," Washington, D.C., 20418, 1972.
(14) Poet, S. E., Moore, H. E., Martell, E. A., "Lead 210, Bismuth 210, and Polonium 210 in the Atmosphere: Accurate Ratio Measurement and Application to Aerosol Residence Time Determination," *J. Geophys. Res.*, 77, 6515–27 (1972).
(15) Rasool, S. I., ed., "Chemistry of the Lower Atmosphere," Plenum Press, New York, N.Y., 1973.

Received for review September 9, 1974. Accepted August 20, 1975. Work supported in part by the Chadron State College Research Institute.

Performance of Charcoal Tubes in Determination of Vinyl Chloride

John E. Cuddeback*, William R. Burg, and Shelton R. Birch[1]

Department of Environmental Health, University of Cincinnati, Cincinnati, Ohio 45267

■ The adsorption characteristics of airborne vinyl chloride on activated charcoal was examined for use as an analytical sampling device. Data are presented to show that charcoal has a limited yet useful capacity for adsorbing low levels of vinyl chloride. Breakthrough volumes, sampling rates, and storage characteristics are presented that indicate a 100-mg portion of activated charcoal in a sampling tube has a capacity of at least 65 μg of vinyl chloride with a twofold safety factor when sampling air containing 5 ppm of vinyl chloride. Analytical methodology is described that produced a 90% recovery of vinyl chloride even after two weeks of sample storage.

The need for analysis of ambient air for low levels of vinyl chloride monomer (VCM) was recognized January 22, 1974. It was on this day that it was made public that three polymerization reactor cleaning personnel at the B. F. Goodrich Co. plant in Calvert City, Ky., had died of a rare form of liver cancer. The results of this announcement was an immediate implication of VCM as a cancer suspect agent. The ensuing investigation (*1*, *2*) indicated the need for an accurate analytical method for low level work.

The Environmental Protection Agency (EPA) and the National Institute of Occupational Safety and Health (NIOSH) were concerned with monitoring personal and environmental exposure to VCM. The EPA was concerned with airborne concentrations of VCM that were transported beyond the plant boundaries into the surrounding community and would be covered under the National Hazardous Pollutant Standards. On the other hand, NIOSH required in-plant exposure data in order to advise the Occupational Safety and Health Administration (OSHA) on safe working standards. After the announcement by B. F. Goodrich Co. there was a flurry of measurement and standards-setting activity; the OSHA standard went from 500 ppm (*3*) to 50 ppm (*4*) to 1 ppm (*5*). As of this writing the EPA has yet to set an emission standard, however, a large amount of data has been obtained from the ambient air in the vicinity of polyvinyl chloride plants (*6*), and this may be the basis for future research.

The general sampling method finally chosen by the EPA and NIOSH was based on absorption of VCM on charcoal followed by desorption by CS_2 and gas chromatographic analysis. The major difference in the methods of the two agencies was the size of the sampling device and amount of charcoal used; the EPA used an 18-in. tube with three 3-in. sections of charcoal (*6*) and NIOSH used a smaller tube with about one inch of charcoal divided into two unequal sections (*7*, *8*). The EPA is finalizing a method for air sam-

[1] Present address, USAF Environmental Health Laboratory, Kelly AFB, Tex.

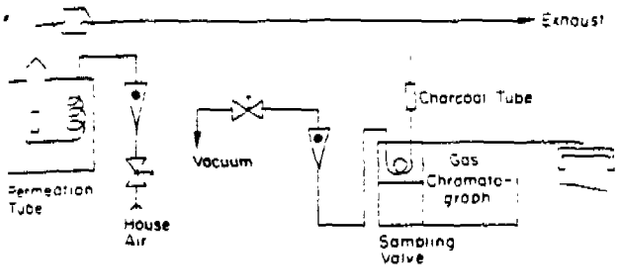

Figure 1. Dynamic dilution system for charcoal tube testing and calibration of gas chromatograph

