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Environmental News

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FOR IMMEDIATE RELEASE THURSDAY, APRIL 4, 1974

EPA FORMS VINYL CHLORIDE TASK FORCE

The Environmental Protection Agency has formed an internal task force to assess the overall environmental impact of vinyl chloride, a gaseous chemical, and the plastic, polyvinyl chloride.

Vinyl chloride has been implicated in the recently reported deaths of ten workers at plants where the gas is used to produce the polyvinyl chloride. All died from a rare form of cancer, called angiosarcoma of the liver.

The task force, chaired by Glenn E. Schweitzer, Director of EPA's Office of Toxic Substances, is charged with assessing possible environmental and health risks associated with the manufacture, distribution, and disposal of vinyl chloride and polyvinyl chloride.

At present, the task force is reviewing, collecting and assessing data on 1) the ambient emission and effluent levels of vinyl chloride in air and water from vinyl chloride and polyvinyl chloride manufacturing plants 2) the environmental impact of all disposal methods for vinyl chloride and polyvinyl chloride wastes, including landfill, incineration, deep-well injection, and ocean dumping 3) ecological effects of vinyl chloride in the environment.

The task force plans to meet with environmental and consumer groups to discuss its mission and exchange information. A similar meeting has taken place between the task force and the chemical industry. The task force is also working with other Federal

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agencies concerned with vinyl chloride, including the Department of Labor; the Department of Health, Education and Welfare; the Consumer Product Safety Commission, and the Department of Commerce.

Vinyl chloride is used as a propellant in 23 pesticide aerosols currently registered by EPA. The gas helps expel the contents from the pesticide containers.

In a March 28 letter to the Health Research Group, a Washington D.C. based public interest organization, EPA said that it will shortly notify the manufacturers, formulators and distributors of these products of the need to substitute another substance for vinyl chloride. A copy of the letter is attached.

The Agency said that, "Even though the health data for vinyl chloride are limited, we believe that it is prudent public policy for us to request the manufacturers of these pesticides to make a voluntary change..."

If a currently ongoing EPA evaluation of these pesticides indicates a substantial risk or imminent hazard to the user, and if voluntary compliance has not been obtained, the Agency will invoke suspension of the products or other enforceable remedies.

On March 27, EPA mailed letters to the manufacturers giving them ten days in which to state any objections to the Agency's making public the brand names of the 23 products. This period for comment is required since the existence of vinyl chloride in the pesticides may be considered part of the products' confidential formulations.

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THE NEW YORK ACADEMY OF SCIENCES
WORKING GROUP
ON
TOXICITY OF VINYL CHLORIDE-POLYVINYL CHLORIDE

"ENVIRONMENTAL CONCERNS BEYOND THE WORKPLACE"

Glenn E. Schweitzer
Director, Office of Toxic Substances
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Presentation to the Working Group on
Toxicity of Vinyl Chloride-Polyvinyl Chloride
The New York Academy of Sciences
New York City, New York
May 11, 1974

"ENVIRONMENTAL CONCERNS BEYOND THE WORKPLACE"

Glenn E. Schweitzer
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Environmental Protection Agency
Washington, D. C.

During the past several months vinyl chloride has awakened all elements of the environmental community to the presence of the plastics industry. In some respects it is fortunate that we have been alerted in a rather dramatic fashion to the need for greater attention to this important segment of our industrial base which will surely continue to expand in the years ahead. While this symposium is directed to the existing and potential risks involved in the manufacture, distribution, and use of vinyl chloride monomer (VCM) and polyvinyl chloride (PVC), many of the types of considerations and uncertainties that punctuate these deliberations undoubtedly characterize a far broader swathe of concerns over chemicals in general. Hopefully, we can extrapolate from our current experiences with VCM and PVC in identifying problems with other potentially important commercial chemicals early in their embryonic stage and thus minimize the economic dislocations attendant to corrective actions.

Unfortunately, the proposed Toxic Substances Control Act has been lodged in a Joint Committee of the Congress for ten months. Thus, a very powerful tool for addressing the vinyl chloride problem, and similar problems with other chemicals, in an adequate manner is not available to the Federal Government. We must rely on other statutory authorities and on the power of persuasion in our efforts to insure that our population is not being unnecessarily exposed to concentrations of VCM and other chemicals used in connection with VCM. It is particularly distressing that until this statutory authority is on the books, the Federal Government will not be equipped -- in terms of experienced personnel and supporting resources -- to grapple with the intricacies of this type of toxic substance problem in a manner which will insure full attention to the balancing of risks and benefits.

Today I will report to you on the preliminary investigations undertaken by the Environmental Protection Agency during the past three months. We are still several weeks away from reaching even tentative conclusions as to what additional steps, if any, should be taken by the Agency concerning VCM/PVC activities. Our monitoring data are not yet

in hand. Similarly, our analytical studies are not yet completed. Nevertheless, we are pleased to share with you some of our initial thoughts. We will welcome your comments on the efforts to date and on further steps which are necessary. In this regard, the prioritization of our efforts is particularly important in view of the speed with which this problem is evolving and the limitations on our resources.

At the outset it is important to underscore that the progress made to date would not have been possible without the extensive cooperation of other federal agencies, industry, and environmental groups. We have profitted greatly from our discussions with these organizations, through our on-site industrial visits, and through constructive suggestions that we have received.

