# Analytical Procedure

Research & Development Department

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PROCEDURE NO. GCF-4.0
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## DETERMINATION OF VINYL CHLORIDE CONTENT OF POLYVINYL CHLORIDE RESIN SLURRY SAMPLES

Alternate Method to EPA Test Method 107
(FR 41:46569, 10/21/76; FR 42:29008, 6/7/77)

### 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. Suitable precautions must be taken by both sampling and analytical personnel to avoid exposure to vinyl chloride (VCM), a carcinogen.

### 1. PRINCIPLE AND APPLICABILITY

1.1 This method is based upon direct injection of a sample solution into a gas chromatograph to separate and determine the residual vinyl chloride monomer content (RVCM).

1.2 Procedure GCF-4.0 is applicable to polyvinyl chloride (PVC) reactor slurry samples from both suspension and dispersion processes. No interferences with the VCM peak have been observed in the analyses of the subject slurry samples, using the columns specified in Section 5.3.2. If the resolution of the VCM peak is not satisfactory for a particular sample, then chromatograph parameters may be altered provided that the precision and reproducibility of the analysis of the calibration standards are not impaired. If there is reason to believe that interferences are occurring from another compound with identical retention time, supplemental confirmation of the VCM peak must be performed by GC-Mass Spectrometry. The GC column used should be identical to, and operated under, the conditions specified in this method.

2. RANGE AND SENSITIVITY

The hydrogen flame ionization detector of the Perkin Elmer Model 3920, and equivalent instruments, is capable of detecting approximately 0.2 nanograns of vinyl chloride. The limit of detection in slurry samples, using the sample concentration specified in Section 7.2.2, is approximately 0.25 parts per million based on total sample. With proper calibration, the upper limit may be extended as needed.

3. PRECISION AND REPRODUCIBILITY

A slurry sample containing 116.1 ppm of residual VCM, when analyzed eight times showed a standard deviation of 9.78%.

4. 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 and when necessary the vapor must be routed to the outside air in an approved laboratory hood. Leave hood on at all times when VCM solutions are present.

5. APPARATUS

5.1 Sampling

5.1.1 Sample Bottles - 4 oz., wide mouth, with Poly-Seal screw on tops, for PVC samples.

5.1.2 Electrical Tape - for securing bottle tops.

5.2 Sample Recovery

5.2.1 Volumetric Flasks, 25 ml - Pyrex, Corning No. 5640 for the preparation of the tetrahydrofuran (THF) solutions.

weight cont
corrected for volume
See 7.2.1

5.2.2 Analytical Balance - Capable of weighing to ± 0.001 gram.

5.2.3 Magnetic Stirring Bars - 1 x 5/16 inches, Bel-Art F51111 for use in sample bottles.

5.2.4 Magnetic stirring bars - 7/8 x 3/16 inches Bel-Art F371111

5.2.5 Magnetic stirring plate

5.2.6 Oven for total solids - capable of holding 105-110°C

5.2.7 Evaporating dishes - aluminum, disposable, 57 mm.

5.2.8 Medicine droppers - for sample transfer

5.3 Analysis

5.3.1 Gas chromatograph - Perkin Elmer model 3920 or equivalent equipped with hydrogen flame ionization detector and column oven temperature programmer.

5.3.2 Chromatographic column - Stainless steel, 0.125 inches x 10 feet, packed with 15% UCON LB-550X on Anakrom ABS, 60-70 mesh. A 0.25 inches x 5 feet column containing 20% Octoil S on Chromosorb P, 30-60 mesh, acid washed, can be used in place of the UCON column (or a 0.25 inch x 20 feet, packed with 10% SP-1000 on 80-100 mesh Supelcoport can be used in place of the UCON column).

5.3.3 Potentiometric Recorder - 1.0 millivolt full scale response with approximately 30 in/hr chart speed.

5.3.4 Injection liners - glass or stainless steel

5.3.5 Integrator - Spectra Physics, Model 6300, or equivalent.

5.3.6 Syringe, 10 microliter - Pressure-Lok Syringe 120022 or equivalent

5.3.7 Filter drier assembly - Applied Science Laboratories, Inc. No. 14503 or equivalent. One unit required for each gas cylinder.

