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40 CFR Part 61

[AD-FRL-2070-8]

Appendix B; Test Methods; Revised Methods 106 and 107; and Appendix C, Quality Assurance Procedures 1 and 2; Revision

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: Revised Test Methods 106 and 107 for vinyl chloride were proposed in the Federal Register on November 18, 1980 (45 FR 76346). This action promulgates the revised test methods. The intended effect of this action is to require all sources of vinyl chloride specified to conduct emission tests under Subparts A and F of 40 CFR Part 61 to hereafter (see effective date below) use these methods for determining compliance.

Appendix C, Quality Assurance Procedures 1 and 2, was proposed in the Federal Register on April 18, 1980 (45 FR 26682). This action promulgates

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Procedures 1 and 2 of Appendix C. The intended effect of Procedure 1 is to provide a method for determination of gas chromatograph (GC) column resolution, and the intended effect of Procedure 2 is to provide a method for auditing GC sample analysis.

EFFECTIVE DATE: September 7, 1982.

Under Section 307(b)(1) of the Clean Air Act, judicial review of this rulemaking is available only by the filing of a petition for review in the U.S. Court of Appeals for the District of Columbia Circuit within 60 days of today's publication of this rule. Under Section 307(b)(2) of the Clean Air Act, the requirements that are the subject of today's notice may not be challenged later in civil or criminal proceedings brought by EPA to enforce these requirements.

ADDRESSES: Summary of Comments and Responses. The summary of comments and responses for the proposed test methods may be obtained from the U. S. EPA Library (MD-35), Research Triangle Park, North Carolina 27711, telephone number (919) 541-2777. Please refer to "Revised Test Methods 106 and 107—Summary of Comments and Responses, EPA 450/3-82-002." The document contains (1) a summary of the changes made to the test methods since proposal and (2) a summary of all the public comments made on the proposed revised methods and the Administrator's responses to the comments.

Docket. A docket, number A-80-50, containing information considered by EPA in the development of the test methods and docket number OAQPS 79-3 Part 2 that contains background information pertaining to Appendix C are available for public inspection between 8:00 a.m. and 4:00 p.m., Monday through Friday, at EPA's Central Docket Section (A-130), West Tower Lobby, Gallery 1, 401 M Street, S.W., Washington, D.C. 20460. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Roger T. Shigehara, Emission Measurement Branch, Emission Standards and Engineering Division (MD-19), U. S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone (919) 541-2237.

Public Participation

The revised test methods were proposed and published in the Federal Register on November 18, 1980 (45 FR 76346). Public comments were solicited at the time of proposal. The public comment period was from November 18,

1980, to January 19, 1981, with an extension to February 19, 1981.

Five comment letters were received concerning issues relative to the proposed test methods. The comments have been carefully considered; and where determined to be appropriate by the Administrator, changes have been made in the proposed revisions to the test methods.

Procedures 1 and 2 of Appendix C were proposed and published in the Federal Register April 18, 1980 (45 FR 26660). Public comments were solicited at the time of proposal. The public comment period was from April 18, 1980, to August 21, 1980.

No comment letters were received.

Significant Comments and Changes to the Proposed Test Methods

Comments on the proposed revisions to the test methods were received from industry, industry counsel, engineering firms, and equipment manufacturers. A detailed discussion of these comments and responses can be found in the summary of comments and responses which is referred to in the ADDRESSES section of this preamble. The summary of comments and responses serves as the basis for the revisions which have been made to the test methods between proposal and promulgation. The major comments and responses are summarized in this preamble. Most of the comment letters contained multiple comments. The comments have been divided into the following areas:

Proposal of Revised Test Methods 106 and 107

One commenter felt that EPA should publish a notice in the Federal Register to clarify the November 18, 1980, notice on Test Methods 106 and 107 (45 FR 76346) as to whether the changes in the methods were proposed or final amendments. The EPA considered the suggestion to be reasonable; and a notice was published in the Federal Register on January 6, 1981 (46 FR 1318) to clarify that the changes in Methods 106 and 107 published on November 18, 1980, were proposed changes.

Sample Analysis Procedure—Method 106

One commenter suggested that Section 7.2.2, Preparation of Chromatograph Calibration Curve, be changed to require calibration at least once every 8 hours of continuous operation of the chromatograph, whereas the method requires daily calibration. The EPA has decided it would be an unnecessary burden to arbitrarily set 8 hours as a cutoff point for valid calibration. However, the

comment has identified the need for instruction in the method as to the use of multiple calibration curves in data interpretation, and Section 7.2.2 has been revised to provide that instruction.

One commenter questioned the use of Figure 106-2 because it appeared to illustrate a standards preparation procedure different from the one described in the method. Figure 106-2 did illustrate a different sample preparation procedure and has been deleted from the method.

Sample Collection and Analysis Procedure—Method 107

One commenter questioned the need for the sample prepressurization procedure that is included in the revised test method. The Agency believes the prepressurization procedure is valid as prepressurization of sample vials prior to analysis has been shown to produce k_p values which agree with theoretical values. A paper describing a study of this technique has been added to the bibliography section of the method as an aid in the use of this procedure.

Quality Assurance—Method 106

One commenter requested that Section 5.2.4, Audit Cylinder Standards, further describe commercial gas manufacturers as an alternative source of these standards. The Agency considered the request to be reasonable, and Section 5.2.4 has been revised to define the acceptability of audit cylinders obtained from commercial gas manufacturers.

Docket

The docket is an organized and complete file of all the information considered by EPA in the development of this rulemaking. The docket is a dynamic file, since material is added throughout the rulemaking development. The docketing system is intended to allow members of the public and industries involved to readily identify and locate documents so that they can intelligently and effectively participate in the rulemaking process. Along with the statement of basis and purpose of the proposed and promulgated test methods and EPA responses to significant comments, the contents of the docket will serve as the record in case of judicial review [Section 307(d)(7)(A)].

