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BFG TECHNICAL DOCUMENT

BFGoodrich
Chemical Division

RESEARCH AND DEVELOPMENT REPORT

Vinyl Chloride Monomer Concentration in Working Environments as Related to the Residual Vinyl Chloride Monomer Concentration in Stripped Latex Products

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EXECUTIVE SUMMARY

OBJECTIVE

Develop technical information to support a business decision to remove cancer hazard labels from vinyl latex products.

SIGNIFICANT RESULTS

Test data were used to relate ambient vinyl chloride monomer (AVCM) concentrations to residual vinyl chloride monomer (RVCM) levels in [illegible] products. Worst case conditions were simulated. It was determined that exposure of workers to AVCM concentrations above the OSHA action level is unlikely in real workplace situations.

CONCLUSIONS

- In a typical Geon 578 compounding operation the AVCM concentration is estimated to be well below the OSHA action level.
- [illegible] at Rhinelander Paper Company, [illegible] clear coating operation, the [illegible] is estimated to be well below the
- [illegible] at Sanitas, who use [illegible] concentration is [illegible] action level.
- [illegible] different labs at [illegible] that the AVCM [illegible] the OSHA action level.
- [illegible] layer, has [illegible]

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SUMMARY

This report documents technical information that supports a business decision to remove cancer hazard labels from latex products containing vinyl chloride monomer. Controlled experiments in a closed, unventilated room relate ambient concentrations of vinyl chloride monomer (AVCM) to residual vinyl chloride monomer (RVCM) in stripped vinyl latexes. Commercial latex consuming operations have also been analyzed to estimate work place AVCM. Measurements were made by personnel monitoring in one of these operations. Our current standard of 25mg/kg maximum RVCM (wet basis) for vinyl latex products is well within the necessary limit for compliance to standards described by the Occupational Safety and Health Administration (OSHA).

Critical latex RVCM concentrations are defined. At the critical RVCM, the air in a closed, unventilated room will reach the OSHA action level, time weighted average (TWA), 95% confidence, in a 4 hour test period. Test results for three vinyl latexes are:

Latex	Latex Temperature, °F	Critical RVCM, mg/kg
Geon 576	110	22
Geon 450X20	110	38
Geon 352	110	>58

These results are translated to other vinyl latex products based on [illegible] partial pressure data. The assumption is made that [illegible] through the latex-air interface is the controlling [illegible] water loss assumption.

Plasticizer, [illegible]	Base Resin	Latex Temperature, °F	Calculated Critical RVCM, mg/kg
[illegible]	—	110	29
[illegible]	Geon 351	110	29
[illegible]	Geon 352	110	17

[illegible] calculated data, the critical RVCM is [illegible] plasticized latexes based on Geon 351 and [illegible]

[illegible]	[illegible]	Geon 352	110	29
[illegible]	[illegible]	Geon 352	110	29

Obviously, current stripping practices in [illegible] are sufficient to keep our vinyl latex products below [illegible] limit. The product specifications for Geon 576 and [illegible] could be changed to 15mg/kg and 15mg/kg maximum RVCM respectively.

A typical Geon 576 compounding operation was modelled. At up to 40mg/kg RVCM, the OSHA action level is not exceeded where ordinary industrial ventilation is provided, viz., 6 turnovers per hour.

A coating operation at Rhinelander Paper Co. was analyzed. A clear coating of Geon 576 at 70mg/kg RVCM will not create non compliance AVCM concentrations even if all the RVCM transfers to the air between the coater and the ovens. This again assumes ordinary industrial ventilation. At 22mg/kg RVCM, the AVCM is about 0.10 ppm using the same assumptions.

Both the BFGoodrich Corporate Environmental Health Laboratory and Wausau Insurance Companies, a private environmental health engineering service laboratory, confirmed AVCM concentrations at Rhinelander to be well under the OSHA action level.

Saniflex coats paper with two different pigmented Geon 580X52 compounds. The base coat and the top coat are applied in a single pass through the coating and drying system. We have estimated that the OSHA AVCM concentration limit is reached with Geon 580X52 at 25mg/kg [illegible] when all of the [illegible] of the [illegible] every [illegible].

DISCUSSION

Introduction

In October 1974, the Occupational Safety and Health Administration (OSHA) published a safety and health standard concerning exposure of industrial workers to vinyl chloride monomer (VCM). This standard set a permissible exposure limit of 1 ppm by volume in air as a time weighted average (TWA) over an 8 hour period. Excursions up to 5 ppm are permitted over a period not to exceed 15 minutes. The standard is written for, but not limited to, employers who handle VCM. Employers in the fabricating industry are also subject to the standard where exposures approach the permissible limits. Employers handling or using fabricated products are excluded from the standard based on the absence of "adequate evidence of exposure to vinyl chloride in these operations." A fabricated product is defined as a product made wholly or partly from PVC which does not require further processing at temperatures, and at times, sufficient to cause mass melting of the PVC. In many applications latex may be considered a fabricated product and therefore the user can be excluded from the standard. Where latex may be considered as being used in the fabricating industry, exposures are not likely to approach the permissible limits.

OSHA describes an "action level" at 1/2 the permissible exposure limit, viz. 0.5 ppm TWA over an 8 hour period. Initial [illegible] where vinyl chloride is used [illegible] product or [illegible] containing PVC are fabricated. [illegible] only where levels are measured [illegible] Monitoring may be [illegible] 5 days apart show [illegible] if the employer [illegible] 95%

[illegible]

0.25 [illegible]
0.5 [illegible]
>1. [illegible]

[illegible] is the action level to [illegible]

1) [illegible]

2) [illegible]

2112003

3) provide medical surveillance on workers

4) post signs and labels

5) limit access to regulated areas

All of these requirements add expense to manufacturing operations. The expense can be avoided only by eliminating vinyl chloride or by showing that the concentration of vinyl chloride in the working environment cannot be greater than 0.5 ppm TWA for 8 hours.

OSHA states in their written standard that exemptions on the basis of residual vinyl chloride in a polymer are "not justified nor necessary". Employers are given the opportunity to "discontinue many duties" upon a showing of no exposures above the action level.

The purpose of this work is to provide objective laboratory data to support what we already know: vinyl latexes stripped to 25mg/kg RVCM (wet basis) can be handled, where ordinary industrial ventilation is in operation, without the liklihood of exposing workers to ambient VCM concentrations above the OSHA defined action level. With such objective laboratory data, the management of the Latex Division can support a business decision to remove cancer hazard labels from vinyl latex products. It is suspected that these labels are unnecessarily inhibiting sales of labeled latex products.

II. Residual Vinyl Chloride Monomer (RVCM) Stripped Latex Products

Vinyl latex [redacted] polymerized to maximum conversion consistent with [redacted] chemical stability and good reactor [redacted] VCM [redacted] remains at the [redacted] is reduced by [redacted] the [redacted] compl[redacted] solutions we begin to attack [redacted] base[redacted] the containers. The containers begin to coll[redacted] [redacted] of [redacted] pers[redacted] cancer [redacted] for vinyl [redacted] the problem.

We have made continuous efforts since 1975 to improve stripping operations in the plants by process studies and by capital improvements. We are now able to routinely produce vinyl latex products at RVCM contents of 25mg/kg (wet basis) maximum. There is one exception, Geon 350X2, is a latex stabilized by a heat sensitive emulsifier system that cannot be stripped in the conventional manner. This product is sold to only one customer. It is acceptable to this customer at a specified RVCM content of 250mg/kg. They are able to handle the latex without OSHA compliance problems.

Plant stripping experience for most of 1980 is summarized in Table I. The average RVCM level is well below the specification level of [illegible] mg/kg for all the major products.

TABLE I

[illegible] - RVCM, MB/RG - MAJOR PRODUCTS

	576	800X119	580X158	460X6 460X9	460X45 460X46	590X4	652
	7.8	6.6	7.0				
	61	60	6				
	[illegible]	3-10	4-9				
	[illegible]	[illegible]	10.1	5.5	9.9	3.7	12.1
	[illegible]	[illegible]	27	32	6	10	30
	[illegible]	[illegible]	4-22	0-14	3-18	0-11	0-32

III. Experimental Plan

A plan was developed which could allow us to relate AVCM concentrations to RVCM concentrations in the latex. Three latex products were chosen for this study: 1) Geon 352, our highest volume vinyl chloride resin latex, 2) Geon 576, our highest volume externally plasticized vinyl chloride resin latex, and 3) Geon 450X20, a high solids, internally plasticized, acrylic modified vinyl chloride latex. The original data set of 12 experiments included the three latexes at two latex temperatures (72°F and 110°F) and at two RVCM levels (as obtained from the plant and after adding a measured quantity of VCM.) The original set was later extended in efforts to improve the quality of the data correlation. A detailed description of the experimental procedure follows in the next section.

IV. Procedure - R. E. Shaffer

A. Latex Spiking

A 12 gallon aq Geon 576, Lot 2005139, was charged to a 15 gallon reactor. The reactor was sealed and the latex stirred at [illegible] rpm.

[illegible]

D. **Pump Calibrations**

The pumps were calibrated by personnel from the ALTC environmental group to provide an air flow rate through the charcoal tubes of ≈15 cc/min. The flow rate was increased to 50 cc/minute for the 15th through the 20th experimental runs where glass disposable charcoal sampling tubes from the Mine Safety Appliance Corporation were used in place of the s.s. tubes.

E. **Air Sampling Pump Locations**

1. For four hours preceding a latex run, duplicate "blank" air samples were taken in the closed work area. Two pumps were placed on a lab bench approximately 3.7 inches off the floor and about 1 foot from the wall.

2. During the 4 hours of a latex test, two pumps were placed side by side 37 inches off the floor and within 2 inches of the wall. Two pumps were placed in the center of the room 37 inches off the floor and directly over the latex. One more pump (4 total) was placed 57 inches off the floor directly over the latex. Silastic tubing was connected to the [illegible] of the pumps. The air [illegible] tubes were [illegible] before each use by [illegible] hours of [illegible] running with nitrogen. [illegible] at 250°C. [illegible] eliminated.

3. [illegible] were taken, a pail of [illegible] placed on the floor in [illegible] used to provide good [illegible] latex agitated, [illegible] latex and room temperature [illegible] sampler with tubes [illegible]

7. After 4 hours the pumps were turned off, temperatures were recorded and another 4 oz. latex sample was taken.

8. The latex samples were analyzed at ALGCP for residual vinyl chloride by gas chromatography. The analyses are routinely done there (BFG Proc. No. 1005-E).

9. The charcoal tubes were analyzed for VCM at ALTC by Pete Dymterko. The thermal exhaustion technique was used for the analysis. The analysis results were converted to ambient vinyl chloride concentration (AVCM) based upon the pumping rate, the time and the VCM adsorbed.

10. The test area was ventilated for ~16 hours before collecting more "blank" samples. Latex testing conditions were, 1) spiked with VCM, 2) as received, 3) 110°F latex temperature, 4) room temperature. The air was at room temperature for all the experiments.

A schematic diagram of the experimental apparatus is shown in Fig. 1.

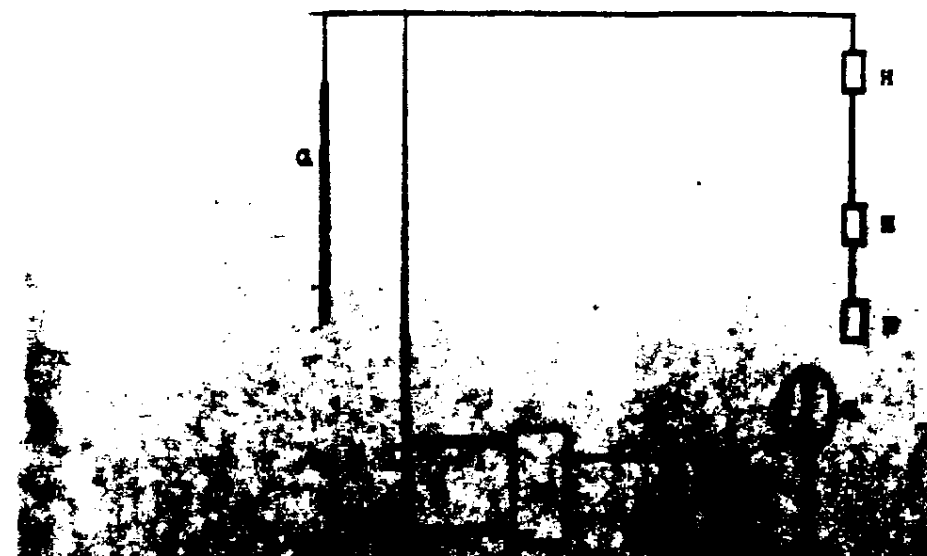
G. Special Test--Controlled VCM Release

1. Data from the charcoal tube analyses were not as reproducible as expected, so after run #8, a different experiment was tried. A cylinder of VCM was put in the test area and a small, known amount of VCM was metered continuously at a constant rate into the closed room for 4 hours. Six charcoal collection tubes and pumps were placed in the usual locations. These data are [illegible] the tubing between tests #8 and #9. This [illegible] by Pete Dymterko.

H. [illegible]

I. Run #[illegible] a thick film over the latex start[illegible] the end of the 4 hour test there [illegible] of clear latex surface visible. [illegible] with foam and polymer. Later [illegible] index increased to 34.6% T.S. [illegible] reduced shining.

[illegible] temperature, some of the Bendix [illegible] used from test #15 [illegible] incremented on test #19.


R
E
B
A

3. During test #7, 352 at 110°F, one of the heating elements apparently overheated and started to decompose some polymer. The test area filled with smoke. A considerable amount of smoke was detected in adjoining rooms as well. This test was stopped after 195 minutes. The tubes were later analysed as in other tests.

Glass charcoal sampling tubes from Mine Safety Appliance Corporation were used for tests #15 through #20. These replaced the stainless steel collection tubes used through test #14. Carbon disulfide extraction replaced thermal [illegible] as an analytical technique. The data are recorded in Table XII.

Experimental data are in books 911-83 pages 128 - 161 and [illegible] pages 3 - 18.

