

SUMMARY SHEET 107
Vinyl Chloride

		Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 107			
Job No.		FDS 107			
Sampling Location		FDS 107			
Sample ID #		FDS 107			
Test Date		FDS 107			
Sample Time		FDS 107			
Abs Amb Temperature ($t_1 + 273$), K	T_1	LDS 107			
Barometric Pressure, kPa	P_b	LDS 107			
Response Factor, area counts/ppm	R_f	LDS 107			
Sample Weight, g	m	LDS 107			
Total Solids, fraction	TS	LDS 107			
Equilibrium Temperature, 90°C	t_2	LDS 107			
Abs Equilibrium Temp ($t_2 + 273$), K	T_2	SS 107			
Vial Volume, cm^3	V_v	LDS 107			
Vinyl Chloride Concentration (A_g/R_f), ppm	C	LDS 107			
Volume of Vapor Phase, cm^3	V_g	SS 107			
Vinyl Chloride Monomer, ppm	C_{vvc}	SS 107			

$$V_g = V_v - \frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9653}$$

$$C_{vvc} = \frac{CP_b}{T_1} \left[\frac{62.5 V_g}{62360 m} + 6.52 \times 10^{-6} (TS) T_2 + 7 \times 10^{-7} (1 - TS) T_2 \right]$$

FIELD PROCEDURE 107
Vinyl Chloride Content of Inprocess Wastewater Samples,
Polyvinyl Chloride Resin, Slurry, Wet Cake,
and Latex Samples

A. PVC Sampling

1. Purge tap line on the tank or silo with the resin or slurry.
2. Fill a 60-mL sample bottle under the tap, and immediately cap the bottle. To prevent the cap from loosening, wrap adhesive tape around the cap and bottle.
3. Label each bottle, and record the date, time, and sample location both on the bottles and in a log book.
4. Keep samples refrigerated until analysis.

B. Water Sampling

1. Fill the vials bubble-free to overflowing so that a convex meniscus forms at the top.
2. Carefully place the sealing disc, with the Teflon side down, on the opening of the vial.
3. Place the aluminum seal over the disc and the neck of the vial, and crimp into place.
4. Label the vial. Record the date, time, and sample location both on the vials and in a log book.
5. Keep samples refrigerated until analysis.

LABORATORY PROCEDURE 107
Vinyl Chloride

A. Sample Preparation

1. Tare sample vials including the septum and aluminum cap to $\pm 0.7\%$. Obtain all weights to within $\pm 0.7\%$.
2. Resin Samples
 - a. For suspension resins, prepare a volumetric cup to hold 0.1 to 4.5 g. Open the sample bottle, and add the cup volume of resin to the tared sample vial. Weigh, then add 100 μL or ~ 2 equal drops of water, and immediately seal the vial.
 - b. For dispersion resins, weigh the sample in an aluminum dish, transfer the sample to the tared vial, and weigh.
 - c. Prepressurize the samples. This is not required if the sample weight is < 0.2 g or if the absolute prepressurization value is within 30% of the atmospheric pressure.
3. Suspension Resin Slurry and Wet Cake Samples
 - a. Decant the water from a wet cake sample, and turn the sample bottle upside down onto a paper towel.
 - b. Wait for the water to drain, place ~ 0.2 to 4.0 g of the wet cake sample in a tared vial, seal immediately, and weigh.
4. Dispersion Resin Slurry and Geon Latex Samples
 - a. Do not filter the samples. Thoroughly mix the sample, and immediately add to a tared vial ~ 8 drops (0.25 to 0.35 g) of slurry or latex with a medicine dropper.
 - b. Seal the vial as soon as possible and weigh.
5. Inprocess Wastewater Samples
 - a. Quickly add ~ 1 cc of water sample using a medicine dropper.
 - b. Seal the vial as soon as possible, and weigh.

B. Equipment Preparation.

1. Install the chromatographic column and condition overnight at 160°C . In the first operation, purge the Porapak columns for 1 hr at 230°C . (Do not connect the exit end of the column to the detector while conditioning. Ensure that the H_2 and air to

the detector are turned off while the column is disconnected.)

2. Adjust N_2 carrier flow rates, calculate the prepressurization pressure (P), adjust the burner air supply flow rate, H_2 supply flow rate, set the temperatures for the oven, dosing line, injection block, sample chamber, and water temperature, ignite the flame ionization detector, balance the amplifier, and program the chromatograph. See LDS 107.
3. With a soap film flowmeter and stopwatch, measure the flow rate at the exit end of the column, check the burner air supply flow rate, and the H_2 supply flow rate.
4. After setting the N_2 , calculate "P."
Note: Because of gauge errors, the apparatus may over-pressurize the vial (indicated by an audible double injection). Too low vial pressures cause inadequate time for head-space gas equilibrium. Therefore, run several standard gas samples at various pressures around the calculated pressure, and then select the highest pressure that does not produce a double injection.