Miscellaneous

This rulemaking does not impose any additional emission measurement requirements on facilities affected by this rulemaking. Rather, this rulemaking revises the test methods to which the

affected facilities are already subject. The revisions do not affect the present emission standards. If future standards impose emission measurement requirements, the impacts of the revised test methods promulgated today will be evaluated during development of those standards.

Under Executive Order 12291, EPA must judge whether a regulation is "major" and, therefore, subject to the requirement of a regulatory impact analysis. This regulation is not major because it will not have an annual effect on the economy of \$100 million or more; it will not result in a major increase in costs or prices; and there will be no significant effects on competition, employment, investment, productivity, innovation, or on the ability of U.S.-based enterprises to compete with foreign-based enterprises in domestic or export markets.

The regulation was submitted to the Office of Management and Budget for review as required by Executive Order 12291.

Pursuant to the provisions of 5 U.S.C. 605(b), I hereby certify that the attached rule will not have a significant economic impact on a substantial number of small entities.

List of Subjects in 40 CFR Part 61

Air pollution control, Asbestos, Beryllium, Hazardous materials, Mercury, Vinyl chloride.

(Secs. 112, 114, 301(a) of the Clean Air Act, as amended (42 U.S.C. 7412, 7414, 7601(a))

Dated: August 24, 1982.

John W. Hernandez,
Acting Administrator.

PART 61—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS

40 CFR Part 61 is amended by revising Test Methods 106 and 107 of Appendix B to read as follows:

Appendix B—Test Methods

Method 106—Determination of Vinyl Chloride From Stationary Sources

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Applicability and Principle

1.1 Applicability. The method is applicable to the measurement of vinyl chloride in stack gases from ethylene

dichloride, vinyl chloride, and polyvinyl chloride manufacturing processes. The method does not measure vinyl chloride contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to GC analysis using a flame ionization detector (FID).

2. Range and Sensitivity

This method is designed for the 0.1 to 50 ppm range. However, common GC instruments are capable of detecting 0.02 ppm vinyl chloride. With proper calibration, the upper limit may be extended as needed.

3. Interferences

The chromatographic columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic, provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

4. Apparatus

4.1 Sampling (see Figure 106-1). The sampling train consists of the following components:

4.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing (as stack temperature permits) equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Lines. Teflon, 6.4-mm outside diameter, of sufficient length to connect probe to bag. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon completion of the test.

4.1.3 Quick Connects. Stainless steel, male (2) and female (2), with ball checks (one pair without), located as shown in Figure 106-1.

4.1.4 Tedlar Bags. 50- to 100-liter capacity, to contain sample. Aluminized Mylar bags may be used if the samples are analyzed within 24 hours of collection.

4.1.5 Bag Containers. Rigid leak-proof containers for sample bags, with covering to protect contents from sunlight.

4.1.6 Needle Valve. To adjust sample flow rates.

4.1.7 Pump. Leak-free, with minimum of 2-liter/min capacity.

4.1.8 Charcoal Tube. To prevent admission of vinyl chloride and other organics to the atmosphere in the vicinity of samplers.

4.1.9 Flowmeter. For observing sampling flow rate; capable of measuring a flow range from 0.10 to 1.00 liter/min.

4.1.10 Connecting Tubing. Teflon, 6.4-mm outside diameter, to assemble sampling train (Figure 106-1).

4.1.11 Tubing Fittings and Connectors. Teflon or stainless steel, to assemble sampling train.

4.2 Sample Recovery. Teflon tubing, 6.4-mm outside diameter, to connect bag to GC sample loop for sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon conclusion of analysis of those bags.

4.3 Analysis. The following equipment is required:

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0- to 5.0-ml heated sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1-ppm vinyl chloride that is at least as great as the average noise level. (Response is measured from the average value of the base line to the maximum of the wave form, while standard operating conditions are in use.)

4.3.2 Chromatographic Columns. Columns as listed below. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.")

4.3.2.1 Column A. Stainless steel, 2.0 m by 3.2 mm, containing 80/100-mesh Chromasorb 102.

4.3.2.2 Column B. Stainless steel, 2.0 m by 3.2 mm, containing 20 percent GE SF-96 on 60/80-mesh Chromasorb P AW; or stainless steel, 1.0 m by 3.2 mm containing 80/100-mesh Porapak Q. Column B is required as a secondary column if acetaldehyde is present. If used, column B is placed after column A. The combined columns should be operated at 120° C.

4.3.3 Flowmeters (2). Rotameter type, 100-ml/min capacity, with flow control valves.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to 1° C, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around GC during sample analysis.

4.3.7 Pump. Leak-free, with minimum of 100-ml/min capacity.

4.3.8 Recorder. Strip chart type, optionally equipped with either disc or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator on recorder, to measure chromatograph peak areas.

4.4 Calibration. Sections 4.4.2 through 4.4.4 are for the optional procedure in Section 7.1.

4.4.1 Tubing. Teflon, 6.4-mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar Bags. Sixteen-inch-square size, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringes. 0.5-ml and 50- μ l, gas tight, individually calibrated to dispense gaseous vinyl chloride.

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4.4.4 Dry Gas Meter, with Temperature and Pressure Gauges. Singer model DTM-115 with 802 index, or equivalent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

3. Reagents

Use only reagents that are of chromatograph grade.

5.1 Analysis. The following are required for analysis.

5.1.1 Helium or Nitrogen. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen. Zero grade.

5.1.3 Oxygen or Air. Zero grade, as required by the detector.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Vinyl Chloride. Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride, for use in the preparation of standard gas mixtures in Section 7.1. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysis may have been performed on this supply rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

5.2.2 Nitrogen. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (50-, 10-, and 5-ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 7.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ± 3 percent or better (see Section 5.2.3.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ± 5 percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

5.2.3.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 50 and 100 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 5 and 10 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source

of error and correct it, then repeat the three-point calibration.

