UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

RECEIVED
DEC 12 1977
R. N. WHEELER, JR.

DEC 9 1977

Mr. R. N. Wheeler, Jr.
Union Carbide Corporation
P. O. Box 8004
South Charleston, West Virginia 25303

Dear Mr. Wheeler:

Attached you will find a copy of my memorandum to the EPA Regional Offices which you have indicated as containing Union Carbide facilities affected by the vinyl chloride test method requirements. Also attached is a copy of the approved alternate test Method 107 which was sent with the memorandum.

Please note that I have slightly modified the applicability statement in order for it to be consistent with the one contained in reference Method 107. You will also find that I deleted the statement in Section 3 regarding adjustment of homopolymer analysis results, as we agreed. I also changed the statement about standard renewal in order to remove any ambiguity. It is my impression that a requirement of standard renewal every three months would not be unduly burdensome, but advise me if you object.

I expect to soon prepare a new draft of this method in preparation for proposal in the Federal Register along with revised Methods 106 and 107. In the course of this project, your continued assistance would be greatly appreciated.

Sincerely yours,

William Grimley

William Grimley
Test Support Section
Emission Measurement Branch
Emission Standards and
Engineering Division

2 Enclosures

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

SUBJECT: Alternate Vinyl Chloride Test Methods Resubmitted by Union Carbide

DATE: December 9, 1977

FROM: William Grimley, Test Support Section
Emission Measurement Branch, ESED (MD 19)

TO: Director, Surveillance and Analysis Division,
Regions II, III, IV, VI, IX

In accordance with requests from Regions IV, IX, and Union Carbide, we have reviewed the vinyl chloride test items which Union Carbide has resubmitted for consideration as alternate procedures. This review has been done in collaboration with the Quality Assurance Branch of the Environmental Monitoring and Support Laboratory. The items resubmitted were as follows:

1. Method 106, Section 4.3.2. Alternate chromatographic column - Stainless Steel, 6.1 m x 3.2 mm, packed with 20 percent Tergitol E-35 on 60/80 mesh Chromasorb W AW.

2. Method 107. Entire method; attached.

Based on the additional supporting information supplied by Union Carbide, both items are now judged acceptable as alternate procedures.

Because of widespread interest, the alternate Method 107 (draft copy attached) will, with some refinement, be proposed as such in the Federal Register. Acceptance of the enclosed draft should satisfy Union Carbide's needs for the present. They will be expected to follow the method as it is finally promulgated, of course.

For your information, we also expect to propose changes in both Methods 106 and 107 so that it will be possible for the method user to perform a self appraisal to determine acceptance of a particular column as an alternate procedure. This change should greatly reduce the number of requests for alternate procedure approvals.

Should you have any questions, please contact me. My FTS phone is 629-5276; commercial phone is 919 541 5276.

Enclosure

cc: Robert Ajax (MD 13)
Richard Biondi (EN 341)
Alvin Chun, Region IX
John Clements (MD 77)
Joe Knoll (MD 77)
James Wu, Region IV
Susan Wyatt (MD 13)

EPA Form 1320-6 (Rev. 6-72)

DRAFT

DEC 9 19

Method 107 - Alternate Method - Determination of Vinyl Chloride Content of Inprocess Wastewater, Solvents, Resin-Solvent Solutions, Polyvinyl Chloride Resin, Resin Slurry, Wet Resin and Latex Samples

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph nor by those unfamiliar with sampling and analytical laboratory procedures, as there are many details that are beyond the scope of this presentation.

1. Principle and Applicability

1.1 The basis for this method lies in the direct injection of a liquid sample into a chromatography and the subsequent evaporation of all volatile material into the carrier gas stream of the chromatograph, permitting analysis of all volatile material including vinyl chloride.

1.2 This procedure is suitable for determining the vinyl chloride content of inprocess wastewater, solvents, resin solvent solutions, PVC resin, wet cake slurries, latex and fabricated resin samples. The column employed has been shown to resolve vinyl chloride from other materials such as acetaldehyde, acetone and vinyl acetate. However, if a resolution of the vinyl chloride peak is not satisfactory for a particular sample, then chromatograph parameters may be altered provided that the precision and reproducibility of the analysis of vinyl chloride cylinder standards are not impaired. If there is reason to believe that some other compound with an identical retention time is present in the sample, then supplemental confirmation of the vinyl chloride peak through an alternate analytical method, such as mass spectroscopy should be performed.

