

BUSINESS CONFIDENTIAL

PROJECT REPORT

VINYL CHLORIDE MONOMER:
USE OF MIRAN I PORTABLE INFRARED GAS ANALYZER
FOR CONTINUOUS AREA AIR ANALYSES

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SUMMARY The Miran I Portable Infrared Gas Analyzer can be used to continuously monitor for vinyl chloride monomer in air. With the instrument parameters chosen for the present work it was possible to determine concentrations in the 5 to 300 ppm range. While the manufacturer lists 0.7 ppm as the minimum detectable amount we feel that a more realistic value would be 1 to 2 ppm with the appropriate instrument settings.

The most serious problem in obtaining reliable results is caused by baseline drift. In field monitoring in the South Charleston Dispersion Vinyl Resins Unit it was found that daily adjustment of the baseline was necessary to maintain accuracy. A Miran II system, designed for such continuous monitoring, automatically and continuously corrects for such drift.

Polyethylene tubing was determined to be suitable for drawing sample for analysis from remote locations as distant as 100 feet.

Variation in moisture content of the sampled air could produce minor errors in the analysis. However, the error was small in 53 percent relative humidity air if calibration was done in 31 percent R.H. air.

Because of the urgent need for monitoring, we relied on interference data supplied with the Miran which indicated possible interferences from 20 compounds "likely" to be present in processes which use vinyl chloride. After the on-site investigation, some additional compounds were checked for possible interference. At the unit monitored vinyl acetate was used in some batches. We found it does interfere at 10.7 μ , so that, where both the chloride and the acetate were used, the vinyl chloride values will be high. In the range under 30 ppm, the response is equivalent; while over 30 ppm the response to the acetate is 50 to 60 percent of that due to the chloride.

INTRODUCTION With the recently recognized need for reducing exposure to vinyl chloride, a need has developed for continuous location

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monitoring in addition to personal sampling. Since infrared absorption is one of the most promising methods for air analysis for vinyl chloride monomer, and we had a Miran I Portable Infrared Gas Analyzer it was decided to evaluate this instrument for continuous area monitoring.

The Miran I Portable Infrared Gas Analyzer (Wilkes Scientific Corp.) was described recently in a report by J. E. Neff (1) who evaluated its use for methyl isocyanate monitoring. Being a single beam dispersive instrument it can be set at any wavelength within the range 2.5 to 14.5 μ or it can be used to scan the entire range. Thus, its operating principles are those of a typical infrared analyzer. Its uniqueness lies in the variable path gas cell provided which permits determination of chemicals in air in the parts per million range. In the list of compounds supplied by Wilkes which are amenable to IR analysis the minimum amount of vinyl chloride detectable with the Miran I is given as 0.7 ppm. A pump, supplied, can be used to draw sample air into the gas cell in order to monitor continuously for any contaminant.

This report gives the results of the laboratory investigation and discusses the use of the Miran I for continuous monitoring in the Dispersion Vinyl Resins Unit at the South Charleston plant.

The Laboratory Investigation

A. Calibration Curve

For an initial plant application where the vinyl chloride concentration variation was not known it was decided to choose instrument parameters such that a range of about 20 to several hundred ppm of vinyl chloride could be determined.

In the instrument, pictured in Figure 4, the black section on the left is the gas cell. The sample path length in the gas cell was set at 20 meters for the analysis and a 2.0 mm slit width was chosen. Standard samples were prepared in Saran bags by adding measured microliter quantities of pure vinyl chloride to known volumes of air. These standard samples were drawn into the evacuated infrared gas cell. A curve was prepared from the measured absorbance of vinyl chloride at 10.7 μ which covered the range of 10 to 300 ppm (Figure 1).

B. Remote Sampling

The infrared light source is a heated nichrome wire (820° C). For this reason the instrument is not intrinsically safe. Therefore, usage in a plant requires either some means to make it safe or operation in a non-hazardous area with sample tubing extended to remote areas where monitoring is desired. For an expedient solution we chose to use remote sampling for monitoring in the Dispersion Vinyl Resins Unit at South Charleston.

