→ G. V. Suhr –

B. F. GOODRICH CHEMICAL COMPANY

Standard Test Procedure No. 999-T

TITLE: Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins

TYPE OF ANALYSIS: Vapor Space Equilibrium, Gas Chromatographic

PRODUCT: Polyvinyl Chloride Resin, Finished Product

I. SCOPE

This procedure is suitable for determining the residual vinyl chloride monomer content of polyvinyl chloride (PVC) resins. The method cannot be used for polymer in other forms such as compounds or final fused products.

II. PRINCIPLE

The basis for this method relates to the vapor equilibrium which is established between residual vinyl chloride monomer (RVCM), PVC resin and air in a closed system. It has been demonstrated that the RVCM in a PVC resin will equilibrate in a closed vessel quite rapidly, provided the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

III. INTERFERENCES

1) Normally this vapor will contain only air, vinyl chloride monomer and traces of water. Any other volatile material present in the closed vessel could change this equilibrium relationship. Impurities in the low ppm range will generally have only a very small influence on this equilibrium relationship.

2) Any material which elutes from the chromatographic column at approximately the same time as vinyl chloride will cause high RVCM results.

IV. PRECISION AND REPRODUCIBILITY

Initial data obtained with this method, covering a range of 0.0025 to 0.2000 wt. percent, indicates that one standard deviation (determined from duplicate results) is approximately 2.1%. Absolute accuracy has been checked by comparing results to another, totally independent method. In this case agreement between the two methods is ± 5% in the range 0.0025 to 0.2000 wt. %. These results were obtained by two operators in one laboratory.

V. SAFETY

1) Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting and purging with vinyl chloride - air mixtures must be held to an absolute minimum. When venting and/or purging is required the vapor must be routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. It can be vented into a properly functioning fume hood.

2) Be careful not to come into contact with heated parts of the chromatograph, such as the injection port, detector, heated column, etc. Handle all electrical connections with care.

VI. APPARATUS

1) Gas Chromatograph, Hewlett Packard Model 5711A, dual flame ionization detector, equipped with following options:

(a) 005 Dual flow controller

(b) 006 Substitute linear oven programmer (5702A) for isothermal oven controller

(c) 011 Substitute auxiliary heated zone controller (5708A)

(d) 017 Substitute universal heated injection port with disposable glass liners (18747)

(e) 024 Rotometer kit for carrier gas

2) Integrator -- Hewlett Packard Model 3380A with built-in recorder

Alternate Integrator -- AutoLab System 4

3) Chromatographic Column -- An 8 ft. x 1/8 in. stainless steel column packed with 80/100 Poropak QS and conditioned at 200° C.

4) Oven, forced draft capable of maintaining a constant temperature of 90° ± 1.0° C. (Fisher Cat. No. 13-244-176 Isotemp Oven)

5) Gas Sampling Bottles, 250 ml capacity equipped with glass stopcocks on both ends plus a septum fitting (Fisher Cat. No. 11-134-190)

6) Serum Bottles, 10 cc volume with rubber septums (Fisher Cat. No. 210B serum bottles and Cat. No. 3-215 rubber stoppers.

7) Analytical Balance, capable of weighing to ± .0001 gram

8) Hydrogen Cylinder with regulator

9) Flowmeter, 0 to 2 liters per minute

VI. APPARATUS (continued)

10) Helium Cylinder with regulator
11) Clean air supply at 25 psig
12) Bubble Flow Indicator

VII. REAGENTS

Calibration gases, vinyl chloride in air mixtures

1) Low level between 15 and 25 parts per million
2) A high level between 800 and 1200 parts per million

These can be obtained from:

Precision Gas Products, Inc.
P. O. Box 538
Linden, New Jersey 07036

VIII. PREPARATION OF GAS CHROMATOGRAPH

1) Install the 8 ft. x 1/8 in. Poropak QS column and condition at 200° C.

