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Memorandum

Center for Disease Control
National Institute for Occupational Safety & Health
1014 Broadway, Cincinnati, Ohio 45202

TO : Chief, Physical and Chemical Analysis Branch
Chief, Engineering Branch
Coordinator, Analytical Services, Salt Lake City

DATE: June 24, 1974

FROM : Chief, Organic Methods Development Section

SUBJECT: Vinyl Chloride Research

Since March 1974 Ann Saalwaechter, Tom Lockwood and Bob Hill of the Physical and Chemical Analysis Branch and Jim Woodfin and Chuck McCammon of the Engineering Branch have worked to develop a reliable sampling and analytical method for vinyl chloride. In the attached "Vinyl Chloride Research Summary" I have consolidated their results and made suggestions for areas of future study.

We gratefully acknowledge the cooperation of Tano Lucero of the Salt Lake City Lab.

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Attachment

VINYL CHLORIDE RESEARCH SUMMARY

21 June 1974

Solid Sorbents

Around 20 sorbents were tested for usefulness in solid sorbent devices for collecting vinyl chloride from air. A sampling of the results are given in Table A. The experiments were run with synthetic atmospheres of vinyl chloride in clean air, generated either in Tedlar bags (≥46 ppm) or dynamically by flowing nitrogen over a permeation tube containing vinyl chloride and diluting the stream with clean air (~2.5 ppm). The sorbents were packed in beds measuring 1.5 cm X 4 mm (i.d.) (0.19 cm^3), except that the charcoal beds were 100 mg or 1.9 cm X 4 mm (i.d.) (0.24 cm^3). At a measured flow for a measured period of time synthetic atmosphere was drawn through a sorbent bed followed by either of two monitoring devices--a flame-ionization detector or a gas sampling valve which interfaced the system with a gas chromatograph--thus monitoring the bed effluent for vinyl chloride. The effective capacity of the sorbent is given by the breakthrough volume--that volume of atmosphere that passed through the bed before the concentration of vinyl chloride in the bed effluent reached 5% of the initial concentration. The total capacity is that volume of atmosphere that passed through the bed before the concentration of vinyl chloride in the bed effluent equalled the initial concentration.

The first 13 sorbents listed are unsatisfactory for collecting vinyl chloride. Of the remaining sorbents, carbonized Saran--obtained from Dr. T.A. Davis of Southern Research Institute--appeared superior, with Carbosieve B and coconut charcoal next in capacity. Of still lower

capacity were petroleum charcoal, carbonized polystyrene and molecular sieves 4A and 5A. The data on lines 14, 15, and 16 suggest that sampling flow has a large effect on the breakthrough capacity.

The primary (100 mg) section of the 150-mg two-section charcoal sampling tube occupies a little over 0.2 cm^3. Thus, the tabulated data indicate that if coconut charcoal is used in these devices and the sampling rate is around 50 ml/min, they should be adequate for collecting vinyl chloride from roughly 2-10 ℓ of air, depending on the concentrations of vinyl chloride and possible interferences. This is the subject of continuing studies. Further investigation of carbonized Seran is also planned.

Desorption of vinyl chloride from petroleum charcoal

Desorption efficiencies were determined by sampling known volumes of synthetic atmospheres of vinyl chloride in clean air, desorbing the vinyl chloride with carbon disulfide, and determining it by gas chromatography. Concentrations thus obtained were compared with those from the gas chromatographic analysis of aliquots of the synthetic atmosphere to give the desorption efficiency (DE):

$$DE = \frac{\text{weight vinyl chloride on charcoal/volume atmosphere sampled}}{\text{concentration of vinyl chloride in synthetic atmosphere}}$$

Desorption efficiencies for about 270 μg of vinyl chloride on charcoal tubes has been around 0.8. Variation of the desorption efficiency with vinyl-chloride loading on the charcoal, desorption procedure, and charcoal batch has not been investigated.

Preliminary experiments indicatd that dichloromethane, tetrahydrofuran, trichloroethylene, methanol, and ethanol would offer little, if any, improvement over carbon disulfide in the desorption of vinyl chloride from charcoal.