C. Calibration

1. Prepare two vials each of 50-, 500-, 2,000-, and 4,000-ppm calibration standards as follows:
 - a. Use a 1/8-in. stainless steel line from the cylinder to the vial (Do not use rubber or Tygon tubing). Purge the sample line from the cylinder into a properly vented hood for several minutes before filling the vials.
 - b. Place 100 μL or about two equal drops of distilled water in the sample vial, then fill the vial with the VCM/ N_2 standard, rapidly seat the septum, and seal with the aluminum cap.
 - c. 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 1/8-in. filling tube to minimize the size of the vent opening and prevent mixing air with the standard in the vial.

- d. Wearing rubber gloves, purge each vial with standard for 90 sec, during which time gradually slide the filling tube to the top of the vial. After the 90 sec, remove the tube with the septum, and simultaneously seal the vial.
- e. Pressurize (if required for samples) the sealed vial for 60 sec using the vial prepressurizer. Test the vial for leakage by placing a drop of water on the septum at the needle hole.

D. Vinyl Chloride Analysis

1. Analyze samples within 24 hr after collection.
2. Prepressurize samples (if required) for 1 hr (not to exceed 5 hr).
3. Condition all samples and standards at 90°C for 1 hr.
4. If the aluminum sample vial caps have a center section, remove it before placing into sample turntable to avoid damaging the injection needle.
5. Place the numbered sample vials in the corresponding numbered positions in the turntable. Insert samples in the following order:
 - a. Positions 1 and 2: If the analyzer has not been used for ≥ 24 hr, old 2000-ppm standards (for conditioning).
 - b. Position 3: 50-ppm standard, freshly prepared.
 - c. Position 4: 500-ppm standard, freshly prepared.
 - d. Position 5: 2000-ppm standard, freshly prepared.
 - e. Position 6: 4000-ppm standard, freshly prepared.
 - f. 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.)
 - g. Position rest of samples, then insert the second set of 50-, 500-, 2000-, and 4000-ppm standards.

6. Start the analysis program according to the manufacturer's instructions.
7. After the instrument program advances to the "B" (backflush) mode, adjust the nitrogen pressure regulator to balance the nitrogen flow rate at the detector as was obtained in the "A" mode.
8. Plot A_c , the integrator area counts for each standard sample, versus C_c , the concentration of vinyl chloride in each standard sample.
9. Draw a straight line through the points derived by the least squares method.
10. Perform a calibration for each 8 hrs the chromatograph is used.

E. Total Solids

For wet cake, slurry, resin solution, and PVC latex samples, determine total solids (TS) for each sample as follows:

1. Weigh the aluminum pan, add ~3-4 g sample, and weigh before and after placing in a draft oven (105-110°C).
2. Dry samples 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.

F. Alternatives

An alternative to step D10 is as follows:

1. Calibrate with duplicate 50-, 500-, 2,000-, and 4,000-ppm standards (a four-point calibration) on a monthly basis.
2. Analyze in duplicate the 500-ppm standard [2,000-ppm standard for dispersion resin (excluding latex resin) samples] once per shift, or once per chromatograph carousel operation (if less frequent than once per shift).
3. If both analyses are within $\pm 5\%$ of the most recent four-point calibration curve, step F1 may be continued. If not, perform a complete four-point calibration.

LABORATORY DATA SHEET 107
Vinyl Chloride

Client/Plant Name _____ Job No. _____

City/State _____ Date _____

Gas Chromatograph ID # _____ Analyst _____

Amb. Temp, T₁ _____ °C _____ K Bar. pressure. P_b _____ mm Hg/7.5 _____ kPa

Vial Volume _____ cc

Sample Preparation

Sample ID#	Tare (g)	Samp + Tare (g)	Sample, m (g)	<0.2 g? (✓)	Calc P (kPa)	± 30% P _b (✓)

$$P = \frac{T_1}{363} (P_1 - 67.47) - 10$$

_____ All unchecked samples prepressurized?

where: P₁ = GC abs. dosing pressure "A" mode, kPa

Selected P₁ = _____ kPa (Highest that does not produce a double injection).