EPA Regulatory Authorities

To date EPA has exercised its authority in the pesticides area to suspend the use of vinyl chloride as a propellant in all pesticide products registered for indoor use in homes, food handling establishments, hospitals, and other enclosed areas, with a mandatory recall of stocks in the channels of trade. In addition, in response to the Agency's request, all registrants of pesticides which are used outdoors have agreed either to withdraw their registrations or to amend them to provide for the substitution of another propellant in their products.

We are currently investigating what regulatory actions, if any, are needed with regard to air emissions, water effluents, and solid waste disposal at facilities involved in VCM and PVC activities. In addition the Agency has responsibility in the areas of drinking water standards, ocean disposal, and municipal waste disposal -- all areas of some relevance to the VCM/PVC concerns.

As previously mentioned a principal authority which is currently missing is the Toxic Substances Control Act. The requirements for reporting of industrial production data envisaged in the Act would enhance our knowledge of the types and extent of different uses of VCM. The testing provision would enable us to obtain much needed data -- and particularly data on toxicity and persistence -- for assessing the risks associated with low concentration levels of VCM, including those levels that are likely to persist beyond the workplace. The proposed regulatory provisions would provide a mechanism for addressing those products using VCM not now subject to regulation under other laws. Also, if considered appropriate, steps might be taken to limit the amount of unreacted VCM in certain PVC products which may eventually migrate out of these products to pose an unnecessary risk.

The Materials Balance

EPA's initial concern in this area centered on reports in February of a materials loss of six percent in the PVC production process. Our detailed investigations indicate that these initial reports were in the correct range. Clearly, the percentage of losses will vary with the type of process, the age of the plant, the level of technology that is employed, and manufacturing practices. However, there is no doubt that in the United States substantial amounts of VCM -- probably exceeding 200 million pounds annually -- and large quantities of PVC -- probably exceeding 50 million pounds -- are being discharged into the environment during the PVC production process. Most of the VCM escapes directly into the atmosphere as air emissions, with lesser amounts dissolved in water effluent streams and entrapped in sludge and solid wastes. PVC losses occur as particulate in air emissions, suspended solids in water effluents, and components of solid wastes.

Clearly, a principal area of VCM leakage is associated with the operation of the polymerization kettles, including losses when they are opened for recharging, cleaning, or sampling. Other losses occur during the transfer of VCM from tank cars to storage, during the drying process, and from leaks at a variety of valves, flanges, and pump seals throughout the process. Polymer losses are similarly distributed among a variety of activities including dust collector losses, disposal of oversize particles, and sampling losses. The enclosed flow diagram for a typical suspension process reflects such losses which according to our estimates usually range from four to eight percent. In this regard two aspects are particularly significant: there are a variety of PVC processes with differing problems and control possibilities, and in every case the number of potential leakage points is very large.

For economic reasons and in view of the fire hazard from VCM, industry has always been concerned with reducing its losses down to a point. Now some plants are taking steps to reduce these losses further in view of worker and environmental concerns. We understand that the tightening up on maintenance and housekeeping activities can indeed have a significant impact, and several PVC plants reportedly are now operating close to the four percent level for total losses.

The data needed for conducting material balance analyses during VCM production and PVC compounding and fabrication processes are less readily available. However, we do not believe that these activities pose as serious an environmental concern beyond the fence line of the plant, at least at the present time, as the polymerization process. At the same time in the absence of constant vigilance VCM losses to the atmosphere during the latter phases of the VCM production process and during transfer to and from storage can be significant. Also, throughout the process there are many seals and valves which inevitably lead to leaks. With regard to compounding and fabrication, unreacted monomer is inevitably

associated with the polymer following the polymerization process. In some cases this monomer concentration reaches 7000 ppm although a more representative level probably is in the range of 500 to 1000 ppm. During the mixing and heating processes in the compounding and fabrication plants, some of this VCM undoubtedly escapes into the environment. Now, in efforts to reduce further the level of unreacted VCM in the final product many companies are introducing new techniques which increase the migration rates during this phase of production.

The Need for Epidemiological and Toxicological Studies

Since some elements of our population in addition to the plant worker are being exposed to some level of VCM, we must address the question: What is the risk of such exposure?

In considering non-worker populations, we are confronted with a host of new unanswered questions. How relevant to this concern are the data generated for estimating worker exposure risks? Can meaningful extrapolations be made from toxicological tests at relatively high dose levels to the lower levels of the dose-response relationship? Can realistic extrapolations be made from intermittent exposure, which characterizes the past and present toxicological and epidemiological investigations (e.g. eight hours per day, five days per week) to sustained exposure at the same dose levels or at lower levels? Are synergistic effects that result from exposure to other chemicals as well as VCM influencing the worker's response to VCM, and are there similar opportunities for such synergism within a non-worker population?

There are not sharp answers to these questions, and indeed they go to the heart of many of the fundamental uncertainties of the biological sciences. To date the epidemiological and toxicological data that have been generated have been directed almost exclusively to concerns over workers. This is the data base that we in EPA presently have available. I doubt that anyone is more aware of its inadequacy than are those of us responsible for regulatory actions based on this data. Unfortunately, we often have no choice but to make judgemental decisions using whatever scientific information is available.