2. Range and Sensitivity

The lower limit of detection of vinyl chloride in dry PVC resin is 0.2 ppm. For resin solutions, latexes and wet resin this limit rises inversely as the nonvolatile (resin) content decreases.

With proper calibration the upper limit may be extended as needed.

3. Precision and Reproducibility

A comparison of precision and reproducibility between the alternative method and Method 107 using a suspension resin homopolymer sample showed the alternative method had a standard deviation of 0.95 percent at the 340 ppm level and yielded mean results ten percent higher than Method 107. Method 107 in the same test had a standard deviation of 1.89 percent.

A standard sample of latex containing 181.8 ppm vinyl chloride analyzed ten times by the alternative method showed a standard deviation of 7.5 percent and a mean error of 0.21 percent.

A sample of vinyl chloride copolymer resin solution was analyzed ten times by the alternative method and showed a standard deviation of 6.6 percent at a level of 35 ppm.

The increase in standard deviation on the latex and the resin solution samples is due to the correction of the analysis from a gross basis to a contained dry solids basis. Both the latex and resin solution samples contained acetaldehyde along with other monomers and solvents.

4. Safety

Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be minimized and when necessary must be routed to the outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory.

5. Apparatus

5.1 Sampling

5.1.1 Bottles - Sixteen-ounce wide mouth with polyethylene lined screw caps.

5.1.2 Vials - 51 ml Hypo-vials,[1] sealed with Teflon faced Tuf-Bond discs or equivalent for water samples.

5.2 Sample Recovery

5.2.1 Vials - 20 ml with polycone screw caps.

5.2.2 Analytical balance - Capable of weighing to ±0.01 gram.

5.2.3 Syringe - 50 microliter with removable needle.

5.2.4 Frittedglass sparger fine.

5.2.5 Aluminum weighing dishes.

5.2.6 Sample collar to effect sample solution.

5.3 Analyses

Chromasorb W AW 60/80 mesh.

[1] Mention of trade names or specific products does not constitute endorsement

5.3.3 Valco Instrument Six Port Rotary Valve for column back flush.

5.3.4 Septa for H.P. chromatograph injection port.

5.3.5 Injection port liners - H.P. chromatograph.

5.3.6 Regulators for required gas cylinders.

5.3.7 Soap film flow meter Hewlett Packard No. 0101-0113 or equivalent.

5.4 Calibration

5.4.1 Analytical Balance capable of weighing to $\pm$0.1 mg.

5.4.2 Erlenmyer Flask with glass stopper 125 ml.

5.4.3 Pipets 0.1, 0.5, 1, 5 and 10 ml.

5.4.4 Volumetric Flasks - 10 ml and 100 ml.

6. Reagents

6.1 Analysis

6.1.1 Hydrogen gas - zero grade

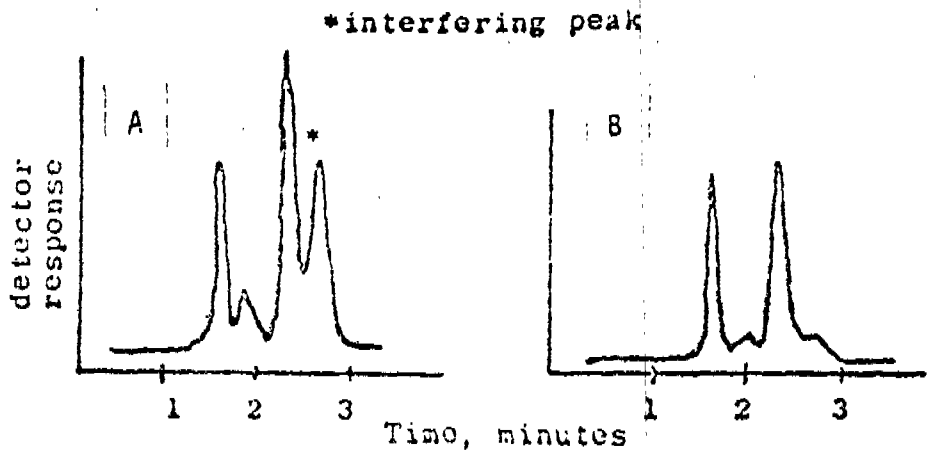
6.1.2 Nitrogen gas - zero grade

6.1.3 Air - zero grade

6.1.4 Tetrahydrofuran - reagent grade

Analyze the tetrahydrofuran (THF) by injecting 10 microliters into the prepared gas chromatograph. Compare the THF chromatogram with that shown on the next page. If the chromatogram is comparable to A, the THF should be

determine if the THF is acceptable for use. If the scan is comparable to B, the THF should be acceptable for use in the analysis.