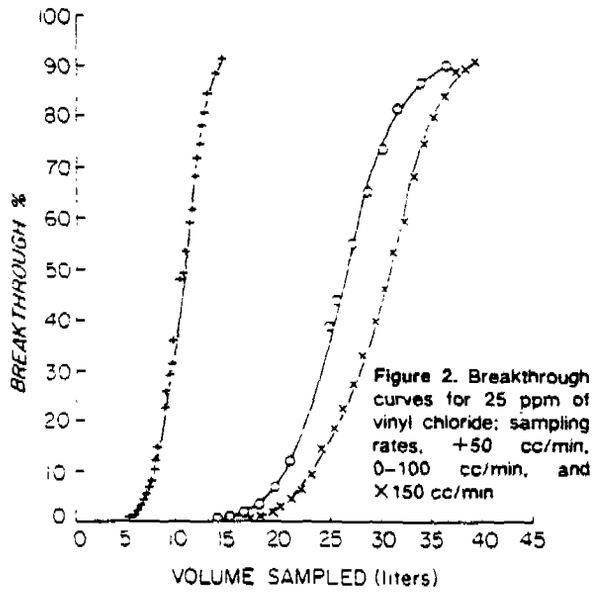

Figure 2. Breakthrough curves for 25 ppm of vinyl chloride; sampling rates, +50 cc/min, 0–100 cc/min, and ×150 cc/min

pling at this time (*9*). The charcoal-filled tubes have been extensively used by both of the agencies for field studies of VCM levels in air: however, there has not been a thorough description of the performance parameters and thus our laboratory undertook an examination of the charcoal tube absorption method for VCM.

Experimental Apparatus and Procedures

Calibration and Standards. Known concentrations of VCM were obtained in the flow dilution system (Figure 1) with a gravimetrically calibrated permeation device made as described previously (*10*). A combination of two different permeation devices and variation of dilution air provided a concentration range of 0.5–50 ppm VCM. Solution standards were also made by injecting known volumes of VCM into volumetric flasks containing measured quantities of carbon disulfide. The flasks were sealed with a silicone rubber septum before injecting the VCM, and adjustment was made for atmospheric conditions assuming ideal gas behavior. Solution standards were made fresh daily as needed. Samples from the dynamic flow dilution system were periodically checked against solution standards so that solution standards were not often needed and served only as a cross-check.

Sampling Equipment. Samples were obtained by drawing a metered stream of air through charcoal tubes obtained from the Mine Safety Appliance Co. The tubes were the small type used for personal monitoring (*8*) and were from a single batch of charcoal. The sampling system is schematically shown in Figure 1. The regulated house vacuum system was used to draw samples through the charcoal tubes thus providing a constant flow. Effluent from the charcoal tube was sampled by means of a stainless steel seven-port sampling valve with a calibrated (*11*) loop system, the loop could be used for direct air sampling when the charcoal tube was not in line.

Table I. Retention Data for Vinyl Chloride on Charcoal Tubes

Vinyl chloride concn, ppm	Sample rate, ml/min	Mass VCM flow rate, μg/min	Retention volume, l[a]	Retention time, min[a]	Total mass, μg[a]
5	50	0.639	10.0	200	127.9
5	100	1.278	9.8	98	125.2
5	150	1.916	29.3	195	373.6
25	50	3.19	7.9	158	504
25	100	6.38	22.8	228	1456
25	150	9.58	20.5	137	1312
50	50	6.38	9.0	180	1285
50	100	12.78	18.1	181	2311
50	150	19.16	14.8	98.7	1891

[a] At 10% breakthrough from front section of tube.

Analytical Equipment. Analysis of flow system gases was performed directly using a Tracor MT 160 chromatograph equipped with a flame ionization detector. The operating conditions were as follows: column 6 ft × ⅛ in. stainless steel, column packing Poropak Q, column temperature 135°C, inlet temperature 150°C, detector temperature 175°C, carrier gas flow rate 30 cc/min of nitrogen. Peak areas were computed by means of a Disc Integrator. The detection limit for VCM was 1 ng.

Sample Analysis. Analyses of air samples were made directly using the calibrated gas-sampling loop. Air was drawn through the sampling loop for 30 sec at 100 cc/min before injection to achieve reproducible results. The detection limit was less than 0.1 ppm VCM when using a 3.81-ml sample volume. A charcoal tube was placed in series with the sample loop and the effluent analyzed when determining sampling efficiencies. The charcoal tubes were analyzed for VCM by placing the charcoal in a 2-ml glass vial and sealing the vial with a silicone rubber septum. The vial was then cooled to dry ice temperatures for several minutes before injecting 0.5 ml of room temperature carbon disulfide through the septum. The vial was removed from the dry ice when the bubbling produced by the mixing of the carbon disulfide and charcoal ceased. The vial was allowed to stand at room temperature for 5 min before removing 5 μl of the solution from the sealed vial for injection into the chromatograph.