Other reports presented at this symposium review past, current, and future studies directed to VCM. While they will undoubtedly be helpful to our assessment of the environmental problem, from our point of view they are clearly not adequate in improving the basis for estimating non-worker risks. Let me cite three examples of the types of studies which appear to be needed:

- Epidemiological investigations of populations near chemical plants that are likely to have been exposed to low ambient levels of VCM over a prolonged period of time. It is the

responsibility of industry to support such efforts which will help clarify whether manufacturing activities pose a risk to neighborhood residents. At the same time we recognize the complexities involved in designing and carrying out such studies, the advantages of drawing on governmental experience in this area, and the prototypic nature of such an undertaking. Therefore, it seems likely that EPA will be prepared to participate in such efforts along with industry and other interested parties.

- Toxicological tests at appropriate dose levels, with a sufficiently large number of animals, and with appropriate exposures to provide the basis for meaningful conclusions concerning the likely health effects of VCM in ambient air near chemical plants. Such tests are clearly the responsibility of industry. Indeed, industrial responsibility for the testing of the safety of its products is a basic tenet of the Toxic Substances Control Act. At the same time, we are aware that some industrial firms are concerned about the possible inadequacy of commercial test facilities to accommodate the needed tests. Therefore, if necessary, the National Center for Toxicological Research, which is supported by FDA and EPA, is prepared to work with industry toward suitable arrangements for utilizing available buildings in Jefferson, Arkansas.
- Research on animals and in vitro experiments to help clarify the toxicological significance of impurities in VCM, synergistic effects due to exposure to other chemicals in addition to VCM such as vinylidene chloride, and metabolic reactions induced by VCM. Government, industry, and academia all have responsibilities in this area, and EPA is currently considering specific steps that might be taken to contribute to advancing the frontiers of our knowledge.

Monitoring, Persistence, and Migration Studies

We are obviously concerned about current and future background levels of VCM in the air and in the water throughout the country. Our more immediate efforts, however, are being directed to determining ambient and peak levels near chemical plants.

Recently, we initiated a nationwide sampling and analysis program to determine, at least in a preliminary fashion, the VCM levels in ambient air and in water and semi-solid effluents at about ten PVC plants. These activities are currently underway, and we hope to have the results within several weeks.

As a precursor to this nationwide effort, several weeks ago we conducted a preliminary monitoring program at the B. F. Goodrich plant in Louisville using inadequately tested sampling and analysis methods. At that time VCM levels were detected of 1 to 2 ppm in the ambient air outside the plant, 2 to 3 ppm in the primary water effluent, and 100 to 200 ppm in the sludge at the plant site. However, these numbers could be in error by as much as an order of magnitude due to the pioneering nature of the effort, and no conclusions should be drawn at this time.

During the past several weeks we have made a major effort to develop credible and standardized sampling and analysis procedures, building on this initial experience. Our current monitoring efforts are based on this recently improved methodology. The limit of detection for our current technique is approximately .06 mg/liter in water and .06 ppm (volume/volume) in air. However, when vacuum cans are used, the detection limit is .2 ppm because the gas sample must be diluted. The technique we are using is now publicly available with the hope that our efforts toward standardization will lessen the chaos characterizing current monitoring efforts of several federal agencies and industry.

While the near-term objective of these monitoring efforts is to gain a limited perspective of the levels of VCM near PVC plants, we should also learn more about the persistence of VCM in air and water from our measurements. Samples are to be taken during daytime and at night, and there undoubtedly will be a range of temperature and humidity conditions. However, we have not structured the measurements with research as a principal objective, and we will not be able to quantify persistence characteristics with any degree of precision.

Limited laboratory experiments are also being attempted to clarify persistence characteristics of VCM. Related to our decision to suspend pesticide sprays containing VCM, one laboratory test showed that in an unventilated and unlighted chamber, less than one percent of the VCM initially present was dissipated after four days. Current efforts are directed to clarifying the rate of retention of VCM entrapped in water effluent streams, as well as further work to understand the effect of light, heat, and moisture on VCM in air.

There has been considerable discussion of the amount of unreacted VCM monomer remaining in PVC and the rates of migration out of the PVC. Many companies are now seized with this problem, and I suspect the number of samples being taken to determine VCM concentrations and migration rates has increased considerably in recent weeks. We do not know whether such migration from finished products contributes significantly to background levels of VCM, but as you are aware FDA is seized with several aspects of this problem directly related to food. Should there be high levels of VCM background in the environment, then our concern over all sources of VCM -- including migration from many products -- should intensify.

In all of these areas industry has a major responsibility for determining and alerting the public about the behaviour of its products. I would hope that in the months and years ahead industrial monitoring efforts at the fence line will increase dramatically; persistence will become a key concern; and the ultimate fate of chemicals will be less uncertain. Already some chemical establishments have rather broad sampling and analysis programs, and as a direct result of VCM concerns, others are also making new efforts in this regard.

At the same time EPA has a responsibility to help insure the adequacy of the national effort in keeping abreast of the chemical cross-section of our environment.

Concerns over Disposal of PVC

While we tend to lump all types of PVC into one category, I am sure you are aware of the variances in the chemical and physical properties of different grades of PVC. Also, end products made from PVC include a variety of other chemicals which are added throughout the production cycle.

To date EPA's principal concerns relating to PVC have been directed to possible problems attendant to its disposal -- either in incinerators or landfills. We have not investigated in depth any of the special problems associated with inhalation or ingestion of low concentrations of PVC particulate.

With regard to incineration, HCl is a primary product of concern. Also, toxic metals may be present as additives and thus cause inhalation problems, either as metal or oxide vapors.