5.2.3.2 Verification of Manufacturer's Calibration Standards. Before using a standard, the manufacturer shall verify each calibration standard (a) by comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.1 or (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The audit cylinder standards shall be identically prepared as those in Section 5.2.3 (vinyl chloride in nitrogen cylinders). The concentrations of the audit cylinder should be: one low-concentration cylinder in the range of 5 to 20 ppm vinyl chloride and one high-concentration cylinder in the range of 20 to 50 ppm. When available, the tester may obtain audit cylinders by contacting: Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711. Audit cylinders obtained from a commercial gas manufacturer may be used provided: (a) the gas manufacturer certifies the audit cylinder as described in Section 5.2.3.1, and (b) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined here to mean analysis performed by an individual different than the individual who performs the gas manufacturer's analysis, while using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is complete and acceptable when the independent analysis concentration is within ± 5 percent of the gas manufacturer's concentration.

6. Procedure

6.1 Sampling. Assemble the sample train as shown in Figure 108-1. A bag leak check should have been performed previously according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connection between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow that will fill over 50 percent of bag volume in the specific sample period. After allowing sufficient time to purge the line several times, change the vacuum line from the container to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. At all times, direct the gas exiting the rotameter away from sampling personnel. At the end of

the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample storage. Keep the sample bags out of direct sunlight. When at all possible, analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection. Aluminized Mylar bag samples must be analyzed within 24 hours.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to 100-ml/min rotameter with flow control valve followed by a charcoal tube and a 1-in. H₂O pressure gauge. The tester may maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

6.4 Analysis. Set the column temperature to 100° C and the detector temperature to 150° C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatography operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for 30 seconds at the rate of 100 ml/min, shut off flow, allow the sample loop pressure to reach atmospheric pressure as indicated by the H₂O manometer, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), sample number, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record the barometric pressure. From the chart, note the peak having the retention time corresponding to vinyl chloride as determined in Section 7.2.1. Measure the vinyl chloride peak area, A_m , by use of a disc integrator, electronic integrator, or a planimeter. Measure and record the peak heights, H_m . Record A_m and retention time. Repeat the injection at least two times or until two consecutive values for the total area of the vinyl chloride peak do not vary more than 5 percent. Use the average value for these two total areas to compute the bag concentration.

Compare the ratio of H_m to A_m for the vinyl chloride sample with the same ratio for the standard peak that is closest in height. If these ratios differ by more than 10 percent, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2.2).

6.5 Determination of Bag Water Vapor Content. Measure the ambient temperature

and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. Preparation of Standard Gas Mixtures, Calibration, and Quality Assurance

7.1 Preparation of Vinyl Chloride Standard Gas Mixtures. (Optional Procedure—delete if cylinder standards are used.) Evacuate a 18-inch square Tedlar bag that has passed a leak check (described in Section 7.3.2) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5-ml syringe to inject 250 μ l of 99.9+ percent vinyl chloride gas through the wall of the bag. Upon withdrawing the syringe, immediately cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppm. In a like manner use the 50 μ l syringe to prepare gas mixtures having 10- and 5-ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 10 days from the date of preparation, after which time new gas mixtures must be prepared. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2 Calibration

7.2.1 Determination of Vinyl Chloride Retention Time. (This section can be performed simultaneously with Section 7.2.2.) Establish chromatograph conditions identical with those in Section 6.4 above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions with the equipment plumbing arranged identically to Section 6.3, and flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures. Then activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity divided by the chart speed is defined as the retention time. Since other organics may be present in the sample, positive identification of the vinyl chloride peak must be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a GC measurement

of each gas mixture standard (described in Section 5.2.3 or 7.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard mixtures, and activate the sample valve. Record the concentration of vinyl chloride injected (C_c), attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the barometric pressure. Calculate A_m , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus C_c . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after the analysis of each emission test set of bag samples, whichever is more frequent. For each group of sample analyses, use the average of the two calibration curves which bracket that group to determine the respective sample concentrations. If the two calibration curves differ by more than 5 percent from their mean value, then report the final results by both calibration curves.

7.3 Quality Assurance

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. Checking of bags for leaks is required after bag use and strongly recommended before bag use. After each use, connect a water manometer and pressurize the bag to 5 to 10 cm H₂O (2 to 4 in. H₂O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: An alternative leak check method is to pressurize the bag to 5 to 10 cm H₂O and allow it to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations

8.1 Determine the sample peak area, A_c , as follows:

$$A_c = A_m A_f \quad \text{Eq. 106-1}$$

Where:

A_m = Measured peak area.

A_f = Attenuation factor.

8.2 Vinyl Chloride Concentrations. From the calibration curves described in Section 7.2.2, determine the average concentration value of vinyl chloride, C_c , that corresponds to A_c , the sample peak area. Calculate the concentration of vinyl chloride in the bag, C_b , as follows:

$$C_b = \frac{C_c P_r T_i}{P_i T_r (1 - B_{wd})} \quad \text{Eq. 106-2}$$

Where:

P_r = Reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_i = Sample loop temperature on the absolute scale at the time of analysis, °K.

P_i = Laboratory pressure at time of analysis, mm Hg.

T_r = Reference temperature, the sample loop temperature recorded during calibration, °K.

B_{wd} = Water vapor content of the bag sample, as analyzed.

9. Bibliography

1. Brown D.W., E.W. Loy, and M.H. Stephenson, Vinyl Chloride Monitoring Near the B. F. Goodrich Chemical Company in Louisville, KY. Region IV, U.S. Environmental Protection Agency, Surveillance and Analysis Division, Athens, GA, June 24, 1974.
2. G.D. Clayton and Associates, Evaluation of a Collection and Analytical Procedure for Vinyl Chloride in Air. U.S. Environmental Protection Agency, Research Triangle Park, N.C. EPA Contract No. 68-02-1408, Task Order No. 2, EPA Report No. 75-VCL-1, December 13, 1974.
3. Midwest Research Institute, Standardization of Stationary Source Emission Method for Vinyl Chloride. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-600/4-77-028, May 1977.
4. Scheil, G. and M.C. Sharp, Collaborative Testing of EPA Method 106 (Vinyl Chloride) that Will Provide for a Standardized Stationary Source Emission Measurement Method. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/4-78-058, October 1978.