5.3.8 Soap film flow meter - Applied Science Laboratories, Inc. No. 13000, or equivalent.

5.3.9 Regulators - for required gas cylinders.

5.4 Calibration

5.4.1 Volumetric flasks (5) - 100 ml, glass stoppered

5.4.2 Dewar flask - capacity to hold a 100 ml volumetric flask.

5.4.3 Pipettes - volumetric, 20 ml, 10 ml, 5 ml, 3 ml

5.4.4 Syringe, 0.5 ml - Hamilton 1750 N, or equivalent

5.4.5 Syringe, 10 microliter - see section 5.3.6

5.4.6 Vials - SKC No. 226-02-100, Development vials with teflon lined septum caps, for storage of standard solutions.

6. REAGENTS

6.1 Analysis

6.1.1 Hydrogen gas - zero grade

6.1.2 Helium gas - zero grade

6.1.3 Air - zero grade

6.1.4 Tetrahydrofuran (THF) - Baker analyzed reagent No. 3-9450, or equivalent. Ten microliters of THF, when injected into the gas chromatograph operated as specified in Section 7.3, must not show any peak eluting at the retention time shown by the VCM in the standards or slurry samples.

6.2 Calibration

6.2.1 Vinyl chloride - Approved sample bomb containing liquid monomer. Must have grounding cable. The commercial material assaying more than 99.9% is satisfactory.

7. PROCEDURE

7.1 Sampling

7.1.1 PVC Slurry Sampling - allow the slurry to flow from a tap on the tank until the tap line has been well purged. Extend a 4 oz. sample bottle under the tap, fill, and immediately tightly cap the bottle. Wrap electrical tape around the cap and bottle to prevent the top 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.

7.2 Sample Recovery - samples must be run within 24 hours.

7.2.1 Sample Preparation - mix the slurry sample thoroughly. To prevent settling during sampling, add a stir bar and agitate the slurry on a stirring plate. Using an eye dropper, transfer approximately 2 grams to a tared 25 ml volumetric flask and determine the weight of sample to $\pm$ 0.005 grams. Immediately add THF to the mark, stopper, and mix the contents by repeatedly inverting the flask. Add a small magnetic stir bar and place the flask on a stirring plate at room temperature until the sample is dissolved.

7.2.1.2 Unused portions of the samples shall be returned to the blend tanks.

7.3 Analysis

7.3.1 Preparation of gas chromatograph - install the chromatographic column and condition overnight at 150°C. Do not connect the exit end of the column to the detector while conditioning.

7.3.1.1 Flow Rate Adjustment - Adjust the flow rates as follows:

a. Helium carrier gas - set cylinder regulator at 60 psig. Adjust chromatograph regulator for a flow rate of 30-40 ml/min as measured with a bubble flow meter. Use 60 ml/min for the octol S column.

b. Burner Air Supply - set cylinder regulator at 60 psig.

c. Hydrogen Supply - set cylinder regulator at 30 psig. Optimize flow rates for b and c with the chromatograph regulators following instrument instruction manual. Record the flow rates obtained.

7.3.1.2 Temperature Adjustments - set temperatures as follows:

a. Column oven - 55°C
b. Injector block - 120°C
c. Detector - 200°C

7.3.1.3 Ignition of flame ionization detector - follow instrument manual directions.

7.3.1.4 Electrometer range - use setting of 1 or 10, as required.

7.3.2 Operating the chromatograph - allow the baseline to stabilize and condition the column at the start of each day by injecting 5 microliters of the 160 ppm standard. When the baseline stabilizes, inject 10 microliters of sample solution, Sect. 7.2.1. Record the integrated area and retention time of the VCM peak. Immediately after elution of the VCM peak, program the column oven at maximum rate to 150°C to purge the solvent. Hold eight minutes at 150°C and cool to 55°C at maximum rate in preparation for the next sample. Injection liners should be changed twice a week or whenever baseline instability becomes a problem.