Landfill disposal operations have traditionally assumed that PVC is stable with little likelihood of biological degradation or undesirable leachates. Taking a long-term perspective these assumptions seem clearly overly simplistic, and we should address in greater depth problems attendant to the disposal of plastics. Experiences in the tropics, for example, have demonstrated the effect of bacteria on PVC which has not been specially treated for use in humid areas.

The Risks, the Benefits, and the Costs

The current problems with VCM have brought into sharp focus the practical aspects of balancing the risks and benefits associated with commercial chemicals. The costs involved to reduce these risks substantially may be formidable -- or indeed may be prohibitive. The aspect which is perhaps the most troublesome goes to the heart of this meeting -- What is the risk now and under alternative regulatory approaches?

In the years ahead more chemicals will be in commerce, the properties of many chemicals will be better understood, and consequently the list of chemicals considered to be hazardous to man and the environment will undoubtedly be much longer. Also, improved research and analytical capabilities will show that the effects of these chemicals -- acting individually and synergistically -- are much farther reaching than currently suspected effects.

As these realities of the chemical age unfold, there must be a far greater sophistication in approaches to responsible regulation. Fully, we will develop the necessary precautionary measures that will limit exposure to chemicals when necessary, but not unnecessarily curtail commercial activities.

ENCLOSED IN BUILDINGS



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Interim Method for Monitoring Vinyl Chloride
in Water Effluents and Air Emissions
Being Used by the Environmental Protection Agency

The sampling and analysis method described in the enclosure reflects current state-of-the-art and undoubtedly will be improved in the months and years ahead. Indeed, it should be recognized that these interim procedures have not been adequately tested.

Several additional caveats should be recognized. It is exceedingly difficult to prepare stable aqueous calibration solutions of VCM. For this reason carbon tetrachloride solutions of vinyl chloride are used to calibrate the gas chromatograph for aqueous samples of vinyl chloride. Even these are difficult calibration solutions with which to work. The calibration procedure developed by the Southeast Environmental Research Laboratory is described in the enclosure. Another weakness is that the stock solution of VCM in carbon tetrachloride must be determined against mixtures of VCM in zero nitrogen. The FFAP on Gas Chrom Q packed columns which is used for aqueous sample analysis is not well suited to analysis of gas samples of VCM.

At present, there is no adequately tested method for continuously monitoring vinyl chloride. Based upon the experiences of the National Institute of Occupational Safety and Health and EPA Region IV, the carbon adsorption column is being used. Time constraints have made it necessary to specify Fischer Scientific activated coconut shell charcoal for standardization of interim EPA procedures although other charcoals or adsorbents may prove to be more efficient.

Vinyl chloride to be used for calibration purposes (50 ppm in zero air) is being obtained from Scott Laboratories and tedlar bags from Fluorodynamics, Inc. However, the use of these sources of supply in no way reflects endorsement of their products as preferable to comparable products of other organizations.

Should there be questions concerning these procedures, Dr. Robert B. Medz (Area Code 202, 426-2382) may be able to clarify further the methodology that has been developed.

Environmental Protection Agency
5/2/74

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METHOD FOR VINYL CHLORIDE (VC) IN INDUSTRIAL
WASTE WATER EFFLUENTS AND ATMOSPHERIC EMISSIONS

1. Scope and Application

- 1.1. This method is applicable to VC monomer determinations in industrial effluents, sludges and scums, and atmospheric emissions.
- 1.2. The limit of detection is approximately 0.06 mg/l in water (0.06 ppm v/v in air samples). When vacuum cans are used, the detection limit is 0.2 ppm because the gas sample must be diluted from 100 ml to about 350 ml.

2. Summary

- 2.1. Water composite and air and water grab samples are analyzed without cleanup by gas chromatography (GC). Separations are effected by selection of one of two types of columns depending upon the nature of the sample. Detection is by means of the flame ionization detector (FID). Tetrahydrofuran extracts of sludges and scums are used for injection into the G.C. Air continuous samples on activated carbon are extracted with carbon disulfide and analyzed by G.C.
- 2.2. VC confirmation may be made by mass spectrometric analysis of the GC eluent. Independent confirmation may also be made in the event of extraordinarily high VC concentration samples by submitting the samples to NERC-RTP for long-path Fourier transform I.R. spectrophotometry (requires 20 cu. ft. air samples but for high levels 2-3 cu. ft. of sample can be diluted).

3. Interferences

- 3.1. Certain volatile hydrocarbons have elution characteristics similar to VC. None of these have been shown to be present in discharge or air samples which have been analyzed in the limited field experience so far.

4. Apparatus and Materials

- 4.1. Gas Chromatograph.
- 4.2. Flame ionization detector.
- 4.3. Recorder - any potentiometric strip chart recorder which is compatible with the detector system.

4.4. GC Column Materials.

4.4.1. For waste water, sludge or scum samples.

4.4.1.1. Borosilicate glass tube - 6' x 2.5 mm I.D. preferred. When G.C. oven configuration requires shorter columns, these should be used.

4.4.1.2. Solid Support - 60/80 mesh Gas Chrom Q.

4.4.1.3. Liquid Phase - 4% FFAP on solid support (weight percent).

4.4.2. For air samples.

4.4.2.1. Borosilicate glass tube - 8' x 2.5 mm I.D. preferred. When G.C. oven configuration requires shorter columns, these should be used.