Results and Discussion

Sample Capacity. Testing of the charcoal tubes was undertaken to determine their capacity for vinyl chloride. In these tests only the front portion of the two-section charcoal tube was used. Figure 2 illustrates a set of breakthrough curves obtained when sampling from a 25-ppm VCM in dry air (less than 20% r.h.). The general sigmoid shape of the breakthrough curves remained the same for 5- and 50-ppm samples. Data for three concentrations of vinyl chloride are presented in Table I. There is not a definite trend with sample concentration and breakthrough volume nor is there a firm trend with sampling rate and breakthrough volume. It is apparent, however, that the 50-cc/min sample rate had a 10% breakthrough volume that was lower than when sampling at higher flow rates in all cases.

Table II gives packing data for the front section of charcoal tubes from two manufacturers. As can be seen there is considerable variation both in total content and how effec-

packing of the charcoal tubes may explain lack of consistency between the 100- and 150-cc/min sample rates as noted in Table I, however, this does not explain the consistently lower retention volume for the 50-cc/min flow rate. One further point should be made concerning the possible differences when used in the field with a reciprocating piston-type pump: The flow in the system used in our experiments was a constant vacuum source and did not have the pulsed flow observed with the small personal pumps. The pumping system may radically alter the retention characteristics and give more consistent results between the high flows and the low flows.

The variability of charcoal in absorbing VCM can be readily seen in Table III which presents data on respirators as well as charcoal tubes. Respirator data were obtained by NIOSH (*12*) on commercially available charcoal scrubbers used in respirators. The major feature of interest is the difference in capacity of the charcoal in the three situations examined. Again the difference must be explained as a combination of flow rate and packing characteristics. The data obtained on the charcoal tubes were taken at a much lower relative humidity which may explain the appreciably greater capacity of the tubes.

Recovery of VCM. Desorption of a substance from charcoal is dependent on variables such as compound to be desorbed, solvent, charcoal source, temperature, and sample age. Table IV presents the recovery data for charcoal tubes stored for up to two weeks. The recovery figures indicate an average initial recovery of vinyl chloride of about 87.5% which diminishes somewhat with age, about 7% in one week. Additional storage beyond one week apparently has little effect on the higher concentration sample. However, if only the two variables, storage time and concentration, are considered, a 16% decrease in recovered vinyl chloride was noted for the low concentration samples after 14 days.

During sample storage there was migration of the vinyl chloride from the front section to the back section of the tubes and this made analysis of both sections mandatory in order to determine total VCM. The tubes were stored at room temperature and the migration could have been minimized by storing under refrigeration. This migration may explain the slight decrease in the average sample recovery upon storage if it is assumed that the charcoal retains a certain fraction of vinyl chloride. Thus, there is an added amount of charcoal that must be considered after migration. A straightforward linear approach indicates that the amount retained would be 1.5 times greater than if all of the vinyl chloride were on the front section—i.e., the total amount of charcoal would be 150 mg instead of 100 mg on front only. As shown in Table III, the average loss with no storage is 13% and increases to an average of 19% for 7 days and 24% for 14 days whereas a linear approximation would predict 19.5% average loss due to the additional charcoal.

Migration was observed between the sections of the charcoal tube and led to the examination of the effects of temperature plus the possibility of losses by migration out of the tube to ambient air. To examine variations in migration with temperature and losses from the tubes, a series of tubes were stored at 43°, 22°, and 4°C, sealed by ordinary plastic caps supplied with the tubes or fused closed by means of a torch. Table V presents the data from 24 samples. There is one immediately apparent factor: storage at 4°C limits migration severely during the seven-day storage period. Even at the end of 15 days the migration of vinyl chloride between the two sections was appreciably hindered. Thus, there is a definite effect of storage temperature on the migration of vinyl chloride throughout the tube; however, this migration did not affect the total recovery of the vinyl chloride.