A 100 ft. length of 0.5 inch polyethylene tubing was tested for use as a sampling line in a total recycle system as shown in Figure 2. To determine if there was any loss of vinyl chloride by absorption or reaction on the polyethylene

after 1 ng contact the f ll wing sequence was foll wed:

1. A nominal 50 ppm vinyl chloride sample made by adding a calculated measured volume of the pure gas to a clean 20 liter Gas Cylinder and pressurizing with dry air to 300 psig was drawn into the evacuated Miran sample cell. A trans-mission reading of 78 percent was obtained indicating 48 ppm of vinyl chloride.
2. The entire system shown in Figure 2, pump, 100 ft. of tubing and cell was purged several times with this standard mixture. To do this the cell was evacuated and then filled to 0 psig with the standard sample. This was recirculated through the system including the polyethylene tubing to purge out the air in the pump and tubing. After several minutes circulation was stopped, the cell evacuated and the purge process was repeated. Readings obtained after successive purges were 78, 77.5, 78.0 per cent indicating steady state conditions.
3. Using the pump, a Neptune dyna-pump (Model 3) fitted with a teflon diaphragm, the standard sample was recycled in the system at 4.6 lpm for 65 minutes. A 79 percent transmittance indicating 46 ppm vinyl chloride was obtained. This indicates that there was essentially no loss of vinyl chloride in the polyethylene tubing.

Wall absorption for short term contact was tested as follows:

The polyethylene tubing and the Miran gas cell were evacuated. Then 10 ppm concentration of vinyl chloride in dry air was introduced at the remote end of the tubing. The instrument showed 12 ppm vinyl chloride, which was the same as was found by sampling without the 100 feet of tubing.

C. Effect of Moisture

To determine the effect of moisture, the instrument was set to 61 percent transmittance in dry air. Purging with room air, relative humidity (RH) 31 percent, changed the reading to 58 percent. With 53 percent relative humidity air the transmittance was 57 percent. The instrument was calibrated with room air of 31 percent relative humidity. We conclude that there is very little effect of moisture to 53 percent RH when calibration is made at 30 percent RH.

D. Interference

In the limited time available prior to the field monitoring, no attempt was made to determine possible interference at the 10.7 μ wavelength chosen. (This is the most sensitive band for vinyl chloride). We relied on a Wilkes Report

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(2) which discussed possible interferences. These are shown in table 2 for the predominant vinyl chloride bands.

Subsequent to the monitoring in the Dispersion Vinyl Resins Unit, a limited laboratory investigation showed interferences of some compounds associated with UCC vinyl chloride units. These are listed in table 3, together with absorption at 10.7 and 13.8 μ . From this it can be seen that vinyl acetate would interfere at 10.7 μ giving high vinyl chloride results, if present.

The extent of the vinyl acetate interference at 10.7 μ is shown in figure 5. For 200 ppm vinyl acetate, the calibration curve for vinyl chloride would show 105 ppm. At concentrations under 30 ppm the response is almost 1:1.

Field Monitoring

The instrument was transferred to the South Charleston plant where it was set up in the Dispersion Vinyl Resins Unit. The monitor was placed in the control room of Building 190 with 100 ft. of 0.5 in polyethylene tubing leading to a portable remote sampling probe placed in the unit. A filter at the probe served to keep dust out of the system. The monitor system shown in Figure 3, includes a carbon trap for providing ambient air free of vinyl chloride for instrument zeroing. The septum is useful for injecting known volumes of vinyl chloride for calibration.

Monitoring for vinyl chloride started on March 12 and was almost continuous until about May 3. Some of the Miran results are given in Table I along with gas chromatographic analyses on similar samples. Initially, there were brief excursions to higher levels of vinyl chloride during periods when filters were dumped, reactors were being steamed or dumped, charging lines washed, etc. The levels reached varied, with some of the earlier higher values being over 350 ppm vinyl chloride. On one such excursion where a Miran value of 250 ppm was obtained the TLV Sniffer (Bacharach Instruments) showed 240 ppm. More recently values above 50 ppm have been infrequent.