4.4.2.2. Solid Support - Carbowax A.

4.4.2.3. Liquid Phase - 0.4% Carbowax 1500 on solid support (weight percent).

4.6. Continuous Air Monitoring Materials.

4.6.1. Tubing, pyrex glass, 18" x 3/8" O.D.

4.6.2. Activated coconut charcoal, 8-16 mesh, Fischer Scientific Company.

4.6.3. Becton-Dickson 27 gage 3/8" hypodermic needle flow control.

4.6.4. Vacuum pump.

4.6.5. Air flow meter.

4.10. Pressure Gas Regulator (0-5 PSIG).

4.12. Microsyringes - 10, 25, 50, and 100 ml.

4.13. Gas-tight sample syringes - 1 ml, 50 ml graduated.

4.14. Vacuum Sampling Cans - 370 ml steel Vacu-Samplers.

- 4.15. Tedlar Bags - 12" x 12", 36" x 36", equipped with sampling system.
- 4.16. Automatic sampler - compositor (manual sampling optional) equipped with sample refrigeration capabilities, a means to prevent loss of vinyl chloride from open bottles.
- 4.17. Glass sampling bottles with teflon lined screw type caps - 50 ml capacity (or other depending upon sampler requirements).
- 4.18. Septum-sealed vials - 1 to 10 ml capacity.
- 4.19. Dedicated G.C./M.S. for confirmatory test.
- 4.20. Barometer.
- 4.21. Thermometer.

5. Reagents, Solvents, and Standards

- 5.1. Carrier gas - zero nitrogen, and helium.
- 5.2. FID gas - zero hydrogen, oxygen.
- 5.3. Tetrahydrofuran.
- 5.4. Carbon tetrachloride (G.C. grade).
- 5.5. Carbon disulfide (G.C. grade).
- 5.6. Standards.
 - 5.6.1. VCM in zero air, 50 ppm (+ 2%) v/v.

6. Sampling

6.1. Water Sample

- 6.1.1. All waste water discharge points identified in NPDES permits should be sampled for VCM. Three successive 24-hour composite samples of each site should be taken. Compositing interval should be 1 hour (manual or automatic sampling is optional). Compositing interval of 20 minutes may be used if automatic sampler has this capability. Samples should also be taken at waste water treatment units such as clarifiers,

and scum and sludge separators. Two 8-hour composites should be taken from the effluents from each of these points, and one 8-hour composite should be taken of scum and sludge from each separator unit. Compositing interval should be 1 hour. Three grab samples of clean process water (city or well) should be taken as blanks.

6.1.2. Samples should be taken in 50 ml bottles with gas tight, teflon sealed, screw-cap closures, or in equivalent containers required by the characteristics of automatic samplers. All water, sludge, and scum samples should be refrigerated during collection and storage. Compositing volumes should be selected to assure head space above the samples are minimized to avoid losses of VOC by its partitioning into the gas phase. Provisions should be made to avoid such losses when using continuous monitors.

6.1.3. Estimates of discharge flow should be made using any appropriate measuring device (venturi, weir, magnetic meter, etc.).

6.1.4. Samples should be preserved by refrigeration until they are ready for analysis. They should also be protected from sunlight.

6.2. Air Samples

6.2.1. Sampling sites should be selected which are downwind and in the plume of the atmospheric emissions from the plant. Samples should be collected only in areas where local residents or neighboring industries would be exposed. Sampling should be conducted over a period of five days. Sampling sites should be selected in the following array: one site immediately upwind (A) and one immediately downwind (B) of the plant site; 4 sites about 0.4 miles from the plant site, one laterally left (C) and one laterally right (D) of the plant site on a line roughly perpendicular to the prevailing wind direction and two (E,F) downwind from the plant site; two sampling sites (G,H) approximately 0.5 miles downwind; one sampling site each at distances approximately 0.6 (I), 0.8 (J), 1.0 (K), and 3.0 (L) miles downwind from the plant site. If wind is fish-tailing severely, locate sampling sites G and H approximately 0.5 mile upwind (prevailing wind direction orientation) from the plant.

The sites specified are a minimum. Additional sites may be selected contingent upon overriding micro-meteorological considerations that must be determined by the sampler in consultation with the Regional meteorologist. These may be at ground or some elevated level.

6.2.2. <u>Sampling Sites</u>		<u>Minimum Sampling Schedule</u>			
Prevailing Wind Direction					
<u>Miles</u>		<u>Time</u>	<u>Mon.</u>	<u>Wed.</u>	<u>Fri.</u>
	A				
	C <u>Plant</u> D	0800	A,A,B	A,B,B	A,A,B
	B	1000	C,D,F	C,D	C,D,D
0.4	E F	1200	A,E	A,G,G	A,E
0.5	G H	1400	B,B,F	B,H	B,B,G
0.6	I	1600	C,G	E,K	I,J
0.8	J	1800	D,I	-	L,L
1.0		K 2000	-	H,L,L	-
3.0	L	All times are $\pm$ 30 minutes			

- 6.2.3. Grab samples are to be taken in 50 ml gas tight syringes, 370 ml "Vacu-Sampler" metal cans, or 12" x 12" capacity Tedlar bags. The "Vacu-Sampler" is evacuated and back-filled to pressure of 10" Hg with zero nitrogen (equivalent to 246.6 ml at 760 mm Hg if can is filled at 21°C). A nozzle on top of the can allows a sample to be taken and sealed until analyzed. Assume perfect gas laws to estimate volumes. Hypodermic syringes are flushed several times, then the sample is taken and the syringe is locked and sealed until it is ready to be analyzed.