2) Adjust flow rates for the H. P. 5711A according to the operating manual (30 cc's per minute helium carrier gas, 30 cc's per minute hydrogen and 130 cc's per minute air.)

3) Set conditions for analysis as follows:

Injection port - 150° C.
Detector - 250° C.
Oven - 160° C.

4) After these conditions have been reached and the chromatograph has stabilized it is ready for calibration.

IX. CALIBRATION

1) Fill the clean glass 250 ml gas sample bottle with the low level (15 to 25 ppm) vinyl chloride air standard. The procedure for doing this is detailed in Attachment 1. Always use the same bottle for this low level standard.

2) With the 1 cc gas syringe draw out of the calibration bottle, through the septum, in excess of 1 cc of the gas sample. After the plunger on the syringe is pulled all the way, wait five seconds before removing the syringe needle from the bottle septum. BOR 005821

3) After the five second delay remove the needle from the septum and move plunger to read exactly 1 cc on the syringe.

IX. CALIBRATION (continued)

4) Immediately inject the 1 cc sample into the chromatograph injection port (as rapidly as possible).

5) Remove the needle from the injection port and start the chromatograph recorder and integrator.

6) In approximately three minutes the vinyl chloride will elute.

7) Wait one minute after the VCl elutes and starting at Step 2 above repeat Steps 2 through 6. Do this four times.

8) Fill in the data obtained in the four runs above on the calibration sheet (Attachment 2).

9) If the peak areas from these four runs do not deviate more than 5% from the average of the four runs, this step is complete. If there is a deviation greater than 5% from the average, repeat Steps 1 through 8. See Note 1.

10) After the above calibration is completed, recharge the second glass calibration cylinder with the high level (800 to 1200 ppm) vinyl chloride air standard. Starting at Step 2 above repeat this procedure through Step 9 using the high level standard.

11) This calibration is complete if the requirements of Step 9 are met. If Step 9 is not met, refer to Note 1.

12) For the third calibration point use the high level standard, but in this case use only a 0.5 cc sample.

13) Draw out an excess of 0.5 cc with the gas syringe.

14) Wait five seconds after the plunger is pulled back before removing the syringe needle.

15) After the five second delay remove the syringe and adjust the plunger to read exactly 0.5 cc.

16) Inject this sample into the chromatograph and record the peak area on the calibration sheet.

17) Repeat Steps 13 through 16 four times.

18) If the peak areas from these four runs do not deviate more than 5% from the average of these four runs, this calibration is complete. If there is a deviation greater then 5% from the average, repeat Steps 13 through 16. See Note 1.

IX. CALIBRATION (continued)

19) The data generated in the above calibration is used to calculate the response factor for the calculation of residual vinyl chloride in the samples analyzed. The response factor calculations are detailed on the calibration sheet.

Note 1: If the deviation is still greater than 5%, shut down and locate the source of the problem.

X. SAMPLE ANALYSIS (Samples must be run at same range and attenuation used for calibration standards. If range or attenuation is changed for the sample, then new standards must be run at this range and attenuation.

1) All samples should be kept in tightly sealed glass jars. Samples must be run promptly (within 30 minutes) from the time they are received in the laboratory. Within 30 minutes the sample should be weighed into the serum bottle and placed in the oven. The exact total volume of the serum bottles must be measured. See Attachment 5.

2) Prepare duplicates for each sample. Take one serum bottle plus rubber septum, mark with identification and obtain a tare weight to four decimal places. Record tare weight on analysis work sheet. See Attachment 3.

3) Remove serum bottle from balance, remove septum and pour in the proper amount of resin to be analyzed. Replace rubber septum. Be certain that rubber septum is fully seated and sealed.

Approximate Bottle Volume	Add
12 cc	2 grams ± .5

A simple technique can be devised based on a volumetric resin addition. Small cups, having the proper volume, can be used to rapidly obtain the resin sample. This can then be added to the serum bottle with a tiny funnel.

4) Replace serum bottle on balance and record the weight to four decimal places.

5) Remove bottle from balance.