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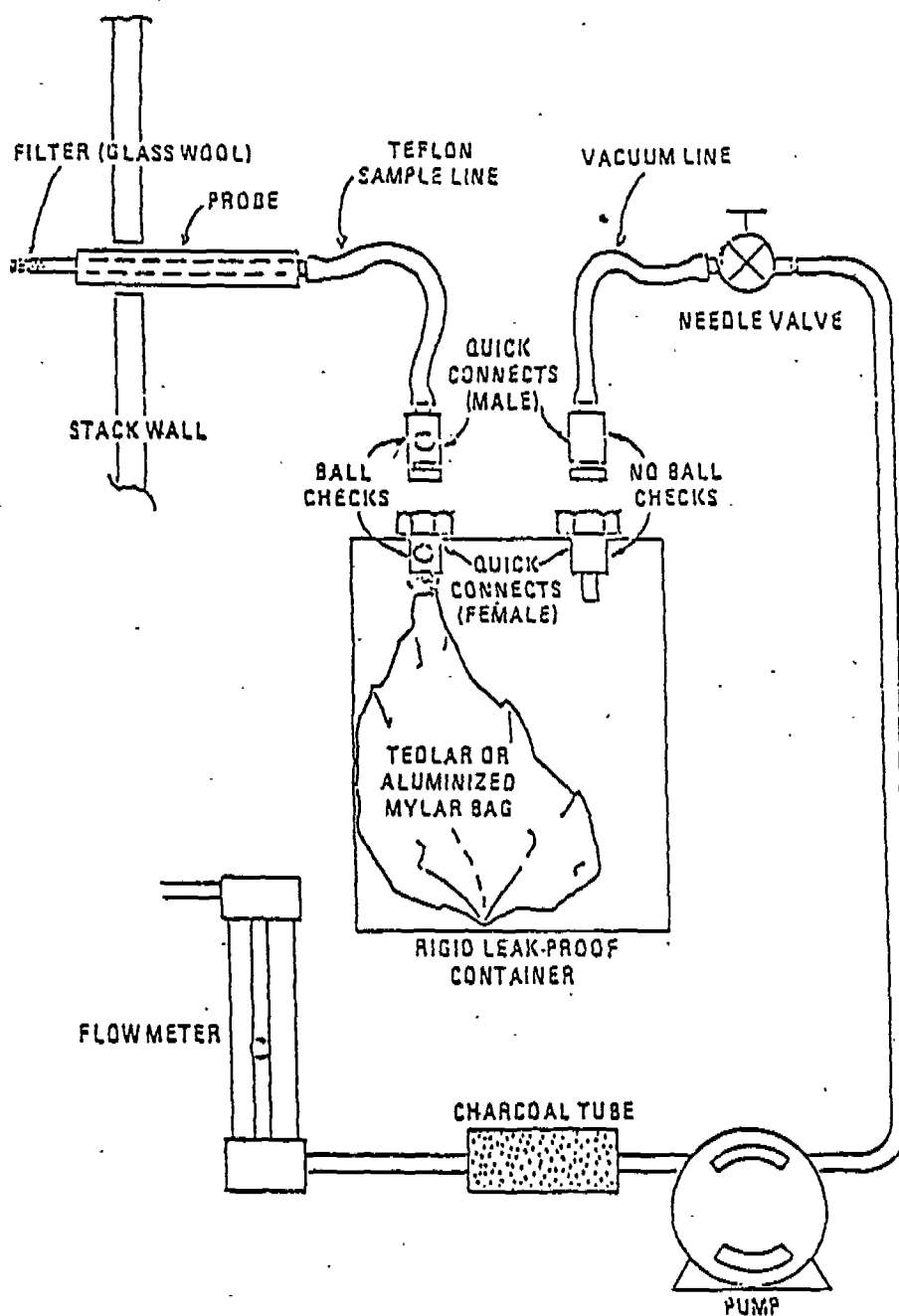


Figure 106-1. Integrated-bag sampling train. (Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)

Method 107—Determination of Vinyl Chloride Content of Inprocess Wastewater Samples, and Vinyl Chloride Content of Polyvinyl Chloride Resin, Slurry, Wet Cake, and Latex Samples

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC), nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Applicability and Principle.

1.1 Applicability. This method applies to the measurement of the vinyl chloride monomer (VCM) content of inprocess wastewater samples, and the residual vinyl chloride monomer (RVCM) content of polyvinyl chloride (PVC) resins, wet cake, slurry, and latex samples. It cannot be used for polymer in fused forms, such as sheet or cubes. This method is not acceptable where methods from Section 304(h) of the Clean Water Act, 33 U.S.C. 1251 et seq. (the Federal Water Pollution Control Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

1.2 Principle. The basis for this method relates to the vapor equilibrium that is established between RVCM, PVC resin, water, and air in a closed system. The RVCM in a PVC resin will equilibrate rapidly in a closed vessel, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

2. Range and Sensitivity. The lower limit of detection of vinyl chloride will vary according to the chromatograph used. Values reported include 1×10^{-7} mg and 4×10^{-7} mg. With proper calibration, the upper limit may be extended as needed.

3. Interferences. The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

4. Precision and Reproducibility. An interlaboratory comparison between seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.63 percent for a sample with a mean of 2.09 ppm, 4.16 percent for a sample with a mean of 1.66 ppm, and 5.29 percent for a sample with a mean of 62.66 ppm.