The only problem of consequence in the Miran I operation has been the instrument baseline drift. Daily adjustment has been necessary to maintain a reasonable degree of accuracy. The maximum drift produced values where the Miran read 10 ppm while gas chromatograph samples gave only 0.5 to 1 ppm.

DISCUSSIONS AND CONCLUSIONS The Miran I is a suitable instrument for monitoring for vinyl chloride in production units if the following factors are considered:

1. Not being intrinsically safe, it must be placed in a non-hazardous area and sampling done remotely using inert tubing.

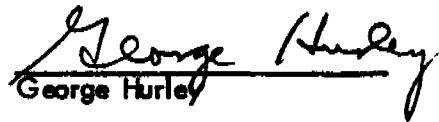
2. An absorption band must be chosen which will be free of interfering compounds.
3. Baseline drift must be corrected periodically - probably daily.

Under satisfactory conditions, it is sensitive to about 1 ppm and will perform reliably for continuous field monitoring.

For more permanent installations, the Miran II system should be used. Here, by virtue of having a double beam instrument, the effect of baseline drift is continually corrected. Also, the effect of one interfering element can be corrected by electronically cancelling its absorbance at the chosen wavelength. Results on the double beam instrument would be less effected by moisture on the salt window and dust on the mirror surfaces.

REFERENCES

1. Evaluation of the Wilkes Miran Infrared Portable Gas Analyzer for Determining Methyl Isocyanate and Other Compounds in Air, J. E. Neff, File No. 17992, Jan. 19, 1973.
2. Infrared Analysis of Vinyl Chloride at Concentrations Below 100 ppm, Application Report No. 4, Wilkes Scientific Corp.


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Attachments: 3 Tables, 5 Figures
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TABLE 1

VINYL CHLORIDE ANALYSES IN DISPERSION VINYL RESINS UNIT
AT SOUTH CHARLESTON

<u>Date</u>	<u>Sampling Point</u>	<u>Miran Anal. ppm</u>	<u>Gas Chrom. Anal., ppm</u>	<u>Remarks</u>
3-13	Standard	90	98	
3-13	Miran cell exit	0	2	
3-13	"	0	10	Miran zero drift effect
3-13	Miran probe in unit	0	2	
3-22	"	12	6	No Miran zero adjustment
3-13	"	0	3	for 3 days previous
3-14	Miran cell exit	12	18.4	
3-14	"	8	7.6	
3-14	"	10	5.7	
3-14	"	8	5.6	
3-14	"	10	7.1	
3-19		10	13	
3-19		10	12	
3-19		8	9	
3-19		6	7	
3-19		8	6	
3-19		6	6	
4-4	Control room air	5	3.3	
4-5	Control room air	7	6	
4-5	"	8	9.3	

TABLE 2

POSSIBLE INTERFERENCES WITH VINYL CHLORIDE ANALYSIS

Vinyl Chloride Analytical Bands				
Compound	6.15 μ	9.8 μ	10.7 μ	13.8 μ
Acrylonitrile			W	
Allyl Chloride			S	W
Chlorobromomethane				W
Chloroform				W
Ethylene		M	S	
Ethylene Dichloride				S
Freon - 11			W	
Freon - 12	W		S	
Freon - 13		S	M	W
Methacrylonitrile	W	W	S	W
Methyl Chloroform				S
Methylene Chloride		W		M
Methyl Methacrylate	W		W	
Perchloroethylene			S	
Styrene			M	
Tetrahydrofuran			M	
Trichloroethylene			M	
Toluene	W		W	S
Vinylidene Chloride	S			
Vinylidene Fluoride	S		S	

KEY: W= Weak, M= Medium, S= Strong

Wilkes data (ref. 2)

