INTER-OFFICE MEMO **TENNECO CHEMICALS, INC.**

TO	E. Schwartz	AT	Burlington	DATE	October 18, 1977
FROM	R. Fanter	AT	Piscataway	COPY TO	J. Jacob J. Sandstedt J. Sweeney
SUBJECT	ESR 498 Flemington Incinerator				

As you are aware, present plans call for not running the spare Incinerator at Flemington. The primary reason for this is that there is not enough effluent water available to cool two units.

A method of operation was proposed that might allow running of the spare: to cool the spare with well water and discharge the well water directly to the river. It was thought this might be allowed since the spare would be burning only fuel oil. John Sandstedt and I discussed this and we believe that this method of operation is not possible. The primary reason this cannot be done is that the water comes into direct contact with the "stack" gases and thereby becomes an "untreated process stream" and this cannot be discharged into the river. Another problem is the temperature of the water, which also prevents it from being discharged into the river.

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Analytical Procedure

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Procedure No. GCF-5.0
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DETERMINATION OF VINYL CHLORIDE CONTENT OF IN PROCESS WASTE WATER 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 of in process waste water into a gas chromatograph to separate and determine soluble vinyl chloride monomer content (VCM).

1.2 Procedure GCF-5.0 is applicable to waste water samples from polyvinyl chloride manufacturing facilities. No interference occurs in the presence of acetaldehyde, acetic acid or vinyl acetate. If the resolution of the VCM peak is not satisfactory for a particular sample, then chromatographic 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 water samples, using the sample size specified in Section 7.2.2, is approximately 0.02 parts per million. With proper calibration, the upper limit may be extended as needed.

3. ACCURACY AND REPRODUCIBILITY

Accuracy:	± 11% relative at 0.3 ppm
Reproducibility:	± 12% relative at 0.3 ppm

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 Vials - 50 ml Hypo-vials with Teflon faced rubber laminate discs (Pierce Chemical's No. 12969 and 12420, respectively- or equivalent).

5.1.2 Hand Crimper - Pierce Chemical No. 13212, or equivalent for sealing sample vials.

5.2 Sample Recovery

5.2.1 Refrigerator, suitable for storage of chemicals - for keeping sample vials of water at approximately 40°F prior to analysis.

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, 0.250 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, aqua regia washed, can be used in place of the UCON column, or a 0.25 inch x 20 feet, packed with 10% SP-1000 on 80-20 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 - Precision sampling syringe, No. 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. 1300 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 Pipets, volumetric - 25, 10, and 2 ml.

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

5.4.5 Syringe, 10 microliter - Precision Sampling syringe, No. 120022 or equivalent.

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

6.2 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.

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

7. Procedure

7.1 Sampling - Prior to use, the 50 ml vials (without the discs) must be capped with aluminum foil and muffled at 400°C for at least one hour to destroy or remove any organic matter that could interfere with analysis. At the sampling location fill the vials

7.1 Sampling (continued)

bubble-free, to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, Teflon side down, on the opening of the vial. Place the aluminum seal over the disc and 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.

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

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 150 ppm standard. When the baseline stabilizes, inject 10 microliters of sample solution, Sec. 7.1. 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.

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 150 ppm standard.

8.1 Preparation of Standards - Standards containing VCM in the range of 3 to 150 ppm (wt/vol) are prepared in THF as described below. With the sample size specified in Section 7.3.2, these standards cover up to 150 ppm of VCM in waste water. By altering the dilution, the range may be extended as needed.

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 100 ml 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 0.06% wt/volume. Accurately dilute 8.1.1 by pipetting 2 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 0.5, 2, 10 and 25 ml of solution 8.1.2 into 100 ml volumetric flasks partially filled with THF. Transfer the 0.5 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 Solutions - In a well ventilated hood, transfer sample, VCM stock solutions and spent calibration standards to a beaker containing several grams of Ionol. Allow 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 water 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 slope of the calibration curve in integrator area counts per microgram of VCM.