6.2 Calibration

6.2.1 Vinyl chloride 99.9+% - For preparation of standard solutions.

7. Procedure

7.1 Sampling

7.1.1 Sampling Other Than Water - Allow the liquid or dried resin to flow from a tap on the tank, silo or pipeline until the tap has been purged. Fill a wide-mouth pint bottle and immediately tightly cap the bottle. Place an identifying label on each bottle and record the date, time, sample location and material on the label.

7.1.2 Water Sampling - Prior to use, the 50 ml type-

bubble-free to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, Teflon-side down on the opening of the vial. Place the aluminum seal over the disc and neck of the vial and crimp into place. Affix an identifying label on the vial and record the date, time and sample location on the label. All samples must be kept refrigerated until analyzed.

7.2 Sample Recovery. Samples must be run within twenty-four hours.

7.2.1 Resin Samples

Weigh nine grams of tetrahydrofuran to the nearest 0.01 gram in a tared 20 ml vial. Add one gram of resin to the tared vial containing the tetrahydrofuran. Close the vial tightly with the screw cap and shake or otherwise agitate the vial until complete solution of the resin is obtained. This may take several minutes to several hours depending on the nature of the resin.

7.2.2 Suspension resin slurry and wet resin samples. Slurry must be filtered using a small Buchner funnel with vacuum to yield a wet resin sample. The filtering process must be continued only as long as a steady stream of water is exiting from the funnel. Excessive filtration

the same as the resin sample. A sample of the wet resin is used to determine total solids. This is required for calculating the RVCM. (Section 7.3.5)

7.2.3 Latex and Resin Solvent Solutions - Samples must be thoroughly mixed. Accurately weigh one gram of the latex or resin-solvent solution into a 20 ml vial containing nine grams of THF as for the resin samples (7.2.1). Cap and shake until complete solution is effected. Determine the total solids of the latex or resin solution sample. (Section 7.3.5)

7.2.4 Inprocess waste water, solvents and non-viscous liquid samples. No preparation of these samples is required. The neat samples are injected directly into the gas chromatograph.

7.3 Analysis

7.3.1 Preparation of gas chromatograph. Install the chromatographic column and condition overnight at 70°C. Do not connect the exit end of the column to the detector while conditioning.

7.3.1.1 Flow rate adjustments - Adjust the flow

b. Burner air supply. Set regulator on the cylinder at 40 psig. Set regulator on the chromatograph to supply air to the burner to yield a flow rate of 250 to 300 cc per minute using the flow meter.

c. Hydrogen. Set regulator on cylinder to read 60 psig. Set regulator on the chromatograph to supply 30 to 40 cc per minute using the flow meter. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with flow meter and record this flow.

d. Nitrogen back flush gas. Set regulator on the chromatograph using the soap film flow meter to yield a flow rate of 40 cc per minute.

7.3.1.2 Temperature adjustments. Set temperatures as follows.

a. Oven (chromatographic column) 70°C

b. Injection port - 100°C

c. Detector - 300°C

7.3.1.3 Ignition of flame ionization detector. Ignite the detector according to the manufacturer's [illegible]

7.3.2 Chromatographic Analyses

a. Sample injection. Remove needle from fifty microliter syringe. Open sample vial and draw fifty microliters of THF-sample solution into the syringe. Recap sample vial. Attach needle to the syringe and holding the syringe vertically needle upward, eject ten microliters through a [illegible] Wipe needle [illegible] Inject sample into chromatographic system.

b. Back flush. After [illegible] minutes have elapsed after sample injection actuate [illegible] back flush valve to purge the [illegible] from the [illegible] column [illegible] and [illegible] vial.

c. Sample [illegible] the chromatogram [illegible] data [illegible]

d. Elution time. Vinyl chloride elutes at 2.2 minutes [illegible] after five minutes [illegible]

7.3.3 Chromatographic [illegible]

a. Septum. Replace after five sample injections.

b. [illegible] sample [illegible]