5. Safety. Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be held to a minimum. When they are required, the vapor must be

routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. After vials have been analyzed, the gas must be vented prior to removal of the vial from the instrument turntable. Vials must be vented through a hypodermic needle connected to an activated charcoal tube to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

6. Apparatus.

6.1 Sampling. The following equipment is required:

6.1.1 Glass bottles, 60-ml (2-oz) capacity, with wax-lined screw-on tops, for PVC samples.

6.1.2 Glass Vials, 50-ml capacity Hypo-vial, sealed with Teflon faced Tuf-Bond discs, for water samples.

6.1.3 Adhesive Tape. To prevent loosening of bottle tops.

6.2 Sample Recovery. The following equipment is required:

6.2.1 Glass Vials. With butyl rubber septa, Perkin-Elmer Corporation Nos. 0105-0129 (glass vials), B001-0728 (gray butyl rubber septum, plug style), 0105-0131 (butyl rubber septa), or equivalents. The seals must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.2.2 Analytical Balance. Capable of weighing to ± 0.0001 gram.

6.2.3 Vial Sealer, Perkin-Elmer No. 105-0106, or equivalent.

6.2.4 Syringe, 100- μ l capacity, precision series "A" No. 010025, or equivalent.

6.3 Analysis. The following equipment is required:

6.3.1 Gas Chromatograph, Perkin-Elmer Corporation Model F-40, F-42, or F-45 Headspace Analyzer, or equivalent. Equipped with backflush accessory.

6.3.2 Chromatographic Columns. Stainless steel 1 m by 3.2 mm and 2 m by 3.2 mm, both containing 50/80-mesh Porapak Q. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.") Two 1.83 m columns, each containing 1 percent Carbowax 1500 on Carbowax B, have been suggested for samples containing acetaldehyde.

6.3.3 Thermometer, 0 to 100° C, accurate to ± 0.1 ° C, Perkin-Elmer No. 105-0109, or equivalent.

6.3.4 Sample Tray Thermostat System, Perkin-Elmer No. 105-0103, or equivalent.

6.3.5 Septa, Sandwich type, for automatic dosing, 13 mm, Perkin-Elmer No. 105-1008, or equivalent.

6.3.6 Integrator-Recorder, Hewlett-Packard Model 3380A, or equivalent.

6.3.7 Filter Drier Assembly (3), Perkin-Elmer No. 2230117, or equivalent.

6.3.8 Soap Film Flowmeter, Hewlett-Packard No. 0101-0113, or equivalent.

6.3.9 Regulators. For required gas cylinders.

6.3.10 Headspace Vial Pre-Pressurizer. Nitrogen pressurized hypodermic needle inside protective shield. (Blueprint available from Test Support Section, Emission Measurement Branch, Office of Air Quality Planning and Standards, Environmental Protection Agency, Mail Drop 19, Research Triangle Park, N.C. 27711.)

7. Reagents. Use only reagents that are of chromatographic grade.

7.1 Analysis. The following items are required for analysis:

7.1.1 Hydrogen, Zero grade.

7.1.2 Nitrogen, Zero grade.

7.1.3 Air, Zero grade.

7.2 Calibration. The following items are required for calibration:

7.2.1 Cylinder Standards (4). Gas mixture standards (50-, 500-, 2000- and 4000-ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 9.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ± 3 percent or better (see Section 7.2.1.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ± 5 percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a 3-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 4000 and 8000 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 50 and 500 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the 3-point calibration.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.1 of Method 106 or by (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within ± 5

percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

8. Procedure.

8.1 Sampling.

8.1.1 PVC Sampling. Allow the resin or slurry to flow from a tap on the tank or silo until the tap line has been well purged. Extend and fill a 60-ml sample bottle under the tap, and immediately tighten a cap on the bottle. Wrap adhesive tape around the cap and bottle to prevent the cap from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

8.1.2 Water Sampling. Prior to use, the 50-ml vials (without the discs) must be capped with aluminum foil and heated in a muffle furnace at 400° C for at least 1 hour to destroy or remove any organic matter that could interfere with analysis. At the sampling location fill the vials 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, with the Teflon side down, on the opening of the vial.

Place the aluminum seal over the disc and the neck of the vial, and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book. All samples must be kept refrigerated until analyzed.

8.2 Sample Recovery. Samples must be run within 24 hours.

8.2.1 Resin Samples. The weight of the resin used must be between 3.5 and 4.5 grams. An exact weight must be obtained (± 0.0001 g) for each sample. In the case of suspension resins, a volumetric cup can be prepared for holding the required amount of sample. When the cup is used, open the sample bottle, and add the cup volume of resin to the tared sample vial (tared, including septum and aluminum cap). Obtain the exact sample weight, add 100 μ l or about two equal drops of distilled water, and immediately seal the vial. Report this value on the data sheet; it is required for calculation of RVC/M. In the case of dispersion resins, the cup cannot be used. Weigh the sample in an aluminum dish, transfer the sample to the tared vial, and accurately weigh it in the vial. After prepressurization of the samples, condition them for a minimum of 1 hour in the 90° C bath. Do not exceed 5 hours.

Note.—Some aluminum vial caps have a center section that must be removed prior to placing into sample tray. If the cap is not removed, the injection needle will be damaged.

8.2.2 Suspension Resin Slurry and Wet Cake Samples. Decant the water from a wet cake sample, and turn the sample bottle upside down onto a paper towel. Wait for the water to drain, place approximately 0.2 to 4.0 grams of the wet cake sample in a tared vial (tared, including septum and aluminum cap) and seal immediately. Then determine the sample weight (± 0.0001 g). All samples must be prepressurized and then conditioned for 1 hour at 90° C. A sample of wet cake is used to

determine total solids (TS). This is required for calculating the RVC/M.