Chromatograph Operation

Parameter	Setting	(✓)	Parameter	Setting	(✓)
N ₂ Cylinder Pressure	50 psig		Injection Block Temp	170°C	
N ₂ Cylinder Flow	30.0 cc/min		Water Bath Temp, t ₂	90 ± 1°C	
Burner Air Cyl Pressure	50 psig		Dosing Time	2 sec	
Burner Air Flow	275 ± 25 cc/min		Analysis Time	70% of VCM Retention Time	
H ₂ Cylinder Pressure	30 psig				
H ₂ Flow	35 ± 5 cc/min		Backflushing Time	2x Analysis Time	
Oven Temp	140°C		Stabilization Time	0.5 to 1.0 min	
Dosing Temp	150°C		Analysis/Sample	1	

Bubble Flow Meter Checks:

	N ₂	Burner Air	H ₂
Volume, cc	_____	_____	_____
Time, min	_____	_____	_____
Flow Rate, cc/min	_____	_____	_____

Sample Concentration

Samp No.	Sample ID#	Peak Hgt, H _s	Area, A _s	VC Conc, C (ppm)	Samp No.	Sample ID#	Peak Hgt, H _s	Area, A _s	VC Conc, C (ppm)
	50 ppm								
	500 ppm								
	2000 ppm								
	4000 ppm								
						50 ppm			
						500 ppm			
						2000 ppm			
						4000 ppm			

Calculate $R_s = A_s/C_s$ for each of the standards. Then average R_s to obtain R_f if calibration curve passes through zero; otherwise, use the calibration curve to determine each sample concentration. $C = A_s/R_f$

Total Solids Determination

Sample ID#									
Tare (g)									
Tare/Sample (g)									
Wgt Wet Smpl (g)									
Dry Wgt 1 (g)									
Dry Wgt 2 (g)									
Dry Wgt 3 (g)									
Wgt Solids (g)									
Total Solids									

Wgt Solids = Dry Wgt - Tare

Total Solids, fraction = Wgt Solids/Wgt Wet Sample

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____
 Personnel (Signature/Date)

 Team Leader (Signature/Date)

SUMMARY SHEET 107A
Vinyl Chloride

		Run #1	Run #2	Run #3	Avg
Client/Plant Name					FDS 107
Job No.					FDS 107
Sampling Location					FDS 107
Sample ID #					FDS 107
Test Date					FDS 107
Sample Time					FDS 107
Response Factor, ppm/mm	R _f				LDS 107A
Peak Height of Sample, mm	H _s				LDS 101A
Total Solids	TS				LDS 107A
Vinyl Chloride in Resin, ppm	C _{rvc(resin)}				SS 107A
Vinyl Chloride in Volatile Material, ppm	C _{rvc(vol.)}				SS 107A
Vinyl Chloride in Solvents, ppm	C _{rvc(solv.)}				SS 107A

$$C_{rvc(resin)} = 10 H_s R_f$$

$$C_{rvc(vol)} = \frac{H_s R_f (1000)}{TS}$$

$$C_{rvc(solv)} = \frac{H_s R_f}{0.888}$$

FIELD PROCEDURE 107A
Vinyl Chloride in Solvents, Resin Solvents Solutions,
Polyvinyl Chloride Resin, Resin Slurry,
Wet Resin, and Latex Samples

Note: Use FDS 107.

1. Purge the tap on the tank, silo, or pipeline with its contents.
2. Fill a wide-mouth pint sample bottle, and immediately cap the bottle.
3. Label each bottle, and record the date, time, sample location, and material.