6) Place bottle in oven (at 90° ± 1.0° C.) and allow it to remain 15 -0 +1 minutes.

7) At the end of the heating cycle remove the bottle from the oven and immediately insert the needle from the 1 cc gas syringe into the bottle through the septum. (Do not allow the needle to contact the resin sample.)

X. SAMPLE ANALYSIS (continued)

8) Sample Size - Use a 1 cc sample volume when the RVCM content is expected to be less than 100 ppm. Use a 0.5 or 0.3 cc sample for expected higher concentrations.

9) Draw out the proper volume sample (plus slight excess) from the bottle. Wait 5 seconds after pulling the plunger back before removing the needle from the sample bottle.

10) After the 5 second delay remove the syringe needle from the serum bottle and adjust plunger to read the proper volume.

11) Inject the sample into the chromatograph, start integrator and recorder.

12) The vinyl chloride peak will elute in approximately 3 minutes.

13) Wait one minute after the vinyl chloride peak elutes and repeat Steps 7 through 11 using a duplicate sample.

14) Record sample peak area, gas sample size, attenuation, sample identification, etc. on work sheet (Attachment 3).

15) One minute after the vinyl chloride elutes you are ready to run another sample.

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XI. CALCULATION OF RVCM IN SAMPLE

The following information is needed to calculate the residual vinyl chloride content of the resin.

1) Response factor for vinyl chloride = R (counts/nanogram VCl) (as determined in the calibration step)

2) Weight of polyvinyl chloride resin in vial = W (grams)

3) Volume of sample injected into chromatograph = V (cc)

4) Area of the chromatograph peak for the vinyl chloride = A (integrator counts)

5) Volume of sample bottle (serum vial) = B (cc)

6) Atmospheric Pressure = P (mm Hg)

$$\text{ppm RVCM} = \frac{\left[\dfrac{A \times 10^{-1}}{A \times 10^{-9} + (1.16\ RV \times 10^{-3})}\right]}{100 - \left[\dfrac{A \times 10^{-7}}{A \times 10^{-9} + (1.16\ RV \times 10^{-3})}\right]} \times \left[\frac{(29)(363)P}{\underbrace{(29.5)(62.5)}_{295}}\right] \times \left[\left(6.5 \times 10^{-6}\right) + \frac{62.5 \times \left(B - \frac{W}{1.4}\right)}{(62400)(363)(W)}\right]$$

This calculation can very easily be set up on a Monroe 1860 Programmable Calculator. It should not be routinely performed on a hand calculator because of a high probability for errors. The Monroe 1860 program for this method is attached. See Attachment 4.

ATTACHMENT 1

Method for Preparation of Standard VCM/Air Mixtures

1) Clean the 250 ml gas sampling bottles with acetone and blow thoroughly dry with clean air or nitrogen.

2) Apply low vapor pressure stopcock grease to both stopcocks after washing and drying.

3) Attach a septum to the septum stem.

4) Using the proper standard VCM/air cylinder equipped with regulator attach the sample bottle using a short piece of tubing. Attach the other end of the bottle to the rotometer.

5) Open both stopcocks on the gas sampling bottle. Open valve on gas cylinder. Very slowly and carefully open the regulator on the cylinder to provide a flow rate of approximately 1.5 liter per minute.

6) Purge for two minutes. Be certain that the VCM/air mixture is properly vented as stated in Section V.

7) At the end of the purge time turn off the valve at the cylinder and then both stopcocks to off, closing the stopcock closest to the cylinder first.

8) Gas sampling bottle is now ready to use.