8.2.3 Dispersion Resin Slurry and Geon Latex Samples. The materials should not be filtered. Sample must be thoroughly mixed. Using a tared vial (tared, including septum and aluminum cap) add approximately eight drops (0.25 to 0.35 g) of slurry or latex using a medicine dropper. This should be done immediately after mixing. Seal the vial as soon as possible. Determine sample weight (± 0.0001 g). After prepressurization, condition the vial for 1 hour at 90° C in the analyzer bath. Determine the TS on the slurry sample (Section 8.3.5).

8.2.4 Inprocess Wastewater Samples. Using a tared vial (tared, including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight (± 0.0001 g). Prepressurize the vial, and then condition for 1 to 2 hours as required at 90° C in the analyzer bath.

8.3 Analysis.

8.3.1 Preparation of Equipment. Install the chromatographic column and condition overnight at 180° C. In the first operation, Porapak columns must be purged for 1 hour at 230° C.

Do not connect the exit end of the column to the detector while conditioning. Hydrogen and air to the detector must be turned off while the column is disconnected.

8.3.1.1 Flow Rate Adjustments. Adjust flow rates as follows:

a. Nitrogen Carrier Gas. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to produce a flow rate of 30.0 cc/min. Accurately measure the flow rate at the exit end of the column using the soap film flowmeter and a stopwatch, with the oven and column at the analysis temperature. After the instrument program advances to the "B" (backflush) mode, adjust the nitrogen pressure regulator to exactly balance the nitrogen flow rate at the detector as was obtained in the "A" mode.

b. Vial Prepressurizer Nitrogen. After the nitrogen carrier is set, solve the following equation and adjust the pressure on the vial prepressurizer accordingly.

$$P = \frac{T_1}{T_2} \left[P_1 - \frac{P_{w1} - P_{w2}}{7.50} \right] - 10 \text{ k Pa}$$

Where:

T_1 = Ambient temperature, °K.

T_2 = Conditioning bath temperature, °K.

P_1 = Gas chromatograph absolute dosing pressure (analysis mode), k Pa.

P_{w1} = Water vapor pressure @ 90° C (525.8 mm Hg).

P_{w2} = Water vapor pressure @ 22° C (19.8 mm Hg).

7.50 = mm Hg per k Pa.

10 k Pa = Factor to adjust the prepressurized pressure to slightly less than the dosing pressure.

Because of gauge errors, the apparatus may over-pressurize the vial. If the vial pressure is at or higher than the dosing pressure, an audible double injection will occur. If the vial

pressure is too low, errors will occur on resin samples because of inadequate time for head-space gas equilibrium. This condition can be avoided by running several standard gas samples at various pressures around the calculated pressure, and then selecting the highest pressure that does not produce a double injection. All samples and standards must be pressurized for 60 seconds using the vial prepressurizer. The vial is then placed into the 90° C conditioning bath and tested for leakage by placing a drop of water on the septum at the needle hole. A clean, burr-free needle is mandatory.

c. Burner Air Supply. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply air to burner at a rate between 250 and 300 cc/min. Check with bubble flowmeter.

d. Hydrogen Supply. Set regulator on cylinder to read 30 psig. Set regulator on chromatograph to supply approximately 35 $\pm$ 5 cc/min. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with bubble meter and record this flow.

8.3.1.2 Temperature Adjustments. Set temperatures as follows:

a. Oven (chromatograph column), 140° C.

b. Dosing Line, 150° C.

c. Injection Block, 170° C.

d. Sample Chamber, Water Temperature, 90° C $\pm$ 1.0° C.

8.3.1.3 Ignition of Flame Ionization Detector. Ignite the detector according to the manufacturer's instructions.

8.3.1.4 Amplifier Balance. Balance the amplifier according to the manufacturer's instructions.

8.3.2 Programming the Chromatograph. Program the chromatograph as follows:

a. I—Dosing or Injection Time. The normal setting is 2 seconds.

b. A—"Analysis Time." The normal setting is approximately 70 percent of the VCM retention time. When this timer terminates, the programmer initiates backflushing of the first column.

c. B—Backflushing Time. The normal setting is double the "analysis time."

d. W—Stabilization Time. The normal setting is 0.5 min to 1.0 min.

e. X—Number of Analyses Per Sample. The normal setting is one.

8.3.3 Preparation of Sample Turntable.

Before placing any sample into turntable, be certain that the center section of the aluminum cap has been removed. All samples and standards must be pressurized for 60 seconds by using the vial prepressurizer. The numbered sample vials should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

Position 1 and 2—Old 2000-ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

Position 3—50-ppm standard, freshly prepared.

Position 4—500-ppm standard, freshly prepared.

Position 5—2000-ppm standard, freshly prepared.

Position 6—4000-ppm standard, freshly prepared.

Position 7—Sample No. 7 (This is the first sample of the day, but is given as 7 to be consistent with the turntable and the integrator printout.)

After all samples have been positioned, insert the second set of 50-, 500-, 2000-, and 4000-ppm standards. Samples, including standards, must be conditioned in the bath of 90° C for 1 hour (not to exceed 5 hours).

8.3.4 Start Chromatograph Program. When all samples, including standards, have been conditioned at 90° C for 1 hour, start the analysis program according to the manufacturer's instructions. These instructions must be carefully followed when starting and stopping a program to prevent damage to the dosing assembly.

8.3.5 Determination of TS. For wet cake, slurry, resin solution, and PVC latex samples, determine TS for each sample by accurately weighing approximately 3 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110° C). Samples must be dried to constant weight. After first weighing, return the pan to the oven for a short period of time, and then reweigh to verify complete dryness. The TS are then calculated as the final sample weight divided by initial sample weight.

9. Calibration. Calibration is to be performed each 8-hour period when the instrument is used. Each day, prior to running samples, the column should be conditioned by running two 2000-ppm standards from the previous day.