Table II Test Data: MVCH and AVCH, Closed Room Experiments

Duplicate Blanks				Duplicate Samples of Later Experiments											
Lab Bench [illegible]				Room Perimeter, 37" High			Room Center, 60" High			Room Corner, 37" High					
Tot Air Vol,cu	Tot Mixed Gas VCH	ppm VCH Reported	Air Temp, °F Start/ Finish	Tot Air Vol,cu	Tot Mixed Gas VCH	ppm VCH Reported	Tot Air Vol,cu	Tot Mixed Gas VCH	ppm VCH Reported	Tot Air Vol,cu	Tot Mixed Gas VCH	ppm VCH Reported	Later [illegible] Start/ Finish	[illegible]	Tot [illegible] Air Run Start/ Later
3774	[illegible]	[illegible]	70 77	3866	13.90	1.11	3680	.377	.06	3336	5.301	62	110 111	[illegible]	250 240
3660	[illegible]	[illegible]		3866	16.07	1.00	3516	7.94	.07	3496	9.339	1.07			
3357	.[illegible]	[illegible]	70 70.5	3256	17.06	2.12	3626	11.60	1.27	3447	.444	05	60 72.5	[illegible]	241 245
3430	.[illegible]	[illegible]		3106	1.126	.10	3334	1.016	.13	3530	2.773	.31			
3531	.300	.07	70 70	3430	.006	.10	3567	.520	.06	3364	.009	.01	110 111	[illegible]	.240 .242
3663	.000	.01		3026	.061	.10	3416	.560	.07	3400	0302	.004			
3169	-	.00	70 77	3503	1.400	.10	3270	1.252	.10	3253	Lost	-	72 73	[illegible]	40 241
3000	.511	.05		3500	1.210	.14	3105	1.116	.10	3100	.047	.22			
3216	.011	.006	70 70	3442	3.213	.30	3160	.994	.12	3442	1.049	.21	115 110	[illegible]	240 240
3252	.001	.11		3130	2.10	.24	3336	1.605	.10	3330	.611	.07			
			74 70	3300	1.000	.13	3004	.750	.09			.10	74 74	[illegible]	[illegible]
3270	.3000	.00		3300	1.300	.16	3400	1.179	.13	3432	1.600	-			
		.02	70 70			-	2700	.132	.00	2700	.200	.00	110 100	[illegible]	240 195
3300	.206	-		3006	.327	.00	2770	.2010	.00	3625	.313	.00		[illegible]	
3616	.200	.00	70 70	3016	5.704	.71	3432	13.06	1.6	3062	2.006	.32	76 75	[illegible]	.00 240
3433	.039	.00		3076	2.300	.31	3260	5.04	.61	3432	.207	.02		[illegible]	
3306	1.30	.16	74 70	3306	.070	.07	3216	1.200	.15	3076	.900	.11			.00 240
3400	.413	.00		3216	1.030	.13	3260	1.530	.10	3260	6.014	.50			
3216	.50	.00	74 77	3216	1.044	.13	3200	.020	.11	3216	1.200	.00	110 110	[illegible]	240 243
3264	.304	.04		3260	3.370	.41	3200	1.003	.20	3260	1.30	.16		[illegible]	
3216	.12	.02	73 74	3264	.110	.01	3216	10.00	2.20	3216	9.004	1.11	73 73	[illegible]	240 240
3276	.044	.11		3206	15.36	1.77	3260	7.007	.93	3260	7.05	.00		[illegible]	
3306	.720	.00	00 00	3260	.007	.003				3264	3.041	.36	110 111	[illegible]	.00 240
3300	.000	.00		3020	5.317	.05	3300	2.700	.22	3256	7.003	.01			
3576	.300	.04	70 70	3260	10.07	1.20	3216	2.006	.30	3406	6.063	.52	75 75	[illegible]	240 240
3576	.702	.00		3260	.527	.00	3076	3.374	.37	3260	4.515	.00			
3216	.000	.01	74 77	3216	1.002	.12	3262	2.517	.30	3400	1.399	.10	72 [illegible]	[illegible]	.01 240
3264	.340	.04		3264	.300	.04	3230	1.167	.14	3260	2.224	.27			
3264	.230	.03	74 70	3264	7.300	.00	3260	6.700	.02	3200	13.35	1.56	[illegible]	[illegible]	[illegible]
3250	.530	.07		3000	15.03	1.00	3062	.670	.00	3026	.377	.00			
			74 76												
11760	2.574	.11	74 75	12000	1.02	.00	11760	6.067	.16	12000	10.120	.11		[illegible]	.240
12000	4.030	.13		11260	5.005	.21	12000	6.443	.15	12000	8.290	.20			
11200	.000	.02	73 75	11760	15.000	.02	12000	13.004	.44	-	-	-	[illegible]	[illegible]	[illegible] .240
12000	.305	.02		12000	18.002	.01	11760	13.070	.05	12000	15.077	.51			
		.01	72 76	12000	27.001	.00	12000	15.000	.52	10760	25.321	.04	[illegible]	[illegible]	[illegible] .240
12000	.100	-		12000	17.700	.05	12000	19.004	.62	12000	24.017	.00			
11760	1.251	.04	74 75	12000	4.705	.16	12000	7.700	.20	12000	5.007	.20	72 72	[illegible]	.240 .240
11200	.074	.03		11700	7.035	.27	12000	4.050	.16	11200	9.110	.17			
11000	.007	.003	74 76	11000	6.242	.21	11240	3.612	.12	11760	6.772	.16	114 113	[illegible]	.240 .240
		0		12000	5.005	.16	12000	4.000	.14	11760	7.002	.27			

V. Testing--Air Sample Tubes - Peter Dmyterko

A. Analysis for Vinyl Chloride

Standard environmental testing techniques were used to measure the concentration of vinyl chloride (VCM) in the air. Air sampling was accomplished by passing the air through charcoal collection tubes for four hours at a known flow rate. The VCM in the air was adsorbed on to the charcoal as the air was drawn through the tubes by a vacuum pump. The VCM level collected on the charcoal was then determined by one of the two following analytical procedures. In the first procedure, the VCM was thermally desorbed from the charcoal using a Bendix Flasher Unit and analyzed by flame ionization chromatography. The second procedure involved desorbing the VCM from the charcoal with carbon disulfide before gas chromatography analysis. The ppm levels of VCM in the air were then calculated from the micrograms of VCM found on a set of tubes and the volume of air sampled.

B. Sampling Procedure

The detailed procedure for sampling the VCM in air using charcoal tubes is presented in [illegible] Sampling Procedure No. [illegible] [illegible] flow and [illegible] sampling [illegible] VCM [illegible] [illegible] Collection [illegible] [illegible] [illegible] preconditioning by the [illegible] and the [illegible] sealed to prevent contamination. The seals at the [illegible] tubes are broken [illegible] before the tubes are to be used for sampling.

[illegible]

[illegible] sampling.

Two tubes in series were used at each sample point. Most of the VCM was adsorbed by the charcoal in the first, and the second tube was present to collect any VCM not adsorbed by the first tube. The pump used to draw air through the tubes was a Bendix Micronair II Air Sampling Pump, a low flow rate battery operated pump.

Before sampling was started, it was necessary to calibrate through each tube set and pump used at the various sampling points. The calibration was performed by the long term six hour exposure technique described in Section VII of Procedure 2506-A. First, the charge on the pump was checked and then the pump was turned on for 15 minutes to warm it up. Next, the pump was attached to the flow rate calibration assembly together with the two conditioned collection tubes in series (see figure in Procedure 2506-A). The breathing air was turned on to the calibration assembly. The flow rate through the tubes adjusted to 7.5 to 15 cc/min. by regulating the speed of the pump with the pump flow rate screw. A soap film flowmeter and a stop watch were used to measure the exact flow rate through the tubes. After the calibration was completed, the pump was stopped and the tubes were disconnected from the calibration assembly and attached directly to the pump.

The pumps and tubes were then placed in the area to be sampled and the pumps were started. The starting time was recorded [illegible] hours of sampling, the final flow rate was [illegible] were stopped and the final time [illegible] the change flow rate [illegible] time were calculated [illegible] was obtained by multiplying [illegible] the total sampling time.

[illegible]

In this [illegible] were [illegible] through [illegible] The flowrate [illegible] step of the analysis. [illegible]

two minutes in order to desorb the VCM from the charcoal. While this step was performed, the tube was isolated from the rest of the system. Next, the flasher was placed in the "inject" mode of operation permitting carrier gas to pass through the tube. The VCM was flash/desorbed from the charcoal and was carried on to a gas chromatography column in the chromatograph. After this column separated the VCM from other organics in the sample, the VCM was detected by a flame ionization detector. The area of the VCM peak produced was measured by an integrator. The VCM peak area was multiplied by a calibration factor to convert it to micrograms of VCM via the External Calibration Procedure. The micrograms of VCM on both tubes in a sampling were combined to obtain the total micrograms of VCM. Finally, the ppm levels of VCM in the air was calculated using the micrograms of VCM on the tubes and the volume of air sampled, using a formula found in Section 8 of Procedure No. 7821-A.

The gas chromatographic conditions used in the thermal desorption procedure are listed in Table III.

Table III

Gas Chromatography Conditions for the Thermal Desorption VCM Analysis

Gas Chromatograph	=	Hewlett and Packard (H&P) 5720A Gas Chromatography with H&P Model 18708A Electrometer and H&P 18791A oven control, flame ionization detector
Integrator	=	H&P 3388A integrator
Column	=	2 ft x 6 ft x 1/8 inch O.D. stainless steel column packed with Porapak QS 80/100 mesh (Waters Co.)
[illegible]	=	Nitrogen
[illegible]	=	150°C
[illegible]	=	[illegible] cc/min.

[illegible] and 6 ft sections of the column [illegible] valve. When the valve was in the [illegible] were connected in series permitting [illegible] sections and to the detector. [illegible] high boiling components [illegible] were forward flushed to the atmosphere, [illegible] the 6 ft section was also main- [illegible] an independent source of carrier gas.

[illegible] employed on the H&P 3388A Integrator:

[illegible] Standard Technique

[illegible] 5.0 minutes.

[illegible] was started.

The Procedure for calibrating the analysis is described in Section VIII of Procedure No. 1021-A. The method involves loading conditioned collection tubes with known levels of VCM from calibration gas mixtures. To calibrate a tube, it is connected to the calibration gas mixture, and the gas mixture is allowed to flow through the tube while the VCM in the gas mixture is adsorbed on to the charcoal. The flow rate through the tube and total time the tube is exposed to the gas mixture are measured. Flow rates were typically in the range of 30 to 40 cc/min and total exposure times were in the order of 4 to 10 minutes. The micrograms of VCM adsorbed by the tube is calculated from the flow rate, exposure time and concentration of VCM in the gas mixture. The flow rate through the tubes was measured by means of a soap bubble flow meter and a stopwatch. The calibration was performed with certified gas mixtures (Matheson Co.) containing: 1.09 ppm, 10.2 ppm and 105.9 ppm VCM in air. Duplicate tubes were loaded at the following approximate levels of VCM: 1 µgm, 4 µgm and 40 µgms of VCM. The tubes were analysed for VCM using the thermal desorption procedure described above and the area for the VCM peak was obtained. A calibration factor for each tube was calculated by dividing the micrograms of VCM on the tube by the VCM peak area. An overall calibration factor was obtained by averaging the factors obtained for all the tubes loaded. The response factors were found to be linear over the calibration range.

In some of the tube, impurity peaks were close enough to VCM peak to prevent full baseline resolution of the VCM peak. In these cases, the [redacted] employed a built-in computer program to determine the [redacted] VCM peak. When this situation occurred for a [redacted] "Interference" was indicated just after the data for [redacted] the data sheets.

In [redacted] whether other components were present [redacted] the VCM peak. The presence of other components under [redacted] would cause an error on the high side for the [redacted] sample. There was no indication [redacted], however.

Occasionally [redacted] results were obtained for one set out of [redacted] which were sampling the same area over the same [redacted] thorough check of the analytical system indicated [redacted] was not related to chromatography analysis. [redacted] problem was never observed during the analysis of [redacted] during the calibration of the analysis. The cause of this problem has not been determined.

D. Carbon Disulfide Desorption Analysis For VCM

The second procedure used in the analysis of VCM adsorbed on the charcoal tubes was the carbon disulfide desorption technique. The method employed was a modification of NIOSH Method No. P&CAM 178, "Vinyl Chloride in Air" (see Appendix). The modifications in the column used and the calibration procedure were based on recommendations of the Corporate Environmental Lab at BFG Research and Development Center.

The analysis is conducted by first desorbing the VCM on the charcoal in carbon desulfide. The charcoal contents of the glass collection tubes were placed into 2 cc glass vials (Wheaton Co.,223682). Then, 1 cc of carbon disulfide (Fisher Co, SC-182) was pipetted into each vial. The vial contents were next crimp sealed with aluminum caps containing a teflon coated rubber seal. Finally, the sample vials were agitated for 1/2 hour at room temperature on an SKC Charcoal Desorber.

Next, one microliter of the carbon disulfide phase of the vials was analyzed by flame ionization chromatography using [illegible] listed in Table IV. An automatic sampler [illegible] from the [illegible] was [illegible] flame ionization detector was determined by [illegible] linear signal [illegible]

[illegible]

Table IV

Chromatography Conditions for VCM
Analysis by the CS_2 Desorption Technique

Chromatograph	=	H & P 7620A Flame ionisation chromatograph
Detector	=	Flame ionisation detector
Integrator	=	Perkin Elmer Sigma 10 Data System
Column	=	20 ft x 1/8 inch O.D. x stainless steel x 10% SP1000 on Supelcoport 80/100 mesh
[illegible]	=	80°C, isothermal
[illegible]	=	250°C
[illegible]	=	250°C
[illegible]	=	30 cc/min
[illegible]	=	[illegible]

The analysis was calibrated by first loading duplicate glass charcoal tubes at the following VCM levels: 1 µgm, 4 µgm, and 40 µgm VCM. The loading procedure used was identical to that described in the calibration procedure for the thermal desorption method. The charcoal in each of these standard tubes was then desorbed in small vials with carbon disulfide as described above. Duplicate analyses were performed on each vial using the above chromatography procedure. The two VCM peak areas obtained for each vial were averaged to obtain the peak area for the standard. A calibration factor for each standard was calculated by dividing the micrograms of VCM loaded on the tube by the average area obtained from the analysis of the standard. An overall calibration factor was determined by averaging the factors for all the individual standards. The calibration was found to be linear over the range of 1 to 40 micrograms of VCM.

At times during the analysis of a series of vials, some drifting of the calibration factor was observed. This problem was found to be related to the use of nickel jets in the flame ionization detector. The carbon disulfide was reacting with the nickel in the jets to form nickel sulfide which tended to coke up the jets. Standards were spaced at intervals throughout the series to compensate for this problem. Eventually, this problem was solved by replacing the nickel jets with stainless steel jets which [illegible]

VI. Data Analysis

[illegible] of Table II, [illegible] of [illegible] evaluation [illegible] data are [illegible] for test #1, [illegible] are omitted, the [illegible] concentration is 0.636 ppm and [illegible]

[illegible] are summarized in Figure 2. One [illegible] were lost. AVCM [illegible] averaging the six air sample test [illegible] closed room test. The AVCM concentration was taken as the average between the test result at the beginning and at the end of a closed room test. There is considerable scatter in the data. Results for [illegible] are particularly poor in agreement with other results.