Analytical Procedure

Solutions or gas samples were analyzed for vinyl chloride by gas chromatography using a flame-ionization detector and one of the following columns:

1) 20-ft 10% SE-30 on 80-100 mesh Chromosorb W AW DMCS at 60°C (isothermal)

2) 20-ft 10% FFAP on 80-100 mesh Chromosorb W AW DMCS at 65°C (programmed)

3) 5-ft 5% SP-1000 on 80-100 mesh Chromosorb W AW DMCS at 65°C (programmed)

The carrier gas was helium flowing at 40 ml/min. With Column (1), the standard curve appeared linear from 0.2 ng/injection, the lower limit of detection, to around 1500 ng/injection.

Solutions of vinyl chloride in carbon disulfide were found to be unstable, especially if contained in a glass-stoppered test tube with a larger headspace volume than solution volume; the rate of loss approached 10% in 30 min. There appears to be loss of vinyl chloride (3%/hr) even from samples desorbed in 2-ml vials which were capped with septa after addition of carbon disulfide to the charcoal. Because of this, desorbed samples were analyzed 30-60 min after addition of the carbon disulfide to the charcoal. The phenomenon will be studied further.

Attempts to prepare standards by the introduction of measured volumes of vinyl chloride gas into carbon disulfide were frustrated by the presence of gaseous impurities in the vinyl chloride. Standards prepared in the following manner gave reproducible and linear standard curves. Concentrated vinyl chloride gas was slowly bubbled into a tared amount of toluene (about 5 ml) contained in a 10-ml volumetric flask. In 3 min, 100-400 mg of vinyl chloride were collected. The solution was reweighed and diluted to the mark with carbon disulfide. Standards were prepared from this stock solution using carbon disulfide for the dilutions.

To determine the magnitude of the loss of toluene during preparation of the stock solution, nitrogen was bubbled through a tared amount of toluene (5 ml) according to the above procedure. The loss of toluene was about 2 mg, which would cause an error of no greater than 2%. During the introduction of vinyl chloride into the toluene, much of the vinyl chloride dissolves. Much less toluene (as vapor) is displaced from the flask than if nitrogen is bubbled through the toluene. Therefore, the actual error due to loss of toluene during preparation of the stock solution is probably much less than 2%.

Chemists at the Salt Lake City Lab prepare their standards by introducing measured volumes of pure vinyl chloride gas into carbon disulfide in 5- or 10-ml volumetric flasks and diluting to the marks. The vinyl chloride is measured in a gas syringe. The carbon disulfide is initially sucked into the syringe and the solution displaced into the flask. The relative accuracies of the two methods needs to be determined.

Storage of vinyl-chloride-on-charcoal samples

Using 150-mg two-section sampling tubes filled with petroleum charcoal, a number of samples containing around 90 μg of vinyl chloride were generated, and stored for varying periods of up to 22 days at -20°C. By day 22 there was no observable loss of vinyl chloride and only 4% of the vinyl chloride had migrated to the backup section. A few such samples were stored at room temperature for 48 hours with no observalbe loss of vinyl chloride, but 2% of the vinyl chloride migrated to the backup section. This experiment will be repeated using coconut charcoal and a lower loading of vinyl chloride.

Interlaboratory Comparison

A rough comparison of our procedure with that of the Salt Lake City Lab (SLCL) was made. Using 150-mg two-section sampling tubes filled with petroleum charcoal, ten 2-ℓ samples of a synthetic atmosphere of vinyl chloride in clean air were taken. Five were analyzed by the Organic Methods Development Section and five at the SLCL. The results are shown in Table B. The SLCL values were 17% higher than ours, a situation that will be subject to further study. The samples sent via air mail to SLCL spent 2 days in transit, followed by 2 days in a refrigerator; thus, the high percentage of vinyl chloride found on the back up section.

TABLE B: INTERLABORATORY COMPARISON

	Average Concentration of Vinyl Chloride	Number of Analyses	Precision (Relative Standard Deviation)	Relative amount of vinyl chloride on back-up Section
OMDS[a] analysis of synthetic atmosphere	132 µg/ℓ	9	6%	
OMDS[a] analysis of samples	108 µg/ℓ[b]	5	1.4%	2%
SLCL analysis of samples	126 µg/ℓ[b]	5	1.0%	25%

[a]Organic Methods Development Section

[b]No desorption efficiency applied