7.3.5 Determination of Total Solids (T.S.)

For wet resin, resin solution and PVC latex samples, determine the T.S. for each sample by accurately weighing approximately three-to five-grams of sample into a tared aluminum [illegible]. The procedure is as follows:

a. Water is the major volatile component. Tare the weighing dish and add three-to five-grams of sample to the dish. Weigh to the nearest milligram.

b. Volatile solvent is the major volatile component. Transfer a portion of the sample to a 20 ml screw cap vial and cap immediately. Weigh the vial to the nearest milligram. Uncap the vial and transfer a three-to five-gram portion of the sample to a tared aluminum weighing dish. Recap the vial and weigh to the nearest milligram. The vial weight loss is the sample weight. Place the weighing pan in a 130°C oven for one hour. Remove the dish and allow to cool to room temperature in a desiccator. Weigh to the nearest 0.1 mg. Total solids is the weight of material in the aluminum pan after heating divided by the net weight of sample added to the pan originally times 100.

8.1 Preparation of standards.

a. Prepare a one percent by weight solution of vinyl chloride in tetrahydrofuran by bubbling vinyl chloride gas from a cylinder into a tared 125 ml glass stoppered flask containing THF. The approximate amount of vinyl chloride should be calculated prior to the operation, i.e., one percent of the weight of THF contained in the tared flask of THF. This must be carried out in a laboratory hood. Adjust the vinyl chloride flow from the cylinder so that the vinyl chloride dissolves essentially completely in the THF and is not blown to the [illegible] Weigh the stoppered flask to nearest [illegible] to determine the exact concentration of vinyl chloride.

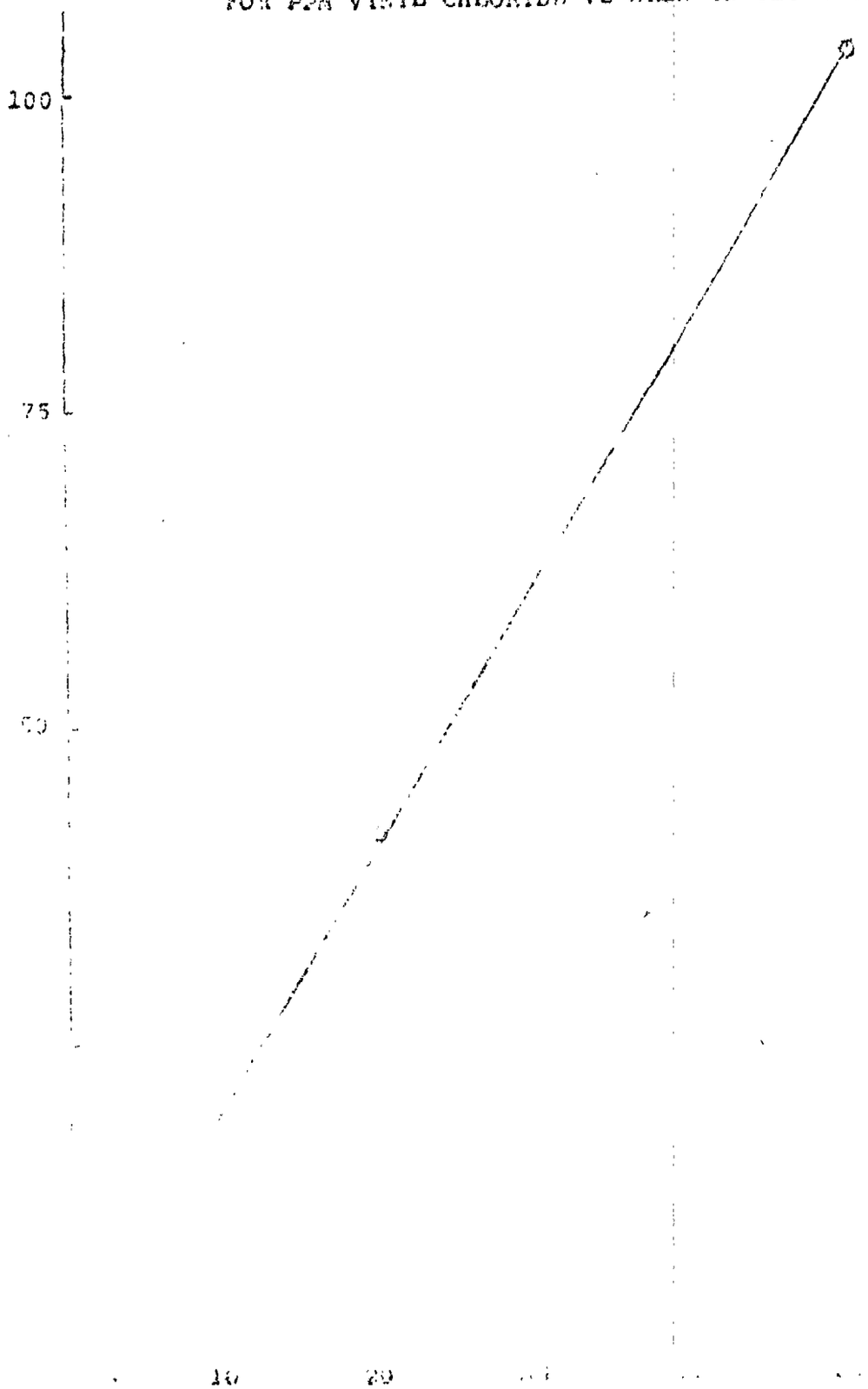
b. Pipet [illegible] ml of the one percent solution from a [illegible] glass stoppered volumetric flask and dilute to the mark with THF and swirl to mix uniformly. This solution contains [illegible] mg/ml.