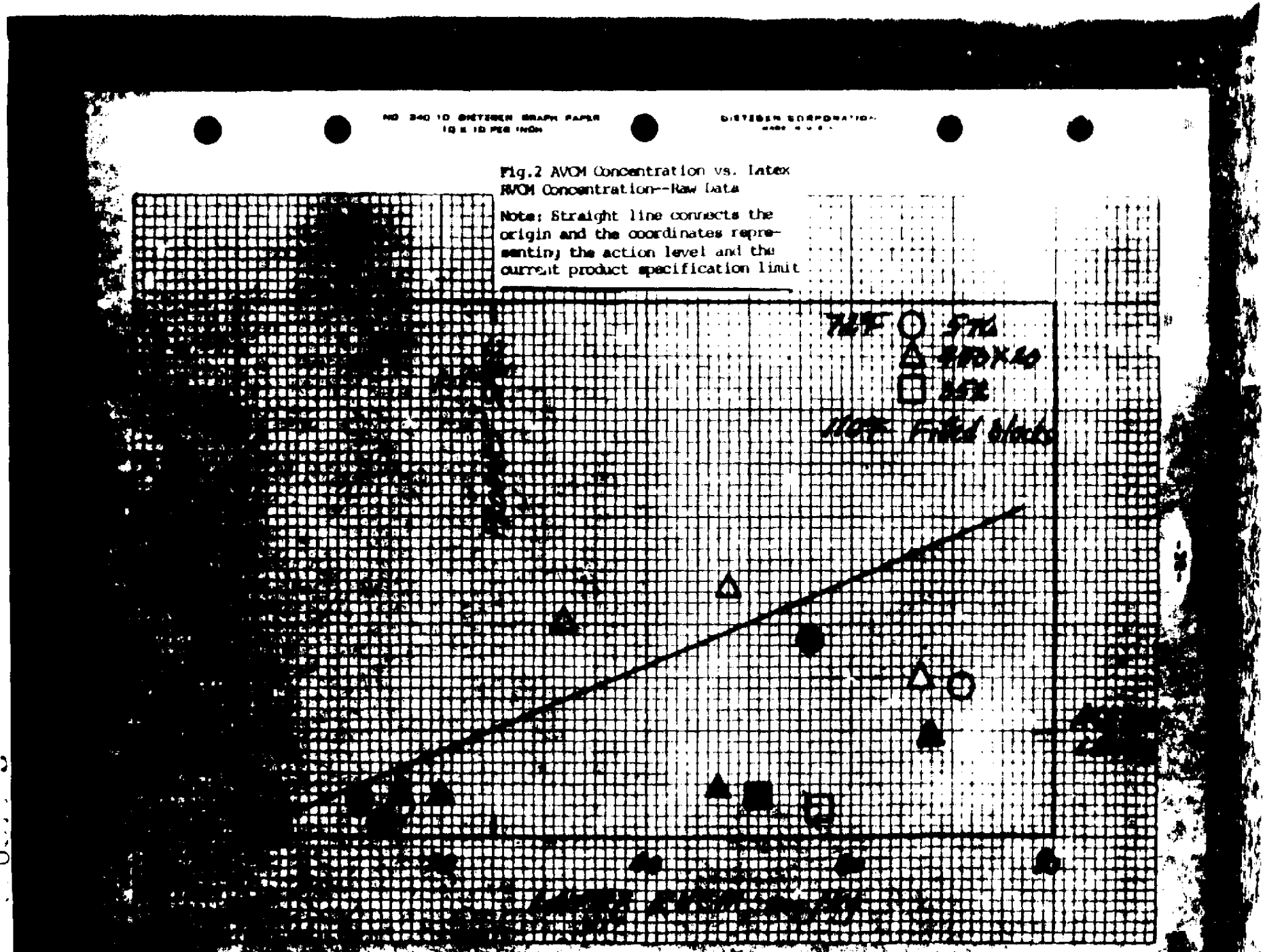


Fig.2 AVOM Concentration vs. Latex
AVOM Concentration--Raw Data

Note: Straight line connects the origin and the coordinates representing the action level and the current product specification limit

Data were submitted to the Statistics and Computer Group for analysis. Details of this analysis are shown in the Appendix. Critical RVCM levels were determined for the three latexes tested. The action level is assured with 95% confidence at 0.5 ppm AVCM if the VCM concentration in the air is 0.33 ppm. The level of 0.33 ppm, therefore, was used in the correlation to determine the critical RVCM concentration in the latex. Results are summarized in Table VI. As explained in the statistical report only 54 of the air sample test results were used; 14 were rejected because carbon tube loadings were out of the range for good accuracy; 4 were rejected because of interference with VCM in the GC analysis.

TABLE VI

Critical Levels of RVCM in Vinyl Latexes--
Closed Room with No Ventilation

Latex	Temperature, °F	Critical RVCM, mg/kg (wet basis) (relates to 0.33 ppm AVCM in 4 hours)
Geon 576	72	53
Geon 576	110	22
Geon 450X20	72	27
Geon 450X20	110	38
Geon 352	72	>50
Geon 352	110	>50

It may be concluded from these results that, under worst case conditions, our vinyl latex products as currently manufactured can be used by formulators without the added manufacturing expense associated with [illegible] requirements. The worst case conditions [illegible]

[illegible] closed working environment, [illegible] of Geon 576 at 110°F, the [illegible] product specification maximum of 25 mg/kg. [illegible], however, since: 1) Geon 576 is [illegible] to Geon 352 base resin; the base [illegible] equilibrating to 25 mg/kg, 2) none [illegible] In [illegible] Table I was at a RVCM [illegible] 3) these experiments are a worst [illegible] for externally plasticized [illegible] effect of dilution of

[illegible] Geon 450X20 at 110°F [illegible] is not physically possible [illegible] for the equilibrium [illegible] pressure increases with [illegible] may be higher at [illegible] of AVCM in [illegible] higher by some unknown [illegible] temperature or by test error. [illegible] more experimental work [illegible] this is not necessary to achieve [illegible]

VII. Translation of Critical RVCM Data to Other Vinyl Latex Products

When the lid is removed from a container of vinyl latex, VCM concentration gradients are created. This causes diffusion of the monomer to occur. There are several steps in series that the monomer must take in the diffusion process. Picture latex in a closed container. The system is in static equilibrium. The monomer is distributed between the phases: polymer, water, and vapor. The concentration in each of the phases depends upon the solubility of vinyl chloride in the polymer and in the water.

Equilibrium data are available for six vinyl latex products representative of the three types: resin, externally plasticized, and internally plasticized. The data relate vapor concentrations in a closed system with concentrations in the latex over a temperature range. No attempt has been made to determine the distribution of monomer between the water phase and the polymer phase. It has not been important for our purposes to do this. The equilibrium data have been fitted to the mathematical model of this form:

$$P_{VCM} = K_1 W^{K_3} e^{-K_2/RT}$$

where: P_{VCM} = partial pressure of VCM, mm Hg
W = weight percent VCM in the latex at STP T.S.
T = absolute temperature, °K
K_1, K_2 and K_3 are curve fitting parameters

Values for the calculated coefficients are shown in Table VII.

[redacted]

Vapor-Liquid Equilibria

[redacted]			[redacted]	[redacted]	
			[redacted]	5413	1.00
		-	[redacted]	4741	1.06
		-	[redacted]	2230	1.03
		351	[redacted]	3075	1.02
576	[redacted]	351	[redacted]	1605	0.92
5[redacted]119	65	352	[redacted]	3453	0.95

The diffusion process starts when the vapor space is suddenly increased to include the air volume surrounding the opened container. The monomer vapor then begins to migrate into the new space as the system tries to establish a new equilibrium. So the monomer begins to move through these steps: 1) diffusion through the air, 2) diffusion through the water-air interface, 3) diffusion through the water, 4) diffusion through the polymer-water interface, and 5) diffusion through the polymer. It is impossible to guess which step controls the rate of increase of RVCM concentration. As a worst case, however, it can be assumed that diffusion through the water-air interface is controlling. The driving force for the diffusion then is the partial pressure of VCM at the liquid-air interface, i.e., the equilibrium partial pressure at the temperature and RVCM concentration of the latex. Equilibrium partial pressures have been calculated for the conditions shown in Table VI. The final result is the average for the six conditions: critical P_{VCM} = 1.36 mm Hg. The standard deviation for this result is: σ = 0.46 mm. This is a large error. The large standard deviation is not surprising considering the large error in the RVCM data. The critical RVCM concentration, 0.21 ppm, when applied to the critical P_{VCM} = 1.36 mm Hg. This [illegible] to calculate the critical RVCM for the other [illegible] Table VII, for which equilibrium data [illegible] the [illegible] products based on [illegible] interpolation of critical [illegible] level. The results of these [illegible] are given in Table VIII. The allowable [illegible] would eliminate the effect of resin dilution with [illegible]

Table VIII

Calculated Critical RVCM Levels in Vinyl Latexes
Based on Equilibrium Partial Pressure

Critical P_{VCM} = 1.38 mm Hg, σ = ± 0.65 mm Hg

Corresponds with AVCM = 0.33 ppm in closed, unventilated room

Latex	Plasticiser phr	Base Resin	Calculated Critical RVCM mg/kg (110°F) (1)		Allowable RVCM Limit for Base Resin mg/kg
352	-	-	35	(>50)	-
351	-	-	29		-
450X20	-	-	38	(38)	-
580X29	22.4	351	29		35
576	38	351	22	(22)	30
[illegible]	65	352	17		28
[illegible]	30	352	27 (2)		35
[illegible]	35	[illegible]	28 (2)		34

[illegible] is the result from statistical
[illegible] Table VI)

[illegible] interpolation of calculated data

[illegible] that for every product the critical RVCM, or [illegible] for base resin used to make the plasticised [illegible] the level allowed by the product [illegible] fragrant plastic products have critical RVCM [illegible] product specifications. With the base [illegible] mg/kg RVCM, Geon 576 would be at 18.5 mg/kg. [illegible] 352, at 28 mg/kg RVCM, Geon 580X118 [illegible] The product specifications for these two [illegible] changed to 18 mg/kg minimum and 15 mg/kg maximum

VIII. Diffusion Rate Estimate.

It is of interest to know the rate of diffusion of VCM from latex to surrounding air space to which it is exposed. From such information it is possible to estimate possible personnel exposure levels in a working environment under known ventilation conditions. Each of our closed room experiments could provide such information. The amount of VCM transferred during the test can be calculated from latex RVCM data at the beginning and at the end of the experiment. This quantity should be in agreement with the quantity measured as the AVCM concentration during the test.

The calculations have been made based on the following assumptions:

1) the rate of transfer from the latex to the surrounding air is constant during the test period,

2) the concentration of AVCM changes linearly with time from 0 at the beginning of the test to a maximum at the end of the test,

3) the measured AVCM for a given test is the average concentration for the test period.

For the measured AVCM value, the average of the statistically validated air samples taken during a test period was used. Air movement within the room during a test was considered sufficient to eliminate gradients in the air space. Statistical analysis [illegible] of AVCM concentration with position of the air [illegible] of the calculations are shown in [illegible] graphically in Fig. 3. The [illegible] Initial tests, described [illegible] the [illegible] cylinder at [illegible] during this time [illegible] in all the [illegible]

[illegible] during a test is [illegible] air

Table IX

RVCM Calculated from RVCM Loss Data

Lot No.	Test Temp., °F	Test Time, min.	RVCM Loss, mg/kg	RVCM Ave., mg/kg
576	56.9	240	19.32	55.8
576	56.9	240	21.46	71.3
576	56.9	240	3.00	14.1
576	56.9	240	0.80	16.1
352	56.9	240	16.00	50.8
352	56.9	240	4.00	56.8
352	56.9	120	-1.10	4.3
352	56.9	240	0.30	4.2
450X20	56.9	240	11.90	47.3
450X20	56.9	240	25.10	48.4
450X20	56.9	240	1.50	4.7
450X20	56.9	240	1.10	4.0
-	-	240	-	-
352	56.9	240	0.23	3.2
450X20	54.0	240	5.07	31.8
450X20	54.0	240	2.45	19.4
450X20	54.0	240	3.37	19.7
450X20	54.0	240	13.71	67.9
450X20	54.0	240	22.35	67.3
450X20	54.0	240	5.00	15.8
576	56.9	240	3.62	11.5

Consolidated RVCM data are excluded, number in parenthesis indicates the number of samples for the test.

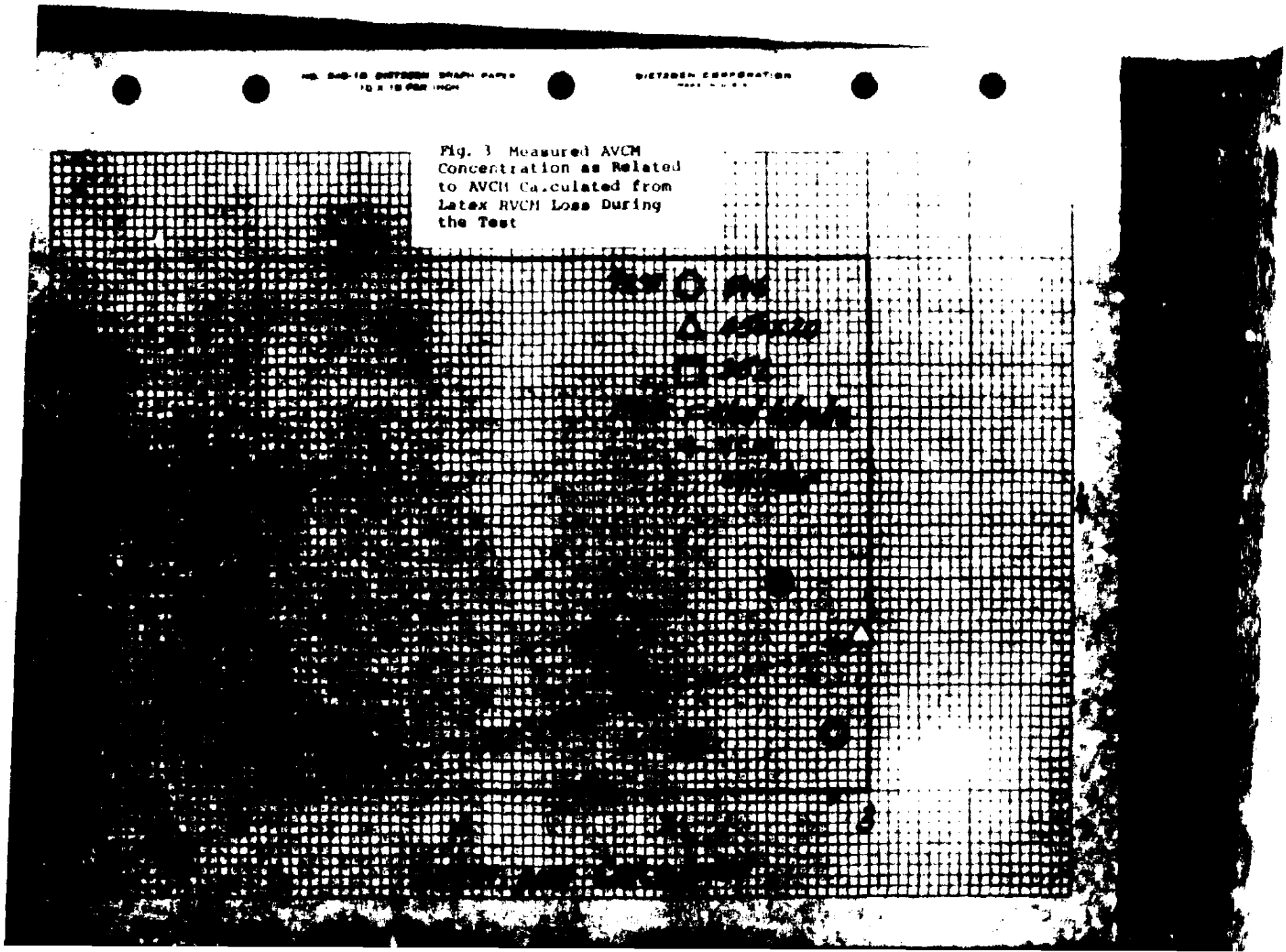


Fig. 3 Measured AVCM Concentration as Related to AVCM Calculated from Latex AVCM Loss During the Test

This finding is based on the overall average for all the validated tests and is represented by the dotted line in Fig. 3. The failure to detect 77% of the VCM released to the atmosphere is explained by diffusion of monomer through the porous ceiling in the closed room and through joints in wall panels. Adsorption of monomer onto surfaces in the room could also account for some of the loss. The loss is equivalent to expanding the original volume of 1000 ft^3 to 4350 ft^3 with new air during the 4 hour test period.