7.3.3 Determination of total solids (TS) - for slurry 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. TS is then calculated as the final sample weight divided by initial sample weight.

8. CALIBRATION - Calibration is to be performed each eight-hour period when the instrument is used. Each day, prior to running samples, the column should be conditioned by running previous days 160 ppm standard.

8.1 Preparation of Standards

Standards containing VCM in the range of 4.5 to 300 ppm (wt/vol)are prepared in THF as described below. With the sample size specified in Section 7.2.1, these standards

cover up to 4000 ppm RVCM in wet slurry.

8.1.1 Stock solution - Approximately 3% (wt/volume). All operations must be carried out in a well ventilated hood. Add about 75 ml of THF (See Section 6.1.4) to a 100ml volumetric flask, stopper and weigh to ± 1 mg. Cool the THF by immersing the flask in a Dewar flask containing dry ice and acetone. Add approximately 3 grams of liquid monomer from the bottom valve of a vertically mounted sample bomb (Fig. 1). Make certain that the bomb is properly grounded. Stopper the flask, invert it gently to mix the contents, and allow it to warm slowly to room temperature. Reweigh the flask to ± 1 mg and calculate the weight of added VCM. Fill the flask to the mark with THF as quickly as possible and mix gently by repeatedly inverting the flask.

8.1.2 Stock Solution - approximately 0.15% (wt/volume). Accurately dilute 8.1.1 by pipetting 5 ml into a 100 ml volumetric flask partially filled with THF and diluting to the mark with THF.

8.1.3 Calibration Standards - Prepare four calibration standards by accurately pipetting 0.3, 3, 10 and 20 ml of solution 8.1.2 into 100 ml volumetric flasks partially filled with THF. Transfer the 0.3 ml aliquot with a precision grade 0.5 ml syringe. Dilute to the mark and mix each flask thoroughly by repeated inversion. Using the original weight of VCM in 8.1.1, calculate the concentration of each calibration standard. For reproducibility of standard preparation see Table I.

8.1.4 Storage of Standards - Transfer the calibration standards to SKC development vials and store under refrigeration. For calibration, remove fresh vials from the refrigerator and allow them to warm to room temperature before use. Standards prepared in this manner have been found stable for periods of 3 to 4 weeks (Table II).

8.1.5 Disposal of THF Solutions - In a well ventilated hood, transfer sample, VCM stock solutions and spent calibration standards to a beaker containing several grams of Ionol. Aloow the contents to evaporate to dryness.

8.2 Preparation of Calibration Curve - Run the calibration standards in duplicate from 8.1.3 in exactly the same manner as the slurry samples. Plot the integrator area counts for each standard vs. the concentration of VCM in that standard. Draw a line of best fit through the points.

9. CALCULATIONS

9.1 Response Factor - calculate the response factor ($F_R$) from the scope of the calibration curve in integrator area counts per microgram of VCM.

9.2 Residual Vinyl Chloride Content - calculate the residual vinyl chloride content of slurry samples as follows:

a. Wet basis:

$$\text{VCM (ppm)} = \frac{\text{Integrator area} \times 5{,}000}{F_R \times S_W}$$

b. Dry basis:

$$\text{VCM (ppm)} = \frac{\text{Integrator area} \times 500{,}000}{F_R \times S_W \times TS}$$

Where $F_R$ = Response factor in counts/microgram
$S_W$ = Sample weight in grams
$T_S$ = Total solids in percent by weight

TABLE I

REPRODUCIBILITY OF STANDARD PREPARATION

| ppm (wt./vol.) as prepared | Response, area/ppm | ppm (wt./vol.) as prepared | Response, area/ppm |
|---|---|---|---|
| 3.82 | 98.0 | 124.9 | 111.4 |
| 42.87 | 101.5 | 225.6 | 109.3 |
| 62.24 | 108.5 | 259.6 | 111.8 |
| 104.5 | 107.6 | 337.8 | 105.5 |
| 120.9 | 110.0 | 382.8 | 112.5 |

