Attachment A

VINYL CHLORIDE MONITORING STUDY (VCMS)

PROTOCOL

Billy

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Field Project Officer

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11,888 - 969

VINYL CHLORIDE MONITORING STUDY (VCMS)

Attachment B

COMMENTS ON THE USE OF MATERIAL BALANCES FOR SURVEILLANCE OF EMISSIONS IN A PVC PLANT

It is submitted that material balances alone will not be adequate to give either the processors or the EPA the information it desires for controlling vinyl chloride emissions in a PVC plant. This method is neither timely nor sufficiently accurate for this purpose.

There is a 24 - 36 hour delay between the time that a specific quantity of monomer is charged to the processes and when the PVC produced from that material is available to measure. The typical PVC plant chosen by EPA as a model produces 417,000 pounds a day of product. This is a dynamic system with the material being held in the form of a reaction mass, a slurry, or an in-process resin in many different tanks, bins and silos. We have found that daily material balances often are in error by as much as 10% and that monthly material balances seldom have an accuracy more than 1% or 2%. Several months of results are necessary before a conclusive trend is apparent. This obviously cannot give us a process control method.

The accuracy of individual measurements may be between 0.1% and 0.5%. This refers to reproductivity and not to precision because there often is a bias or offset in the measuring device itself. Material balance assumes that the difference between two large numbers can be determined with accuracy, but if we subtract 99 from 100 and do not know either of those numbers within $\pm$ 1 that the actual precision of the answer is 1 + or minus 2.

This lack of precision is recognized in the industry because most contracts do not allow for negotiation of differences between billed weights and measured recipes unless this difference exceeds at least ½% and usually 1%. One of our railroads tells us that they will guarantee that the sum of the errors in 50 weighings will be not more than 1% but will not guarantee the accuracy of any one weighing.

Similar problems exist in measuring in-process quantities. The difference in the contents of a 14 ft. silo can be as much as 11,500 lbs or 2.75% of the daily production of the typical plant, depending upon whether or not the cone in the silo points upward, as in a freshly filled silo, or downward, as in one from which material has been withdrawn. Similarly, about the best accuracy which one can obtain in a bagging machine is $\pm$ 4 oz. per bag. This is equivalent to 0.5% in a 50 lb container. In addition, there are fugitive PVC losses as well as monomer losses which show up in the unaccountable portion of any material balance.

Therefore, we would propose that a combination of methods be used to demonstrate the trend in accountability changes in PVC plants. This would include in-process check points where, for example, the concentration of certain major vent streams or the monomer concentration in stripped slurry would be measured. There should also be a program of ambient or perimeter monitoring to demonstrate the concentrations in the surrounding environment. (This method offers some difficulty when two or more plants are located near each other). A continuing system of reporting emergency releases would be the third component of this program, and finally, the use of long term material balances would help to support the data obtained by the three previous methods.

There are extensive differences in the four major processes used to manufacture PVC, and there are equally great differences between technologies within each of these major processes. For this reason, it would be necessary that any monitoring program be tailored specifically for the plant in question. This can be done quite easily by discussions between EPA officials and technical people associated with that plant. It is not possible to average technology nor to set a uniform monitoring method that will apply with equal precision to all processes and plants.

The EPA has used this combination of monitor methods with success in the past. For example, for the control of mercury in the chlorine industry, and we believe it can be applied equally well in the case of vinyl chloride.

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VINYL CHLORIDE MONITORING STUDY
PROTOCOL

I. Introduction

Vinyl Chloride (vc) has been reported as being the cause of a rare form of liver cancer, angiosarcoma, in workers exposed to vinyl chloride. For this reason, it is important that ambient air data be collected to determine the actual concentrations of vinyl chloride around polyvinyl chloride (pvc) and vinyl chloride monomer (vcm) plants. The Office of Air Quality Planning and Standards (OAQPS), Monitoring and Data Analysis Division (MDAD) requested QAEML's involvement in an ambient air monitoring program for vinyl chloride through ORD's air program assistant activity. Two pvc plants and one vcm plant were selected as sites to collect this background data. One of the pvc plants is a "closed" plant and the other is an "open" plant. This means that the reactors in the "closed" plant are enclosed in a building and subsequently higher concentrations of vc may build up inside such a plant as opposed to an "open" plant in which the reactors are well ventilated and thereby reduces the probability of a build up of vc in reactor areas.

II. Purpose

The ambient data from the VCMS will be analyzed and used for the development of an ideal meteorological diffusion model for vinyl chloride and polyvinyl chloride plants and to support an emission standard for vinyl chloride from pvc and vcm plants.

III. Scope

Two plants that produce pvc from vc and one vcm production plant were chosen for the vc monitoring program. Since one of the main purposes of this study is to develop an ideal diffusion model for vc plants, vc must be monitored at sites surrounding these plants. The four most distant sites will be used as control sites while the other sites will be used to monitor the diffusion of vc into the ambient air adjacent to the plant. Approximately 15 sites per plant will be necessary to obtain adequate data for a diffusion model. The desired criteria for selection of the plants were (1) two of the plants must be pvc plants, (2) one of the pvc plants must be the "open" process and one must be the "closed" process, (3) one plant must be a vc monomer plant, (4) predominent wind direction during months of interest, (5) cooperation from plant management, (6) no interfering air pollutants from chemical plants nearby.

The selection of the pvc plants was made using the above criteria. The "open" plant selected was the Continental Oil Company's plant (CONOCO) in Aberdeen, Mississippi. At the time of selection, this plant was not truly "open", but with the installation of new "open" reactors, it was converted to an "open" plant in November, 1974. The "closed" pvc plant chosen was the B. F. Goodrich Chemical Company, Louisville, Kentucky. The vinyl chloride monomer plant chosen was the Shell Chemical Company's plant in Norco, Louisiana.

The criteria considered for selecting the sampling sites at the individual plants were: (1) prevailing wind direction, (2) stack height, (3) mathematical model for location of highest vc concentrations, (4) control sites, (5) adequate facilities for trailer hookup at one site, (6) adequate electrical power adjacent to the sites, (7) simple site lease agreements.

Meteorology stations will be established at one site for each of the plants. The wind direction and wind speed are needed to establish the diffusion of vc into the air and the maximum concentration sites.

IV. Sample Preparation, Handling and Analysis

The only pollutant to be measured will be vc. The monitoring is being carried out by EPA personnel from the EMB, QAEML, using the sampling systems developed by EMB. See Figures 1 and 2. The principal method of measurement is the collection of the vc sample onto charcoal absorbers, which are subsequently extracted with carbon disulfide. See ATTACHMENT A. The resulting solutions are then measured chromatographically using a flame ionization detector. This method is a 24-hour integrated sampling method with the samples being collected twice a week. Duplicate samples will be taken at a minimum of two of the sites at each plant. A contract was awarded to Research Triangle Institute to provide the charcoal absorbers and subsequent analysis of the samples collected. The charcoal absorbers must be shielded from light exposure during sampling and shipment. This is accomplished by covering the glass absorbers with aluminum foil prior to shipping from the contractor. An operational information log book is kept at one site at each of the plants to keep an accurate record of all the conditions during sampling for each sample, e.g., site number, flow rates, time of sample, etc.

A Quality Assurance Plan for the analysis of the 24-hour method has been written by Joe Walling of the ACB, QAEML. See ATTACHMENT B.

A gas chromatograph with a flame ionization detector has been set up at the same site as the meteorology station at the CONOCO plant in Aberdeen, Miss. This gas chromatograph monitors ambient concentration of vc continuously. Initially only this one gas chromatographic system is being used for vc monitoring. The CONOCO plant in Aberdeen, Miss., was chosen because it has the fewest interferences from extraneous air pollutants of the three plants. If this gas chromatographic system demonstrates a minimum of maintenance and interference problems, a similar system may be purchased and used at one site at each of the other plants.

The Quality Control for this gas chromatographic system will consist of the following: (1) an interference study prior to field installation, (2) a monthly 5 point calibration by Bendix using a certified vinyl chloride permeation tube or a National

Bureau of Standards cylinder containing known quantities of vc in N_2, (3) a daily zero and span, (4) a monthly external audit check on span calibration using a NBS standard cylinder supplied by Tom Clark, MSPEB, QAEML.

Another type of sampling system utilizing the Bendix "Flasher" method will be used in the VCMS for a period of one month at the duplicate sites. The absorber in the Bendix "Flasher" method is a 7.6 mm stainless steel tube (0.46 cm I.D.) filled with a specially treated activated charcoal. The ambient sample will be pulled through this charcoal absorber at a flow rate of 5 cc/min $\pm$ 1 cc/min. The charcoal tubes will be analyzed by Bendix using a thermal "flashing" technique to desorb the collected vc from the charcoal directly into the analytical column of a gas chromatograph. Unexposed tubes and "spiked" tubes with known concentrations of vc will be added by EPA to the samples taken in the field to provide external audit checks of the analyses by Bendix. Analytical results will be reported to the Field Project Officer the first working day of each week. At the end of the contract period, the contractor will submit a final report containing additional documentation pertaining to "break-through" tests, sample decay storage tests, quality control results, and analysis data.

A summary of the Field Studies Quality Control Procedures is attached. See ATTACHMENT C.

V. Data Reduction

The collection of the continuous vinyl chloride data by the Bendix gas chromatograph will be made on a strip chart recorder. Manual hourly averages will be determined by the station operator and transferred to a SAROAD format data sheet.

The integrated 24 hour vc samples will be analyzed by RTI. The analysis will be entered on a SAROAD card and sent to the Contract Project Officer along with a typewritten sheet of weekly results.

The values obtained by Bendix from the metal charcoal absorbers will be entered on SAROAD cards by Bendix and sent to the Field Project Officer. Analytical results will be reported to the

Field Project Officer the first working day of each week.

The continuous meteorology data will be reduced by personnel of the Environmental Monitoring Branch for the appropriate days.

All SAROAD forms will be sent to the Statistical Services Staff (SSS) of QAEML for processing. In order to ensure more rapid data turn around time, alternative methods of data reduction such as a desk top minicomputer system and strip chart reduction by a data clerk are also being considered.

VI. Project Start-Up

The proposed start-up schedule for the three plant VCMS is shown in Figure 3. The assumptions made include: (1) an estimated 2 weeks for plant selection, (2) nine days for site selection, (3) three days for transporting trailers to plants, (4) two days set-up time for trailers, (5) six days set-up time for individual samplers at each site, (6) two days set-up of meteorology stations, (7) one week of installation and start-up of continuous gas chromatographic analyzer, (8) one week of check out, and (9) the addition of the metal Bendix charcoal absorbers to sampling system.

VII. Operation Schedule

The routine operation schedule of all sampling systems is shown in Figure 4. Each week will consist of two sampling days per plant. Each sampling day will consist of 15 samples plus two duplicate samples at the NORCO and CONOCO plants and 17 samples plus two duplicate samples at the B. F. Goodrich plant. A map of the location of the sites at each plant is attached. See ATTACHMENT D. For a one month period in the study, 200 Bendix charcoal absorbers will be analyzed by Bendix. The continuous gas chromatograph will be run by EMB personnel and the data reduction to the SAROAD format data sheet will be performed by the field operator.

VIII. Equipment Requirements

The equipment required for sampling is shown in Table I.

Table I.

Meteorology

3 Wind Speed

3 Wind Direction

3 Relative Humidity

3 Temperature

Vinyl Chloride

47 samplers & shelters

*4000 glass absorbers

200 metal absorbers (Bendix)