9.1 Preparation of Standards. Calibration standards are prepared as follows: Place 100µl or about two equal drops of distilled water in the sample vial, then fill the vial with the VCM/nitrogen standard, rapidly seat the septum, and seal with the aluminum cap. Use a ¼-in. stainless steel line from the cylinder to the vial. Do not use rubber or tygon tubing. The sample line from the cylinder must be purged (into a properly vented hood) for several minutes prior to filling the vials. After purging, reduce the flow rate to 500 to 1000 cc/min. Place end of tubing into vial (near bottom). Position a septum on top of the vial, pressing it against the ¼-in. filling tube to minimize the size of the vent opening. This is necessary to minimize mixing air with the standard in the vial. Each vial is to be purged with standard for 90 seconds, during which time the filling tube is gradually slid to the top of the vial. After the 90 seconds, the tube is removed with the septum, simultaneously sealing the vial. Practice will be necessary to develop good technique. Rubber gloves should be worn during the above operations. The sealed vial must then be pressurized for 60 seconds using the vial prepressurizer. Test the vial for leakage by placing a drop of water on the septum at the needle hole.

9.2 Preparation of Chromatograph Calibration Curve.

Prepare two 50-, 500-, 2000-, and 4000-ppm standard samples. Run the calibration samples in exactly the same manner as regular samples. Plot A_{vinyl} the integrator area counts for each standard sample, versus C_{vinyl} the concentration of vinyl chloride in each standard sample. Draw a straight line through the points derived by the least squares method.

10. Calculations.

10.1 Response Factor. If the calibration curve described in Section 9.2 passes through zero, a response factor, R_f , may be used to compute vinyl chloride concentrations. To compute a response factor, divide any particular A_{vinyl} by the corresponding C_{vinyl} .

$$R_f = \frac{A_{\text{vinyl}}}{C_{\text{vinyl}}} \quad \text{Eq. 107-1}$$

Where:

A_{vinyl} = Chromatograph area counts of vinyl

$$C_{\text{PVC}} = \frac{A_{\text{vinyl}} P_a}{R_f T_1} \left[\frac{M_v V_g}{R m} + K_p (TS) T_2 + K_w (1 - TS) T_2 \right] \quad \text{Eq. 107-2}$$

Results calculated using these equations represent concentration based on the total sample. To obtain results based on dry PVC content, divide by TS.

11. References.

1. B.F. Goodrich, Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins, Latex, Wet Cake, Slurry and Water Samples. B.F. Goodrich Chemical Group Standard Test Procedure No. 1005-E. B.F. Goodrich Technical Center, Avon Lake, Ohio, October 8, 1979.
2. Berens, A.R. The Diffusion of Vinyl Chloride in Polyvinyl Chloride. ACS—Division of Polymer Chemistry, Polymer Preprints 15 (2):197, 1974.
3. Berens, A.R. The Diffusion of Vinyl Chloride in Polyvinyl Chloride. ACS—Division of Polymer Chemistry, Polymer

$$C_{\text{PVC}} = \frac{A_{\text{vinyl}} 750}{R_f 296} \left[\frac{55.5 (21.8 - \frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9653})}{62360} + 6.25 \times 10^{-6} (TS) (363) + 7.0 \times 10^{-7} (1-TS) (341) \right]$$

Gas Chromatography. Journal of Applied Polymer Science. 19:3169-3172, 1975.

5. Mansfield, R.A. The Evaluation of Henry's Law Constant (K_p) and Water Enhancement in the Perkin-Elmer Multifract F-40 Gas Chromatograph. B.F. Goodrich, Avon Lake, Ohio, February 10, 1978.

40 CFR Part 61 is amended by adding Appendix C as follows:

Appendix C.—Quality Assurance Procedures

chloride for the sample.

P_a = Ambient atmospheric pressure, mm Hg.
 R_f = Response factor in area counts per ppm VCM.

T_1 = Ambient laboratory temperature, °K.
 M_v = Molecular weight of VCM, 82.5 g/mole.

V_g = Volume of the vapor phase, cm³.
 R = Gas constant, (82380 cm³) (mm Hg/mole) (°K).

m = Sample weight, g.

K_w = Henry's Law Constant for VCM in PVC @ 90° C, 6.52×10^{-6} g/g/mm Hg.

If the calibration curve does not pass through zero, the calibration curve must be employed to calculate each sample concentration unless the error introduced by using a particular R_f is known.

10.2 Residual Vinyl Chloride Monomer Concentration, (C_{vinyl}) or Vinyl Chloride Monomer Concentration. Calculate C_{vinyl} in ppm or mg/kg as follows:

Preprints 15 (2):203, 1974.

4. Berens, A.R., L.B. Crider, C.J. Tomanek, and J.M. Whitney. Analysis for Vinyl Chloride in PVC Powders by Head-Space

TS = Total solids expressed as a decimal fraction.

T_2 = Equilibrium temperature, °K.

K_w = Henry's Law Constant for VCM in water @ 90° C, 7×10^{-7} g/g/mm Hg.

Assuming the following conditions are met, these values can be substituted into Equation 107-2:

P_a = 750 mm Hg.

V_g = Vial volume—sample volume (Fisher vials are 22.0 cm³ and Perkin-Elmer vials are 21.8 cm³).

T_1 = 23° C or 296° K.

T_2 = 90° C or 363° K.

Procedure 1—Determination of Adequate Chromatographic Peak Resolution

In this method of dealing with resolution, the extent to which one chromatographic peak overlaps another is determined.

For convenience, consider the range of the elution curve of each compound as running from -2σ to $+2\sigma$. This range is used in other resolution criteria, and it contains 95.45 percent of the area of a normal curve. If two

peaks are separated by a known distance, b , one can determine the fraction of the area of one curve that lies within the range of the other. The extent to which the elution curve of a contaminant compound overlaps the curve of a compound that is under analysis is found by integrating the contaminant curve over the limits $b - 2\sigma$, to $b + 2\sigma$, where σ , is the standard deviation of the sample curve.