ATTACHMENT 2

Calibration Data Sheet and Calculations

Run No.	Sample Identification	Injected Sample Size, cc	Peak Area	Avg. Peak Area	Deviation from Avg.	Counts per Nanogram VCl	Avg. Counts per Nanogram VCl
1	19 ppm Std	1.0	4600		.2		
2	"		4565		1.0		
3	"		4690		.4		
4	"		4585	4610	.5	95.7	
5	805 ppm Std	0.5	95370		.8		
6	"		96485		.4		
7	"		95732		.4		
8	"		96901	96122	.8	94.2	
9	805 ppm Std	1.0	193946		1.4		
10	"		190241		.5		
11	"		189789		1.4		
12	"		190916	191,223	.2	93.7	94.53

Using a 1.0 cc sample, each ppm VCl in the standard contains 2.5352 nanograms VCM.

Runs 1 through 4 each contain (19)(2.5352) = 48.17 nanograms VCM
Runs 5 " 8 " " (805)(2.5352)(.5) = 1020.4 nanograms VCM
Runs 9 " 12 " " (805)(2.5352) = 2040.8 nanograms VCM

ThenAverage Peak Area ÷ Nanograms VCM = Counts per Nanogram VCM
The Response Factor = Avg. Counts per Nanogram VCM = 94.53

ATTACHMENT 3

Analysis Work Sheet and Results

Date ____________

GC Run No.	Sample Identification	Sample Weight (grams) W	Vapor Sample Volume (cc) V	GC Peak Area A	Atm. Pressure mm P	Response Factor R	Volume of Serum Bottle B	PPM RVCM in Resin
1	"A"	2.0012	1	43,210	753	94.53	12.0	6.4
2	"B"	1.9873	.3	769,343				213
3	"C"	2.1249	.5	143,356				22.6
4	"D"	2.0141	.5	19,423				3.2
5	"E"	1.9981	.5	117,324				19.4
6	"F"	2.0476	.5	4,422				0.7

ATTACHMENT 4

Program for Calculating % RVCM in Resin - Monroe 1860

Operating Procedure:

1) Br ( ) ( ); 0; 0

   Program No. 133 prints

2) Enter

   A) Area Counts

   B) Response Factor, counts/nanogram VCM

   C) Syringe Volume, cc

   D) Atm. Pressure, mm

   E) Sample Weight, grams

   F) Volume of Serum Bottle, septum in place, cc

3) Prints answer in ppm RVCM in resin

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      133.0000 ———————— PROGRAM NO.
 ................
   144,735.0000 ———————— AREA COUNTS
        94.5300 ———————— RESPONSE FACTOR
         0.3000 ———————— SYRINGE VOLUME
       753.0000 ———————— ATM. PRESSURE
         2.0012 ———————— SAMPLE WEIGHT
        12.0000 ———————— SERUM BOTTLE VOLUME

        39.8641        A
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4	003	3
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6	176	
7	056	
8	110	↓
9	001	1
0010	060	
1	056	
2	110	↓
3	002	2
4	060	
5	056	
6	110	↓
7	003	3
8	060	
9	056	
0020	110	↓
1	004	4
2	060	
3	056	
4	110	↓
5	005	5
6	060	
7	056	
8	110	↓
9	010	8
0030	060	
1	065	
2	111	↑
3	001	1
4	023	X
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6	001	1
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6	001	1
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8	026	(
9	001	1
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3	013	−
4	027	)
5	020	=
6	021	+
7	026	(
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9	002	2
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8	111	↑
9	007	7
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6	005	5
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9	176	
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ATTACHMENT 5

Establishing True Volume of Serum Bottle

1) Clean serum bottle (water and detergent) and rinse with acetone. Air dry thoroughly.

2) Allow to condition for at least 15 minutes at room temperature.

3) Weigh serum bottle plus septum to 0.0001 gram on an analytical balance.

4) Using distilled water which has been conditioned to within ± 2° F. of room temperature fill the bottle to the very top.

5) Carefully insert and seal the septum. This will tend to force a small amount of water out of the bottle.

6) Dry the outside of the bottle and weigh again on the analytical balance.

7) Knowing the temperature of the water, determine, using a table of density of water at various temperatures, the volume of the bottle.

8) Check three bottles and average the results. Individual results should not differ more than ± 0.3 cc from the average. (Bottles normally have a volume of approximately 12.0 cc.)