**1 gas chromatograph

**1 Bendix calibrator

*Includes 1000 extra tubes

**Option to purchase 2 more

Vinyl Chloride Duplicate Sampler

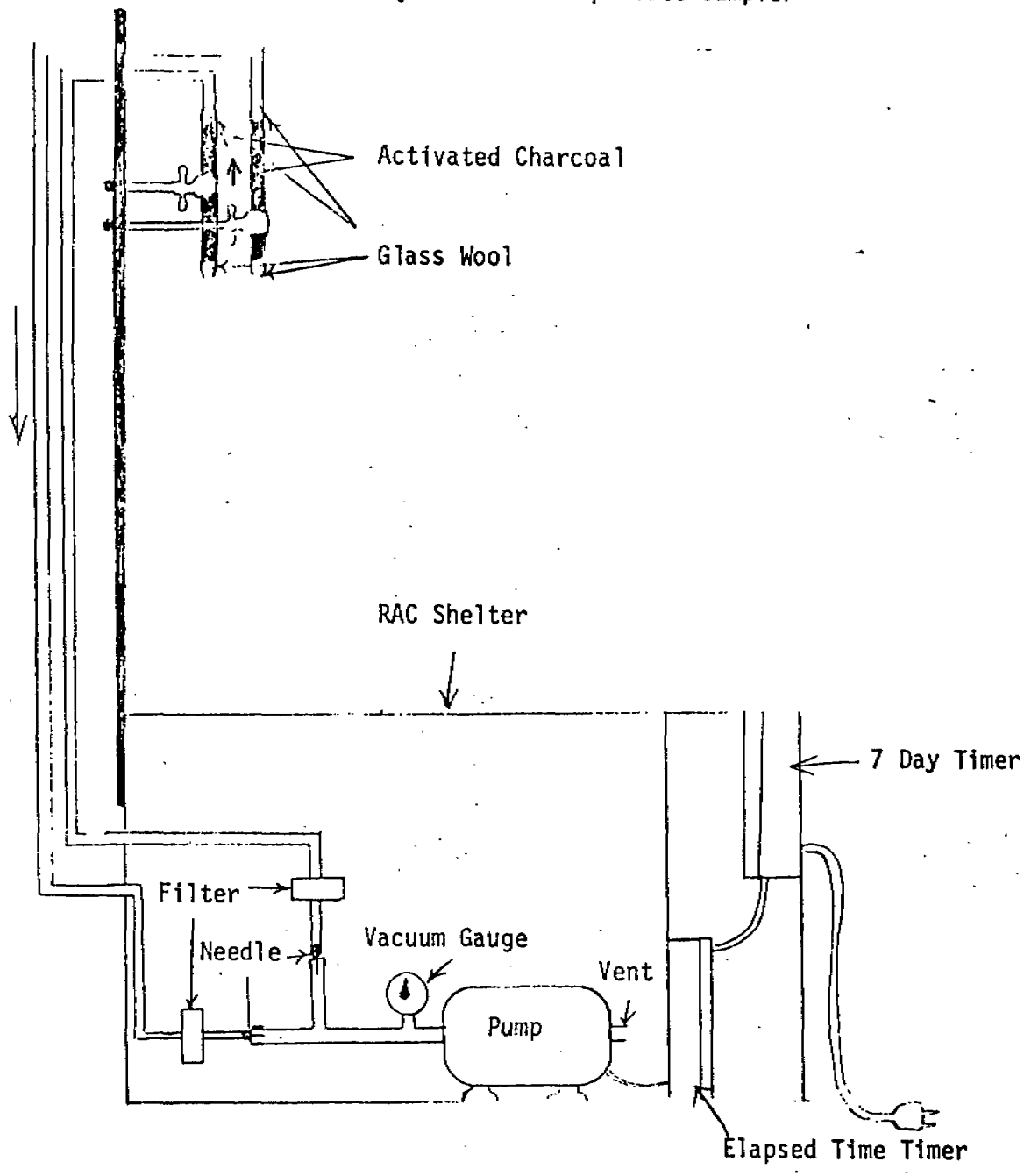

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Figure 1

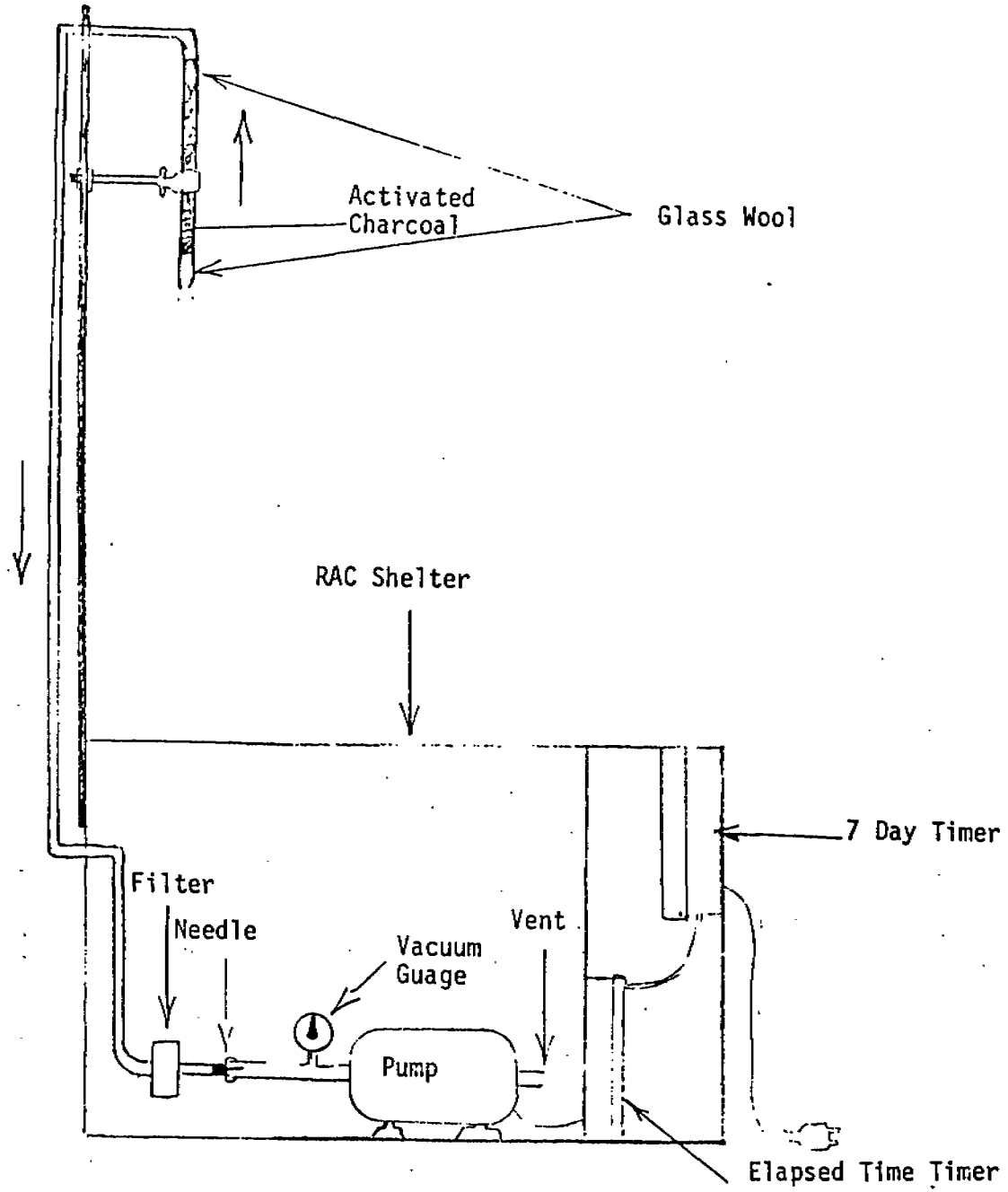

Figure 2

ATTACHMENT A

TENTATIVE METHOD FOR THE DETERMINATION OF VINYL CHLORIDE IN THE ATMOSPHERE (24-HOUR INTEGRATED SAMPLING)

OCTOBER 1974

This method has been drafted from available information and reviewed editorially within the Methods Standardization and Performance Evaluation Branch, QAEML. The method has received no laboratory evaluation, is still under investigation and, therefore, is subject to revision.

U.S. ENVIRONMENTAL PROTECTION AGENCY
METHODS STANDARDIZATION AND PERFORMANCE EVALUATION BRANCH
QUALITY ASSURANCE AND ENVIRONMENTAL MONITORING LABORATORY
NATIONAL ENVIRONMENTAL RESEARCH CENTER
RESEARCH TRIANGLE PARK, NORTH CAROLINE 27711

October 22, 1974

TENTATIVE METHOD FOR THE DETERMINATION OF VINYL CHLORIDE IN THE ATMOSPHERE BY 24-HOUR INTEGRATED SAMPLING

1. Principle and Applicability.

1.1 Vinyl chloride (chloroethene) is absorbed from air onto charcoal adsorbers, which are subsequently extracted with carbon disulfide. The resulting solutions are then measured chromatographically, using a flame ionozation detector.

1.2 The method is applicable to the measurement of vinyl chloride in ambient air using a 24-hour sampling period.*

2. Range and Sensitivity. The limit of detection is approximately 0.003 mg/m^3 (1 ppb). The maximum of the range is 20 mg/m^3 (8 ppm); it may be increased by extending the calibration range or by diluting the sample.

3. Interferences. At the present time, there are no known common pollutants in the ambient atmosphere in sufficient concentrations to interfere with the measurement of vinyl chloride. However, certain volatile hydrocarbons and Freons have elution characteristics similar

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*Warning: Vinyl chloride is a suspected carcinogen. Care must be exercised to protect operators from breathing vinyl chloride fumes. Carbon disulfide is toxic and its vapors form explosive mixtures with air. Work with this material in a well ventillated fume hood.

to vinyl chloride. Among the latter is Freon 12 (dichlorodifluoromethane). Under certain conditions, a peak is associated with the injection and subsequent withdrawal of the microsyringe into and from the G.C. septum. These peaks can also give interferences with the vinyl chloride peak.

4. Precision and Accuracy. Replicate gas chromatographic analyses of standard gas mixtures and sample aliquots should not deviate by more than 3 per cent relative standard deviation. When the entire analysis is repeated, preliminary studies indicate that relative standard deviations of 6 per cent are attainable. No information is presently available on accuracy.

5. Apparatus.

5.1 Sampling - Air Monitoring materials

5.1.1 Pump - Capable of maintaining an air pressure differential greater than 0.5 atmospheres at the desired flow rate.

5.1.2 Critical Orifice - Twenty-seven gauge 3/8" hypodermic needle. To control flow rate at approximately 200 ml/min.

5.1.3 Tubing - 18 cm length of 10 mm O.D. borosilicate glass with tapered ends, to prepare adsorption tube.

5.1.4 Serum caps - 5 x 9 mm and 7 x 11 mm sizes.

5.1.5 Vibrator - To achieve close packing of the adsorption tube.

5.1.6 Air flow meter - Rotometer type; 1 - 260 ml/min range. To calibrate critical orifice.

5.1.7 Furnace, muffle - To operate at 400° C.

5.2 Sample recovery.

5.2.1 Graduated cylinder - Glass stoppered; capacity, 25 ml (TC).

5.2.2 Pipette, dropping - 2 ml.

5.2.3 Serum bottle - Narrow mouth for septum sealing; 2 ml.

5.2.4 Serum cap - With Teflon coating on the side of the septum exposed to the sample 5 x 9 mm size. (Hewlett-Packard #5080-8713[1] has been found to be satisfactory.)

5.2.5 Aluminum serum cap seal.

5.2.6 Crimper - For use with aluminum serum cap seals.

5.3 Analysis.

5.3.1 Gas chromatograph - With flame ionization detector and potentiometric strip chart recorder.

5.3.2 Chromatographic column - Borosilicate glass, 2.5 m x 2 mm I.D., containing 0.4% Carbowax 1500 on Carbopak A packing. (w/w)

5.3.3 Microsyringes - 0 to 10 and 0 to 100 microliter range, graduated.

5.3.4 Syringes, sampling - Gas tight, 1 ml and 50 ml, graduated.

5.3.5 Sampling loop - one ml.

5.3.6 Flow meter - Rotometer type, 0 to 100 ml/min capacity.

5.3.7 Gas regulator - 4 to 50 psig range.

5.3.8 Gas sample bags - Poly(vinyl fluoride). Sixteen inch square and seven inch square sizes.

5.3.9 Stop watch - To time gas flow in preparation of standard gas mixtures.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6. Reagents

Unless otherwise indicated, it is intended that all reagents be chromatographic grade or conform to the specifications established by the Committee of Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use best available grade.

6.1 Sampling

6.1.1 Charcoal - Activated coconut shell charcoal. (Fisher Scientific Company,[1] 6 to 14 mesh is effective.)

6.1.2 Glass wool - borosilicate

6.1.3 Aluminum foil.

6.2 Sample recovery.

6.2.1 Carbon disulfide.

6.3 Analysis.

6.3.1 Nitrogen gas - Zero grade, for chromatographic carrier gas and for preparation of standard gas samples.

6.3.2 Vinyl chloride - 128 mg/m^3 at 25° C, 1 atm (50 ppm v/v) in zero nitrogen. Analyzed. For calibration.

6.3.3 Combustion Air - Containing less than 1.3 mg/m^3 hydrocarbons (2 ppm as methane). To operate flame ionization detector.

7. Procedure.

7.1 Sampling

7.1.1 Activation of charcoal - Heat charcoal to 400° C for one hour to remove adsorbed gases. Store in a sealed container.

7.1.2 Preparation of adsorption tube - Insert glass wool into tubing (see Section 5.1.3) and tamp into position at one end to a depth of approximately 2.5 cm. Mount tube on vibrator in a verticle position. Add charcoal a little at a time and vibrate after each addition to prevent channelling. Fill tube to a depth of 13 cm with charcoal. Insert glass wool into remainder of tube. Prepare additional adsorption tubes in a similar and uniform manner. Cover ends of tubes with serum caps. Wrap with aluminum foil to protect tubes from light during storage and subsequent use. Insert critical orifice through septum at one end of tube. Retain until calibration, sampling and recalibration procedures have been completed.

7.1.3 Twenty-four hour sample collection. Remove serum cap from one end of the adsorption tube and mount it with open end downward. Connect critical orifice to the sampling train. Begin drawing air through the tube. Record time and adsorption tube number. Continue sampling for at least 23 hrs 45' but for not more than 24 hrs 15'. At end of sampling interval, record time, disconnect adsorption tube from sampling train and protect open end with serum cap. Remove sample to analytical area. Protect tube from light.

7.2 Sample recovery. Fill the graduated cylinder to the 25 ml mark with carbon disulfide, stopper and cool in an ice bath. Remove cap and glass wool from one end of the adsorption tube and, with continued cooling, rapidly add charcoal to the carbon disulfide. Stopper cylinder immediately. (Note: The mixing of charcoal and carbon disulfide is an exothermic process that causes local boiling of the solution. The

mixture must be cooled and the container stoppered to prevent loss of vinyl chloride). Mix thoroughly. Allow mixture to stand for one half-hour in the ice bath. Mix thoroughly and draw off two ml of the supernatant liquid. Completely fill 2 ml serum bottle, cap and sea

7.3 Analysis.

7.3.1 Column preconditioning. Prior to its initial use, the chromatographic column is heat treated to remove impurities. To do this, establish a 40-60 ml/min flow of zero nitrogen through the column and raise its temperature from ambient by 2° C/min to 200° C. Maintain these conditions for 48 hours, or until base line drift is eliminated.

7.3.2 Chromatographic analysis. Set the column temperature to 60° C and the sample inlet port temperature to at least 170° C. Operate the flame ionization detector at the temperature specified by the manufacturer. Using zero 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 40 ml/min has been shown to produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base-line drift has ceased. Inject a 2.5 microliter aliquot of the supernatant solution of the sample into the gas chromatograph. Mark the injection point on the chart. (The injection point is defined as the position of the pen on the chart at the time of sample injection.) Record the sample number, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. From the chart, select the peak having

the retention time corresponding to vinyl chloride. (See Sect. 8.3 below). Measure the peak height, H_m, the distance in chart divisions from the average value of the baseline to the maximum of the wave form. Record H_m and the retention time. Purge the column at 160°C for five minutes.

8. Calibration and Standards.

8.1 Calibration of absorption tube flow rates. Connect absorption tube to sampling train as in 7.1.3, above. Connect flowmeter in series. Turn on pump and measure flow rate. Record flow rate and adsorption tube number. Repeat flow rate calibration procedure after sample collection. Denote flow rate before sampling as F_1; denote flow rate after sampling as F_2.

8.2 Preparation of vinyl chloride standard gas mixtures. Evacuate a 16-inch square gas sample bag and meter-in 2.00 liters of the 128 mg/m^3 (50 ppm) standard vinyl chloride gas mixture into the bag. Meter-in 3.00 liters of zero nitrogen. This gives a concentration of 51 mg/m^3 (20 ppm) of vinyl chloride. In a like manner, prepare dilutions having 12.8 (5 ppm), 2.55 (1 ppm), 0.51 (0.2 ppm) and 0.15 (0.06 ppm) mg/m^3 vinyl chloride concentrations. (Alternately, calibration samples may be prepared from 99% vinyl chloride gas, using appropriate dilution factors.)

8.3 Determination of vinyl chloride retention time. Establish chromatographic conditions identical with those in 7.3.2, above. Set attenuator to X 1 position. Flush 1.0 ml sampling loop with zero nitrogen and inject into gas inlet port. Mark the injection point on the chart and record the column temperature, the carrier gas flow rate, the chart

speed and the attenuator setting. Record peaks and detector responses that occur in the absence of vinyl chloride. Maintain conditions. Flush 1.0 ml sampling loop with 5 ml of the 0.16 mg/m^3 (0.06 ppm) vinyl chloride calibration mixture and inject into gas chromatograph. Mark the injection point on the chart. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart in mm from the injection point to the peak maximum. This distance, divided by the chart speed in mm/min, is defined as the retention time. Record.

8.4 Preparation of chromatograph calibration curve. Make a gas chromatographic measurement of each standard gas mixture described in Section 8.2 (0.16 mg/m^3 through 128 mg/m^3), using conditions identical with those listed in Section 7.3.2, above. Flush the 1.0 ml sampling loop with at least 5 ml of standard gas mixture and inject into gas chromatograph. Record W_{VC}, the quantity of vinyl chloride injected (in nanograms), the attenuator setting, chart speed, peak height and retention time. Calculate H_C, the peak height multiplied by the attenuator setting. Plot W_{VC} vs H_C. Repeat until replicate measurements do not deviate by more than 3 percent relative standard deviation and draw a smooth curve through the points. Check calibration after every fifth analysis using the 0.16 mg/m^3 (0.06 ppm) standard gas mixture. Recalibrate daily, and whenever remeasurement of a standard gas sample deviates from its calibration value by more than 6%.

9. Calculations.

9.1 Uncorrected volume. The volume of air sample is not corrected to S.T.P., because of the uncertainty associated with 24-hour average

temperature and pressure values. Determine the air sample volume taken for analysis.

$$V_m = \frac{F_1 + F_2}{2} \times T \times 10^{-6},$$

where:

V_m = The volume of gas sampled (uncorrected), m^3.

F_1 = The measured flow rate before sampling, ml/min.

F_2 = The measured flow rate after sampling, ml/min.

T = The sampling time, min.

9.2 Determine the sample peak height as follows:

$$H_c = H_m A_m,$$

where:

H_c = The sample peak height, chart divisions.

H_m = The measured peak height, chart divisions.

A_m = The attenuator setting.

9.3 Vinyl chloride concentration.

9.3.1 Calculate the vinyl chloride concentration as mg/m^3. From the calibration curve described in Section 8.4, above, select the value of W_{vc} that corresponds to H_c, the sample peak height.

$$C_{vc} = \frac{W_{vc} V_s}{V_m V_i}$$

$$= \frac{W_{vc}}{V_m} \times 10^{-2},$$

where:

C_{vc} = The concentration of vinyl chloride in the air sample, mg/m^3.

W_{vc} = The quantity of vinyl chloride measured by gas chromatography, ng.

V_s = The total volume of carbon disulfide in which the vinyl chloride sample is contained, 25 ml.

V_m = The uncorrected sample volume, from 9.1 above, m^3.

V_i = The volume of carbon disulfide solution injected into the chromatograph for analysis, 0.0025 ml.

9.3.2 If desired, the concentration of vinyl chloride may be calculated as parts per million vinyl chloride,

ppm VC = mg VC/m^3 x 0.3915.

10. Effects of storage: Charcoal tubes containing adsorbed vinyl chloride have been found to be stable for more than seven days, though there is some evidence that they are adversely affected by strong sunlight. Carbon disulfide solutions lose vinyl chloride to the atmosphere but have been stored unchanged for more than a month in sealed serum bottles having minimum headspace. Gas standards may be kept in poly (vinyl fluoride) gas sample bags for several weeks without undergoing concentration changes. However, present knowledge of the stability of vinyl chloride samples is based on studies with pure substances. No information is available on the storage of samples containing other active substances as are commonly found in ambient air.