TABLE 3

MEASURED INTERFERENCES WITH VINYL CHLORIDE ANALYSIS

<u>COMPOUNDS</u>	<u>TRANSMISSION FOR 100 ppm</u>	
	<u>at 10.7 μ</u>	<u>at 13.8 μ</u>
Vinyl Acetate	70 %	99
Toluene	95	
Trichloethylene	32	
Acetone	92	
Methyl Ethyl Ketone	80	
Isopropanol	71	
(Vinyl Chloride	61	57)

20 meter path, 2 mm slit

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FIGURE 1

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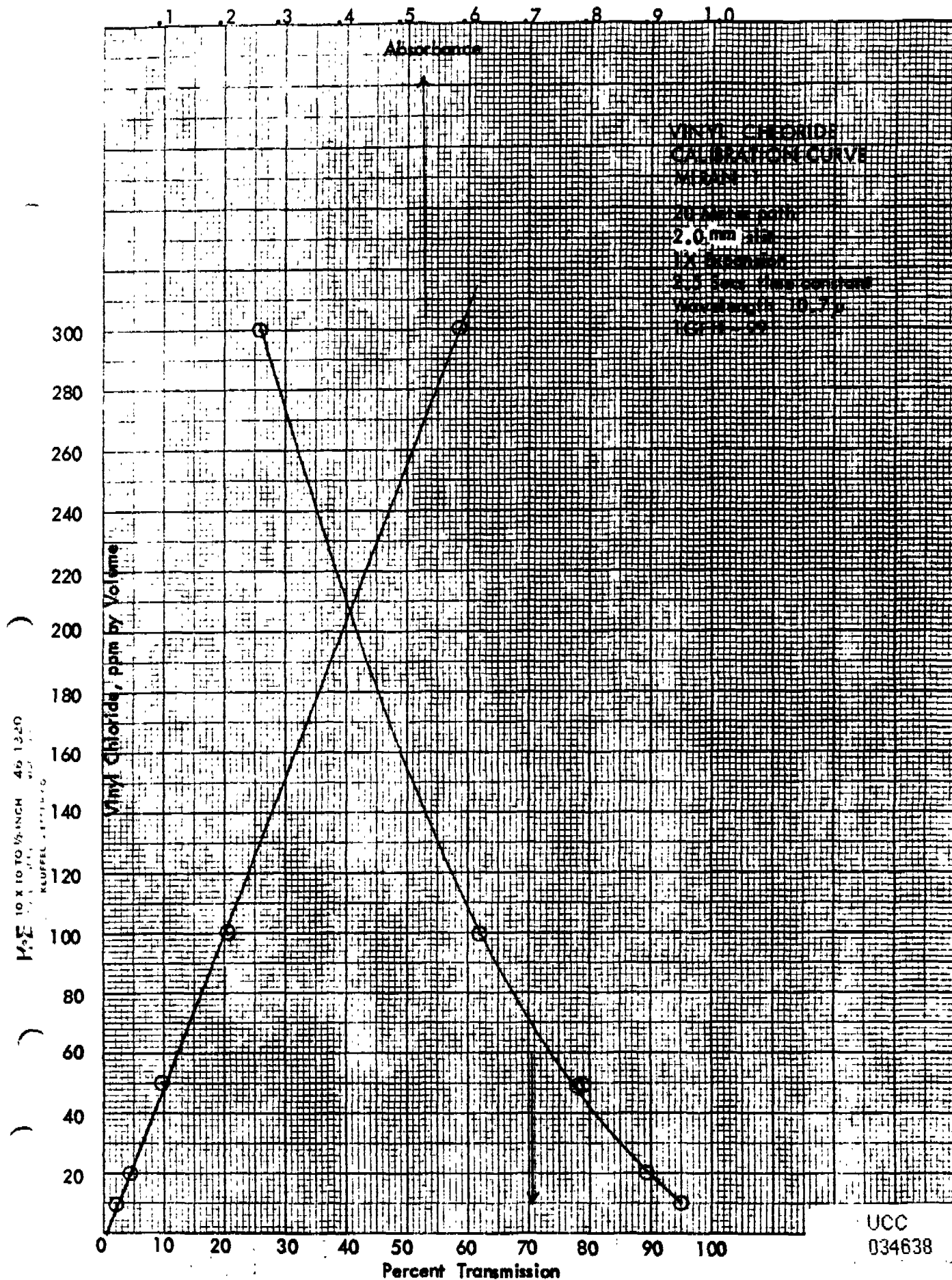