So, in a case where 0.33 ppm AVCM is the measured concentration as determined by collection of air samples over a 4 hour test period, it can be determined that 42 lb. of latex in the 5 gallon container would have to release 10.57 mg of VCM per kg of latex. And assuming that the rate of release is constant, the diffusion rate is: (11.09) (10^{-5}) lb/hr. To generalize the result, the latex-air interfacial area (0.6303 ft^2) is taken into account and the diffusion rate becomes: (1.76)(10^{-4}) lb/ft^2-hr. This then is the diffusion rate of VCM from latex to air where temperature and concentration conditions are such that the equilibrium partial pressure of VCM is 1.30 mm Hg.

Knowing the rate of evolution of VCM from the latex to the room, an equivalent air flow can be calculated that will maintain 0.33 ppm AVCM. The corresponding air flow is 2117 ft^3/hr. Since the room volume is 1000 ft^3, this is equivalent to 2.1 turnovers/hr. Earlier [illegible] reported [illegible] 1.2 air turnovers/hr. in [illegible] conditions. The system [illegible] monomer diffusing from [illegible]

It is safe to assume that the diffusion rate varies linearly with the equilibrium partial pressure of the latex. To check this assumption, equilibrium partial pressures have been calculated for the [illegible] and latex [illegible] Fig. 4 [illegible] partial [illegible] pressure. [illegible] the original coordinates [illegible] fit is good considering the poor

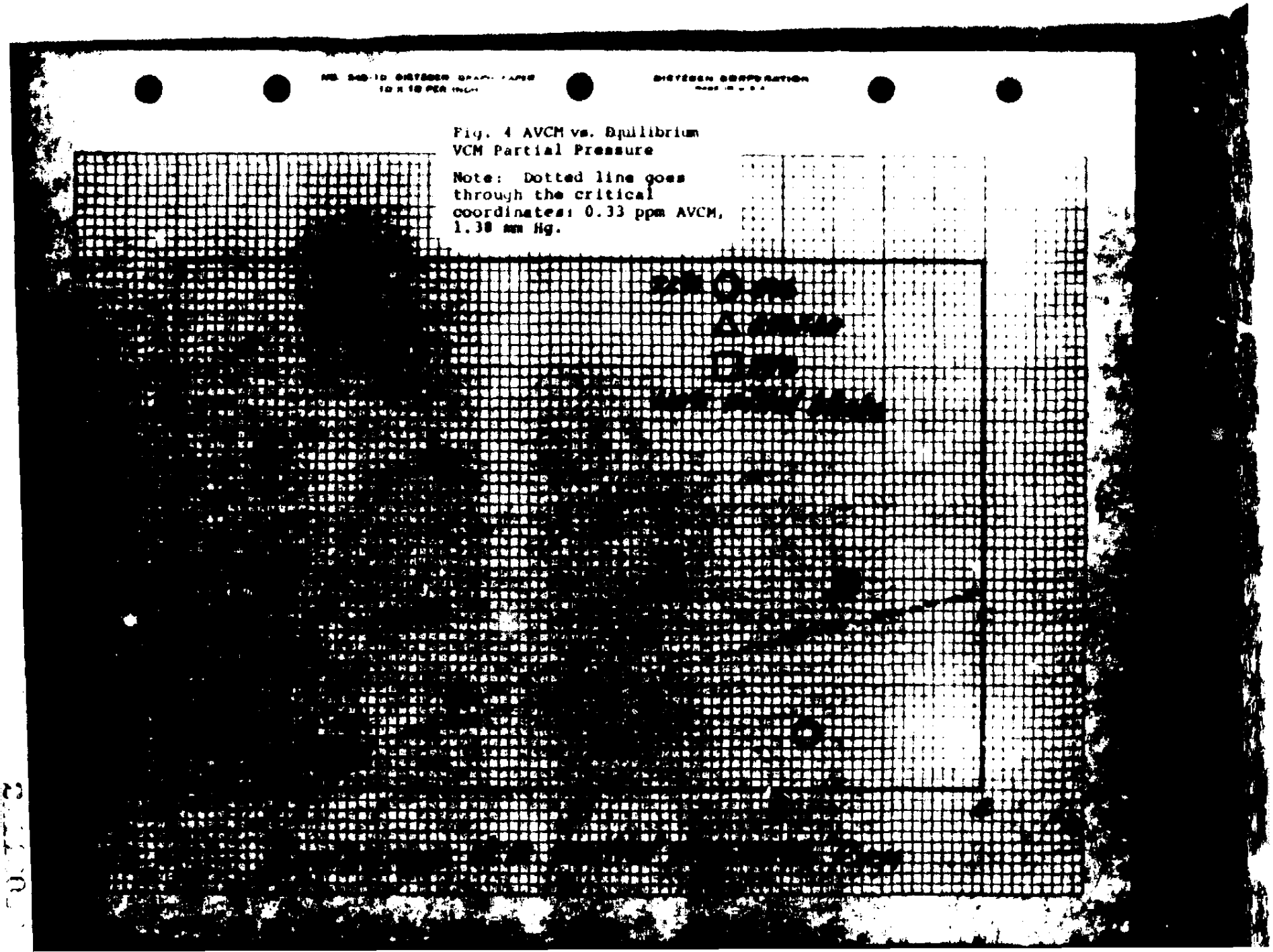


Fig. 4 AVCM vs. Equilibrium VCM Partial Pressure

Note: Dotted line goes through the critical coordinates: 0.33 ppm AVCM, 1.38 mm Hg.

X. VCM Estimate for a Typical Compounding Operation

A hypothetical compounding operation has been conceived in order to calculate possible VCM exposure levels in a real work area.

Work space: volume 20 ft x 40 ft x 25 ft
(= 20,000 ft³)

air temperature 90°F
barometric pressure 750 mm Hg
ventilation variable

Compound mix tank:

volume 1000 gal.

diameter 60 in.
(liquid-air interface 2830 in²)

agitated

Mixer: Cmcm 576, 576 r.p.m., [illegible] variable

temperature 110°F

[illegible]

[illegible] index of the air mixed is [illegible]

[illegible] index [illegible]

[illegible] ppm. [illegible]

[illegible] liquid is not [illegible]

[illegible] the ventilation requirement at [illegible] to maintain the VCM concentration at [illegible] partial pressure of VCM in the air at

[illegible] ft.³/min (lbs⁻¹)[illegible] p_g = [illegible] mm Hg,

[illegible] the [illegible] concentration at

The calculations are summarized in Fig. 5. Typical industrial ventilation gives 6 turnovers of air per hour. At this level of ventilation, the Geon 576 used in a typical compounding operation could be at 40 mg/kg RVCM without exceeding the OSHA action level. At the proposed specification limit for Geon 576, 18 mg/kg, only 3 air turnovers per hour are required to stay in the OSHA compliance region.

X. Paper Coating Operation at Rhinelander Paper Company

Geon 576 is used at Rhinelander Paper Company to apply a clear coating to paper.

Work space: volume 20 ft x 150 ft x 100 ft
(= 300,000 ft^3)

air temperature 90°F

barometric pressure 750 mm Hg

ventilation 6 turnovers/hr.

Coating operation:

[illegible] 40 lbs (wet)/ream
([illegible] ream x 3000 ft^2)

[illegible] 300 ft/min.

[illegible] in.

[illegible] 10 ft.

[illegible]

[illegible] could [illegible] unlikely [illegible]

[illegible] levels

[illegible]

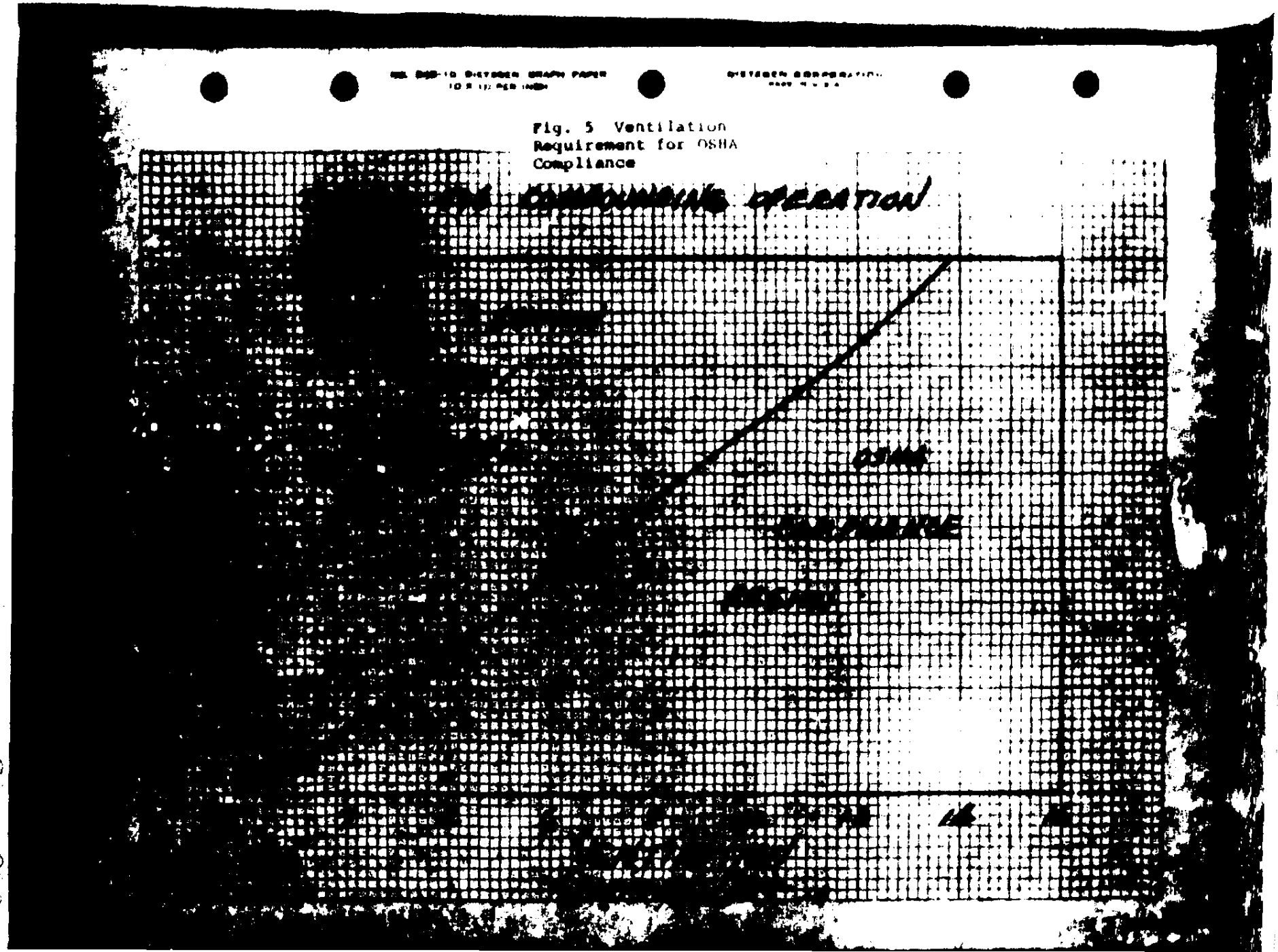


Fig. 5 Ventilation Requirement for OSHA Compliance

The working environment at Rhinelander was monitored during a coating operation using Geon 576. Results were reported by two different laboratories accredited by AIHA:

1) the BFGoodrich Corporate Environmental Health Laboratory in Brecksville, Ohio, and

2) Wausau Insurance Companies, Wausau, Wisconsin.

These reports are included in the Appendix of this report. Results are consistent with our calculated data.

XI. Scrim Coating Operation at Benitez

Geon 576X13 is used as a pigment binder at Benitez in a double coating operation. A base coat compound is applied to the scrim on the first station. The base coat is dried in an oven. A top coat compound, also based on 576X13, is then applied and the material is again dried in an oven. All these operations take place in one pass through the coating line.