11. References.

Lodge, J. P., Pate, J. B., Ammons, B. E. and Swanson, G. A. "The Use of Hypodermic Needles as Critical Orifice in Air Sampling." J. Air Pollution Control Association. 16:4, 197-200, (1966

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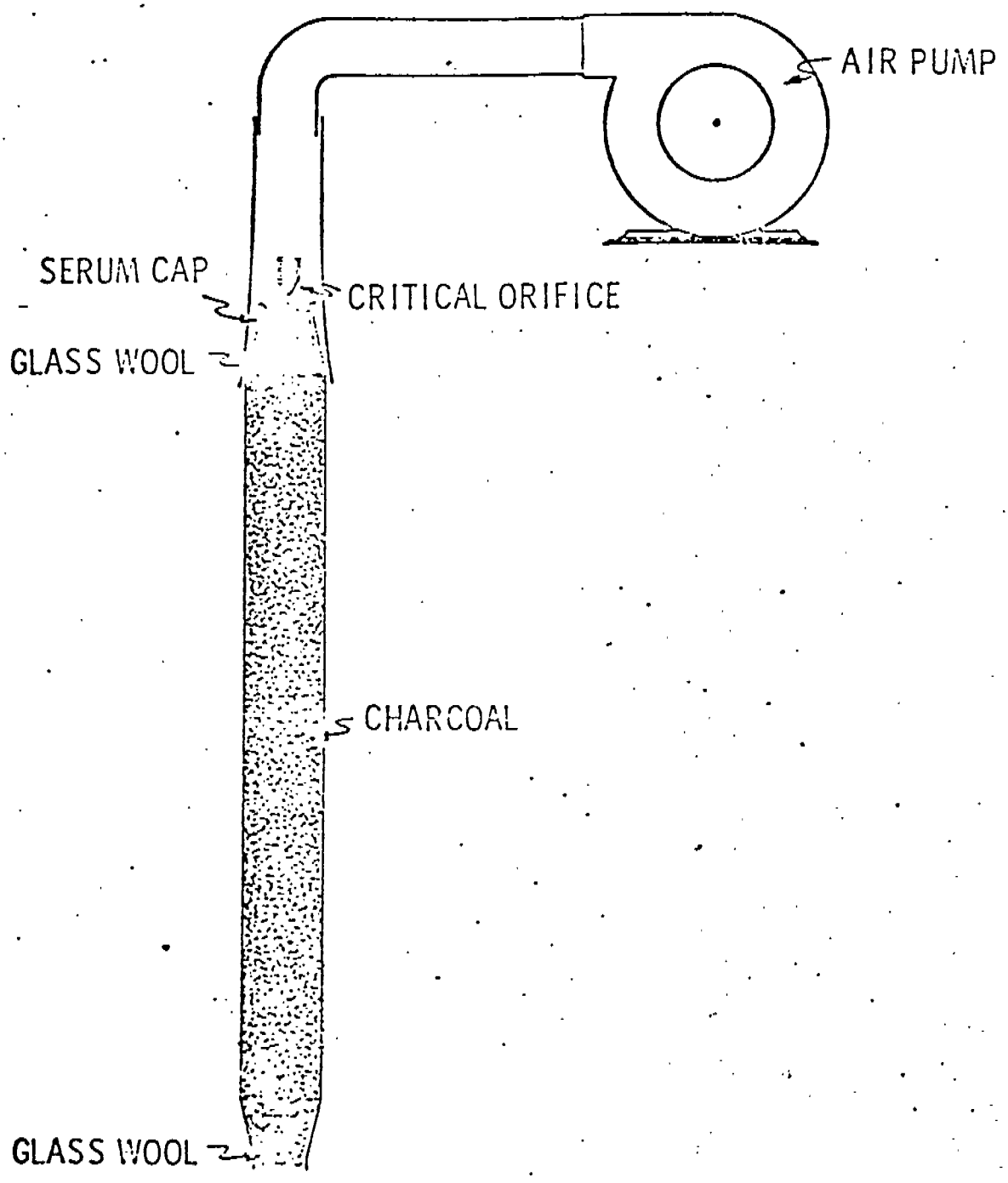


Figure 12-1. Air monitoring apparatus.

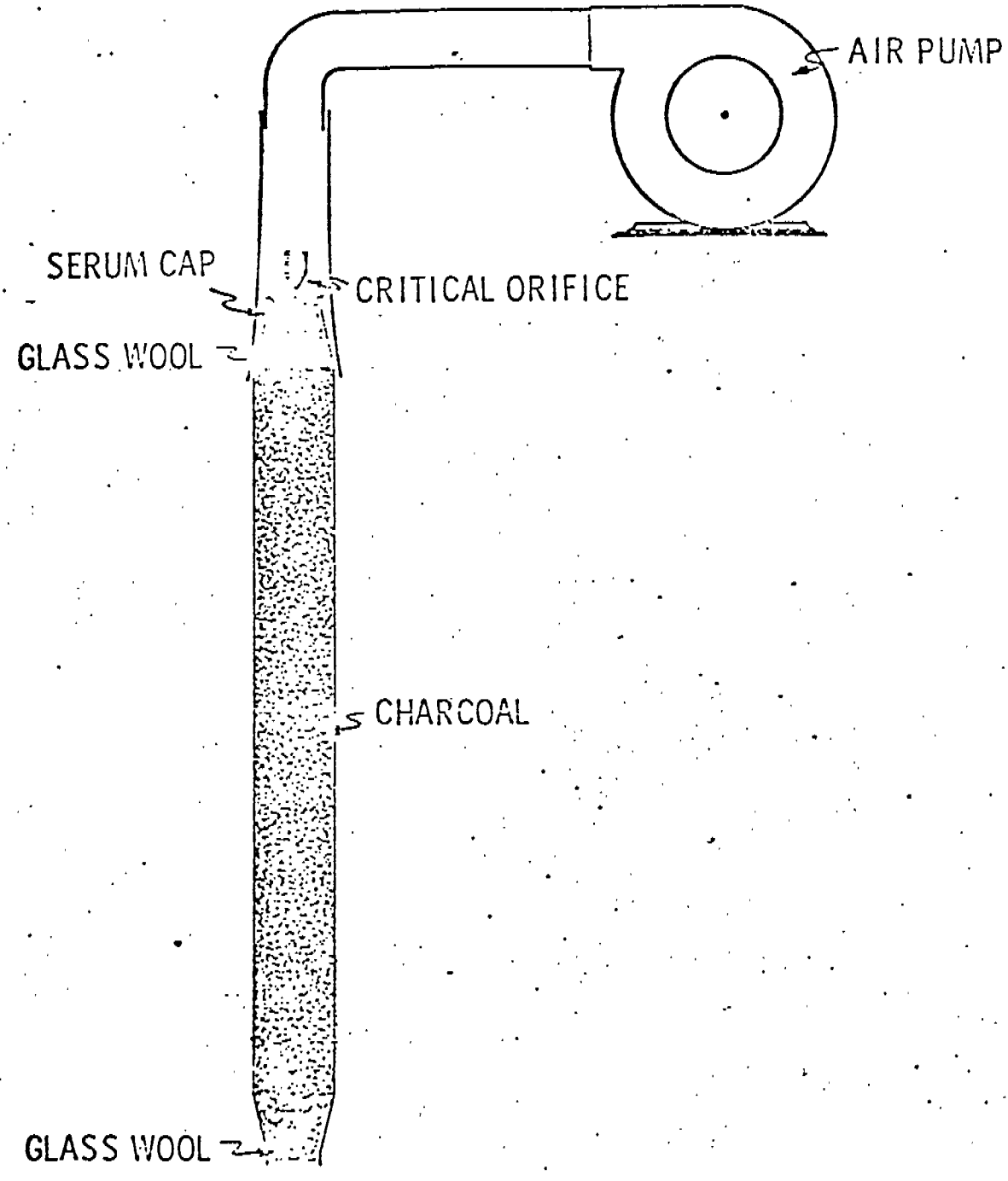
Vinyl Chloride Contract QC Plan

Contractor Activities

1. Calibration

A. One cylinder of 1 ppm VC in N_2 will be supplied at the outset to be used routinely as a calibration check. Periodically another cylinder will be supplied. When this happens run "overlap duplicates" i.e., cyl 1, cyl 2, cyl 1, cyl 2, as a run sequence and report the four values to the project officer by phone promptly each time and receive instructions about the shipping of one of the cylinders.

B. One cylinder of 50 ppm VC in N_2 will be supplied at the outset to be used as calibration material. Periodically another 50 ppm cylinder will arrive. Prepare three concentrations of this material in a fashion similar to that used for the calibration material. Calculate differences between the concentration you calculate and those calculated using your calibration curve. Report promptly by phone the observed differences for each concentration (expect.



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B. One cylinder of 50 ppm VC in N_2 will be supplied at the outset to be used as calibration material. Periodically another 50 ppm cylinder will arrive. Prepare three concentrations of this material in a fashion similar to that used for the calibration material. Calculate differences between the concentration you calculate and those calculated using your calibration curve. Report promptly by phone the observed differences for each concentration (expect

calibration curve) to the project officer and receive instructions about shipping of one of the cylinders.

2. Operational Activities (Some of these activities, e.g., frequency of standards, blanks, etc., are specified in the body of the Task Order Agreement.)

A. At the beginning of the project it is hoped that seven QC unknown reference samples of differing concentrations can be obtained. If possible these shall be analyzed acceptably (to the project officer) before any field samples are analyzed.

B. Sample storage condition (temperature, light intensity and duration) shall be standardized. Contractor should propose condition for approval by project officer.

C. Within any sample set, samples should be run in the order in which they appear in the shipping box.

D. Known QC samples, calibration checks, etc., should be acceptable to the operator and project officer each time or corrective action should be undertaken before proceeding with field sample analyses.

Vinyl Chloride Contract QC Plan

EPA Activities

1. T. Clark will place the tubes in shipping boxes introducing in random positions 2 QC unknowns in each box of samples. Some of these unknowns should be blanks, i.e., tubes containing no VC.

2. T. Clark will distribute the duplicate field samples at his convenience so that by the end of the study approximately the following distribution of analyses will have been done:

   1/3 both analyzed by contractor
   1/3 1 by contractor, 1 by referee 1
   1/3 1 by contractor, 1 by referee 2

3. T. Clark will ship the 1 and 50 ppm cylinders so that if possible by the end of the project each laboratory will have used each cylinder at least once.

4. T. Clark will introduce not less than 5 QC unknowns per month into shipments to referee laboratories.

5. G. Akland will process sample data routinely, but upon receipt of results will promptly pull out data on duplicates, standards, calibration replications and QC unknowns to provide estimates on per batch and cumulative bases of the following:

i repeatability within given lab

ii precision and bias mappings between labs

iii characterization of stability of each 1 ppm and 50 ppm cylinder

iv an overall estimate of bias and precision at the contractor's operation

Referee Laboratory Activities

Each laboratory should analyze:

1. No more than 60 replicate samples
2. Not less than one duplicate analysis of each 1 ppm and 50 ppm cylinder with "overlap"
3. Not less than 5 QC unknowns/month
4. Report results to project officer by phone as well as in writing

Summary of the Field Studies Quality Control Procedures

For The Vinyl Chloride Monitoring Study

I. 24-Hour Integrated Sampler

The flowrate through the charcoal absorbers is checked at the time of installation on the sampler and at the time of removal from the sampler using a calibrated rotameter whose calibration is checked once a month with a calibrated Hastings Mass Flowmeter. The flowrate should be 240 cc/min $\pm$ 20%. The start and end flowrates must agree with each other $\pm$ 15%. The sampler is checked during the day of sampling to make certain that the sampler is operating properly during the 24 hour sampling period. Elapsed timers will be installed when received so that the exact time of sampling can be recorded. The hypodermic needle (#27 guage) and filter are changed every four months or as needed to insure that the flowrates are kept constant.

The charcoal absorbers are received capped with rubber systems from the contractor. Upon removal from the sampler, the charcoal absorbers are capped immediately to prevent the escape of the collected vinyl chloride from the charcoal. The charcoal absorbers are then mailed via air mail special delivery to the project officer at NERC, RTP, N.C. on the day they are removed from the sampler unit. The flowrates and total volume sampled are validated by the VCMS project officer and the absorbers and SAROAD cards are sent to the MSPEB for the addition of Quality Control.

II. Continuous Gas Chromatograph

An interference study of compounds that might interfere with the vinyl chloride analysis was performed prior to field installation by the manufacturer (Bendix). A five point calibration was performed

by Bendix upon installation in the field using a calibrated VC permeation tube. A five point calibration curve will be performed monthly by Bendix using the calibrated VC permeation tube. A zero and span will be performed daily using the VC permeation tube for the span concentration. If the daily span check is off by more than $\pm$ 15%, then the instrument will be calibrated by Bendix. A cylinder containing VC in N_2 will be supplied monthly by MSPEB for an external audit check on the calibration procedure.

The data from the continuous gas chromatograph will be entered on SAROAD Forms and keypunched by personnel of the SSS. The printout will then be validated against the strip charts obtained from the gas chromatograph by EMB personnel.

III. Continuous Meteorology Stations

The MRI Weather Station was set up at each plant by selecting a point with known coordinates and aligning the MRI Stations with this point.

The time of day, operator, and location will be recorded on the MRI strip chart daily. If necessary, the time of day on the strip chart will be reset daily to the correct time.

Monthly checks will be made on the orientation of the MRI Stations and the overall operation of the MRI Stations. All MRI data will be reduced to the SAROAD forms weekly by the field operator. The SAROAD forms will be validated against the MRI charts by personnel of the Environmental Monitoring Branch.

IV. Bendix "Flasher" System

The collection columns will be tested by the manufacturer (Bendix) for "breakthrough" of vinyl chloride under 24 hour sampling conditions. The percentage of the collected vc that is retained by the collection columns must be shown for periods up to 14 days. Unexposed collection columns and "spiked" collection columns with known concentrations of vc will be added by EPA to

the samples taken in the field to provide external audit checks of the analyses by Bendix. The results will be reported to the field project officer the first working day of each week. At the end of the contract period, the contractor will submit a final report containing additional documentation pertaining to "breakthrough" tests, sample decay tests, quality control results, and analyses data.

ATTACHMENT D

SITE DESCRIPTIONS

SITE DESCRIPTION - ABERDEEN, MISS.

Site #1 - Located on Conoco's property, approx. 1000 ft. NNE of plant operations. Site of meteorology station and continuous gas chromatograph.

Site #2 - Located on Conoco's property, approx. 800 ft. north of operation.

Site #3 - Located on Conoco property, by truck entrance road approx. 600 ft. north of operation.

Site #4 - Located at Catalytic freezer shed, Conoco property, approx. 400 ft. west of operation.

Site #5 - Located on Conoco property by plant entrance approx. 900 ft. NNW of operation.

Site #6 - Located near VCM storage tanks, Conoco property, approx. 800 feet WNW of operation.

Site #7 - Located on Conoco property, approx. 700 ft. WSW of operation.

Site #8 - Located at waste treatment lagoon, Conoco property, approx. 1000 ft. south of operation.

Site #9 - Located at propane storage tanks, Conoco property, approx. 750 ft. east of operation.

Site #10- Located on banck of fire pond, Conoco property, approx. 700 ft. northeast of operation.

Site #11- Located at Thaxton residence at 102 Pinehurst St., approx. 1 mile north of operations.