FIGURE 2

REMOTE SAMPLING TESTING

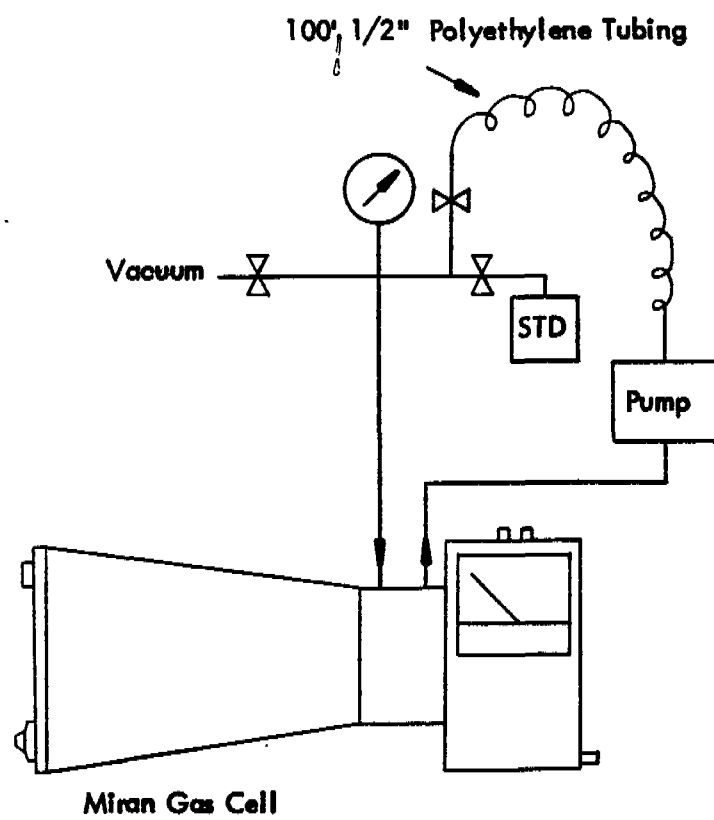


FIGURE 3
PLANT MONITORING SYSTEM