9.2 Soluble Vinyl Chloride Content - Calculate the vinyl chloride content of water samples as follows:

a. Wet basis:

$$\text{VCM (ppm)} = \frac{\text{Integrator area}}{F_R \times S_w}$$

Where F_R = Response factor in counts/microgram
S_w = Sample weight in grams (injection volume in ml may be used).

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

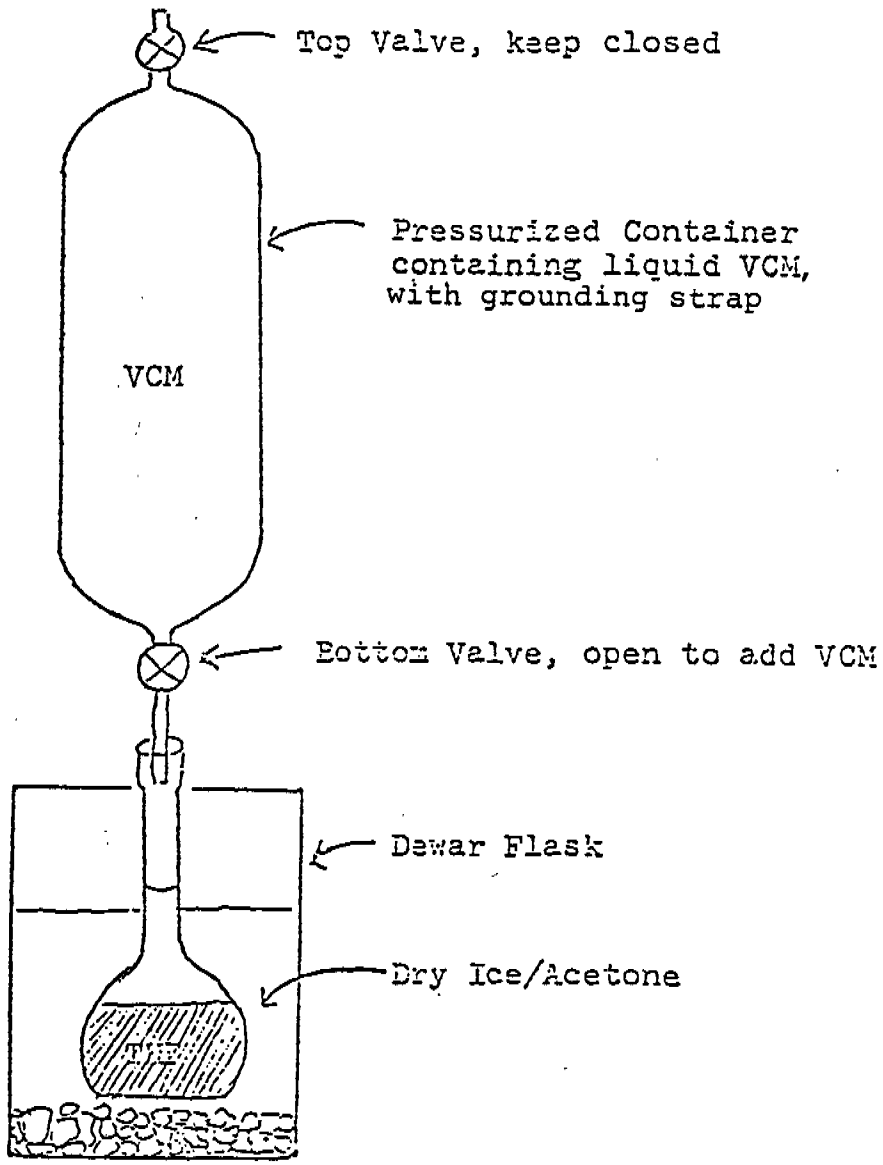
Average Response, area/ppm = 107.6
Average Deviation = 3.57
Standard Deviation = 4.71

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