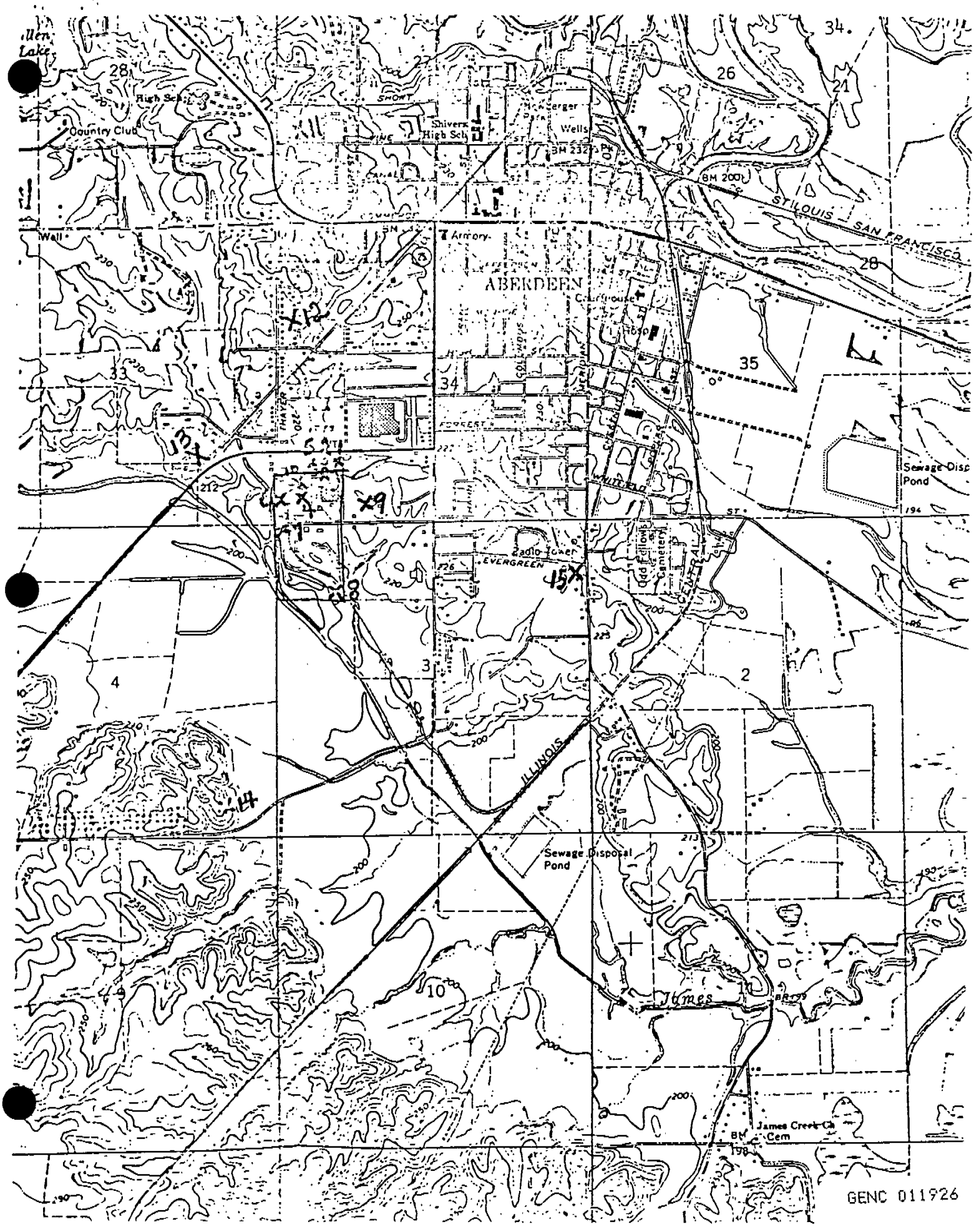
Site #12- Located at Carter residence on Glendale Circle, Approx. 1/3 mile north of operations.

Site #13- Located at Nason residence on Thayer Ave., approx. 2400 ft. northeast of plant operation.

Site #14- Located at Ausburn residence on old Hwy. 25, approx. 1 mile south of plant.

Site #15- Located at Flynn residence on Meridian St., approx. 3/4 mile WSW of plant.

SITE NUMBER	SAROAD IDENTIFICATION NUMBER
Aberdeen	
1	250020201
2	250020202
3	250020203
4	250020204
5	250020205
6	250020206
7	250020207
8	250020208
9	250020209
10	250020210
11	250020211
12	250020212
13	250020213
14	250020214
15	250020215


Allen Lake
Country Club
High Sch
Shivers High Sch
Wells
BM 2327
BM 2001
ST LOUIS SAN FRANCISCO
Armory
ABERDEEN
Court House
Water
THAYER
FORREST
COLLEGE
MERIDIAN
Sewage Disp Pond
Radio Tower
EVERGREEN
Odd Fellows Cemetery
CENTRAL
ILLINOIS
Sewage Disposal Pond
James
James Creek Ch Cem
BM 198
GENC 011926

SITE DESCRIPTION - LOUISVILLE, KY

Site #1 - Located directly across the street, approx. 700 ft. north of B.F. Goodrich, in yard of Midsouth Coating Co., 4300 Bells Lane. Site of meteorology station.

Site #2 - Located at Gilland residence at intersection of Bells Lane and 41st Street, approx. 1200 feet northeast of plant.

Site #3 - Located on roof of Greater Shepherd Missionary Baptist Church, 3705 Bells Lane, approx. 2500 ft. east of plant.

Site #4 - Located at Hunter residence at 4216 Algonquin Pkwy., approx. 1500 ft. north of plant.

Site #5 - Located at Mohawk Industries, 4110 Algonquin Pkwy., approx. 1800 feet northeast of plant.

Site #6 - Located in yard of Ashland Bulk Plant, Algonquin Pkwy., approx. 2100 feet northeast of plant.

Site #7 - Located at Sewage Disposal Plant, approx. 3500 feet northwes of plant.

Site #8 - Located at Ashland Chemical, Algonquin Pkwy., approx. 3500 feet north of plant.

Site #9 - Located on roof of Kennedy School, approx. 4500 ft. NE of plant.

Site #10 -Located at Fire Training Tower, Algonquin Pkwy., approx. 3900 feet north of plant.

Site #11 -Located at Jefferson Co. A.P.C. Trailer at end of 43rd Street, approx. 6000 ft. north of plant.

Site #12 -Located at guard station to L.P. & E., West end of Bells Lane, approx. 4800 feet west of plant.

Site #13 -Located at front gate to B.F. Goodrich, Bells Lane, approx. 500 ft north of plant.

Site #14 -Located at sand-blasting shed on B.F. Goodrich property, approximately 1300 ft. southwest of plant.

Site #15 -Located by a black building on B.F. Goodrich property, approx. 600 ft. south of plant.

LOUISVILLE, KY.

Site #16 - Located at Beam residence, 3613 Campground Rd., approx. 3300 ft. south of plant.

Site #17 - Located at St. Denis School, Cane Run Rd., approx. 8000 ft. south of plant.

SITE NUMBER	SAROAD IDENTIFICATION NUMBER
Louisville	
1	182380201
2	182380202
3	182380203
4	182380204
5	182380205
6	182380206
7	182380207
8	182380208
9	182380209
10	182380210
11	182380211
12	182380212
13	182380213
14	182380214
15	182380215
16	182380216
17	182380217

STATE OF KENTUCKY
KENTUCKY GEOLOGICAL SURVEY
UNIVERSITY OF KENTUCKY

SITE DESCRIPTION - NORCO, LA.

Site #1 - Located by the U.S. Corp of Engineers building at the east end of the Bonnet Carre Spillway, just off River Rd., approx. 1800 feet SSW of the VCM process stack.

Site #2 - Located by the high pressure dump tank at the intersection of B Street and West Fence Rd. on Shell property, approx. 800 feet southwest of the VCM process stack.

Site #3 - Located inside a fenced area where the pipeline from the barge loading dock crosses the crown of the levee, approx. 1900 feet south of the VCM process stack.

Site #4 - Located by the oxygen storage tank on Seventh Street, Shell property, approx. 350 feet NNE of the VCM process stack.

Site #5 - Located between two of the VCM storage tanks on Shell property, approx. 750 ft. NNE of the VCM process stack.

Site #6 - Located at the west end of a dead end street just north of the VCM storage area on Shell property, approx. 1100 ft. NNE of the VCM process stack.

Site #7 - Located by the West Fence Road in the northwest corner of Shell property, approx. 1450 ft. NNE of the VCM process stack.

Site #8 - Located on the roof over the walkway at Norco Elementary School, 102 Fifth Street in Norco, approx. 2200 ft. NNE of the VCM process stack.

Site #9 - Located beside the Poche residence at 679 West Pine St. in Norco, approx. 4800 ft. NE of the VCM process stack.

Site #10- Located on top of one of the stirrers at Norco Sewage Treatment Plant on Edgewood St., off of U.S. 61, approx. 8700 ft. NE of the VCM process stack.

Site #11- Located beside the Parquet residence at 306 Bethene St. in Norco, approx. 1400 ft. ESE of the VCM process stack.

Site #12- Located on Shell property just off Seventh St., approx. 330 ft. SSW of the VCM process stack.

Site #13 - Located on Shell property at the corner of B Street and Seventh Street, approx. 650 ft. SSW of the VCM process stack. The EPA mobile lab is at this location. Site of meteorology station.

Site #14 - Located on Shell property near the corner of A Stree and Seventh Street, approx. 1000 ft. SSW of VCM process stack.

Site #15 - Located on Shell property just off A Street in a corner adjacent to a parking lot, approx. 1300 ft. SSW of VCM process stack.

SITE NUMBER	SAROAD IDENTIFICATION NUMBER
Norco	
1	192060201
2	192060202
3	192060203
4	192060204
5	192060205
6	192070206
7	192060207
8	192060208
9	192060209
10	192060210
11	192060211
12	192060212
13	192060213
14	192060214
15	192060215


Oil Well
Pipeline
Sandpit
Campground
Picnic Area
Norco
Gaging Station
Light
MISSISSIPPI

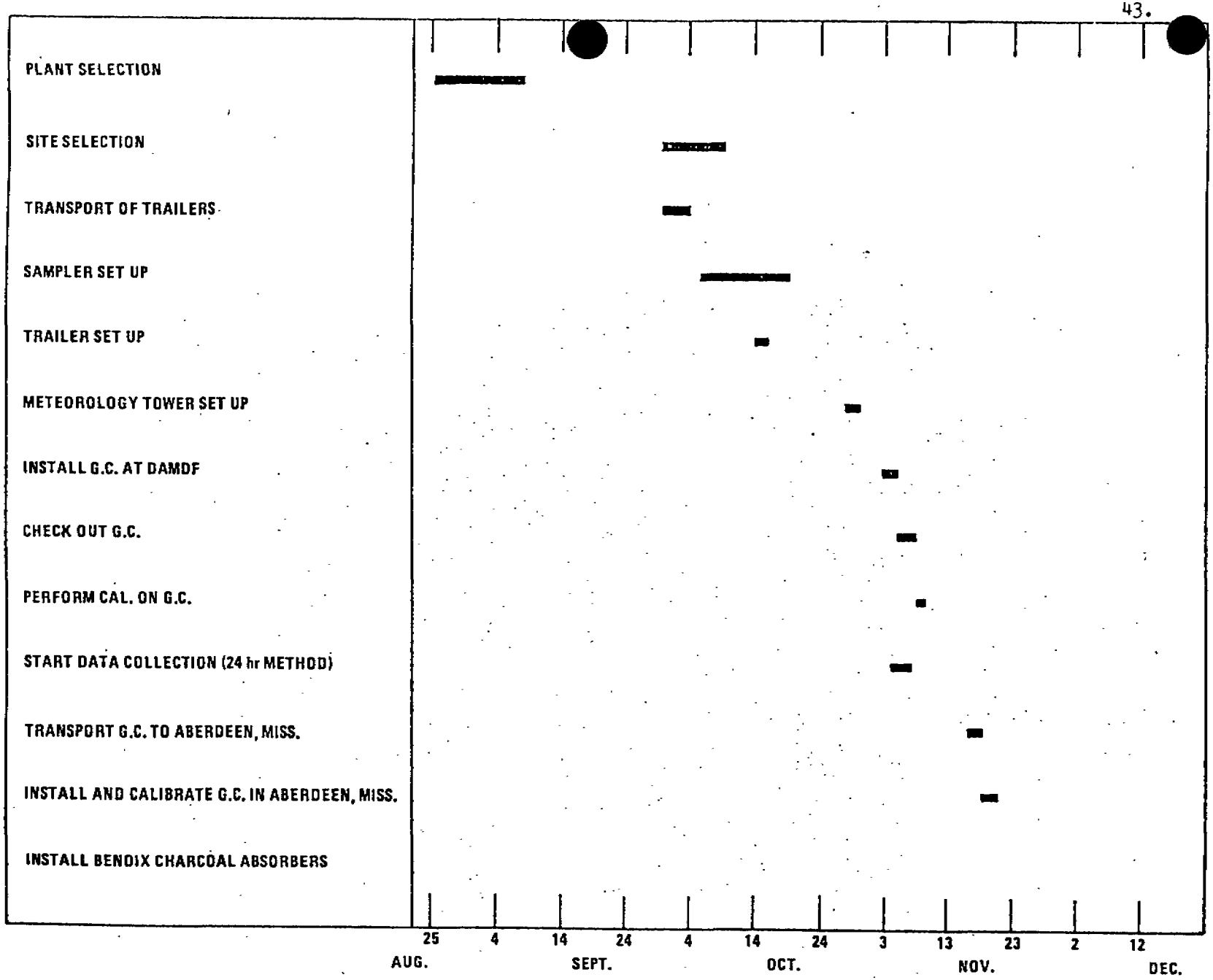


Figure 3. Start up schedule.

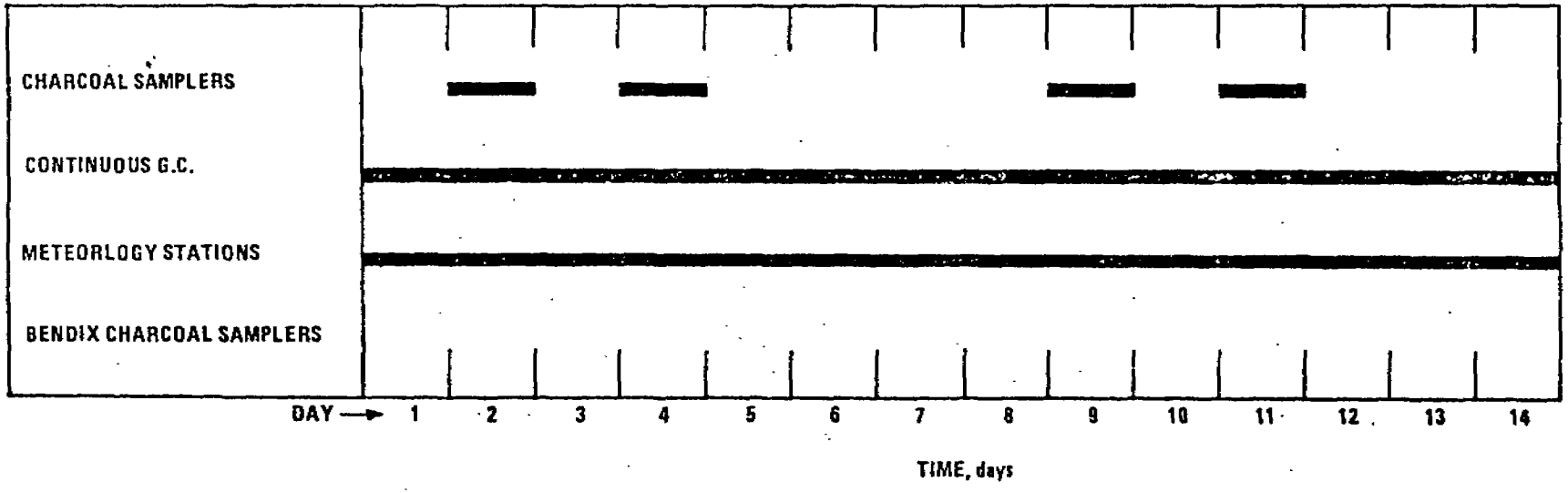


Figure 4. Operation schedule.

We would hope that since dispersion resin products are only 12% of the total PVC production, EPA could develop an alternative control requirement if not permanently, at least on a temporary basis to allow for development of feasible control systems. For those plants which produce various PVC products, i.e. suspension, latex, dispersion, etc., EPA may wish to consider emission "averaging" or "balancing".

QUESTION 6: Compliance schedules for installation of stripping systems at existing plants. Use of incineration, solvent absorption, and/or carbon adsorption to reduce the vinyl chloride concentration of the dryer exhaust to less than 10 ppm. (Cost, capability.)

Answer: In response to this question and assuming that we consider the term stripping loosely as we did in Question 5, let me first say that across the board the industry plans to accomplish VCl reductions by stripping. We believe that we must and can remove residual VCl before drying or before exposing our products to large volumes of air. No company to my knowledge, and this has been discussed at our full committee meetings, plans any other technique and certainly not incineration, solvent absorption or activated carbon adsorption. These techniques are not considered feasible. We are somewhat confused with this question, but assume you mean stripping to less than 400 ppm before drying or reducing VCl to 10 ppm in the dryer exhaust whichever we so choose as a course of control.

