Organization Resources
Counselors, Inc.
1625 I Street, N.W.
Washington, D.C. 20006
(202) 872-1080
Cable Address: ORESCON

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MAR 12 1976
MEDICAL DEPARTMENT

Larry: You may want to send this to Frank Lussier + Len Greco

Memorandum

March 9, 1976

To: ORC Occupational Safety and Health Standards Group
Vinyl Chloride Task Force

From: William E. Nichols

The attachment was received from Nick Wheeler of Union Carbide, we though you might be interested in seeing it.

WEN/cs
Enclosure

TRIP REPORT
VISIT TO WESTERN AREA OCCUPATIONAL HEALTH LABORATORY, SALT LAKE CITY, UTAH

R. N. WHEELER, JR.

DATE: September 4, 1975

PROJECT NO.: 510E05

FILE NO.: 21058

SUMMARY Representatives from several producers or users of vinyl chloride met with OSHA officials at the Western Area Occupational Health Laboratory at Salt Lake City, Utah, on July 8, 1975. The method for sampling and analysis for vinyl chloride by the OSHA charcoal tube procedure was discussed with representatives from OSHA and NIOSH.

The major item discussed was the procedure used by OSHA for eliminating interferences from compounds other than vinyl chloride which may be in the location sampled or from contamination during handling or storage. At present, the retention time on an SE-30 column is used for vinyl chloride identification. They have analyzed several other compounds which have been reported to be interferent with vinyl chloride or present in area sampled. None have been found with the same retention time as vinyl chloride on the SE-30 column. They have on order a Fourier Multiplex Infrared Spectrometer which they intend to eventually use as a means of verifying the presence of vinyl chloride in any questionable sample. To prevent contamination, the charcoal tubes are stored in a refrigerator reserved for these samples only; no other samples or chemicals are to be stored in this refrigerator.

The only external report of analyses of the charcoal tube samples analyzed by this Laboratory is sent to the compliance officer who took the samples. It is left to his discretion as to whether or not to report the actual values obtained by the Laboratory.

DISCUSSION Representatives from several vinyl chloride users met with personnel from NIOSH and OSHA at the Western Area Occupational Health Laboratory in Salt Lake City, Utah, on July 8, 1975. This visit was arranged by ORC (Organizational Resources Counselors) to discuss vinyl chloride sampling and analyses. Those attending the meeting were: John Whitney, Goodrich; G. A. (Bud) Bedford and Paul Bankovich, Goodyear; Bert Boeneke, Allied Chemical; Steve Levitam, Diamond Shamrock; Floyd Madsen, Mike Shulsky (Chemist), and Curtis A. Foster, OSHA; and Dr. Russell Hendrick, NIOSH.

The following information was sought from OSHA personnel. interferences

1. What procedure is used to analyze for vinyl chloride.
2. What is being done to eliminate inferences in the method.
3. What is the precision and accuracy of the method.

Copies of the actual vinyl chloride method used by OSHA were not readily available. Mr. Madsen will mail each attendee at the meeting a copy of the method when he receives them. The chromatographic conditions employed by OSHA are listed in Table 1. Samples are analyzed on a Hewlett-Packard Model 5380A gas chromatograph equipped with an automatic sampler.

The entire contents of a charcoal tube sample are placed in the 1 ml sample vial and 1 ml of CS_2 pipetted into the vial. The vial is then capped, sealed and placed in the automatic sampler. Because of the problem of migration or diffusion of vinyl chloride between the primary and backup sections of carbon in the charcoal sampling tubes, the entire contents are analyzed together. Compliance officers who sample for vinyl chloride are instructed to use a second charcoal tube in series with the primary tube to serve as a backup.

Samples are analyzed on the gas chromatograph using n-heptane as an internal standard. Calibration for vinyl chloride is done by injecting 50 microliters of the gas into a volumetric flask containing 50 mls of CS_2 with 0.01 percent n-heptane added. This procedure was questioned as loss of vinyl chloride at this point would cause the analyses of charcoal tube samples to be reported erroneously high. All the industrial representatives at the meeting use a sealed system to prepare the vinyl chloride standards. OSHA personnel defended the use of the glass-stoppered volumetric, saying that when they prepared vinyl chloride in air samples in plastic bags (believed to be Milar) and sampled with charcoal tubes from the bags, they were within limits of the accuracy of the method.