A multivariant analysis was performed on the data displayed. In Table V the four variables, storage temperature, time, quantity of VCM, and sealing method, were examined for effect on recovery of the VCM. The multivariant analysis included two additional variables not included in the result indicated in Table IV—storage temperature and method of sealing the tubes. The hypothesis that each of the indicated variables had no effect was tested at the 0.01 level and in none of the cases was this hypothesis rejected. The effect of the above variables on partition of the VCM between the sections of the tubes was also tested and as might be expected, temperature had an effect on the partition; however, the storage time and quantity of VCM ab-

Table II. Packing Variations in Charcoal Tubes

Supplier		Front section packed length, mm	Front section wt. of packing, mg	Wt, g/mm
MSA[a]		18.2	103.1	5.66
MSA[a]		14.6	92.8	6.36
MSA		16.6	103.2	6.22
	Av	16.5	99.7	6.08
	% rel. std. deviation	10.9%	6.0%	6.1%
SKC[b]		15.1	85.0	5.63
SKC		15.2	82.4	5.42
SKC		14.1	86.2	6.11
SKC		16.6	87.3	5.26
SKC		17.0	90.5	5.32
SKC		17.2	85.9	4.99
	Av	15.9	86.2	5.45
	% rel. std. deviation	7.8%	3.1%	7.0%

[a] Mine Safety Appliance Co. [b] SKC, Inc.

Table III. Ten Percent Breakthrough Capacity of Charcoal Absorbers

Cartridges,[a] sample capacity		Canisters,[b] sample capacity		Charcoal tubes,[c] sample capacity	
Air, l/g charcoal	VCM, mg/g charcoal	Air, l/g charcoal	VCM, mg/g charcoal	Air, l/g charcoal	VCM, mg/g charcoal
44.9	5.7	48.9	12.5	148	18.9
36.6	4.7	53.5	13.3	181	23.1
41.1	5.2	35.8	9.1	90	12.8
40.0	5.1	40.1	10.2		

[a] Flow rate, 30 l/min at 50 ppm and 50% rel. humidity (Ref. 12). [b] Flow rate, 60 l/min at 100 ppm and 50% rel. humidity (Ref. 12). [c] Amounts of 50–100, and 150 cc/min at less than 20% relative humidity.

Table IV. Partition of VCM Upon Storage

Storage time, days	Vinyl chloride sampled, μg	Vinyl chloride recovered, %[a]	Recovered sample in front, %	Recovered sample in back section, %
0	2.55	85	100	0
0	31.9	89	100	0
7	2.55	83	84	16
7	31.9	79	86	14
14	2.55	71	84	16
14	31.9	81	79	21

[a] Average for six tubes at each storage time except for zero storage in which case only one tube was used.

Table V. Charcoal Tube Performance Under Various Conditions

Storage days		High concentration, 31.9 μg						Low concentration, 2.6 μg					
		Capped tubes, °C			Fused tubes, °C			Capped tubes, °C			Fused tubes, °C		
		43	22	4	43	22	4	43	22	4	43	22	4
	Recovery, %	91	71	87	69	79	79	87	84	77	72	86	90
7	Total recovered in back section, %	22	14	3	19	21	3	23	14	0	27	27	10
	Recovery, %	78	98	85	60	81	85	76	67	81	64	69	69
15	Total recovered in back section, %	28	20	11	28	23	15	28	18	6	22	19	1

sorbed also affected the degree of partition. The only factor that did not influence the VCM partition was the method of sealing the tubes.

Analytical Methodology. From the data presented above, it can be seen that the charcoal tubes must be refrigerated if any information is to be gained from a separate analysis of the rear section of the tube. The function of the additional section is to determine breakthrough of VCM during sampling. To achieve this additional bit of information, it is necessary to refrigerate the tubes, preferably at dry ice temperatures, in the interim between sampling and analysis. If the tubes have not been refrigerated during the interim, the analytical procedure should be modified and the tube sections should be analyzed as a combined sample. When the tube sections were combined, the recovery was enhanced considerably over separate analysis. Ten identical VCM samples were obtained, and the charcoal tubes stored at ambient temperature for two weeks. Five of the tubes were analyzed as a unit by combining the front and rear sections before analysis, and the remaining five were analyzed separately. The average total recovery was 90.8% (std dev 5.5%) for the combined section analysis and 78.0% (std dev 4.5%) for the tubes which had each section analyzed separately. Thus, there was a 14% decrease in recovery when analyzing the tube sections separately and this could be significant at low concentrations.