With regard to compliance schedules, it will take from 2 to 2½ years for the industry to provide stripping of suspension, latex, and bulk products. An additional 2 to 2½ years will be required for technology development and equipment installations for dispersion product, or a total of 4 to 5 for dispersion products.

Obviously stripping will be accomplished on some PVC products before these dates. Some plants are currently stripping some products on a makeshift basis and permanent stripping facilities are being installed at some plants for some products.

QUESTION 7: Quantify the reduction in dryer exhaust gas volume that can be achieved by using fluidized bed dryers, flash dryers, and/or by recycling the dryer exhaust after removing the water and vinyl chloride. Discuss the factors that would control the rate at which these techniques can be installed.

Answer: We have studied this question and believe it really to be irrelevant when considering that across the board the industry intends to remove the residual VCl from PVC products prior to drying as I have noted in response to Questions 5 and 6. Therefore, I have no data comparing various dryer systems typical of the industry.

I can, however, provide data typical of B.F.Goodrich operations. Dryer exhaust gas volume is lowest when using a fluidized bed dryer. We estimate 4.3 # air/ # PVC for fluidized bed drying, 11.5 # air/# PVC for flash drying, and 82 to 125 # air/# PVC for spray drying.

Although fluidized bed drying results in the lowest dryer exhaust volume per unit of product, all PVC products cannot be dried using fluidized bed dryers. Most suspension PVC can be (95-99%) but there would be no incentive to switch since the industry approach to VCl reduction is to remove it prior to drying. None of our dispersion resins can be dried using fluidized bed dryers.

As far as treating and recycling dryer gases, we see no incentive either from an energy savings or from a VCl reduction standpoint. Certainly treatment would be required to remove the PVC particulate matter in order to prevent product contamination. Additionally, we believe it to be more difficult to remove the low concentration VCl from high volume dryer exhaust gases than to remove the VCl from the PVC prior to drying.

industry range 10 - 200

QUESTION 14: Sampling and analysis techniques to determine the vinyl chloride content of the resin after stripping.

Answer: The industry has methods of determining residual VCl in resin and will make these procedures available to EPA if desired. I have copies of two B.F.Goodrich techniques which I will leave with you today. These are called "Analyses for Vinyl Chloride in PVC Powders by Head-Space Gas Chromatography" and "Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins".

Attachment D

EVALUATION OF A COLLECTION AND ANALYTICAL PROCEDURE FOR VINYL CHLORIDE IN AIR

FOR

U.S. ENVIRONMENTAL PROTECTION AGENCY

CONTRACT NO. 68-02-1408

TASK ORDER NO. 2

EPA Report No. 75-VCL-1

December 13, 1974

INTRODUCTION

The purpose of Task Order No. 2 was to evaluate the feasibility of source testing for vinyl chloride (VC) using a gaseous grab sampling method with Tedlar bags followed by gas chromatographic analysis. According to this task order, gas-tight syringes were to be used for all sample injections. The completion of this task should provide sufficient data on the reproducibility of the analytical method for 5, 50, 500, and 1000 ppm (v/v) of vinyl chloride in air, the possible interference of a number of specified organic compounds, and the stability of gaseous vinyl chloride samples under a prescribed set of conditions.

EXPERIMENTAL

In executing Step 1 of the Task Order (see Appendix IV), a series of 5-, 50-, 500-, and 1000-ppm gas mixtures of vinyl chloride in air was prepared five times on four separate days using a static dilution procedure. In addition, the 5-ppm vinyl chloride gas mixture was prepared an additional six times each, using a static and a dynamic dilution system. The analysis of each gas mixture was performed in triplicate by gas chromatography.

In performing Step 2, the potentially interfering substances were added in sequence to a 500-ppm gaseous mixture of vinyl chloride in air. Two, 5-ml portions of the mixture were analyzed after preparation of the vinyl chloride-air mixture as well as after each of the sequential 500-ppm additions of the 11 potential interferences which consisted of the following compounds listed in the order of their respective additions: methane, ethane, ethylene, ethyl chloride, n-pentane, 1,1-dichloroethane (ethylidene chloride), vinyl acetate, n-hexane, 1,1-dichloroethylene (vinylidene chloride), 1,1,1-trichloroethane and n-heptane. After the sequential addition and analysis of these mixtures, water vapor was added to yield approximately a 10 percent (v/v) water vapor concentration in the mixture which was then analyzed in duplicate. Hydrogen chloride was then added to yield a 50-ppm concentration and the final set of duplicate analyses for VC was performed.

Step 3 of the Task Order required the determination of the possible degradation of 5 and 500 ppm vinyl chloride-gas mixtures in either of two sets of Tedlar air bags which contained several of the possible interferences

investigated in Step 2; one set was maintained at room temperature, the other at the dewpoint of a 10% water vapor mixture. The two sets of Tedlar air bag gaseous mixtures were prepared by similar procedures and, in addition to 5 and 500 ppm of vinyl chloride contained 500 ppm of each of the following: methane, ethane, ethylene, ethyl chloride, n-pentane, and vinyl chloride, 10 percent water vapor, and 50 ppm of hydrogen chloride. Duplicate analyses were performed on each gas-vapor mixture immediately upon generation and again after 6, 24, and 48 hours.

RESULTS

Reproducibility of the Gas Chromatographic Method

The gas mixtures consisting of 5, 50, 500 and 1000 ppm of vinyl chloride (VC) in air contained in Tedlar bags were analyzed by gas chromatography on Chromosorb 102 using flame ionization detection. The gas mixtures were prepared statically in 19-liter Tedlar bags provided with Nylon fittings, the opening of which was sealed with a rubber serum cap. A 5-ml gas-tight syringe was used to withdraw a portion of the gas mixture for analysis. The results of this study are summarized in Tables I-IV.

As shown in Tables I-IV there was a marked variation in the vinyl chloride equivalent peak areas for the four VC gas mixtures from one trial to the next. However, the mean deviation of repeated analyses of any one trial was within three percent in 17 of the 20 trials.

The observed variations from one trial to another, conducted on different dates, demonstrate the need for repetitive re-standardization of the method with each group of unknown samples. The data shown presented in Tables V and VI are the results of the analysis of 5-ppm VC standards prepared statically with a 50-ml gas-tight syringe (Table V) and dynamically (Table VI). Table V demonstrates that the use of a single 50-ml gas-tight syringe is an improvement over five 10-ml portions. The dynamic preparation of a 5 ppm vinyl chloride standard from a 100 ppm standard produced a sample whose average equivalent areas more closely approximated those obtained for the higher concentrations. However, the mean deviation per trial showed no improvement for this method over the static method of sample preparation. None of the

compounds investigated had a retention time on the Chromosorb 102 column sufficiently close to that of vinyl chloride to constitute a serious qualitative interference.

Table VIII present the measured vinyl chloride peak areas in the presence of the listed interferences, along with the equivalent areas, expressed in terms of mm^2/ppm, adjusted to correct for overnight changes in the sensitivity of the gas chromatographic method (sensitivity changes were observed in Step 1 during the evaluation of the reproducibility of the method).

Degradation of Vinyl Chloride - Gas Mixtures

The deterioration of air mixtures containing vinyl chloride and potential interferences was investigated. Gas-air mixtures containing 5 and 500 ppm each of vinyl chloride plus added potential interferences were analyzed at 0, 6, 24 and 48 hours. Duplicate preparations of the gas mixtures were made; one set being maintained at ambient temperature, the other at the dew point of a 10% water vapor mixture. The results of this study, tabulated in Tables IX and X, give no evidence of degradation of vinyl chloride during the 48-hour residence period in the Tedlar bags.

COMMENTS

The gas chromatograph was allowed to remain completely operational day and night to minimize variable detector response characteristics. In addition, the gas chromatograph was recalibrated daily with a 500 ppm VC-air mixture prepared as described above for Step 1. This calibration was proved to be reproducible in Step 1.

SAMPLING AND ANALYTICAL EQUIPMENT PROCEDURES

Equipment

1. Pye Unicam Series 104 Gas Chromatograph with Flame Ionization Detector.
2. 80/100 mesh Chromosorb 102 Gas Chromatographic Column (2.4 meters x 0.64 cm).
3. Philips Model PM8000 Strip Chart Recorder.
4. Hamilton Gas-Tight Syringes, 1-ml, 5-ml, 10-ml and 50-ml.
5. Hamilton Syringe, 50-µl, Model No. 705N.
6. 19-liter Tedlar Bags, Model No. 1234, Plastic Film Enterprises.
7. Mark III Flowmeter, Fisher Scientific Company.
8. Flowmeter, Type 1211-1355-8506, Brooks Instrument Division.

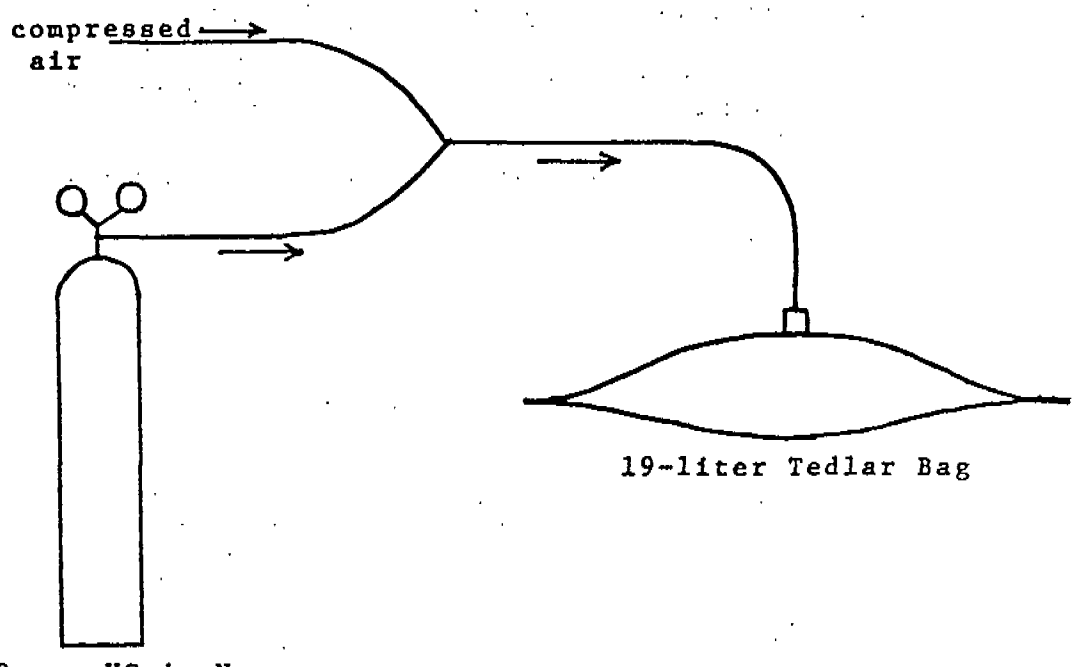
Procedures

Step 1

The 50-ppm vinyl chloride gas mixture was prepared by injecting, with a 1-ml gas-tight syringe, 0.5 ml of pure vinyl chloride gas into an 19-liter Tedlar bag while the latter was being charged with 10 liters of air. The air was purified by passage through 20/50 mesh activated coconut charcoal at a rate of 1.0 liter per minute; the air flow was monitored with a calibrated gas flowmeter. The pure vinyl chloride had previously been transferred from a Matheson lecture bottle into a 250-ml evacuated Saran bag, from which it was withdrawn using the gas-tight syringes for the preparation of the desired concentrations. After preparing each mixture, the inlet tubing was removed and the bag sealed with a rubber serum cap. The 500- and 1000-ppm mixtures were prepared in a similar manner using 5 and 10 ml of vinyl chloride gas, respectively.

The 5-ppm gas mixture was prepared according to the following procedure. While the 19-liter Tedlar bag was being charged with 10 liters of purified air, five 10-ml portions f a previously prepared 1000 ppm vinyl chloride gas mixture were injected into the air line. This method

of 5 ppm vinyl chloride preparation did not yield consistent results and two other methods were investigated. 1) A single 50-ml injection was employed to reduce the number of injections of the 1000 ppm solution from five to one. The results of the subsequent analyses differed only slightly from the previous 5 ppm gas standard. 2) The dynamic dilution of a commercially prepared 100 ppm vinyl chloride gas mixture (Liquid Carbonic). The following schematic diagram depicts the apparatus used to dynamically generate the 5 ppm VC Standard.



The flowrate of the compressed air was nineteen times as great as the flowrate of the 100 ppm vinyl chloride gas standard. The results of the subsequent analyses are tabulated in Tables V and VI.

Each gas mixture was mixed thoroughly. Analysis in triplicate was accomplished by the injection of 5 ml of the mixture onto the gas chromatographic column with a 5-ml gas-tight syringe. The conditions for the gas chromatograph throughout Step 1 were as follows: oven

temperature, 155°C; detector temperature, 225°C; helium carrier flowrate, 40 ml/min.; 2.4 meter x 0.64 cm Chromosorb 102 column.

Step 2

A group of 11 organic compounds, water vapor and hydrogen chloride was evaluated to determine their additive and possible qualitative or quantitative interference on the analysis of vinyl chloride. Due to the problems in reproducing a 5-ppm vinyl chloride mixture, this part was completed only on the 500-ppm gas mixture. A 500-ppm vinyl chloride gas mixture, was prepared, as described in Step 1, and analyzed in duplicate by injecting 5 ml of the mixture on the Chromosorb 102 column using a 5-ml gas-tight syringe. Five ml of methane was then introduced into the Tedlar bag by means of a gas-tight syringe to yield a resulting gas mixture containing 500 ppm of vinyl chloride and 500 ppm of methane. Again, duplicate analyses were performed. The remaining potential interferences were added sequentially with duplicate analysis following each addition. The following organic compounds were investigated for their potential interference in the vinyl chloride analysis: methane, ethane, ethylene, ethyl chloride, n-pentane, 1,1-dichloroethane (ethylidene chloride) vinyl acetate, n-hexane, 1,1-dichloroethylene (vinylidene chloride), 1,1,1-trichloroethane, and n-heptane.

Methane, ethane, ethylene, and ethyl chloride are gases at room teperature and atmospheric pressure and were added to the vinyl chloride gas mixture with a gas-tight syringe. The remaining compounds are liquids at room temperature and atmospheric pressure and were therefore introduced into the gas mixture by means of a 50-µl Hamilton liquid syringe (Model No. 705N). In each case, calculations were performed to determine the amount of each liquid required to yield a 500-ppm concentration in 10 liters of gas. Following the addition of the last contaminant, i.e., n-heptane, water vapor was added from a steam generator to produce a 10 percent (v/v) concentration of water vapor in the Tedlar bag. The water vapor was allowed to condense on the walls of the bag (at room temperature) and duplicate analyses for vinyl chloride were performed. Hydrogen chloride gas (0.5 ml) was then added to the gas mixture. This produced a concentration of 50 ppm of HCl vapor. Duplicate analyses for vinyl chloride were again performed.

A fresh 500-ppm vinyl chloride solution was prepared daily and analyzed. The interferences which had been

added by the time of the conclusion of the previous day's work were then added and the investigatory scheme was continued.

Step 3

This step was performed to evaluate the possible deterioration of vinyl chloride in a Tedlar bag over a period of 48 hours (see Appendix IV). Two sets of two identical bags were charged with air containing 5 and 500 ppm, respectively, of vinyl chloride and 500 ppm concentrations of each of the following contaminants: methane, ethane, ethylene, ethyl chloride and n-pentane. To each gas-mixture water vapor and hydrogen chloride were added as described in Step 2 (10% water vapor and 50 ppm HCl vapor in the final mixtures). Those contaminants whose retention times were greater than twenty minutes were omitted from Step 3 to accelerate the completion of the analyses.

Each mixture was analyzed in duplicate following injection of 5 ml onto the gas chromatographic column. One 5-ppm gas mixture and one 500-ppm gas mixture were stored in a forced-draft oven (Blue M) at 115°F, the water vapor dewpoint of 10 percent water vapor in air (Perry's Chemical Engineer's Handbook, Perry, J.H., (ed.), McGraw-Hill, New York, 1963, p. 15-5). The other two mixtures were maintained at room temperature, which varied from 71-76°F over the 48-hour period. Each gas mixture was subsequently analyzed, in duplicate, after 6, 24, and 48 hours of residence in a Tedlar bag.