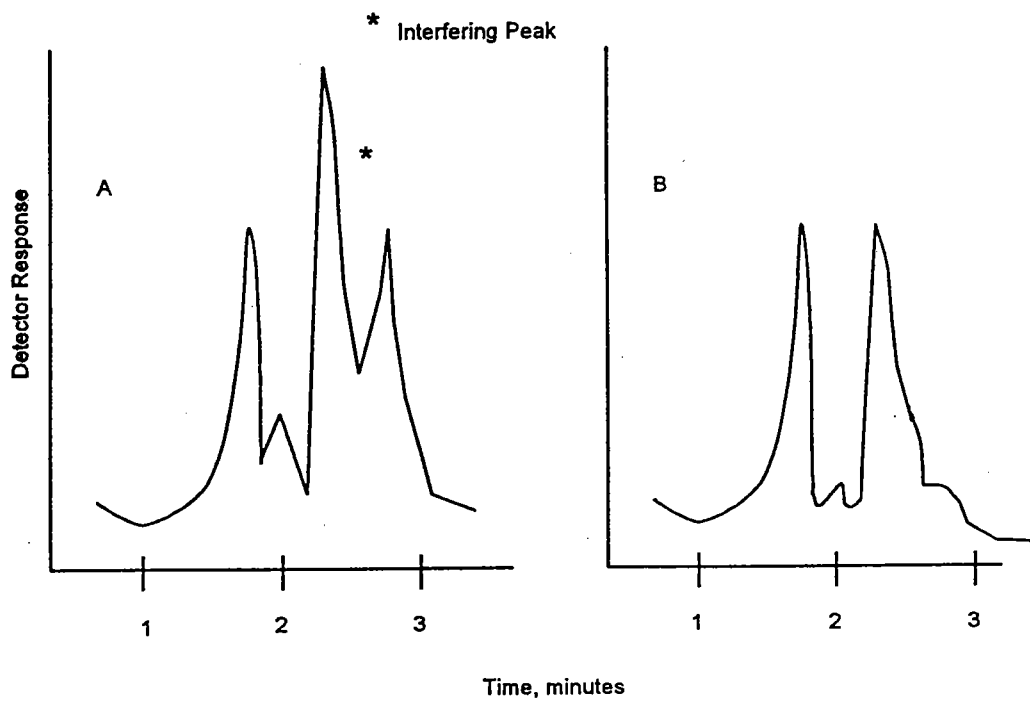


Figure L107A-1.

LABORATORY PROCEDURE 107A
Vinyl Chloride in Solvents, Resin Solvents Solutions, Polyvinyl Chloride Resin,
Resin Slurry, Wet Resin, and Latex Samples.

A. Sample Preparation

1. Tetrahydrofuran (THF). Inject 10 μL THF into the gas chromatograph (GC). For the reagent to be acceptable, the chromatogram must look like Figure L107A-1(B). If the chromatogram looks like Figure L107A-1(A), sparge the THF with pure N_2 for about 2 hr using the fritted glass sparger to remove the interfering peak, and analyze again.
2. Resin Samples
 - a. Weigh 9.00 ± 0.01 g THF or N,N-Dimethylacetamide (DMAC) in a tared 20-mL vial.
 - b. Add 1.00 ± 0.01 g resin, and close the vial tightly with the screw cap, and shake until the resin dissolves completely (may require several minutes to several hours, depending on the nature of the resin).
3. Suspension Resin Slurry and Wet Resin Sample
 - a. Filter the slurry using a small Buchner funnel with vacuum; continue only as long as a steady stream of water is exiting from the funnel. Excessive filtration could cause some loss of vinyl chloride monomer (VCM).
 - b. Perform step A2.
4. Latex and Resin Solvent Solutions
 - a. Thoroughly mix the samples.
 - b. Perform step A2.
5. Solvents and Non-viscous Liquid Samples
Inject the neat samples directly into the GC.

B. Equipment Preparation

1. Install the GC column, and condition overnight at 70°C . Do not connect the exit end of the column to the detector while conditioning.
2. Adjust the N_2 carrier, burner air supply flow rate, H_2 , and N_2 flow rates, optimize the H_2 flow to yield the most sensitive detector response without extinguishing the flame, set the GC oven, injection port, and detector temperatures, ignite the FID (allow 1 hr warmup), set recorder pen at zero and start chart drive, and set attenuation to yield desired peak height (function of VCM content). See LDS 107A.

3. With a soap film flowmeter and stopwatch, measure the N_2 , burner air supply, and H_2 flow rates.

C. Standards Preparation

1. Prepare an $\sim 1\%$ by weight solution as follows:
 - a. Tare a 125-mL glass-stoppered flask, add THF or DMAC, and weigh. Multiply the THF or DMAC weight by 0.01.
 - b. In a hood, bubble vinyl chloride gas into the THF or DMAC. Adjust the vinyl chloride flow from the cylinder so that the vinyl chloride dissolves essentially completely in the THF or DMAC and is not blown to the atmosphere. Take care not to volatilize any of the solution.
 - c. Stopper the flask and swirl the solution to effect complete mixing.
 - d. Weigh the stoppered flask to nearest 0.1 mg.
2. Pipet 10 mL of the $\sim 1\%$ solution into a 100-mL glass-stoppered volumetric flask, and fill to mark with THF or DMAC to obtain $\sim 1,000$ ppm by weight. Cap the flask and invert 10 to 20 times.
3. Pipet 50-, 10-, 5-, 1-, 0.5-, and 0.1-mL aliquots of the $\sim 1,000$ ppm solution into 10-mL glass stoppered volumetric flasks. Dilute to the mark with THF or DMAC, cap the flasks and invert each 10 to 20 times. These solutions contain $\sim 500, 100, 50, 10, 5,$ and 1 ppm vinyl chloride. Calculate the exact concentration of each one. Keep refrigerated in stoppered bottles, and renew every 3 months.