[redacted]

Again, the worst case situation is assumed, i.e., the unlikely situation where all of the VCM in the two compounds would transfer to the surrounding work space. The latex is consumed at a rate of 1134 lb/hr in the base coater and at 303 lb/hr in the top coater. The total consumption rate is 1437 lb/hr and the VCM evolved is 0.0359 lb/hr.

$$P_{VCM} = \frac{vRT}{MV} = \frac{(0.0359)\ (555)\ (550)}{(62.4)(2.4)\ (10^6)\ (6)} = 1.22\ (10^{-5})\ \text{mm Hg}$$

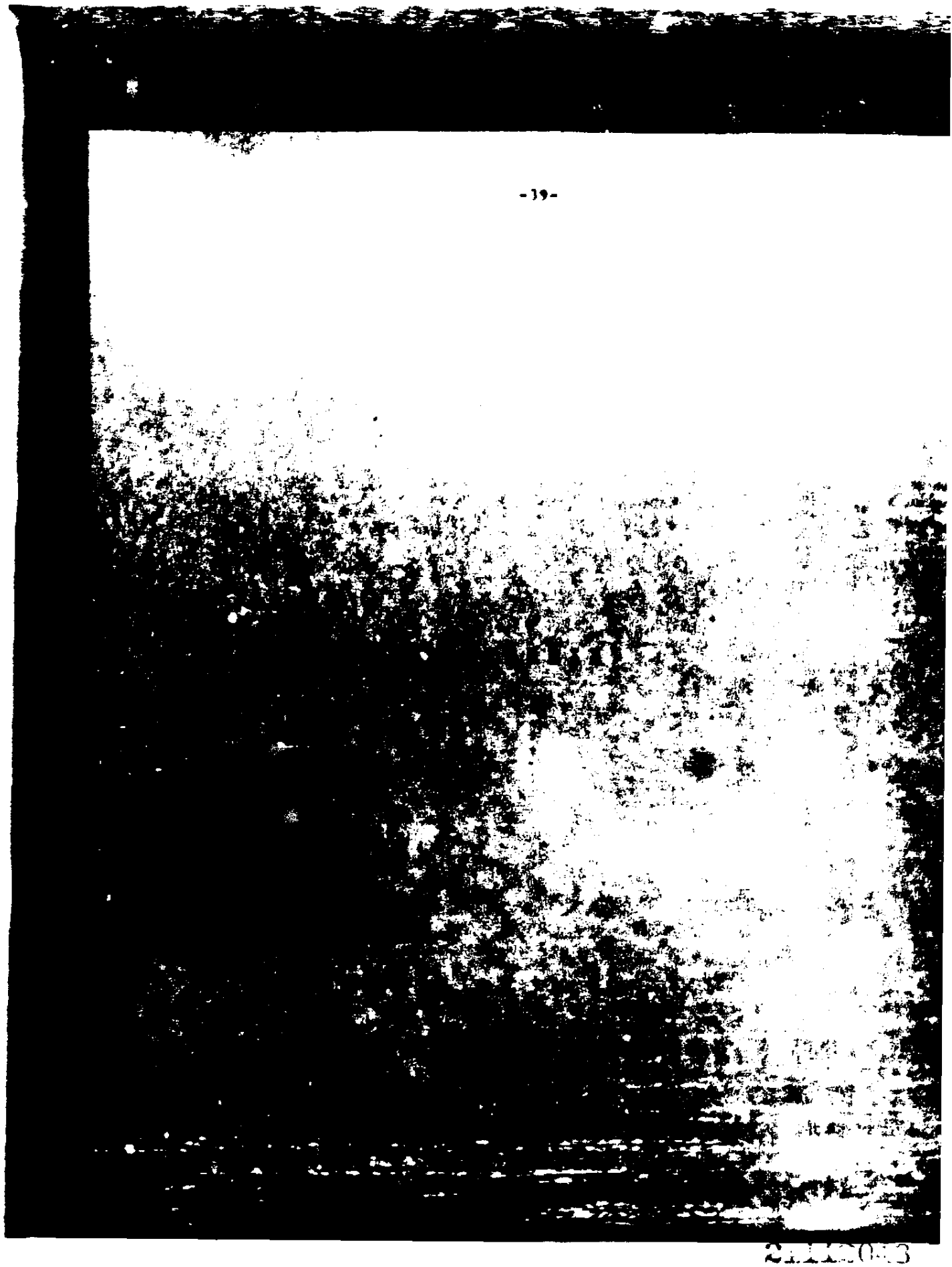
And the AVCM concentration is

$$AVCM = \frac{(1.22)(10^{-5})\ (10^6)}{760} = 0.016\ \text{ppm}$$

This [illegible] the OSHA action level. There is no likelihood that [illegible] emissions to ambient air will create an OSHA [illegible]

ACKNOWLEDGMENTS

The authors are grateful for help from the Environmental Control Group: R. B. Hardesty, R. E. Hattler, and L. A. Hilvig who [illegible] the procedure for testing oil samples; and for data [illegible] of specialists in the Tetra Group: Paul Clots, [illegible] and Ray Branson. [illegible] and D. E. Farley of the [illegible] accumulated.



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7. [illegible]

8. [illegible]

9. [illegible]

B.F.G TECHNICAL DOCUMENT

THE B F GOODRICH COMPANY CHEMICAL DIVISION Statistics and Computer Applications REPORT

D.S.Farley-H.S.Miller	ALTC	12/9/80	
	ALTC	3096-61	

REMOVAL OF "CANCER-HAZARD" LABELS FROM GEON LATEXES

BACKGROUND:

Marketing wants to remove the "cancer-hazard" labels from GEON latexes containing residual vinyl chloride monomer (RVCM). I&S was asked to demonstrate that emission of VCM differing out of scrapped GEON latexes are below the 0.5 ppm [illegible] limit defined by OSHA.

DATA:

The original data set consisted of 12 experiments and 72 samples of airborne vinyl chloride monomer (AVCM). Only 54 AVCM samples were usable. Analytical data for fourteen samples were rejected because the VCM loadings (mg VCM/activated carbon sampling tube) were outside of the 1.0 mg to 10.0 mg range recommended by [illegible] and J. V. [illegible] ([illegible]). Data on four samples were not usable because of interference during the gas chromatographic analysis.

The experimental conditions used are summarized in Table 1, below. A complete list of data used in the correlation analysis can be found in the Appendix (Table 1-A). Rejected data are listed in Table 2-A of the Appendix.

TABLE I

Summary of Experimental Conditions

[illegible]	Average VCM [illegible]	Latex Temp. (°F)	Flow Rate for Sampling Pump ([illegible])	Analytical Method
[illegible]	[illegible]	[illegible]	10 ml/min.	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	50 ml/min.	CS_2 Extraction

[illegible] inside a closed, unventi-[illegible] sampling pumps equipped with [illegible] used to sample the air in the room.

[illegible]

DISCUSSION: (Cont'd)

A. OSHA Regulations (continued)

If HPC could demonstrate that the RVCM levels in OXON latexes will not produce airborne VCM levels in excess of the 0.5 ppm action level, the "cancer-hazard" labels can be removed from these products. Users of HPC vinyl latexes would not need to establish programs for monitoring employee exposures.

B. Simulating OSHA Test Procedures

The procedure OSHA uses to determine employee exposure to airborne VCM is [illegible] program which simulates this procedure [illegible] L. Crume. The program calculates [illegible] of airborne VCM and a specific [illegible] associated with VCM detection and [illegible] and testing error, some AVCM [illegible] in Figure 1.

[illegible] AVCM [illegible] 1980 [illegible] testing of [illegible]

[illegible]

MACHINERY (Cont'd)

C. [redacted] (continued)

All these latexes tested will comply at the 95% level to OSHA regulations, if they are stripped to the levels proposed in the following Table I.

TABLE II

Optimal Levels of EVCM in Vinyl Latexes

Latex Type.	Critical EVCM Level (ppm by wt.)	Proposed EVCM Lvls. (ppm by wt.)
[redacted]		

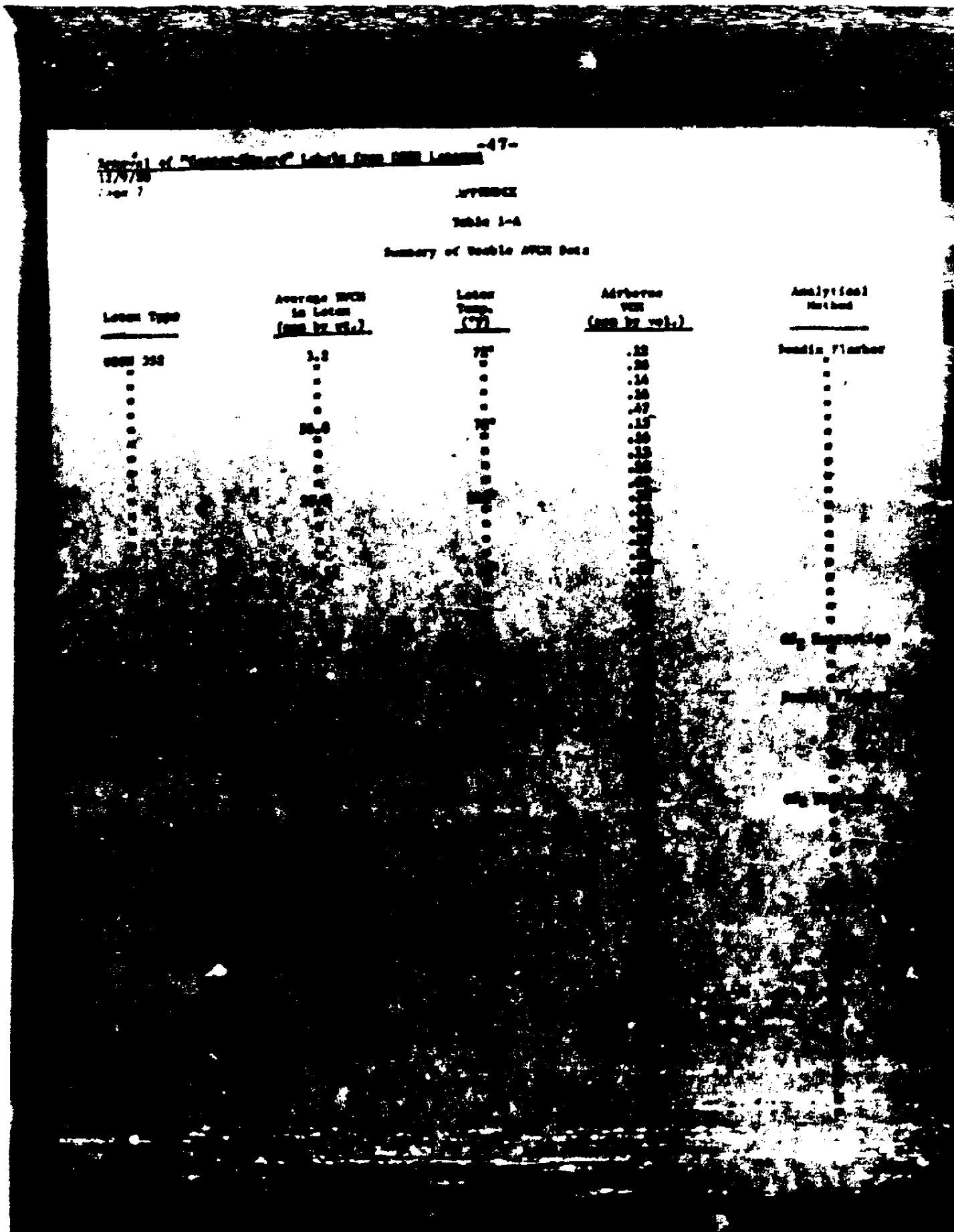
Removal of "Unmanned Vehicle from Base Location
1/31/90
Page 5

FIGURE 1
DOD
EXPLOSIVE PROGRAM

Removal of "Chemo-Sterol" Labels from Open Laboratory
11/4/80
Page 6

FIGURE 3

FIGURE 4



Removal of "Cancer-Causing" Labels from [illegible] Lotions
12/9/80
Page 8

APPENDIX (Cont'd)

Table 2-A

Rejected Data

Lotion	Average EVCH in Lotion (ppm by wt.)	Lotion Temp. (°F)	AVCH Level (ppm by vol.)	VCH Location (nm)
[illegible] 352	6.3	110°	0.65	0.327
"	"	"	0.68	0.122
"	"	"	0.64	0.252
"	"	"	0.64	0.266
"	"	"	0.65	0.312
[illegible] 355	96.6	72°	0.69	0.759
"	3.2	72°	0.68	0.307
"	"	"	1.68	13.98
"	20.6	110°	.39	.85
"	"	"	.37	.021
"	20.6	110°	1.68	13.88
"	"	"	.68	0.377
"	"	"	1.12	17.34
"	"	"	1.38	13.68

(Interference)

B.F. GOODRICH CHEMICAL DIVISION

Standard Sampling Procedure No. 1800-A

TITLE: Sampling Procedure for Vinyl Chloride in Air Using the Bendix Personal Monitoring Collection Column

TYPE: Carbon Adsorption Tube

PRODUCT: Ambient Breathing Air and Related Air Samples

1. SCOPE

The purpose of this procedure is to identify the equipment required, and to outline the [illegible] method of air sample collection used in monitoring the [illegible] chloride exposure (VCM) in air via the Bendix Flasher - [illegible] Collection Column system.

[illegible]

III. INTERFERENCES

1. Flushing and analysis of each tube does not always remove 100% of the VCM from the previous collection period. It is therefore necessary to "pre-flash" or condition each PMCC in the Bendix Manifold Flasher to remove residual material which may remain from the previous analysis.

2. After conditioning and prior to sample collection, the PMCC's are to be capped and stored in a desiccator. Maximum storage time is 24 hrs. Moisture pick-up will reduce the capacity of the PMCC.

3. After the exposure period and prior to laboratory analysis, the PMCC's may be stored in a desiccator or freezer. A separate desiccator is required for storage of exposed tubes. It is recommended that the storage period time should not exceed 24 hours.

4. High [illegible] flow rates for extended time periods contribute to [illegible] breakthrough" (loss of VCM during sampling). Calibrate [illegible] prescribed "safe" flow rates as indicated in this [illegible] when prolonged sampling periods are used to eliminate if breakthrough

[illegible] hydrocarbons in the [illegible] and greatly reduce [illegible] in chemical economy [illegible] relative humidity [illegible] will [illegible] collection pe[illegible] which [illegible] 2B-2.

[illegible] and apply calibration [illegible] at [illegible] period [illegible] section.

IV. [illegible]

IV. SAFETY (cont'd.)

2. Observe all normally accepted safe operating practices pertaining to the specific area being sampled.

3. Use appropriate safe handling procedures associated with compressed air cylinders.

4. Observe all normally accepted safe practices in handling electrically heated equipment.

V. APPARATUS

A. Sampling Equipment

1. [redacted] Personnel Sampler, Part No. [redacted] equipped with battery rechargers, Part No. [redacted] or equivalent unit consisting of [redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

V. APPARATUS (cont'd.)

B. Calibration Assembly (cont'd.)

4. BIOS, Battery Tester - Model 504. BIOS Electronics, Flushing, N.Y. or equivalent.

5. Stainless steel tubing 1/4" and the appropriate fittings to be installed between breathing air source and the PHCC (see attached diagram of the calibration assembly).