APPENDIX I

TABLES

TABLE I

REPRODUCIBILITY OF THE GAS CHROMATOGRAPHIC ANALYSIS OF 5-PPM VC MIXTURES IN AIR

Trial No.	Equivalent Area*		Mean Deviation Per Trial	
	Separate Analyses (mm^2/ppm)	Average (mm^2/ppm)	(mm^2/ppm)	%
1	9284 8704 7752	8580	552	6.4
2	5760 5120 4880	5253	338	6.4
3	3460 3400 3400	3420	27	0.8
4	6436 6356 6124	6305	121	1.9
5	7812 8112 7752	7892	147	1.9

*Equivalent Area = $\frac{\text{Peak Area x Attenuation}}{\text{PPM of Vinyl Chloride in Air}}$

TABLE II

REPRODUCIBILITY OF THE GAS CHROMATOGRAPHIC ANALYSIS OF 50-PPM VC MIXTURES IN AIR

Trial No.	Equivalent Area* Separate Analyses (mm^2/ppm)	Equivalent Area* Average (mm^2/ppm)	Mean Deviation Per Trial (mm^2/ppm)	Mean Deviation Per Trial %
1	7032 7256 7108	7132	83	1.2
2	6396 6552 5680	5781	496	8.6
3	5760 5880 5760	5800	53	0.9
4	9440 9284 9424	9383	66	0.7
5	10804 10716 10716	10745	39	0.4

TABLE III

REPRODUCIBILITY OF THE GAS CHROMATOGRAPHIC ANALYSIS OF 500-PPM VC MIXTURES IN AIR

Trial No.	Equivalent Area*		Mean Deviation Per Trial	
	Separate Analyses (mm^2/ppm)	Average (mm^2/ppm)	(mm^2/ppm)	%
1	7372 7412	7392	20	0.3
2	6450 6145 6095	6209	140	2.3
3	6280 6080 6240	6200	80	1.3
4	9120 9196 9120	9145	34	0.4
5	10180 10300 10184	10221	52	0.5

TABLE IV

REPRODUCIBILITY OF THE GAS CHROMATOGRAPHIC ANALYSIS OF 1000-PPM VC GAS MIXTURES IN AIR

Trial No.	Equivalent Area*		Mean Deviation Per Trial	
	Separate Analyses (mm^2/ppm)	Average (mm^2/ppm)	(mm^2/ppm)	%
1	7270 7125 7220	7205	53	0.7
2	6450 6145 6095	6230	147	2.4
3	6220 6320 6240	6260	40	0.6
4	8626 8970 8932	8843	144	1.6
5	10120 10120 10165	10135	20	0.2

TABLE V

REPRODUCIBILITY OF THE GAS CHROMATOGRAPHIC ANALYSIS
OF 5-PPM VINYL CHLORIDE STANDARDS
PREPARED WITH A 50-ML GAS-TIGHT SYRINGE

Trial No.	Equivalent Area*		Mean Deviation Per Trial	
	Separate Analyses (mm^2/ppm)	Average (mm^2/ppm)	(mm^2/ppm)	%
1	7260 7308	7284	24	0.3
2	7216 7100	7158	58	0.8

TABLE VI

REPRODUCIBILITY OF THE GAS CHROMATOGRAPHIC ANALYSIS OF 5-PPM VINYL CHLORIDE GAS STANDARDS PREPARED BY THE DYNAMIC DILUTION OF A 100-PPM VINYL CHLORIDE STANDARD

Trial No.	Equivalent Area*		Mean Deviation Per Trial	
	Separate Analyses (mm^2/ppm)	Average (mm^2/ppm)	(mm^2/ppm)	%
1	12936 12672	12804	132	1.0
2	12672 12912	12792	120	0.9
3	11772 13164	12468	696	5.6
4	13420 11220	12320	1100	8.9

TABLE VII

POTENTIAL INTERFERENCES INVESTIGATED
AND THEIR ABSOLUTE AND RELATIVE RETENTION TIMES
(Relative to Vinyl Chloride Retention Time = 4.90 minutes)

Name	Formula	Retention Time[a] (min.)	Relative Retention Time[b]
Methane	CH_4	1.0	0.20
Ethylene	$CH_2=CH_2$	1.6	0.33
Ethane	CH_3-CH_3	1.9	0.39
Ethyl Chloride	CH_3-CH_2Cl	9.1	1.9
1,1-Dichloro-ethylene (Vinylidene Chloride)	$CH_2=CCl_2$	14.8	3.0
n-Pentane	$CH_3(CH_2)_3CH_3$	16.7	3.4
1,1-Dichloro-ethane (ethylidene chloride)	CH_3CHCl_2	23.6	4.8
Vinyl Acetate	$CH_2=CHOC(=O)-CH_3$	23.9	4.9
n-Hexane	$CH_3(CH_2)_4CH_3$	37.0	7.6
1,1,1-Trichloro-ethane	CH_3-CCl_3	43.5	8.9
n-Heptane	$CH_3(CH_2)_5CH_3$	87.0	18

[a] Retention Time was measured from time of injection.

[b] Relative Retention Time = $\frac{\text{Retention Time for Compound}}{\text{Retention Time for Vinyl Chloride}}$

TABLE VIII

VINYL CHLORIDE PEAK AREAS IN THE PRESENCE OF POTENTIAL INTERFERENCES

	Mixture Description	Date	Peak Area Range	Peak Area Avg.	Avg. Dev. from a, a′, a″, or a‴
(a)	500 ppm VC	8/27/74	3201-3312	3257	
(b)	(a) + 500 ppm methane	8/27/74	3648-3700	3674	+417 (12.8%)
(c)	(b) + 500 ppm ethane	8/27/74	3293-3441	3367	+110 (3.3%)
(d)	(c) + 500 ppm ethylene	8/27/74	3150-3719	3435	+178 (5.5%)
(e)	(d) + 500 ppm methyl chloride	8/27/74	3293-3690	3492	+235 (7.2%)
(f)	(e) + 500 ppm n-pentane	8/27/74	3528-3756	3642	+385 (11.8%)
(g)	(f) + 500 ppm 1,1-dichloroethane	8/27/74	3626-3682	3654	+397 (12.2%)
(a′)	500 ppm VC	8/28/74	3120-3141	3131	-
(h)	(g) + 500 ppm vinyl acetate	8/28/74	2916-2934	2925	-206 (6.6%)
(i)	(h) + 500 ppm hexane	8/28/74	2826-2952	2889	-242 (7.7%)
(j)	(i) + 500 ppm vinylidene chloride	8/28/74	2983-2993	2988	-143 (4.8%)
(a″)	500 ppm VC	8/29/74	2945-2951	2948	-
(k)	(j) + 500 ppm 1,1,1-trichloroethane	8/29/74	3003-3077	3040	+92 (3.1%)
(l)	(k) + 500 ppm n-heptane	8/29/74	2912-2937	2925	-23 (0.7%)
(a‴)	500 ppm VC	8/30/74	2907-3173	3040	-
(m)	(l) + 10% water vapor	8/30/74	2024-3034	3029	-11 (0.4%)
(n)	(m) + 50 ppm HCl	8/30/74	3024-3028	3026	-14 (0.5%)

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TABLE IX

DEGRADATION OF 5 PPM VINYL CHLORIDE IN GAS MIXTURES
CONTAINING POTENTIAL INTERFERENCES STORED FOR STATED PERIODS

Vinyl Chloride Peak Area (x 1/20)

Time (hours)	100 PPM VC Standard*	Room Temperature			Dew Point Temperature (115°F)		
		Separate Analyses (mm^2)	Average (mm^2)	Deviation** (mm^2)	Separate Analyses (mm^2)	Average (mm^2)	Deviation** (mm^2)
0	1906	2358 2358	2358	-	2376 2327	2352	-
6	1887 (1.0%)	2390 2380	2385	+27 (+1.1%)	2370 2399	2385	+33 (+1.4%)
24	1848 (-3.0%)	2174 2376	2275	-83 (-3.5%)	2301 2299	2300	-52 (-2.2%)
48	2147 (+12.6%)	2793 2910	2852	+494 (+20.9%)	2641 2793	2717	+365 (+15.5%)

* Reference standard, prepared fresh daily without potential interferences

** Deviation from average area at t = 0 hours

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TABLE X

DEGRADATION OF 500 PPM VINYL CHLORIDE IN GAS MIXTURES CONTAINING POTENTIAL INTERFERENCES STORED FOR STATED PERIODS

Time (hours)	500 ppm VC Std.*	Vinyl Chloride Peak Area (x 1/2000)					
		Room Temperature			Dew Point Temperature		
		Separate Analyses (mm^2)	Average (mm^2)	Dev.** ($t-t_o$) (mm^2)	Separate Analyses (mm^2)	Average	Dev.** ($t-t_o$) (mm^2)
0	3257	2309 2603	2456		2363 2633	2498	
6	-	2508 2525	2517	+61 (+2.5%)	2496 2496	2496	-2 (-0.08%)
24	3131 (-3.9%)	2889 2905	2897	+441 (+18%)	2821 2840	2830	+332 (13.3%)
48	2948 (-9.5%)	2868 2868	2868	+412 (+16.8%)	2610 2679	2645	+147 (+5.9%)

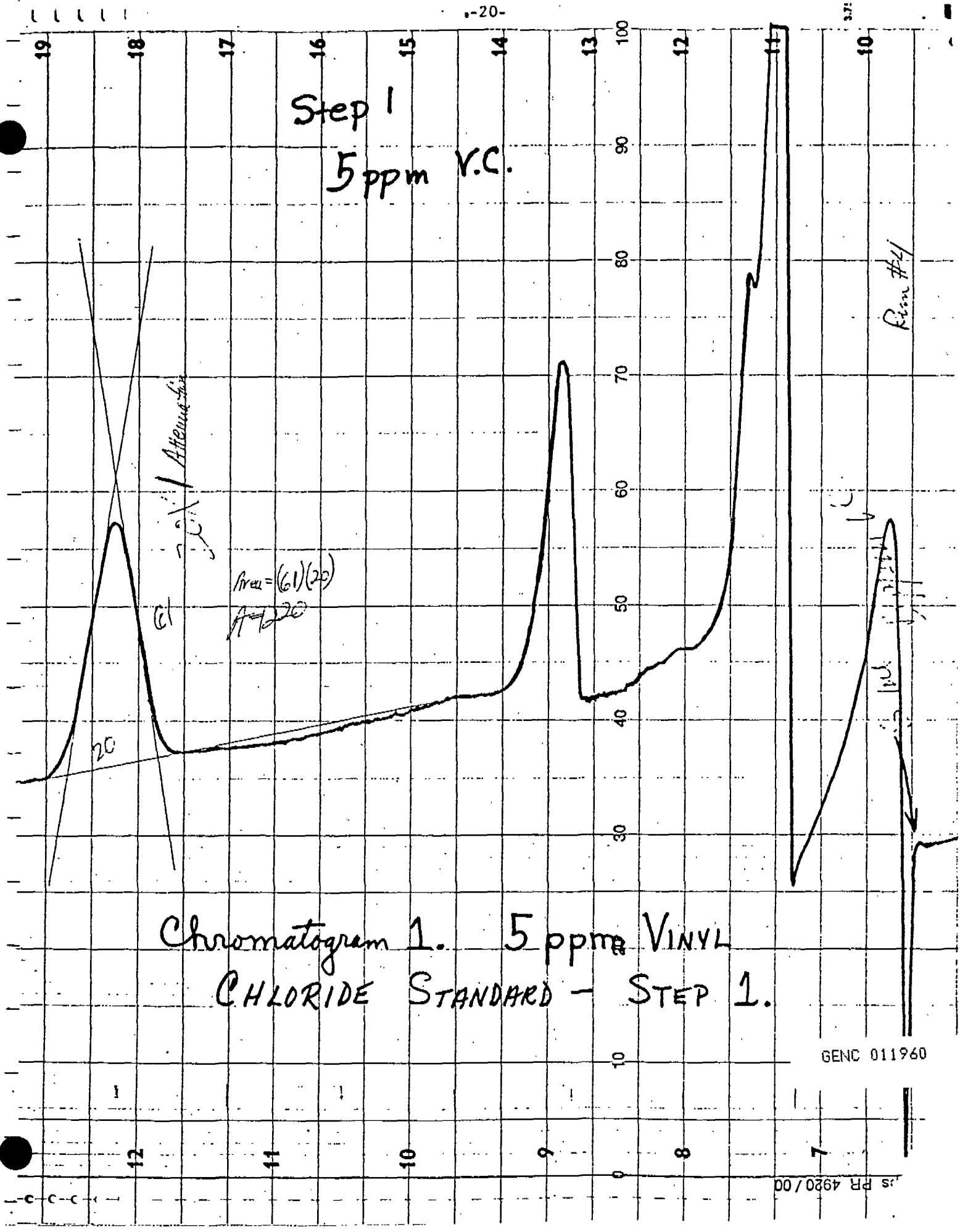
* Reference standard, prepared fresh daily without potential interferences

** Deviation from 0 hours

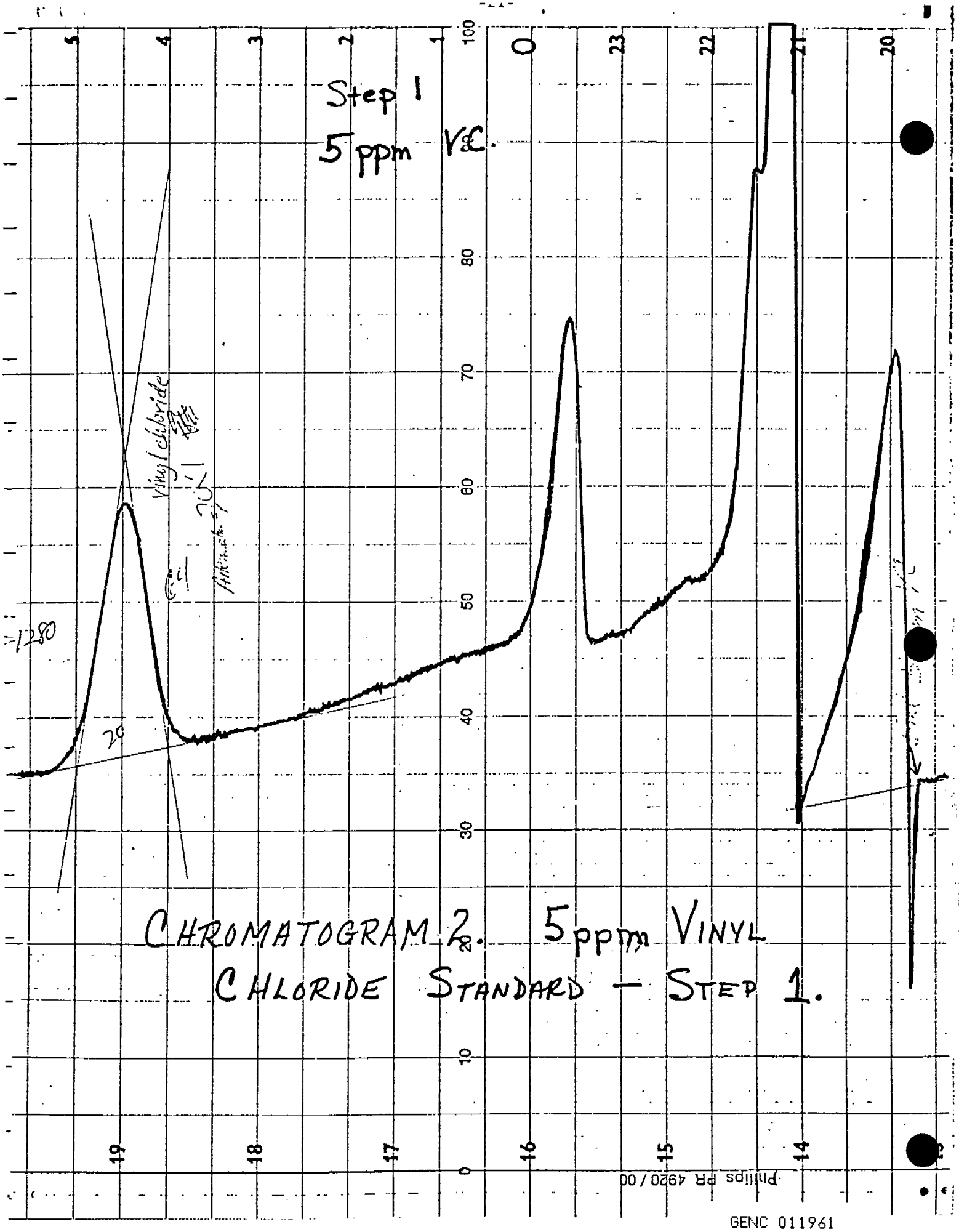
APPENDIX II

CHROMATOGRAMS

1. 5 ppm Vinyl Chloride Standard - Step 1
2. 5 ppm Vinyl Chloride Standard - Step 1
3. 5 ppm Vinyl Chloride Standard - Step 1
4. 500 ppm Vinyl Chloride Standard - Step 1
5. 500 ppm Vinyl Chloride Standard - Step 1
6. 500 ppm Vinyl Chloride Standard - Step 1
7. 500 ppm Vinyl Chloride Gas Mixture plus Potential Interferences - Step 2