The Tedlar bag samplers are filled by pulling the walls of the bag apart to suck in the air sample, and then the bag is sealed until the sample is ready to be analyzed.

All samples should be protected from the sunlight.

- 6.2.4. Continuous samples are to be taken in pyrex tubes (approximately, 3/8" O.D. x 18" long) packed with activated coconut shell charcoal (Fisher Scientific Co., 8-16 mesh). The charcoal is added to the tube

in three 3-inch segments, each separated by a glass wool plug. The two ends of the packed tube are also plugged with glass wool. Both ends of the adsorption tube are plugged with serum caps for transit and storage.

Flow rate through the tube should be controlled by inserting a Becton-Dickson 27 gage, 3/8" hypodermic needle through one of the serum caps, and into the end glass wool plug. Air is sucked through the tube by connecting it to a conventional vacuum pump (the arrangement is similar to that used in the National Air Surveillance Network). Flow rate should be about 200 ml/min. For each adsorption tube, the flow rate should be calibrated in the laboratory using a standard flow meter before a sample is taken and should be verified again in the laboratory after the sample is taken.

The adsorption efficiency of the carbon should be verified in the laboratory by preparing a 3 ppm v/v VCM mixture in air in the 36" x 36" Tedlar bag and drawing this through the adsorption tube. Flow rates through the tube should be verified before and after the experiment.

All collections should be made with the adsorption tubes protected from light - either by wrapping with foil or enclosure in a box.

Each segment of the adsorption sample is worked up separately by etching the tube in the middle of each 3" section with a file, successively breaking each segment and spilling the contents into measured volumes of carbon disulfide in glass stoppered test tubes. The additions should be effected cautiously and with cooling in an ice bath since the interaction of activated charcoal with carbon disulfide is exothermic. A 2 micro liter aliquot of the supernatant solution should be injected on the Gas Chrom supported FFAP column for estimation of the adsorbed VCM. Successive analyses of the three adsorption tube segments will indicate the amount of break-through of VCM through the adsorbent.

The same procedure should be used for taking samples in the field.

6.2.5. Record the temperature and atmospheric pressure at which the samples are taken.

6.2.6 (See page 7a)

7. Calibration

7.1. Calibration for Analysis of Gas samples.

7.1.1. Record ambient temperature and atmospheric pressure.

7.1.2. Prepare dilutions of 50, 1.0, 0.2 ppm (v/v) of vinyl chloride in zero nitrogen by diluting standard VC gas mixture (50 ppm in zero air) with appropriate volumes of nitrogen. Dilutions may be made using Tedlar bags and gas tight syringes.

7.1.3. Inject 1 ml aliquots of the calibration samples into a G.C. equipped with a Carbowax - 1500 (on Carbowax A) packed column and an FID detector. Use zero nitrogen as the carrier gas at a flow rate of 60 ml/min. Operate the inlet and the column at room temperature.

7.1.4. Prepare a calibration curve. Repeat dilutions and G.C. injections until calibration curves are reproducible.

7.1.5. Assume the perfect gas laws to be applicable.

7.2. Calibration for Analysis of Water Samples.

7.2.1. Prepare a stock solution of 10 ppm vinyl chloride by bubbling a slow stream of standard vinyl chloride gas mixture (50 ppm) into a septum-sealed vial which has been completely filled with carbon tetrachloride. During this period, the vial system should provide for free exhaust of the nitrogen dilution gas. If a supply of reagent VC is available it may be used in place of the standard VC gas mixture.

7.2.2. Determine the concentration of the stock solution by G.C. analysis using a FFAP on Gas Chrom Q packed column and FID detector. Operate the G.C. with zero nitrogen carrier gas at a flow rate of 60 ml/min. inlet temperature of 150°C, and a column temperature of 62°C. The stock solution concentration should be determined by comparison to appropriate dilutions of V.C. in nitrogen zero gas.

7.2.3. Prepare dilutions of V.C. in carbon tetrachloride solution at concentrations of 2, 1.0, and 0.2 ppm using

7a

- 6.2.6. Tedlar bags are the grab sampling device of choice and should be used to the maximum degree possible in meeting the minimum sampling schedule. Continuous samples should be taken at sites A, B, C, and D at ground level, unless otherwise specified by the regional meteorologist.

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septum sealed vials which are completely filled with known amounts of carbon tetrachloride.

7.2.4. Inject 2 microliter aliquots of carbon tetrachloride calibration samples into G.C. equipped as described in 7.2.2.

7.2.5. Prepare a calibration curve. Repeat dilutions and G.C. injections until calibration curves are reproducible.

8. Procedure

8.1. Water Sample Analysis

8.1.1. Untreated water samples (1-5 microliter aliquots) are injected directly into the G.C.

8.1.2. A 4% FFAP on "Gas Chrom Q" packed column is used. Nitrogen zero gas is used as the carrier gas at a flow rate of 60 ml/min. Inlet temperature is set at 150°C. The column is operated isothermally at 62°C. Detection is by FID.

8.1.3. Report concentration of VC in sample in mg/l.

8.2. Sludge and Scum Samples

8.2.1. Extract 5 grams of sludge or scum sample with 100 ml of tetrahydrofuran (THF). Analyze THF extract in the same manner used for water samples in 8.1. If VC concentrations are too high, make appropriate dilutions of the THF extracts.