D. Standards and Sample Analyses

1. Remove needle from 50- μL syringe. Open standard or sample vial and draw 50- μL solution into the syringe. Recap the vial. Reattach the needle. While holding the syringe vertically (needle point up), eject 40 μL into an absorbent tissue. Wipe needle with tissue. Then inject 10 μL into the GC.
2. Repeat until two consecutive values for the height of the vinyl chloride peak do not vary more than 5%. Then average the values.
3. Four minutes after sample injection, actuate the back flush valve to purge the first 4 feet of the chromatographic column of solvent and other high boilers.

4. Record on the chromatograph strip chart the sample identification.
 5. Vinyl chloride elutes at 2.8 min. Acetaldehyde elutes at 3.7 min. Analysis is complete when chart pen becomes stable. After 5 min, reset back flush valve and inject next sample.
 6. For the standards, prepare a chart plotting peak height, H_c , obtained from the chromatogram of each solution versus the known concentration, C_c . Draw a straight line through the points derived by the least squares method.
2. If water is the major volatile component, add 3- to 5-g sample to the tared dish and weigh.
 3. If volatile solvent is the major volatile component, transfer a portion of the sample to a 20-mL screw cap vial, cap immediately, and weigh. Uncap the vial and transfer a 3- to 5-g sample to a tared dish. Recap the vial and reweigh.
 4. Place sample in a 130°C oven for 1 hr. Remove, allow to cool to room temperature in a desiccator, and weigh.

E. Total Solids

For wet resin, resin solution, and PVC latex samples, determine the total solids (TS) for each sample as follows:

1. Tare the weighing dish (aluminum) to the nearest mg. Make all weighings to the nearest mg.
1. Replace the septum after five sample injections.
 2. Replace the sample port liner with a clean spare after five sample injections.
 3. If the GC has been shut down overnight, rerun one or more samples from the preceding day to test stability and precision prior to starting on the current day's work

LABORATORY DATA SHEET 107A
Vinyl Chloride

Client/Plant Name _____ Job # _____

City/State _____ Date _____

Gas Chromatograph ID # _____ Analyst _____

Standard Preparation

* DMAC may be used instead of THF

A Tare (g)	B Tare + THF* (g)	C = B - A THF (g)	D VC + B (g)	E = D - B Sample (g)	(100 E)/C VC Conc. (%)

Chromatograph Operation

Parameter	Setting	(✓)	Parameter	Setting	(✓)
N ₂ cylinder pressure	60 psig		H ₂ flow rate	30-40 cc/min	
N ₂ flow rate setting	40.0 cc/min		Oven temperature	70°C	
N ₂ backflush flow rate	40.0 cc/min		Injection port	100°C	
Burner air supply	40 psig		Detector	300°C	
Burner air flow rate	250-300 cc/min		FID stabilized?		
H ₂ cylinder pressure	60 psig				

Bubble flow Meter Checks:

	N ₂	Burner Air	H ₂
Volume, cc	_____	_____	_____
Time, min	_____	_____	_____
Flow rate, cc/min	_____	_____	_____

Total Solids Determination

Sample ID#									
Tare (g)									
Tare/Sample (g)									
Volatile Syr + Samp (g)									
Syr + Samp (g)									
Wet Sample (g)									
Dry Wgt 1 (g)									
Dry Wgt 2 (g)									
Dry Wgt 3 (g)									
Total Solids (TS)									

$$\text{Total Solids} = \frac{\text{Dry Weight}}{\text{Wet Sample}}$$

Sample Concentration

Use the calibration curve to determine each sample concentration and calculate response factor $R_f = C_c/H_c$ for each

Samp No.	Sample Conc, C_c	Peak Hgt (mm)				Response Factor $R_f = C_c/H_c$
		H_{c1}	H_{c2}	$H_{c1}/H_{c2} < 5\%$?	Avg, H_c	
	1 ppm					
	5 ppm					
	10 ppm					
	50 ppm					
	100 ppm					
	500 ppm					

Use exact concentration of VC stock standard to calculate the ppm concentrations of diluted standards.

Samp No.	Sample ID#	Peak Hgt (mm)				VC Conc, $C = R_f H_s$ (ppm)
		H_{s1}	H_{s2}	$H_{s1}/H_{s2} < 5\%$?	Avg, H_s	

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____
 Personnel (Signature/Date)

 Team Leader (Signature/Date)