Pipet [illegible] ml of the [illegible] mg/ml solution into 100 ml glass stoppered volumetric flasks. Dilute to the mark with THF and swirl to mix uniformly. These solu-

[illegible]

response. Figure 1 shows a typical calibration curve.

FIGURE 2
TYPICAL GAS CHROMATOGRAPHIC CALIBRATION CURVE
FOR PPM VINYL CHLORIDE VS AREA IN TETRAHYDROFURAN



9. Calculations.

9.1 Response factor.

From the calibration curve described in Section 8.1 select the value of Cc that corresponds to Hc for each sample. Compute the response factor, R_f, for each sample as follows:

$$R_f = \frac{[illegible]}{Hc}$$

9.2 Residual vinyl chloride monomer concentration or vinyl chloride monomer concentration in resin:

[illegible] R_f

where:

[illegible] concentration of vinyl chloride in the sample [illegible]

Hs [illegible] sample

[illegible] response factor

[illegible] material, [illegible]

[illegible]

$$[illegible] = \frac{[illegible]}{[illegible]}$$

where:

[illegible]

PS. to JPS

SCOPE OF BURLINGTON EPA COMPLIANCE PROJECT

1. INCINERATION SYSTEM - (Gas streams above 10 ppm)

   One incinerator with a caustic scrubber supplied as a package unit from Trane. Caustic storage tanks with pH control system are also required. Quench water for the incinerator to be cooling tower overflow stream which will be diverted to mix box with high salt concentration.

   MAJOR STREAMS

   Vent Condenser Discharge
   Water Stripper Vents (2)
   Vessel Entry as required

2. WATER STRIPPER SYSTEM - (Process water above 10 ppm)

   A continuous steam stripping column with a Nash vacuum pump to control vacuum. Unit includes a new feed storage tank, and feed-bottoms exchanger, and automatic filtration system.

   MAJOR STREAMS

   Foam K. O. Pots
   Fume Scrubber water
   Barometric Sumps Ho & Co

3. SLURRY PUMP PROJECT-(Eliminate nitrogen for strippers)

   One homopolymer and one copolymer transfer pump with interconnecting piping.

4. VESSEL ENTRY - (Less than 2 Vol % VCM to open)

   Provide piping and tie-ins to sources of nitrogen or steam and tie vessels into existing recovery systems.

5. DISPERSION TOWER STEAMING - (Less than 2600 ppm)

   Provide steam piping into top of each dispersion tower with provisions to steam during stripper-tower recovery.

6. COPOLYMER REACTOR RECOVERY - (Less than 2300 ppm)

   Method not as yet selected.
   Alternatives: 1. Steam reactor and install jet cleaning system.
   2. Water spray alone or with jet cleaning system

7. DISPERSION STRIPPING SYSTEMS

Method not determined. Best guess is direct steam heating system for each stripper. What, if any, recovery equipment will be required has not been determined.

Additional projects that will require justification by Manufacturing Dept.:

1. Spare Vent Condenser
2. Spare Brine System
3. Additional Ho/Co Compressor capability
4. Additional Plastisol Compressor capability
5. Well Water quality improvement