8.2.2. Report concentration of V.C. in sample in mg V.C./g of sample.

8.3. Air Sample Analysis

8.3.1. Grab samples.

8.3.1.1. Use a 0.4% Carbowax 1500 on Carbo-Pak A packed column. Use nitrogen zero gas as the carrier gas with a flow rate of 60 ml/min. Operate the column and inlet at room temperature. Use a flame ionization detector.

8.3.1.2. Untreated air samples (1 ml) are injected directly into the G.C.

8.3.1.3. Report concentration of V.C. in gas samples in ppm (v/v).

8.3.2. Continuous Samples

8.3.2.1. Use same procedure as that used in section 6.2.4. for calibration of adsorption tube efficiency.

9. Quality Control

9.1. Duplicate sample analyses are recommended as a quality control check.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Southeast Environmental Research Laboratory
Athens, Georgia 30601

SUBJECT: Determination of Vinyl Chloride
Monomer in Aquatic Effluents

DATE: April 24, 1974

FROM: Alfred D. Thruston, Jr. *DSJ*
Analytical Chemistry Branch

TO: Arthur W. Garrison
Analytical Chemistry Branch.

INTRODUCTION

This technical assistance project was undertaken at the request of Dr. Henry Enos in his memo of March 15, 1974 on "The Availability of an Analytical Method for Vinyl Chloride in Water."

SUMMARY

A method for preparation of quantitative standard solutions of vinyl chloride monomer (VCM) in carbon tetrachloride was developed. Two gas chromatographic techniques to quantitatively determine VCM in aquatic samples were tested. They are based on: (1) direct aqueous injection, and (2) carbon tetrachloride extraction. Both methods were tested on effluent samples from a vinyl chloride plant and shown to be reproducible and quantitative at the mg/l levels. They are adequate for screening at the $\mu\text{g/l}$ level. The presence of vinyl chloride was confirmed by gas chromatography-mass spectrometry.

RECOMMENDATIONS

Water samples containing vinyl chloride should be collected by completely filling a glass bottle and sealed with a teflon-lined cap. Samples should be immediately refrigerated and kept cold during shipping and storage. Quantitative standards should be prepared gravimetrically. Direct aqueous injection GC is the best method for screening samples for mg/l levels of vinyl chloride. Extraction methods should be used to analyze samples containing $\mu\text{g/l}$ amounts of vinyl chloride. Gas chromatography-mass spectrometry is valuable for confirmation of the presence of vinyl chloride. Headspace gas sampling is suggested as an alternate screening method.

ANALYTICAL METHOD

Equipment

1. Vinyl chloride - lecture bottle size (Matheson or equivalent)
2. Carbon tetrachloride (CCl_4) - GC grade
3. 2 ml and 25 ml serum vials with teflon-coated rubber septa

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4. 10 and 100 μ l syringes
5. 1 ml gas syringe
6. Gas chromatograph with flame ionization detector, temperature programmed column oven, and a one millivolt recorder.

Analytical Parameters

Column & Packing -	1/8" OD x 6' long SS or glass filled with 10% FFAP on 80/100 chromosorb W-AW
Column Temperature -	Isothermal at 60° C. until VCM elutes (50 seconds), then raise temperature to 160° C. at 30°/min. until water or solvent is eluted.
Injection Port Temperature -	200° C.
Detector Temperature -	280° C.
Helium Flow Rate -	40 cc/min.
Chart Speed -	1/2" per minute

Sample Preservation

Store water samples in the refrigerator in glass bottles with teflon-lined screw tops. Particulate matter should be allowed to settle. For convenient replicate sampling, several 2 ml septum vials can be filled with samples and capped before analysis.

Standard Solution Preparation

Pipet 25.0 ml CCl_4 in a 25 ml serum vial, cap, and accurately weigh to 0.1 mg. Attach a two-foot length of tygon tubing to the cut-off valve on the vinyl chloride lecture bottle and place the tubing end in a beaker of water. Adjust the lecture bottle valve to give a steady flow of gas as indicated by the bubbles. Pierce the tubing 1 inch from the valve with a 1 ml gas syringe. Flush the syringe twice and then withdraw 800 μ l of VCM (approximately 2 mg). Inject the VCM slowly into the CCl_4 in the serum vial. Care should be taken not to pull any CCl_4 solution into the syringe when removing the syringe from the septum. Shake the vial vigorously for one minute. Reweigh the vial and calculate the concentration of VCM (approximately 80 ng/ μ l). Recap the vial with an unpierced septum or transfer to a bottle closed with a teflon-lined screw cap. (The CCl_4 attacks the septum rubber once the teflon liner is pierced.) Dilute this stock solution to give working standards. Two ml serum vials, which hold about 1.8 ml

to the neck (calibrate), make good containers for the diluted standards. For example: aliquots of 90, 45, and 23 μ l (100 μ l syringe) diluted to 1.8 ml make 4, 2, and 1 ng/ μ l solutions. These solutions must be prepared fresh daily if the septa are pierced.

Analysis

- A. Direct Aqueous Injection - Inject the sample (2 to 3 μ l) directly into the GC. The sensitivity of this technique depends on the condition of the GC. For example, on three different GC's, 50% full scale chart deflection (FSCD) at the most sensitive attenuation corresponded to: (1) 20 ng, (2) 4 ng, and (3) 0.5 ng of VCM. On instrument (1) with a 2 μ l direct aqueous injection, the lower limit of detection (10% FSCD) was 2 mg/l, while on instrument (3) the limit was 0.05 mg/l.