6. Tygon tubing 1/4" I.D. and the appropriate tubing connectors.

7. Stopwatch

8. Stainless steel air reservoir with vent holes. Approximately 200 cc volume. Fabricated as per diagram.

C. [redacted]

1. Sling Psychrometer, Bacharach Inst. Co., Pittsburgh, Pa., +20 to 120°F, Part No. [redacted] or equivalent.

2. [redacted]

VI. [redacted]

VI. CONDITIONING PMCC'S FOR USE (cont'd.)

5. It is recommended that PMCC's stored more than 24 hours be reconditioned prior to use. All new PMCC's must be conditioned prior to initial exposure.

VII. BENDIX PUMP CALIBRATION

For the purposes of both short term "task" sampling breathing air analyses as well as long term "time weighted average" breathing air sampling, there are two standardized sampling time periods associated with specific pump flow rates. The following pump calibration procedure covers the long term, 6-hour exposure period. For instructions on short term sampling, refer directly to step 10 of this section.

1. Remove the Bendix Micronair II pump from its battery charger and record its identification number along with the identification numbers of the primary and secondary conditioned PMCC's in the appropriate space on the laboratory data form.

Check the pump battery with the battery tester. Do not use if not fully charged.

[illegible] and let it run on the bench for 15 minutes while [illegible]

[illegible] calibration assembly along with the two [illegible]. The sampling end of the PMCC is to [illegible] breathing air supply source. The Bendix [illegible] used to connect the PMCC's. See the [illegible] for the flow rate calibration assembly.

[illegible] air supply at a flow rate of approximately [illegible]

[illegible] adjust the [illegible] screw to achieve a [illegible] height of the water column on the U-tube [illegible]. This corresponds a pressure of 2 inches [illegible] pressure.

[illegible] Remember that a reading equivalent than 1.8 or [illegible] flow rate of 2 liters, by the following [illegible]

[illegible] the appropriate space [illegible] the pump flow rate [illegible] 6. [illegible] and [illegible] on the expiration of the [illegible]

VII. SEMIAUTOMATIC CALIBRATION (cont'd.)

8. Turn off the pump and disconnect the PVCC's and pump from the flow rate calibration assembly. Connect the tandem PVCC's to the pump using a length of Tygon tubing and an adapter. The primary PVCC is the one farthest from the pump. Again the serrated end of each tube is to be directed away from the pump.

9. Repeat calibration Steps 1 thru 8 for each pump - PVCC sample collector combination. Pump - sample collection combinations as calibrated must be used within 8 hours. If not employed within this period, pumps are to be put back on charge and PVCC's are to be reconditioned. Recalibration is also necessary prior to use.

10. There are two basic sample collection time intervals, 8 hours, and 15 minutes. The permissible time exposure range for the 8 hour sampling conditions is 6-7 hours, while that of the 15 minute sampling conditions will range from 15 to 30 minutes. The above calibration conditions are for the 8 hour exposure period. The [illegible] conditions [illegible] for the 15 minute exposure [illegible]

VIII. [illegible]

VIII. SAMPLING PROCEDURE (cont'd.)

7. Note should be made of [illegible] by the employee during the sample collection period.

8. At the conclusion of the sample collection period, the pump flow rate is to be measured. The flow rate is to be measured in the field using a portable flow meter and stopwatch. The pump is then turned off and the final flow rate in cc/min. and the time when the pump was turned off are recorded.

IX. REPORTING AND CALCULATIONS

1. Record both the initial and final flow rates (see Appendix #2). Average these to obtain the cc/minute average flow rate over the sampling period. Calculate and record the total volume of air sampled in m3's by multiplying the average cc/minute flow rate by the total minutes of exposure. Record this value on the data

[illegible] relative humidity [illegible] the sample was [illegible] form,

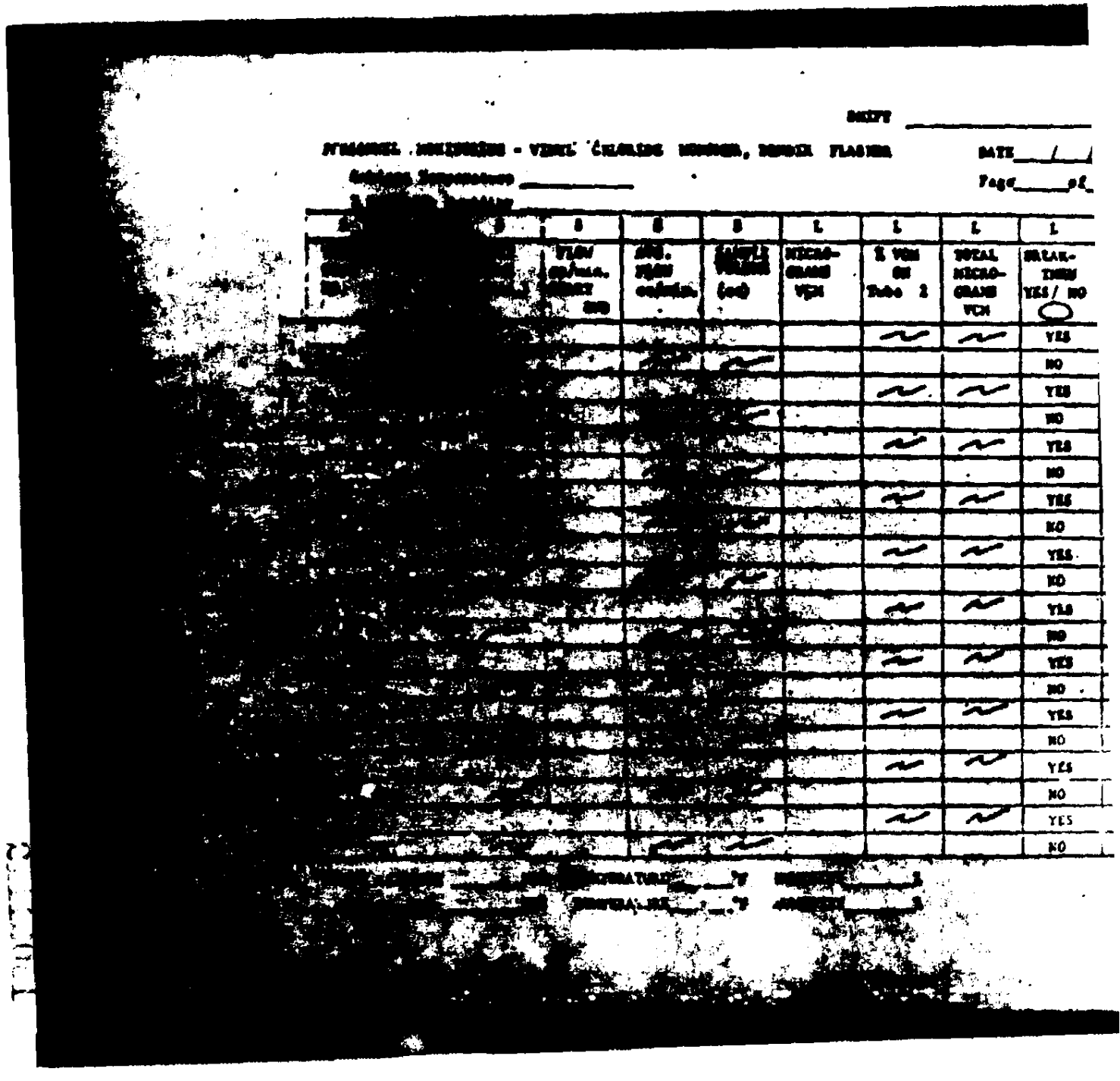
[illegible] report concerning [illegible]

[illegible] values and [illegible] recorded.

X. APPENDIX (cont'd.)

2. Other than battery replacement, there is little maintenance which can be performed on the pumps themselves. However, it is recommended that pump % fall-off rate records be kept for each pump. As much as 35% fall-off in flow rate from the start to the end of an exposure period can be considered normal. Percent fall-off rates greater than this should be investigated for battery failure or pump problems. (Note: This is considered normal for the Bendix, Microsair II pumps. Sipin or other NIOSH approved pumps may exhibit different fall-off flow rate characteristics.)

3. To prevent sampling errors and false breakthrough, the O-rings in the [illegible] and back-up cassettes kits (tandem tube adapters) must be replaced every six months. Replace them with 1/4" I.D., 1/8" O.D., [illegible] diameter O-rings. Use Viton O-rings since they are exposed to [illegible] chamber service.



DATE ____/____/____

Page _____ of _____

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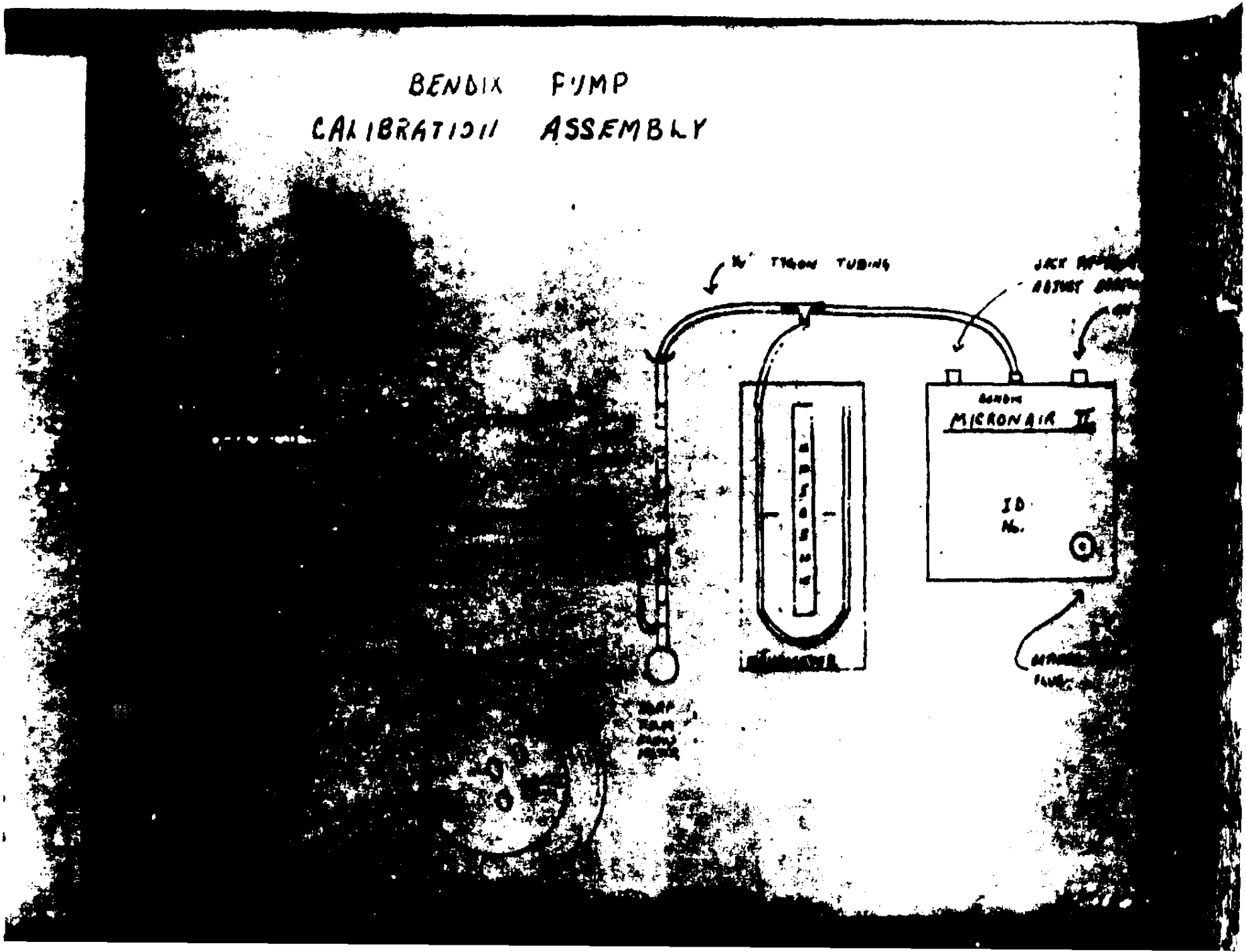
BENDIX PUMP
CALIBRATION ASSEMBLY
MICRONAIR
ID
No.

B.F.GOODRICH CHEMICAL COMPANY

Standard Test Procedure No. 1021-A

TITLE: Analysis of Vinyl Chloride Monomer in Air Via Carbon Collection Tube Thermal Desorption

TYPE: Gas Chromatograph

PRODUCT: Ambient Breathing Air and Related Air Samples

* Sample collection method to be covered by separate procedure (see Note 3)

I. SCOPE

The use of the thermal desorption technique incorporated in this procedure is suitable for monitoring the level of vinyl chloride vapors in air in relation to personnel exposures. The method, with modifications, can also be utilized for determining exposure to other organic vapors.

II. SUMMARY

This system of sampling and measuring industrial vapor enables the collection tubes to be connected directly to the G.C. analytical column after [illegible] collection. The organic vapors are thoroughly flushed/desorbed from the [illegible] collection tube into a [illegible] gas chromatograph for [illegible] of the amount of vinyl chloride adsorbed during [illegible] sampling. A column backflushing technique is [illegible] of high boiling components.

III. [illegible]

[illegible] interferences) which elute from the chromatographic [illegible] and which also on vinyl chloride will adversely [illegible] of this analysis.

[illegible] collection tubes, either samples or standards, beyond [illegible] recommended. Refrigeration (-10°F) of exposed samples [illegible] tube storage of 25 hours without appreciable VCM [illegible] tube standards can be frozen along with samples to [illegible] during storage.

[illegible] material, and to include use of the Century equipment

[illegible]	[illegible]	11/23/76
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

III. **INTERFERENCES** (cont'd.)

3. All collection tubes must be pre-flashed prior to their initial use, and must be conditioned prior to each subsequent exposure.

IV. **PRECISION**

An accurate determination of the total test reproducibility of this method has not as yet been defined. But the standard deviation of the ability to reproduce on calibration standards has been measured at approximately 7% at all three calibration levels of 0.3 µg, 43.0 µg and 430 µg. Data on calibration standards was collected daily over a one month period.

V. **SAFETY**

1. Vinyl chloride monomer is a suspected carcinogen. Do not release vinyl chloride vapors to the laboratory atmosphere during standard preparation. Standard preparation should be performed in a suitable, properly functioning, lab fume hood and the vapor must be vented to the outside air.

2. [illegible] not to come into contact with heated parts of the collection [illegible] chromatograph. [illegible] tubes are to be removed [illegible] needle-nose pliers and should be allowed to [illegible]

3. [illegible]

4. [illegible] from the [illegible] [illegible] off the hydrogen gas flow [illegible] possibility of explosion.

5. [illegible] safe handling procedures associated with com- [illegible]

[illegible]

VI. APPARATUS (cont'd.)

4. 2 ft. and 4 ft. x 1/8" stainless steel columns packed with Porapak Q 50/80 mesh (Waters Associates, Inc.), or equivalent substitute.