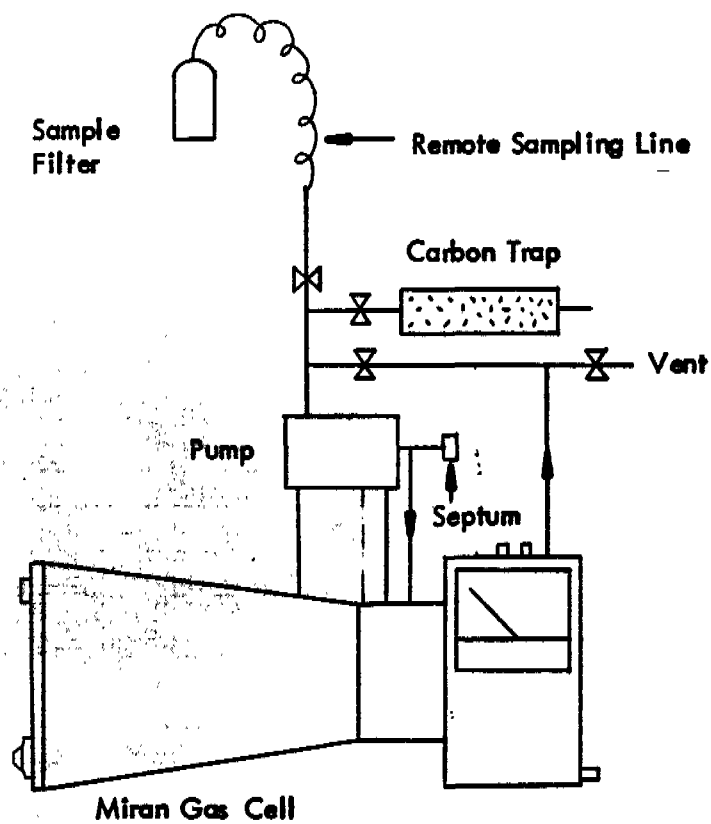


FIGURE 4

MIRAN 1 PORTABLE INFRARED
GAS ANALYZER

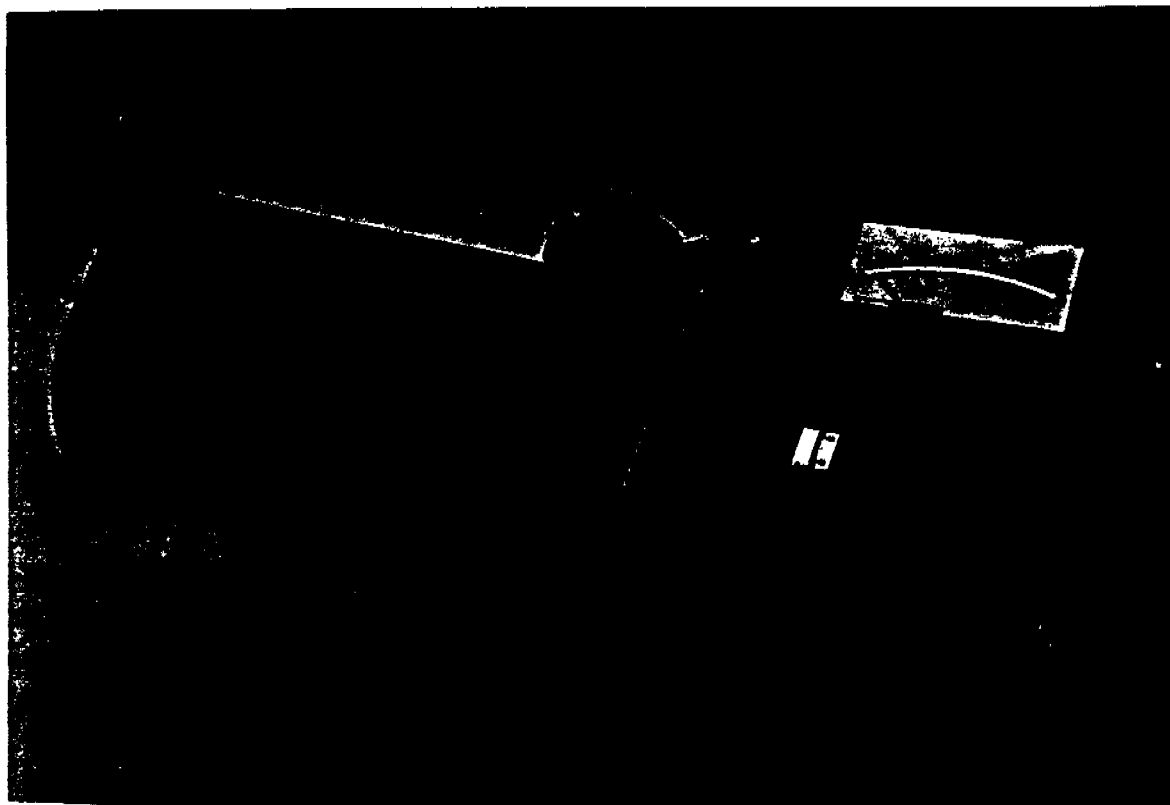