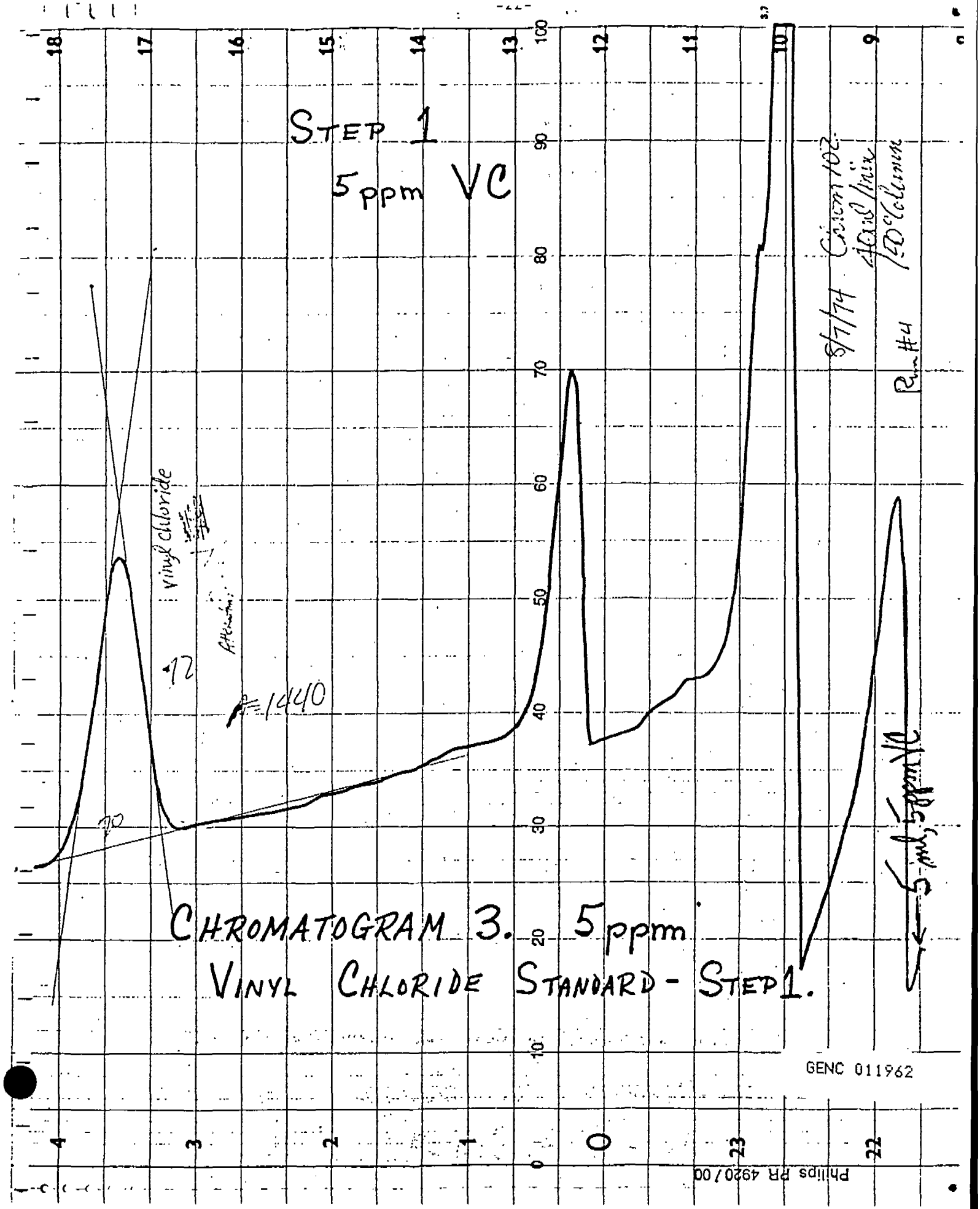


Chromatogram 1. 5 ppm Vinyl Chloride Standard - Step 1.



CHROMATOGRAM 2. 5ppm VINYL CHLORIDE STANDARD – STEP 1.

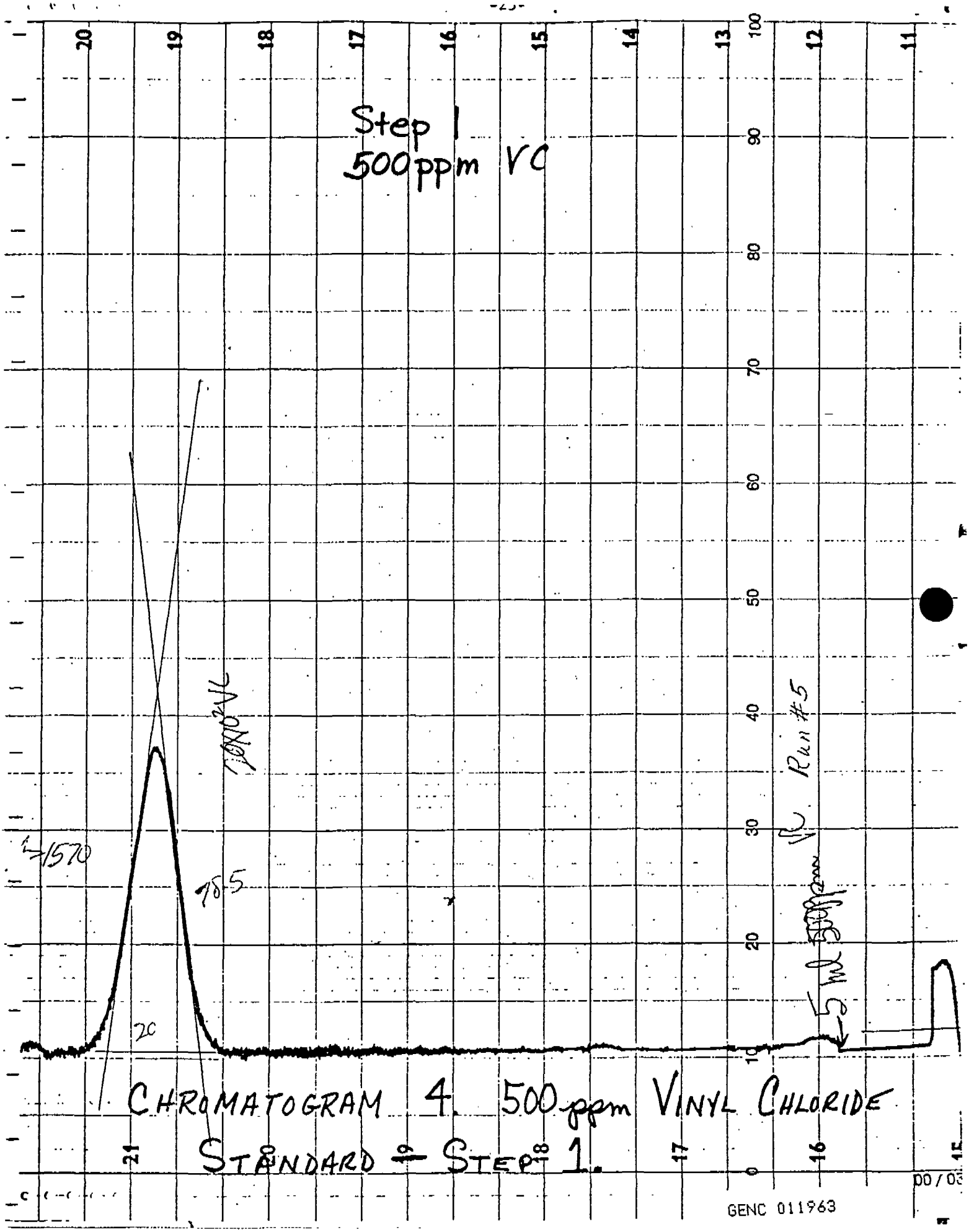
GENC 011961



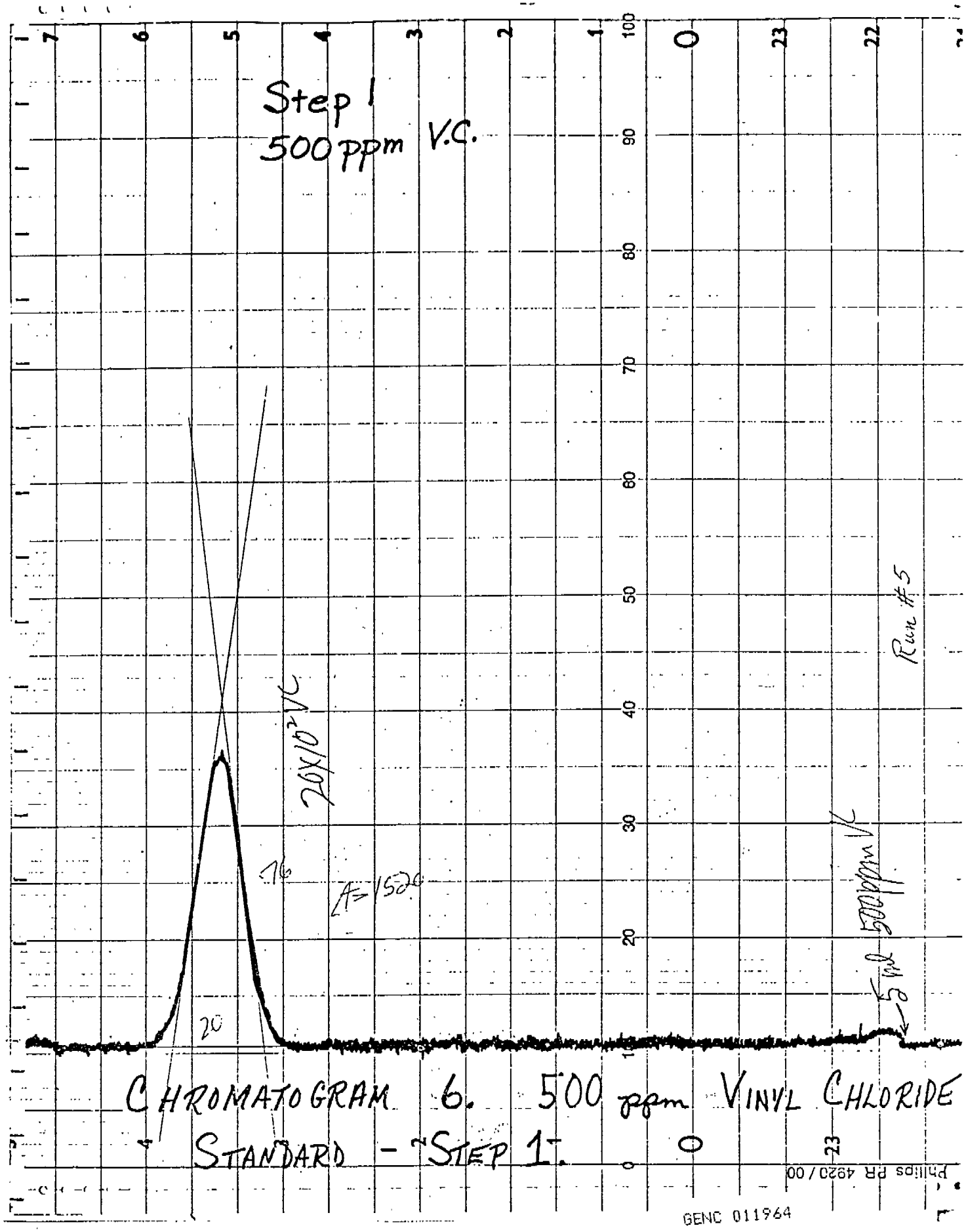
CHROMATOGRAM 3. 5 ppm VINYL CHLORIDE STANDARD - STEP 1.

GENC 011962

Philips PR 4920/00



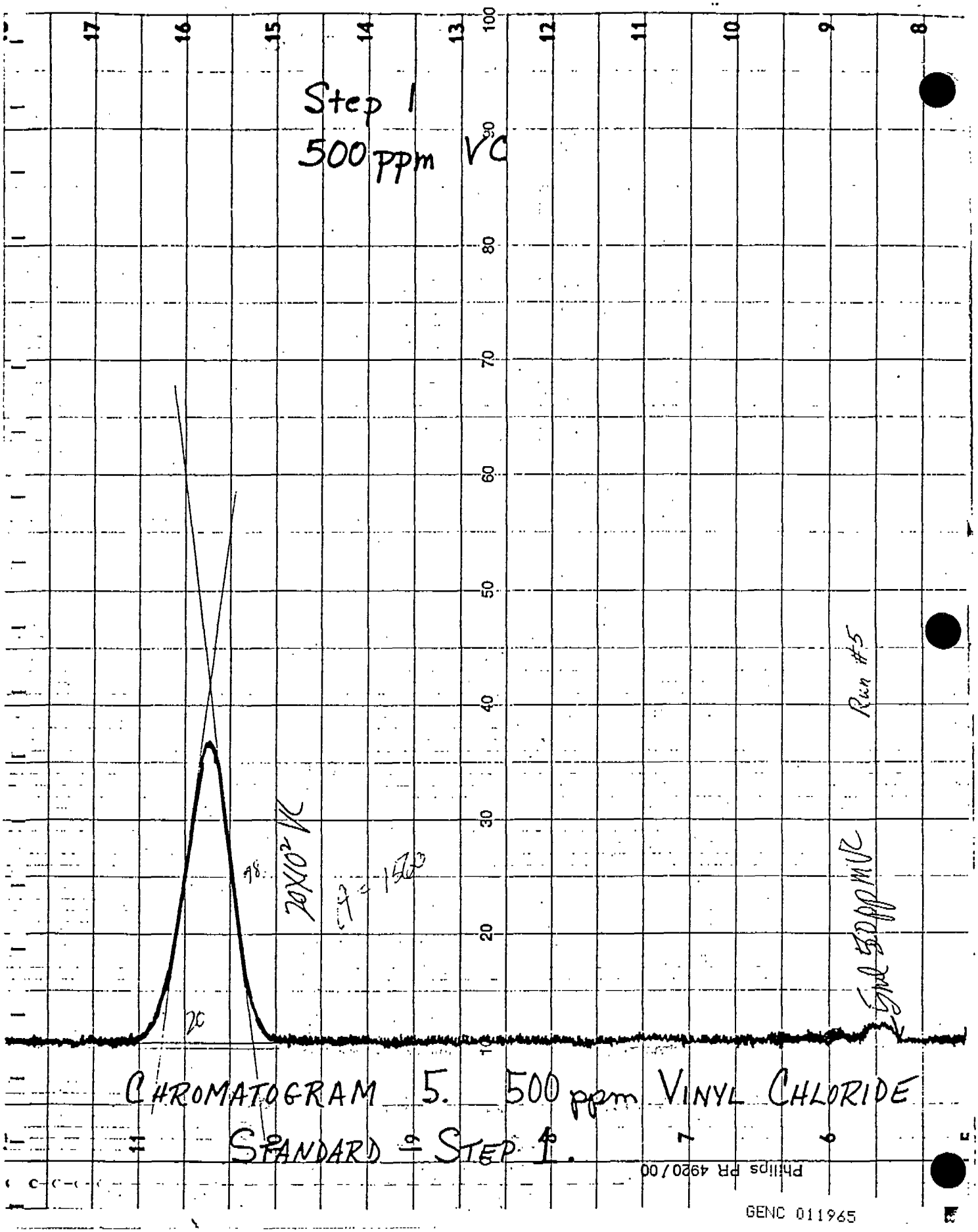
CHROMATOGRAM 4. 500 ppm VINYL CHLORIDE STANDARD ~~1~~ STEP 1.