5. Standard cylinders, vinyl chloride in air at 10, 100, and 1000 ppm by volume, Matheson Gas Products; Joliet, Illinois. When ordering, specify zero grade air (vinyl chloride in nitrogen can be used instead of air if desired).

6. Pressure regulators, No. 8L (CGA) Matheson Gas Products (3) required for item 5 above.

7. Rotameter, No. 7221T, 65 mm, aluminum, 1/4" tubing, Matheson Gas Products, Joliet, Illinois. (To be installed downstream of the pressure regulator in each of the calibration gas lines.)

8. Hydrogen cylinder with regulator.

9. Nitrogen cylinder with regulator.

10. Air cylinder with regulator.

11. Instrument air supply and regulator.

12. [illegible] Timer No. 2230117. One for each [illegible] equivalent).

[illegible] Div. of Emerson Electric Company, [illegible] hydrogen, air and carrier gas lines [illegible] control to the F.I.D.

[illegible] meter (MF 8101-0115).

[illegible] Cat. No. 315-21.) optional
[illegible] 9-531-116.)

[illegible] connectors - Swagelok or [illegible]

[illegible] calibration of equipment.

[illegible] necessary

[illegible]

2.

VII. PREPARATION OF GAS CHROMATOGRAPH (cont'd.)

4. Both solenoid valves are to be interfaced with the timer for automatic sequencing of the backflush cycle. The timer cam(s) are to be selected and adjusted so that the VCM has all eluted into the second column immediately before the timer activates backflushing of the first column. This should take place at about 70% of the VCM retention time in minutes. It can be determined by cutting the cycle progressively shorter until a noticeable response drop is experienced on known VCM standards.

5. Install the filter drier assemblies in each cylinder gas line and adjust the gas flow rates to optimize conditions for the chromatographic system being used. The following are typical flow rates used for the Bendix Series 2300 gas chromatograph:

   a) Nitrogen Carrier Gas - Set the regulator on the cylinder to 50 psig. Adjust the pressure regulator in the N_2 carrier gas line to obtain a VCM chromatograph peak characterized by clean separation from its neighbors. VCM retention time may vary within 2.5 ± 1.0 min. dependent on the particular column system. See also Step 3 above for adjustment of the backflush N_2 flow.

   b) Detector Air Supply - Set regulator on the cylinder to 80 psig. A Brooks flow controller is to be installed in this line to provide the optimum constant air flow to the detector between 280 to 290 cc/min.

   c) [illegible] Supply - Set the cylinder regulator to 20 psig. A [illegible] flow controller is to be installed in this line to provide a constant H_2 flow to the detector between 30 and 40 cc/min.

6. Optimum System Temperatures. The following conditions may be used as starting points:

   [illegible] chromatographic columns) ..... ~100°C
   [illegible] Block ..... ~250°C
   [illegible] Ionization Detector (FID) ..... ~120°C
   [illegible] ..... ~250°C

   [illegible] the HEATING blocks. VM flows are [illegible] while within five seconds. It [illegible] of inspecting the cylinder pressure [illegible] supply of the desired cylinder

   [illegible] Do not connect the [illegible] during the conditioning cycle. Whenever the [illegible] disconnected from the detector, the hydrogen and air flows should be turned off. NOTE: The maximum temperature limit on the column backflush solenoid valves is 150°C. It may be necessary to remove them or condition the columns in [illegible]

VIII. [illegible]

Calibration checks should be performed during the [illegible] period when the [illegible] In addition, [illegible] of time, [illegible] normal operation [illegible]

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VIII. CALIBRATION (cont'd.)

1. Preparation of Calibration Standards (use fume hood)

Prepare three standard calibration tubes, one each of the 10, 100, and 1000 ppm standard VCM gases, in the following manner:

a.) Open the standard cylinder and set the outlet regulator at 5 lbs. and open the needle valve at the regulator.

b.) Set the flow rate, by adjusting the rotameter valve to between 18 and 20 seconds per 10 cc's using the soap film flow meter.

c.) After the flow rate has been adjusted, connect a pre-conditioned collection tube with the appropriate end toward the cylinder and simultaneously start a stopwatch. NOTE: Do not use tygon connections between the standard gas cylinder and collection tubes. Stainless steel connections are recommended.

[illegible] the bubble flow meter to the exit end of the collection [illegible] while it is being exposed to the standard and, using another [illegible] the time in seconds for 10cc volume. Repeat [illegible] the average time to the nearest 0.1 [illegible]

[illegible] collection tube to the standard for [illegible]

[illegible]

[illegible] to the standard calibration [illegible]

[illegible]

[illegible] which readily performs this calculation.

[illegible] calibration exposures and record the [illegible] standard (see also Note 2).

[illegible] calibration tubes is then to be analyzed through [illegible] analytical system [illegible] collection tubes [illegible]

[illegible]

VIII. CALIBRATION (cont'd.)

J. Preparation of Calibration Curve (cont'd.)

c.) After analysing and plotting two sets of calibration standards, the best calibration curve can be drawn through the plotted points. It is recommended that the calibration data be analysed using the two variable linear regression capabilities of a Monroe Model 1860 statistical programmable calculator to obtain the equation of the best fit line for this data, and that this line be plotted as a calibration curve. Monroe program No. 114 can be used to generate the equation for the calibration curve.

d.) Examine the plot of the calibration data carefully. If there appears to be any non-linearity in the log-log plot, it is recommended the curve be segmented into shorter sections, which approach linearity, and that appropriate sample calculation methods are incorporated which are dependent upon VCM level (see Note D).

e.) It is recommended that subsequent calibration checks be control charted. In this manner significant shifts in calibration which may occur will be readily identified. Following control chart rules will also provide a consistent basis for determining if recalibration is necessary. Refer to the B.F.Goodrich Chemical Company "Control Chart Manual" by R.L. Bowles, A.M. Fairlie, [illegible] and R.S. Morgan, March, 1962. If the daily calibra[illegible] violate control chart rules, the analysis system is to [illegible] and troubleshooted until the discrepancy is detected [illegible] that recalibration is necessary.

[illegible] calibration curve used in this analysis [illegible] to J.M. Whitney and F.V. Zemanek [illegible] Monitoring VCM Exposure from [illegible]. A copy of this report is obtain[illegible] at the [illegible] Laboratory.

[illegible] of calibration standards which cover [illegible] excellent reproducibility. This [illegible] certified calibration gas and varying flow [illegible] time to obtain different calibration levels. The [illegible]

[illegible]

IX. SAMPLE ANALYSIS PROCEDURE

3. The collection tube is allowed to desorb for 2 minutes, during which time the recorder baseline, attenuation, and/or integration parameters can be appropriately checked and adjusted.

4. After the desorption step is completed the sample is injected onto the analytical G.C. column and the backflush timer switch is set to "reset". The recorder and/or integrator is also started simultaneously.

5. If using a recorder only, attenuate as necessary to keep the peak height of all peaks in the upper half of the chart. Record the sample identification, analysis start, and attenuation of each peak on the recorder chart. If using an integrator, the logarithmic scale attenuator can be used to keep all peaks on the recorder chart. After 30 seconds have elapsed, switch the timer to "Auto". This will return the backflush timer to the start of the cycle at the completion of the analysis.

6. The recorder will graph the response with time of each low boiling component in the collection tube being analyzed. The backflush of the first analytical column will be automatically actuated by the preset timer immediately after the VCM has eluted from the first column.

If using the Century system, repeat injections may be made on aliquots of single desorbed collection tubes.

7. Record the sample identification, collection tube I.D. number, attenuation, [illegible] peak width and height, (or area counts if an integrator is used) and [illegible] sample pressure volume (supplied with sample) on the appropriate [illegible] data calculation form (see Attachment #3).

X. CALCULATION OF RESULTS (cont'd.)

The above equation can be easily calculated using Monroe Program No. 113.1860.

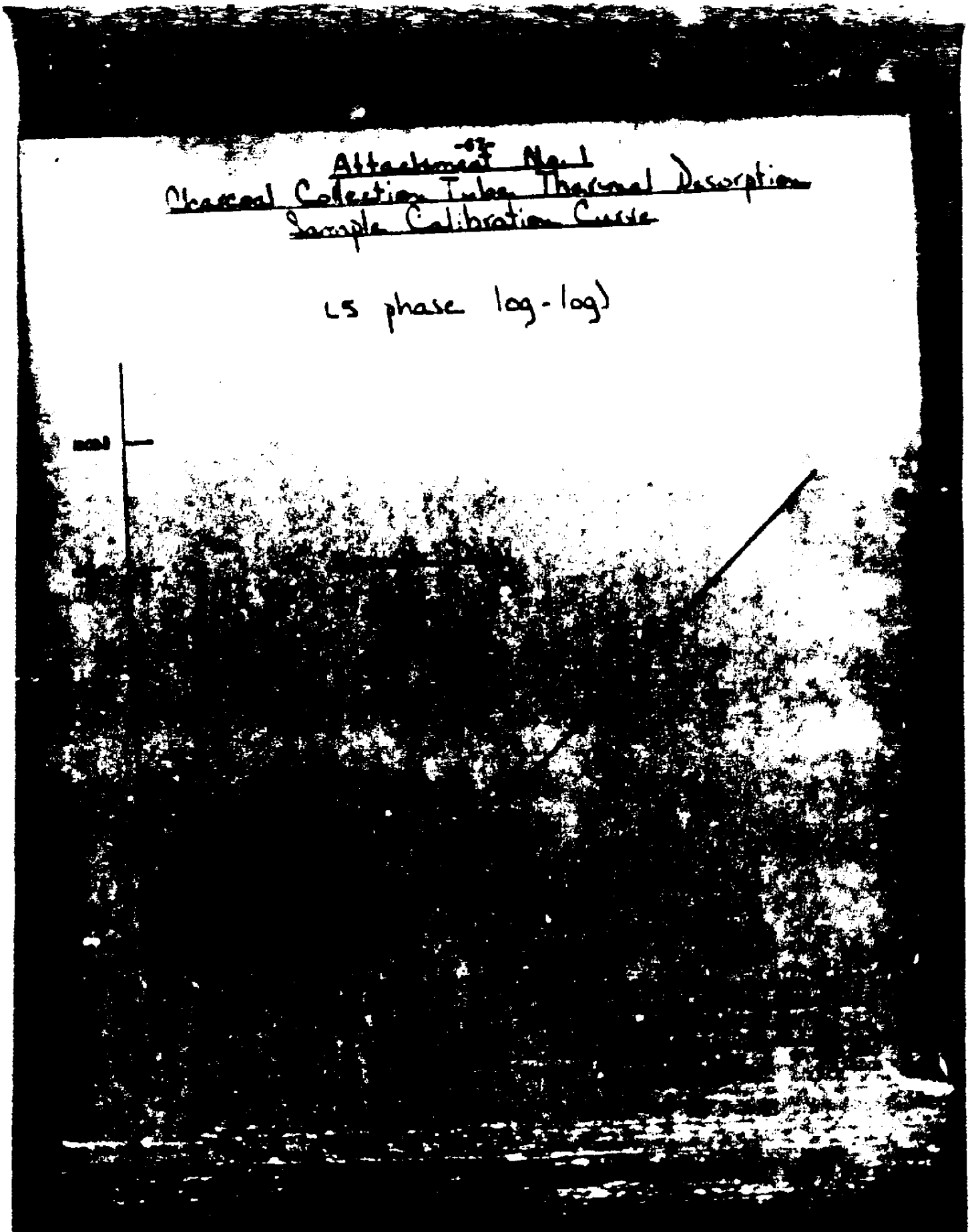
NOTE 3: Although sampling methods are not outlined in this test procedure, it is understood that the capacity of the collection tube has not been exceeded.

It has been found that collection periods characterized by high air flow rates (20lpm/min.), and/or high humidity may lower the capacity of the collection tube dependent upon the length of the collection period and the concentration level being sampled.

[illegible] significant [illegible] should be appropriately adjusted relative [illegible] psychrometric conditions. See also VIII, 2.

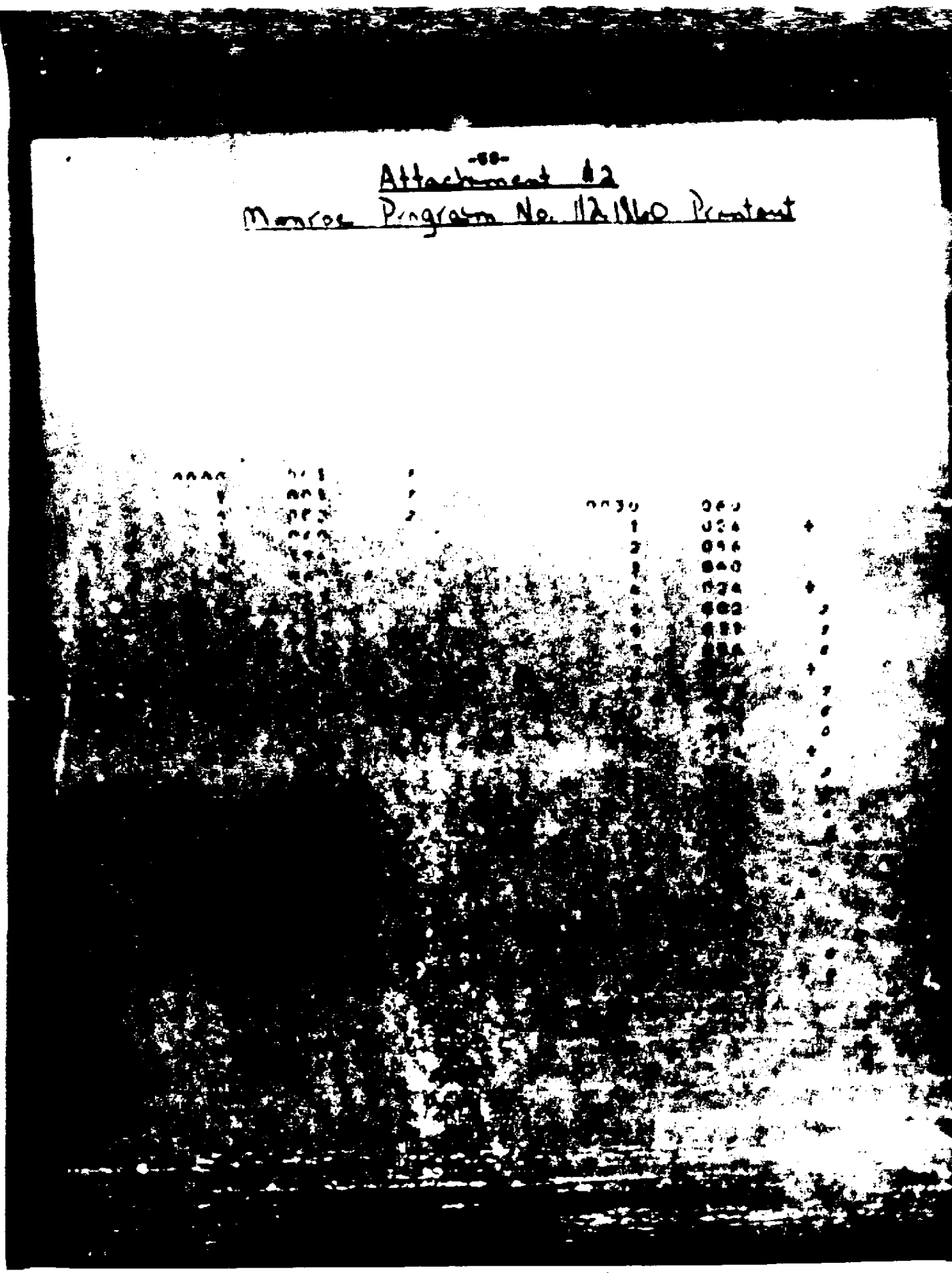
Attachment No. 1
Charcoal Collection Tubes Thermal Desorption
Sample Calibration Curve