Desorption efficiencies are determined by injecting standard solutions of vinyl chloride in CS_2 directly onto the carbon. The sampling of vinyl chloride in air from plastic bags using charcoal tubes is used as an alternate method of determining desorption

1. If any compounds are known to be in the area where vinyl chloride is being sampled, the retention times of the compounds are determined on the column used to analyze vinyl chloride samples. Table I lists the chromatographic conditions employed to analyze vinyl chloride. Also listed in the table are compounds with their retention times which have been tested for possible interference with the method.

2. The retention time of vinyl chloride is determined by injecting standard samples into the chromatograph each day. If the retention time of the peak from a charcoal tube sample differs by more than ± 0.01 minute from the retention time of vinyl chloride, the peak is not considered to be vinyl chloride.

3. The charcoal tube samples when received by mail from the compliance officer are stored in a refrigerator which is restricted in use to charcoal tube samples only. No bulk samples or chemicals are stored in this refrigerator.

   Compliance officers are instructed to mail bulk samples separately from charcoal tube samples. If any charcoal tubes are received containing a bulk sample, the package is returned to the compliance officer and not analyzed.

4. A Fourier Transform Infrared Spectrometer from Digalab has been ordered for the Laboratory. When this instrument is received and operating, any questionable samples will be analyzed on the Digalab instrument to confirm the presence of vinyl chloride.

Precision and Accuracy

OSHA personnel at this laboratory are not responsible for developing the data for precision and accuracy determinations for the method. This is a NIOSH function and is being done at Cincinnati, Ohio. Mr. Madsen suggested that we contact Dr. Bob Hill, who is in charge of the vinyl chloride method statistical evaluation, or Ken Busch, who is the statistician at Cincinnati. We were provided with a preliminary report of the evaluation of the vinyl chloride method. A copy of this document is appended.

Miscellaneous Information

The only external report of analyses of charcoal tube samples from the OSHA Laboratory is sent directly to the compliance officer who took the sample. Release of the actual numerical values obtained on the samples is at the discretion of the compliance officer who receives the report.

The personal sampling pumps used by the compliance officers are returned periodically to Cincinnati for recalibration. The compliance officer should check the flow using a flowmeter before taking each charcoal tube sample, according to Mr. Foster.

J. E. Neff

Attachments:
1 Table
1 Document

Manuscript Date: August 6, 1975
Date Typed: September 3, 1975
JEN:gk

TABLE I

OSHA CHROMATOGRAPHIC CONDITIONS FOR ANALYSES OF VINYL CHLORIDE CHARCOAL TUBE SAMPLES

Instrument	Hewlett-Packard Model 5830A Gas Chromatography
Column	20 ft x 1/8 in stainless steel packed with 10% SE 30 on Chromasorb W
Column temperature	50°C
Injection port temperature	200°C
Detector temperature	250°C
Carrier	Nitrogen, 27 cc/min
Sample size	1 µl, using H-P auto sampler
Internal standard	0.01% n-heptane in CS_2

POSSIBLE INTERFERENCES

Compound	Retention Time, Minutes
Vinyl chloride	2.18
Methyl chloride	2.05
Vinylidiene chloride	3.63
Butadiene	1.13
Ethylene oxide	No peak
Acetaldehyde	6.03

MEMORANDUM

DEPARTMENT OF HEALTH, EDUCATION, AND WELFAR
PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

TO : Barry J. White
Associate Assistant Secretary
for Regional Activities-OSHA

DATE:

FROM : Director, DLCD

SUBJECT: Accuracy and Precision Data for P&CAM 178, Vinyl Chloride in Air

In October, 1974, OSHA requested information on the precision and accuracy of the NIOSH method for vinyl chloride. The data was generated sometime ago, but workloads have not permitted the formulation of this data into a memo until this date. The data indicates that the NIOSH method is within the accuracy and precision limits prescribed by OSHA in the vinyl chloride standard.