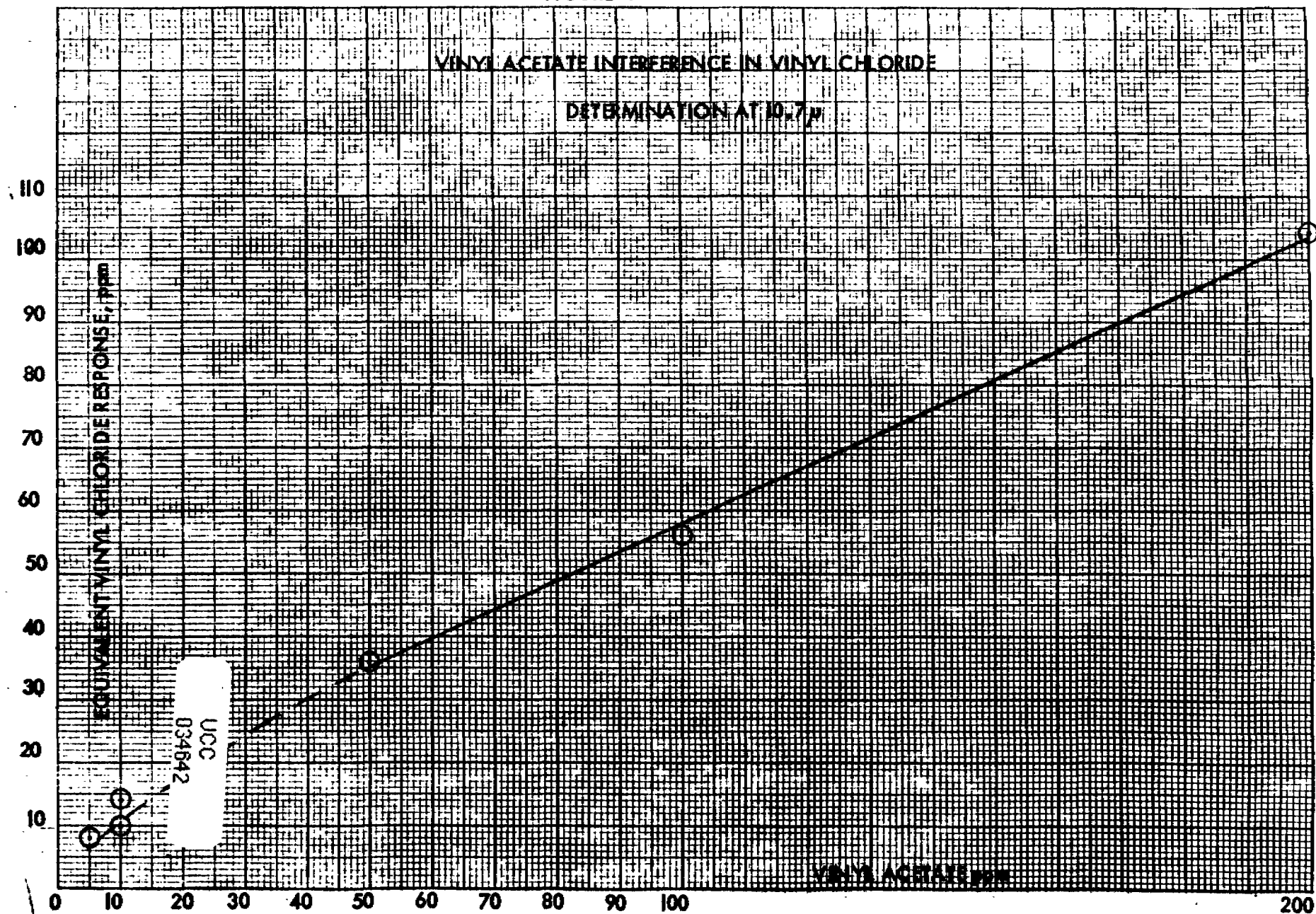


FIGURE 5



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