- B. Extraction with CCl_4 - Carbon tetrachloride quantitatively extracts VCM from water. If a sample contains too little VCM for direct aqueous injection, CCl_4 concentration techniques may be used.

Add 5, 10, or 500 ml of settled sample - depending on the concentration of VCM - to a 15 ml stoppered centrifug tube or a 500 ml separatory funnel containing 1.0 ml CCl_4 . Stopper, shake for 1 minute, allow the layers to separate, and inject 2 μ l of the CCl_4 layer into the GC.

Recovery at the mg/l Level

Aliquots of 1, 2, and 3 ml of an effluent sample containing 7.1 mg/l VCM (as measured by direct aqueous injection) were each extracted with 1 ml CCl_4 . The aqueous and CCl_4 layers from each extraction were analyzed by GC. As shown in Table 1, the concentrations of VCM in the CCl_4 layers indicates essentially complete recovery.

Table 1. CCl_4 Recovery at 7.1 mg/l VCM Level.

Ratio Sample: CCl_4	CCl_4 Layer		Aqueous Layer
	ng VCM*	mg/l in Sample	ng VCM
1:1	17	6.8	<1
2:1	35	7.0	<1
3:1	55	7.3	<1

* Calculated by comparison of GC peak height with that of standard VCM in CCl_4 .

Recovery at the $\mu\text{g/l}$ level

A sample, which analyzed 3.7 mg/l VCM by direct aqueous injection, was diluted from 1 ml to 500 ml with tap water (7.4 $\mu\text{g/l}$ VCM). The 500 ml was extracted with 1 ml CCl_4 - 74% of the VCM was recovered (5.5 $\mu\text{g/l}$).

Another sample that analyzed 0.19 mg/l VCM by direct aqueous injection was diluted 1 ml to 100 with tap water (1.9 $\mu\text{g/l}$). The 100 ml was extracted with 1 ml CCl_4 and 84% of the VCM was recovered (1.6 $\mu\text{g/l}$).

Analysis of Industrial Effluent Samples

Four aqueous samples from three stations at a plastics manufacturing plant were analyzed by both techniques:

- 0468 - clarifier scum removal system discharge
- 0465 and 0472 - primary clarifier discharge (two different days)
- 0463 - plant storm sewer

Results are shown in Table 2.

Table 2. VCM in Aqueous Industrial Effluent Samples.

Sample	Direct Sample Injection mg/l	Extraction with CCl_4	
		Ratio Sample: CCl_4	mg/l
0468*	9.3	1:1	6.8
0465	2.8	3:1	3.0
0472	2.8	3:1	2.9
0463	0.2	50:1	0.2

*Sample was high in particulate matter.

Alternative Analytical Techniques for VCM

- A. Other Columns for Direct Aqueous Injection - Columns 1/8" ID x 2' long packed with Chromasorb 102 or 1/8" ID x 8' long packed with 0.4% Carbowax 1500 on Carbowax A have also been shown to give good results for VCM by Don Brown of the Chemical Service Branch, Surveillance and Analysis Division, Region IV, EPA.
- B. Headspace Screening - This technique (also developed by Don Brown) is a sensitive and fast screening procedure, and is semi-quantitative if standardized. Fill a 2 ml serum vial to half capacity with the aqueous sample, cap, and place in a 40° C oven or water bath. The VCM will equilibrate between the liquid and headspace gas. Withdraw 500 µl of the headspace gas with a 1 ml gas syringe and inject into the GC. After about 10 injections at 60° C, raise the column temperature to 160° to remove water vapor from the column.

Confirmation by Gas Chromatography - Mass Spectrometry

The presence of vinyl chloride is indicated by three prominent ions in the mass spectrum: the vinyl ion at m/e 27, the molecular ion at m/e 62, and the chlorine isotope molecular ion at m/e 64. The ion abundance at m/e 62 and m/e 64 must be approximately 3:1, corresponding to the natural abundance of the chlorine isotopes.

The presence of 0.2 mg/l VCM in sample 0463 was easily confirmed on a Finnigan 1015 GC/MS System. Good spectra were obtained using either a 2 µl direct aqueous injection or 2 µl of CCl₄ extract. To test the sensitivity of GC/MS to VCM, the CCl₄ extract of this sample was diluted to successively lower concentrations and analyzed. Acceptable spectra were obtained with 0.14 ng of VCM injected into the GC — this would correspond to 0.07 µg/l in the original solution.

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EPA QUESTIONS FOR SPI (SOCIETY OF PLASTICS INDUSTRY)

1. list of top 50-100 PVC products by sales volume
2. list of top 50-100 PVC products by volume of plastic in product
3. amounts of unreacted monomer in above products
4. list of PVC compounding plants by name, location, # employees, polymer used, products line, quantities produced
5. list of PVC fabrication plants by name, location, # employees, polymer used, fabrication methods utilized, quantities produced
6. levels of VCM in plants in 4. and 5. by plant area and detection method utilized
7. levels of VCM beyond the plants and detection method(s) used
8. levels of VCM in water effluents
9. decomposition products from various incineration conditions for PVC and quantities of PVC involved
10. amounts of VC leaching out of landfills and total amount PVC buried to date
11. toxicity of PVC resin and products
12. epidemiology studies of workers
13. population within square mile of plants
14. substitutes for VC and PVC
15. Future PVC markets *markets?*
 New products
 New workers for old products
16. Additives used in PVC products

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