The sample losses upon immediate analysis of the charcoal tubes, or when analyzing the combined sections of tubes stored for a period preceding analysis, amounted to approximately 10%. An examination of the head-space gas in sealed 2-ml vials containing standard solutions indicated that VCM was distributed between the gas phase and the carbon disulfide such that the head-space gas should not be neglected. Comparison of solutions of carbon disulfide originally containing 30.1 μg/ml of VCM and the head-space gas above the solution provided an approximate value for the Henry's law constant; the value determined was 8.1 atm. When we use this value and apply Henry's law to the analysis procedure described previously, head-space gas losses would be expected to be on the order of 6% when the head space was 1.5 ml. The remaining losses of VCM can be attributed to irreversible absorption on the charcoal. The Henry's law constant can be used to show typical losses when making-up standards in a 25-ml volumetric flask are on the order of 1% which may be decreased by limiting the head space.

Conclusions

A small charcoal tube is adequate for sampling vinyl chloride if well-controlled conditions are maintained. From the data given above, the recommended sampling procedure is as follows: sample rate, 100 cc/min; maximum sample volume, 5 l; and low-temperature storage, if breakthrough is thought to be a problem. The conditions given above provide a safe limit under most circumstances such that variabilities in temperature and relative humidity will not pose a problem. The analysis of tube contents should be performed on the combined contents of the charcoal tube unless the tubes have been stored at −20°C or less, in the interim between sampling and analysis and the head-space gas over the desorbing reagent, CS_2, should be minimized for highest recovery efficiencies. For accurate determination of recoveries, each charcoal tube batch should be examined by random selection of charcoal tubes from the same batch followed by a performance check using a dynamic flow system to absorb known concentrations on the charcoal. The dynamic system should be used to avoid sample losses that might occur when using a standard vinyl chloride solution in ethyl acetate as previously done (7) for other compounds. Recovery data should be determined over the same time interval as anticipated storage time.

Thus, while the charcoal tube method appears adequate for concentrations of VCM on the order of 1–50 ppm or more, there should be great care taken when using the method for very low levels, such as might be found around the perimeter of a polyvinyl chloride plant. As the concentration of VCM decreases, the scatter in the data and sample losses become a greater factor in analytical accuracy.

Acknowledgment

The authors wish to thank Jeanne Cooper Burg for advice on the statistical analysis.

Literature Cited

(1) Maltoni, C., "Preliminary report on carcinogenicity bio-assays of vinyl chloride," Presented at OSHA Hearing, February 15, 1974.
(2) Tabershaw Cooper Associates, Inc., "Final report epidemiological study of vinyl chloride workers," Presented to Manufacturing Chemists Association, 1974.
(3) *Fed. Regist.*, **36**, No. 105, May 29, p 10505, 1974.
(4) *Ibid.*, **39**, No. 67, April 5, p 12342, 1974.
(5) *Ibid.*, No. 195, October 4, p 35890, 1974.
(6) Environmental Protection Agency, "Preliminary assessment of environmental problems associated with vinyl chloride and polyvinyl chloride," 1974.
(7) White, L. D., Taylor, D. G., Mauer, P. A., Kupel, R. E., *Am. Ind. Hyg. Assoc. J.*, **31**, 225 (1970).
(8) U.S. Dept. of Health, Education, and Welfare, "NIOSH manual of analytical methods," p 127–1, 1974.
(9) Analytical Quality Control Newsletter, p 2, Environmental Protection Agency, No. 24, January 1975.
(10) Saltzman, B. E., Burg, W. R., Ramasuamy, G., *Environ. Sci. Technol.*, **5**, 1121 (1971).
(11) Cuddeback, J. E., Burg, W. R., Birch, S., *Anal. Chem.*, **42**, 355 (1975).
(12) U.S. Dept. of Health, Education and Welfare, "Evaluation of organic vapor respirator cartridges and canisters against vinyl chloride," HEW Publication No. 75-11 (NIOSH), 1974.

Received for review April 7, 1975. Accepted August 14, 1975. Work supported by U.S. Public Health Service Grant ES 00159 and by the Environmental Protection Agency under Research Grant R800869.