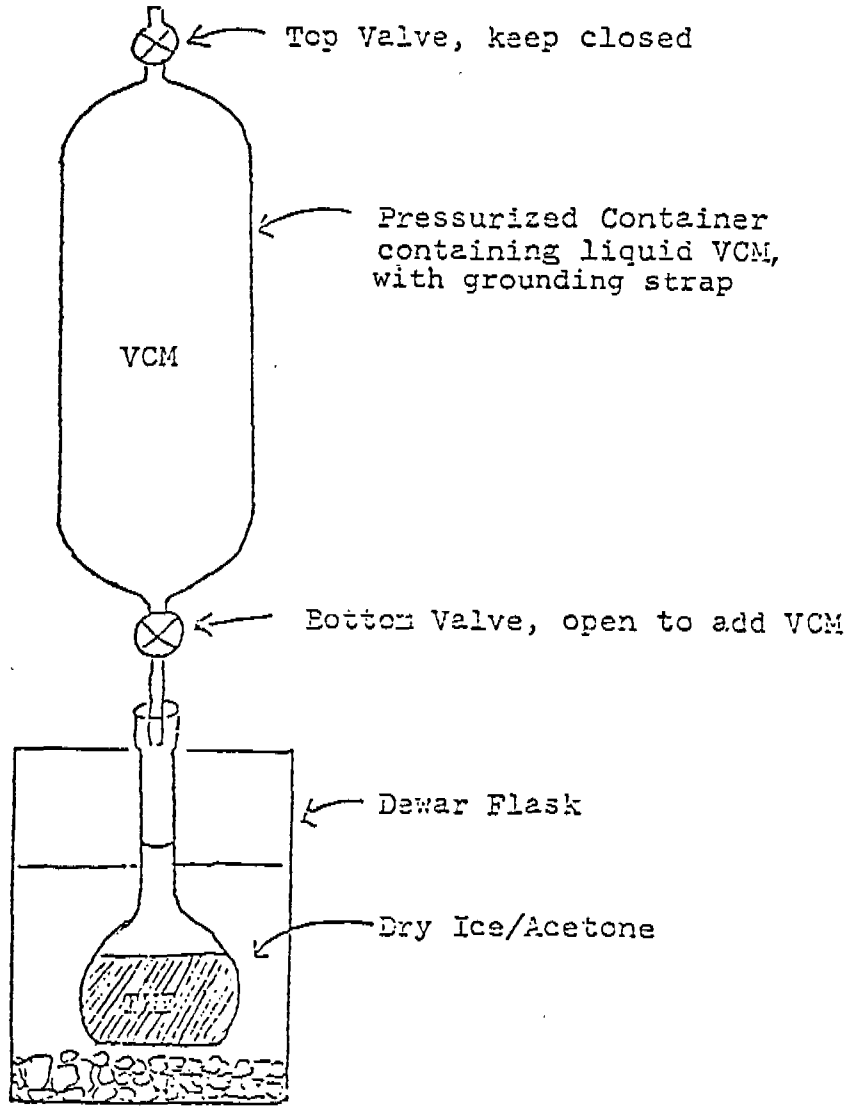
Average Response, area/ppm = 107.6
Average Deviation = 3.57
Standard Deviation = 4.71

TABLE II

STABILITY OF STANDARD SOLUTIONS

| Age, Days | 104.5 ppm Response | 120.9 ppm Response | 62.6 ppm Response | 104.3 ppm Response |
|---|---|---|---|---|
| 0 | 107.6 | 110.0 | 108.5 | 109.7 |
| 3 | 101.6 | 107.0 | 108.3 | 102.6 |
| 6 | 102.1 | 105.9 | - | - |
| 7 | - | - | 97.5 | 105.5 |
| 9 | 110.5 | 112.1 | - | 106.7 |
| 11 | - | - | 107.1 | - |
| 14 | - | - | - | 101.7 |
| 16 | 105.4 | 109.0 | - | - |
| 20 | 107.4 | 94.4 | 90.4 | - |
| 23 | 107.2 | - | - | - |

Fig. 1


Top Valve, keep closed
Pressurized Container containing liquid VCM, with grounding strap
VCM
Bottom Valve, open to add VCM
Dewar Flask
Dry Ice/Acetone