Test atmospheres containing vinyl chloride were sampled and analyzed by P&CAM 178 to give measurements, M_1, M_2,.....M_n, which were then corrected for desorption efficiency (recovery). The desorption efficiency was determined by sampling synthetic atmospheres containing measured amounts of vinyl chloride with charcoal tubes and determining the recovery. The synthetic atmosphere was analyzed directly by gas chromatography to give measurements, X_1, X_2,.....X_n. The desorption efficiency was X/Y. The relative standard deviation (RSD) reflecting the precision of method was calculated from equation (1) which was derived after Ku[1].

$$(RSD)^2 = \frac{S_z^2}{\bar{Z}^2} = \frac{S_m^2}{\bar{M}^2} + \frac{S_x^2}{N_x\bar{X}^2} + \frac{S_y^2}{N_y\bar{Y}^2} \qquad (1)$$

where S_z, S_m, S_x, S_y are standard deviations of the measurements, X, Y, Z, M
$\bar{Z}$, $\bar{M}$, $\bar{X}$, $\bar{Y}$ are means
N_x, N_y are numbers of samples.
M = Analysis of identical charcoal tube samples from synthetic Atmosphere I.
X = Analysis of identical charcoal tubes samples from synthetic atmosphere II used to determine desorption efficiency.
Y = Analysis of replicate gas samples of synthetic atmosphere II used to determine desorption efficiency.

1. H. H. Ku, "Statistical Concepts in Metrology" in Precision Measurement and Calibration, National Bureau of Standards, Special Publication 300 - Volume 1, 1969, p. 315-39.

Synthetic air concentrations of 71.3 µg/l and 7.2 µg/l of vinyl chloride were used to prepare two sets of 29 and 27 charcoal tubes, respectively. These samples were analyzed over a 20-30 day period by various chemists, using in some cases different instrumentation and thus, the data represent two fairly rugged sample groupings. The percent relative standard deviations of these two sets was 7.5% and 7.6% respectively.

Additional experiments were performed to obtain some indication of the accuracy, although accuracy was difficult to evaluate in the absence of a primary standard. These experiments generally involved six charcoal tube samples which were prepared from a synthetic atmosphere, analyzed and corrected for desorption efficiency. The theoretical value was the concentration which the bag was supposed to be, based on the measured amounts of vinyl chloride and air added. Thus the theoretical value was not the "true" value, since it was subject to experimental error. The value found for the charcoal tube and corrected for desorption efficiency, was also compared to that found by direct injection of gas samples from the same synthetic atmosphere used to generate the tubes. The results of these experiments are shown below (± 95% confidence levels reported):

Synthetic Atmosphere of 64 µg/l (theoretical)

Analysis of Gas Samples, Found = 71.2 ± 0.7 µg/l
% R.S.D. of Gas Samples = 1.0%

Analysis of Charcoal Tubes, Found = 69.8 ± 1.5 µg/l
%-R.S.D. of Charcoal Tubes = 2.0%

Synthetic Atmosphere of 13 µg/l (theoretical)

Analysis of Gas Samples, Found = 14.5 ± 0.5 µg/l
% R.S.D. of Gas Samples = 3.4%

Analysis of Charcoal Tubes, Found = 13.6 ±,0.4 µg/l
% R.S.D. of Charcoal Tubes = 2.9%

Synthetic Atmosphere of 2.6 µg/l (theoretical) (1 ppm)

Analysis of Gas Samples, Found = 2.88 ± 0.07 µg/l
% R.S.D. of Gas Samples = 2.4%

Analysis of Charcoal Tubes, Found = 2.91 ± 0.13 µg/l
% R.S.D. of Charcoal Tubes = 4.5%

Synthetic Atmosphere of 1.3 µg/l (theoretical)

Analysis of Charcoal Tubes, Found = 1.27 ± 0.09 µg/l
% R.S.D. of Charcoal Tubes = 6.3%

Elliott Harris, Ph.D.