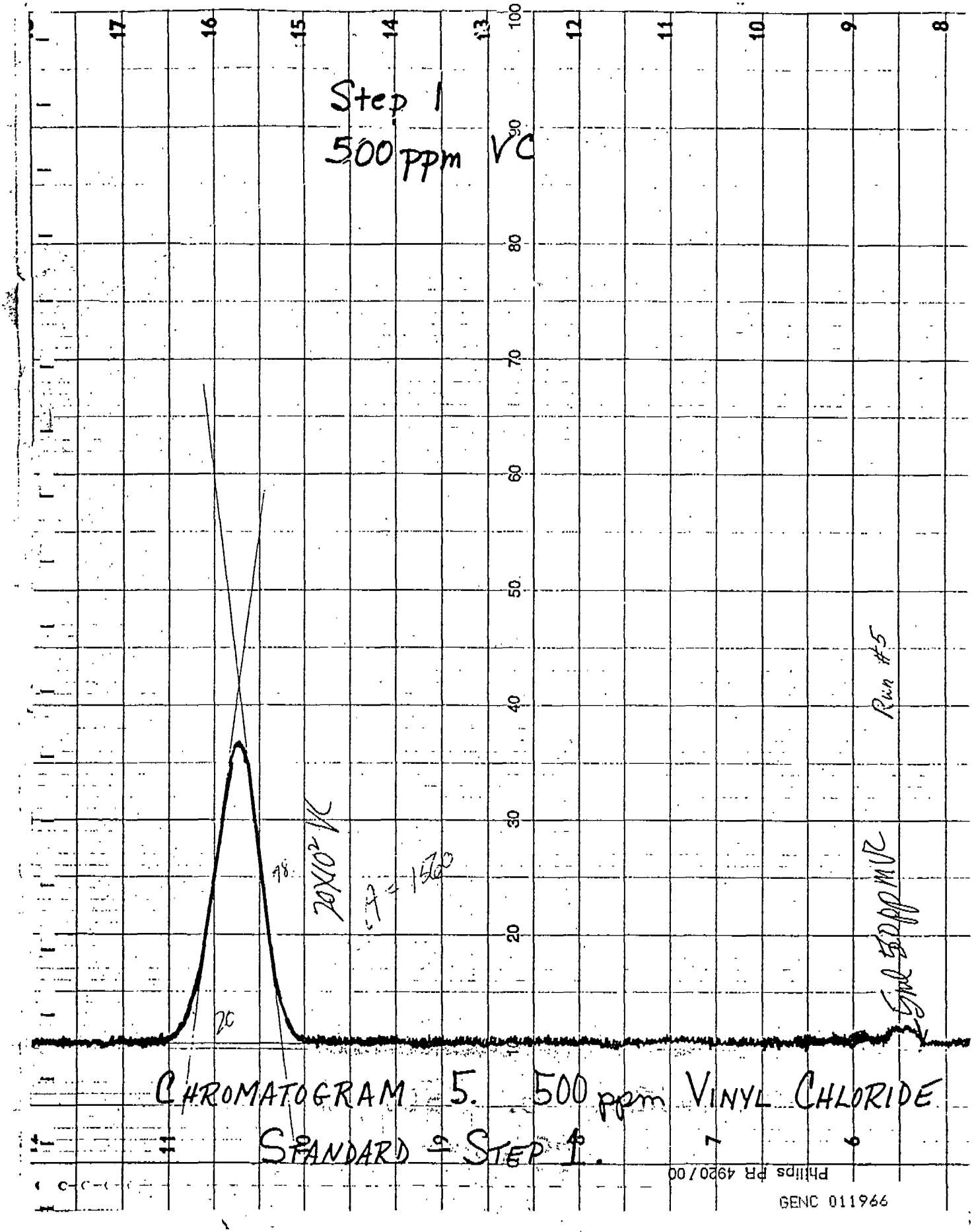
CHROMATOGRAM 6. 500 ppm VINYL CHLORIDE STANDARD - STEP 1.

Philips PR 4920/00

GENC 011964



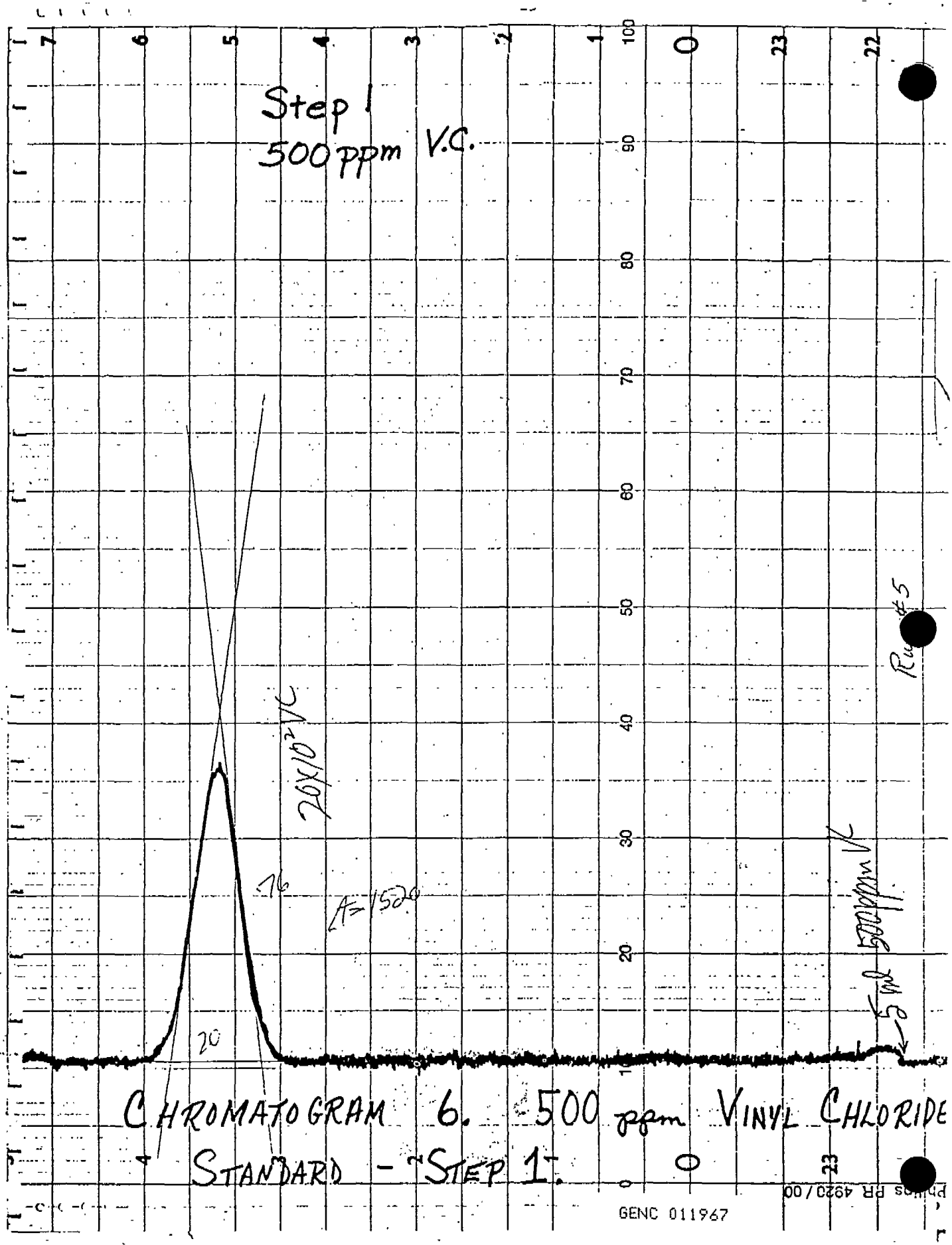
CHROMATOGRAM 5. 500 ppm VINYL CHLORIDE STANDARD = STEP 1.



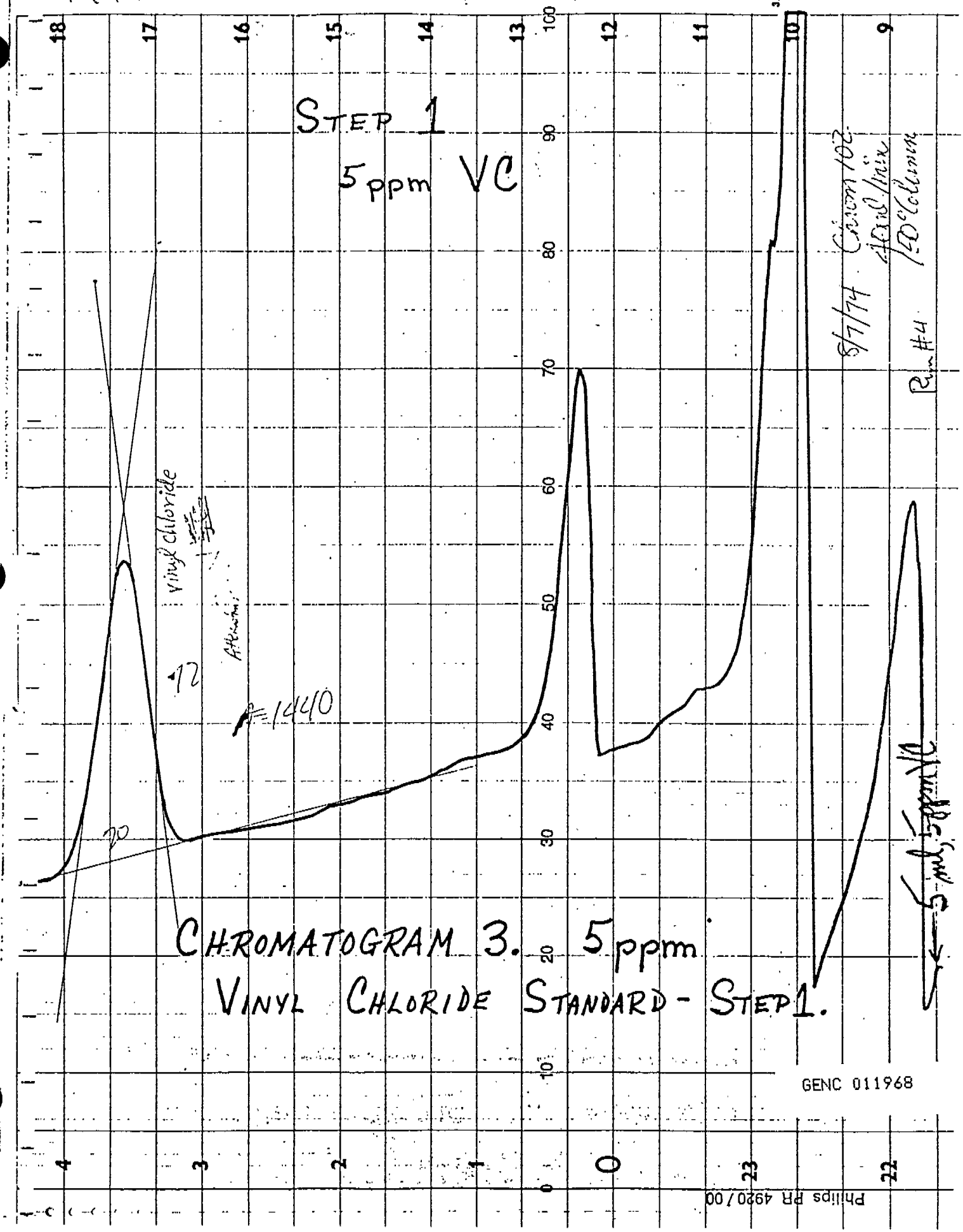
CHROMATOGRAM 5. 500 ppm VINYL CHLORIDE STANDARD & STEP 1.

Philips PR 4920/00

GENC 011966



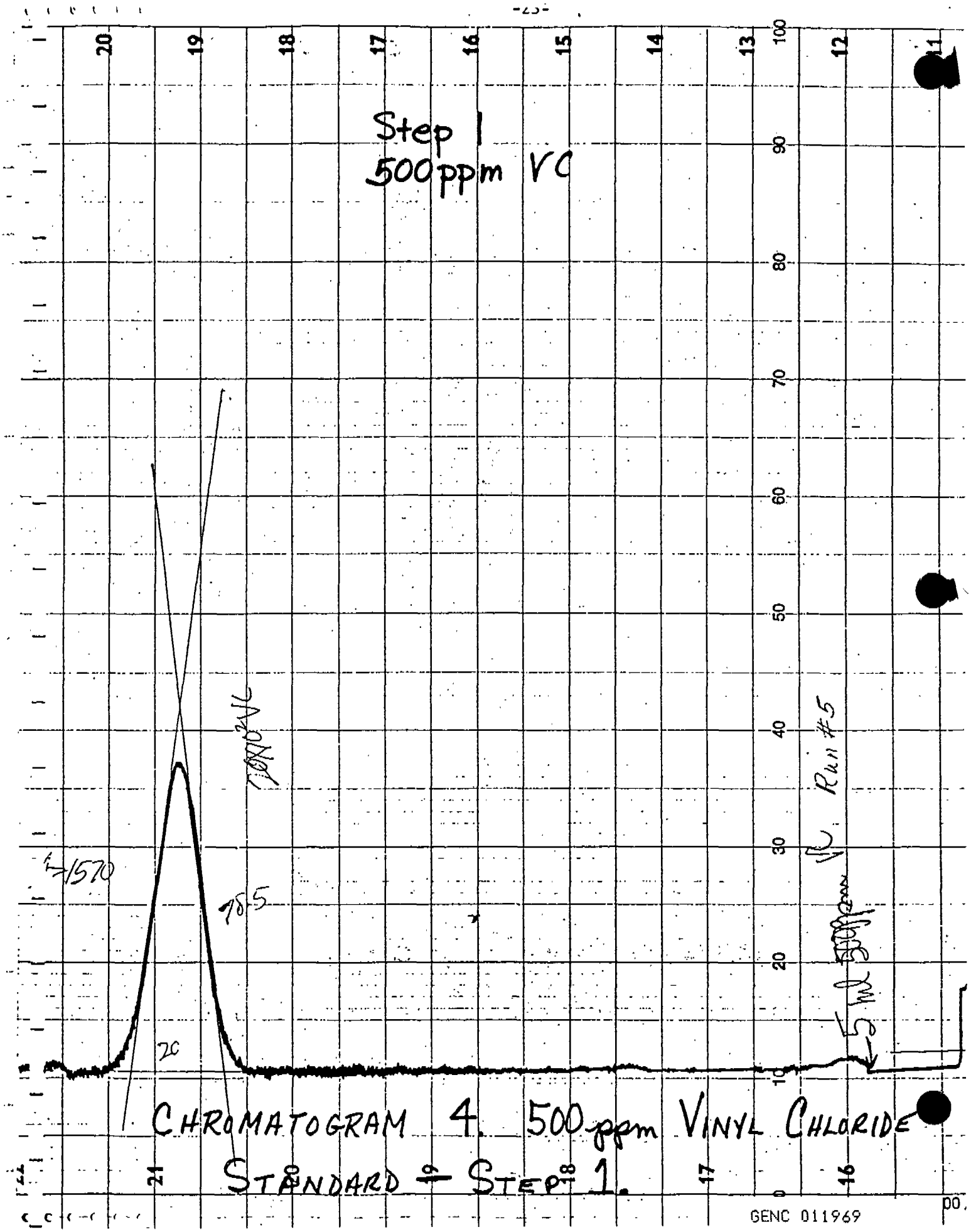
CHROMATOGRAM 6. 500 ppm VINYL CHLORIDE STANDARD - STEP 1.



CHROMATOGRAM 3. 5 ppm VINYL CHLORIDE STANDARD - STEP 1.

GENC 011968

Philips PR 4920/00



CHROMATOGRAM 4. 500 ppm VINYL CHLORIDE STANDARD - STEP 1.