This calculation can be simplified in several ways. Overlap can be determined for curves of unit area; then actual areas can be introduced. Desired integration can be resolved into two integrals of the normal distribution function for which there are convenient calculation programs and tables. An example would be Program 15 in Texas Instruments Program Manual ST1, 1975, Texas Instruments, Inc., Dallas, Texas 75222.

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$$\frac{1}{\sqrt{2\pi}\sigma_c} \int_{b-2\sigma_s}^{b+2\sigma_s} e^{\left(\frac{-t^2}{2\sigma_c^2}\right)} dt = \frac{1}{\sqrt{2\pi}} \int_{\frac{b-2\sigma_s}{\sigma_c}}^{\frac{b+2\sigma_s}{\sigma_c}} e^{\left(\frac{-x^2}{2}\right)} dx = \frac{1}{\sqrt{2\pi}} \int_{\frac{b-2\sigma_s}{\sigma_c}}^{\frac{b+2\sigma_s}{\sigma_c}} e^{\left(\frac{-x^2}{2}\right)} dx$$

The following calculation steps are required:*

$$1. \quad 2\sigma_s = t_s / \sqrt{2 \ln 2}$$

$$2. \quad \sigma_c = t_c / 2\sqrt{2 \ln 2}$$

$$3. \quad x_1 = (b-2\sigma_s)/\sigma_c$$

$$4. \quad x_2 = (b+2\sigma_s)/\sigma_c$$

$$5. \quad Q(x_1) = \frac{1}{\sqrt{2\pi}} \int_{x_1}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx$$

$$6. \quad Q(x_2) = \frac{1}{\sqrt{2\pi}} \int_{x_2}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx$$

$$7. \quad I_o = Q(x_1) - Q(x_2)$$

$$8. \quad A_o = I_o A_c / A_s$$

$$9. \quad \text{Percentage overlap} = A_o \times 100$$

where:

A_s = Area of the sample peak of interest determined by electronic integration or by the formula $A_s = h_s t_s$.

A_c = Area of the contaminant peak, determined in the same manner as A_s .

b = Distance on the chromatographic chart that separates the maxima of the two peaks.

H_s = Peak height of the sample compound of interest, measured from the average value of the baseline to the maximum of the curve.

t_s = Width of sample peak of interest at 1/2 peak height.

t_c = Width of the contaminant peak at 1/2 of peak height.

σ_s = Standard deviation of the sample compound of interest elution curve.

σ_c = Standard deviation of the contaminant elution curve.

$Q(x_1)$ = Integral of the normal distribution function from x_1 to infinity.

$Q(x_2)$ = Integral of the normal distribution function from x_2 to infinity.

I_o = Overlap integral.

A_o = Area overlap fraction.

*In most instances, $Q(x_2)$ is very small and may be neglected.

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In judging the suitability of alternate GC columns or the effects of altering chromatographic conditions, one can employ the area overlap as the resolution parameter with a specific maximum permissible value.

The use of Gaussian functions to describe chromatographic elution curves is widespread. However, some elution curves are highly asymmetric. In cases where the sample peak is followed by a contaminant that has a leading edge that rises sharply but the curve then tails off, it may be possible to define an effective width for t_r as "twice the distance from the leading edge to a perpendicular line through the maxim of the contaminant curve, measured along a perpendicular bisection of that line."

Procedure 2—Procedure for Field Auditing GC Analysis

Responsibilities of audit supervisor and analyst at the source sampling site include the following:

A. The audit supervisor verifies that audit cylinders are stored in a safe location both before and after the audit to prevent vandalism.

B. At the beginning and conclusion of the audit, the analyst records each cylinder number and pressure. An audit cylinder is never analyzed when the pressure drops below 200 psi.

C. During the audit, the analyst performs a minimum of two consecutive analyses of each audit cylinder gas. The audit must be conducted to coincide with the analysis of source test samples, normally immediately after GC calibration and prior to sample analyses.

D. At the end of audit analyses, the audit supervisor requests the calculated concentrations from the analyst and compares the results with the actual audit concentrations. If each measured concentration agrees with the respective actual concentration within ± 10 percent, he directs the analyst to begin analyzing source samples. Audit supervisor judgment and/or supervisory policy determine action when agreement is not within ± 10 percent. When a consistent bias in excess of 10 percent is found, it may be possible to proceed with the sample analysis, with a corrective factor to be applied to the results at a later time. However, every attempt should be made to locate the cause of the discrepancy, as it may be misleading. The audit supervisor records each cylinder number, cylinder pressure (at the end of the audit), and all calculated concentrations. The individual being audited must not under any circumstance be told actual audit concentrations until calculated concentrations have been submitted to the audit supervisor.

Field Audit Report

Part A.—To be filled out by organization supplying audit cylinders.

1. Organization supplying audit sample(s) and shipping address

2. Audit supervisor, organization, and phone number

3. Shipping instructions: Name, Address, Attention

4. Guaranteed arrival date for cylinders
5. Planned shipping date for cylinders
6. Details on audit cylinders from last analysis

	Low conc.	High conc.
a. Date of last analysis		
b. Cylinder number		
c. Cylinder pressure, psi		
d. Audit gas(es)/balance gas		
e. Audit gas(es), ppm		
f. Cylinder construction		

Part B.—To be filled out by audit supervisor.

1. Process sampled
2. Audit location
3. Name of individual audit
4. Audit date
5. Audit results:

	Low conc. cylinder	High conc. cylinder
a. Cylinder number		
b. Cylinder pressure before audit, psi		
c. Cylinder pressure after audit, psi		
d. Measured concentration, ppm Injection #1: Injection #2: Average		
e. Actual audit concentration, ppm (Part A, 6e)		
f. Audit accuracy: Low Conc. Cylinder High Conc. Cylinder		

Percent accuracy = $\frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$

g. Problems detected (if any)

*Results of two consecutive injections that meet the sample analysis criteria of the test method.

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