LS phase log-log)

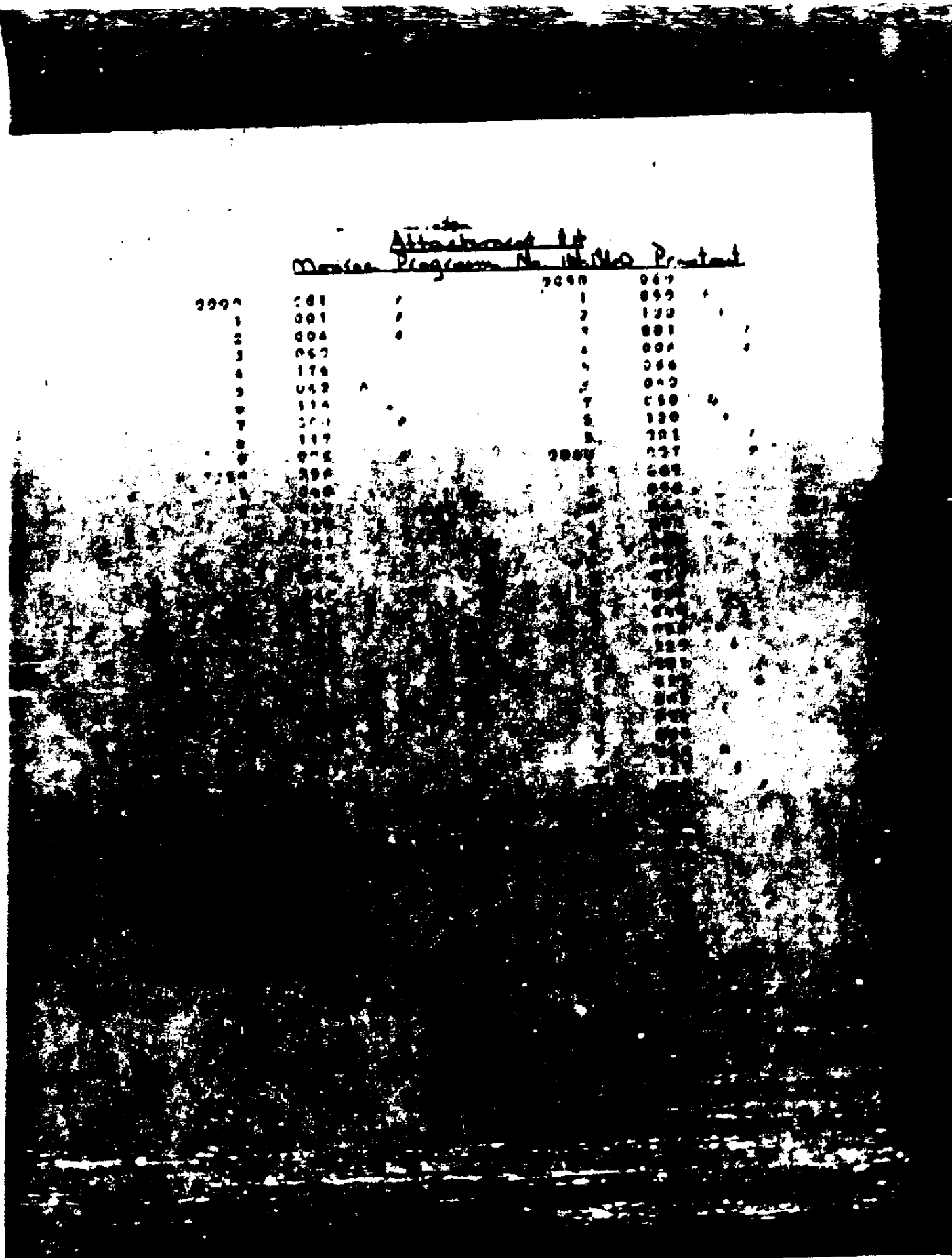


0.1

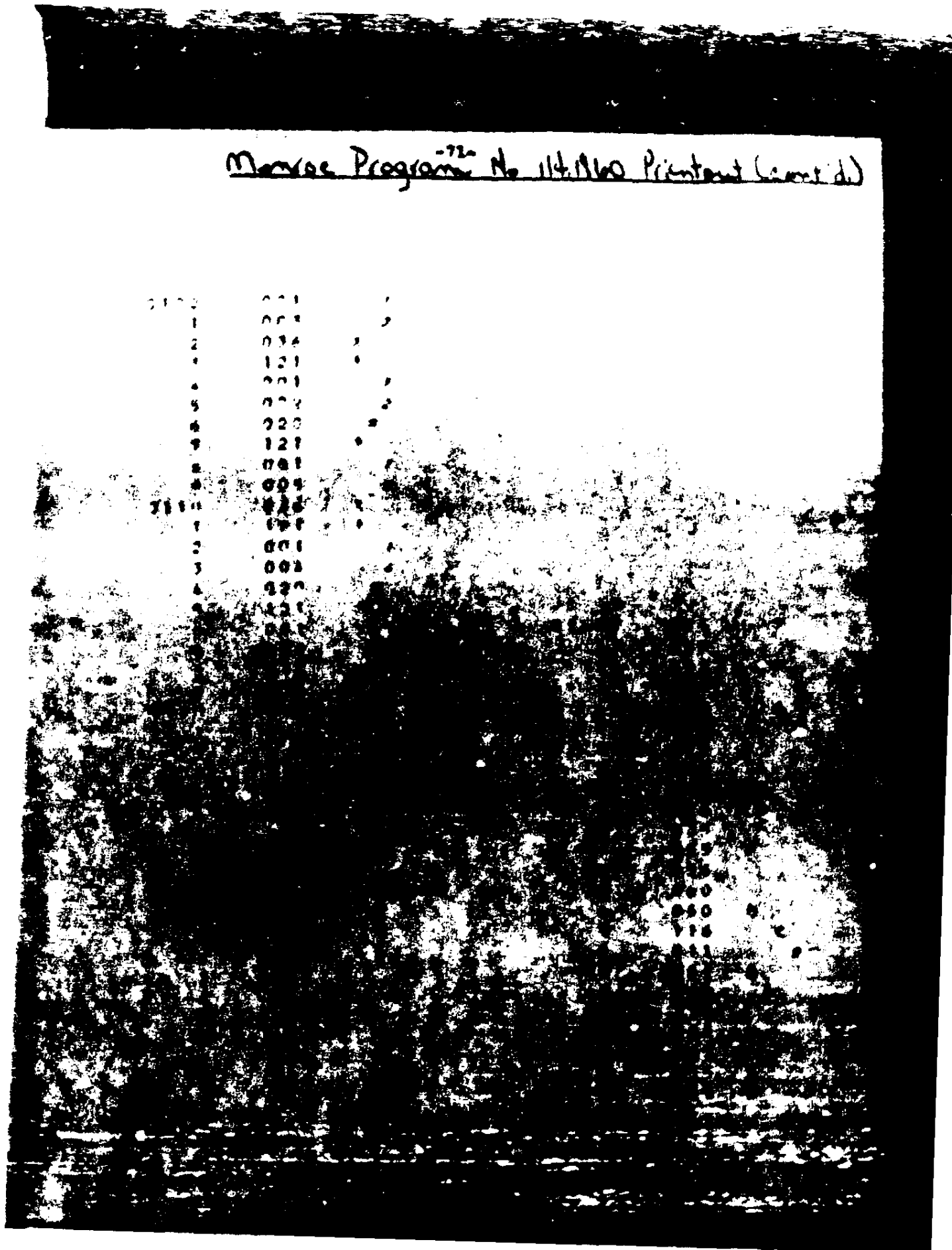
Attachment #2
Monroe Program No. 11A1160 Printout



Attachment 13
Power Program No. 13,110 Pursuant



Macros Program -72- No 11&1160 Printout (cont'd)



Attachment 65

[illegible] ______________ [illegible] ________

[illegible] [illegible], [illegible] [illegible] [illegible] ____/______

[illegible] ______________ [illegible] ______________

[illegible] ______________ [illegible] [illegible] ______________

[illegible]	[illegible]	[illegible]	% VCN ON [illegible] 2	TOTAL [illegible] [illegible] VCN	DECAL- [illegible] YES/ NO	REPORT TTK VCN
[illegible]	[illegible]	[illegible]	✓	✓	YES	✓
[illegible]	[illegible]	[illegible]			NO	
[illegible]	[illegible]	[illegible]	✓	✓	YES	✓
[illegible]	[illegible]	[illegible]			NO	
[illegible]	[illegible]	[illegible]		✓	YES	✓
[illegible]	[illegible]	[illegible]			NO	
[illegible]	[illegible]	[illegible]		✓	YES	✓
[illegible]	[illegible]	[illegible]			NO	
[illegible]	[illegible]	[illegible]		✓	YES	✓
[illegible]	[illegible]	[illegible]			NO	
[illegible]	[illegible]	[illegible]		✓	YES	✓
[illegible]	[illegible]	[illegible]			NO	
[illegible]	[illegible]	[illegible]	✓	✓	YES	✓
[illegible]	[illegible]	[illegible]			NO	
[illegible]	[illegible]	[illegible]	✓	✓	YES	✓
[illegible]	[illegible]	[illegible]			NO	
[illegible]	[illegible]	[illegible]		✓	YES	✓
[illegible]	[illegible]	[illegible]			NO	
[illegible]	[illegible]	[illegible]			YES	✓

VINYL CHLORIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte: Vinyl Chloride	Method No.: P&CAM 178
Matrix: Air	Range: 0.008 to 5.2 mg/m³ in a 5 - liter air sample
Procedure: Adsorption on activated carbon, desorption with carbon disulfide, gas chromatography	Precision (CV_T): 0.08 at levels of 7 and 71 mg/m³
Date Issued: 9/3/74	Classification: B (accepted)
Date Revised: 1/29/76	

1. Principle of the Method

A known volume of air is drawn through two small sorbent tubes in series containing activated coconut shell charcoal which adsorbs the vinyl chloride present in the air. The charcoal in each tube is transferred to a separate vial and desorbed with carbon disulfide, and the desorbed samples are analyzed by gas chromatography. Quantitation is accomplished by the addition of

3. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped effectively. Experiments indicate that high humidity severely decreases the capacity of activated carbon for organic vapors.

3.2 When two or more substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample since these compounds may interfere with the analysis for vinyl chloride.

3.3 Any compound that has the same retention time as vinyl chloride at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, may not provide proof of chemical identity. Often, operating conditions can be modified to eliminate interferences. Samples should be analyzed by an independent method when overlapping gas chromatographic peaks cannot be resolved.

4. Sampling and Analysis

4.1 The [illegible] sampling train, the analysis of [illegible] tube, [illegible] was supplied by a dynamic concentration of 7.3 mg/m³ in the air [illegible] was supplied by a dilute solution (571.3 mg/m³, were 0.876 and [illegible] These values reflect what was supplied [illegible] were as well as [illegible] collection efficiency.

[illegible] indicate the [illegible] more indicative of the accuracy, although [illegible] primary standard. These [illegible] by a capillary [illegible] of the [illegible]

Experiment No.		Concentration, calculated, mg/m³	Concentration, experimental, mg/m³	Estimated error, %[a]
I	Gas samples	64	71.2 ± 0.7[b]	
	Sorbent tubes	64	69.8 ± 1.5	-2
II	Gas samples	13	14.5 ± 0.5	
	Sorbent tubes	13	13.6 ± 0.4	-6
III	Gas samples	2.6	2.88 ± 0.07	
	Sorbent tubes	2.6	2.91 ± 0.13	+1
IV	Gas samples	1.3	-	
	Sorbent tubes	1.3	1.27 ± 0.09	-

a. The estimated error is the average of concentrations determined from sorbent tubes minus the average of concentrations determined from gas samples, divided by the average of concentrations determined from gas samples, multiplied by 100.

b. The sampling error is the plus-minus value of the 95% confidence level. The 95% confidence level is defined as the standard deviation, multiplied by Student's t at the 0.05 significance level, divided by the square root of the number of samples.

5. Advantages and Disadvantages of the Method

5.1 This sampling device is small, portable, and involves no liquids. Interferences are [illegible] and most of these, if the source can be eliminated by closing [illegible] sampling. The [illegible] sampled by means of a valid instrumental [illegible] method by [illegible] simultaneous determination of two or [illegible] gas sample by the [illegible] the same sample by changing gas [illegible] flow rate through the [illegible] temperature-programmed mode of [illegible]

6. Apparatus

6.1 Personal Sampling Pump. The pump should be a properly calibrated personal sampling pump for personal and area samples. It should be calibrated with a representative sorbent tube in the sampling line. A dry or wet test meter or a glass rotameter that will determine the flow rate (50 ml/min) to within ±5% may be used for the calibration.

6.2 Sorbent Tubes. The glass tubes have both ends flame sealed. Each is 7 cm long, 6-mm o.d., 4-mm i.d., and contains two sections of 20/40-mesh activated carbon separated by a 2-mm portion of urethane foam. The activated carbon is prepared from coconut shells and is fired at 600°C prior to packing to remove adsorbed materials. The primary adsorbing section contains 100 mg of sorbent, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silanized glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 2 in. of water at a flow rate of 0.2 l/min.

6.3 Gas chromatograph equipped with a flame ionization detector. [illegible]

[illegible] (or graduated in 0.1-ml increments). [illegible]

[illegible] It is preferable to [illegible]

4.4 Purified hydrogen.

4.5 Filtered compressed air.

5. Procedure

5.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be washed with detergent and thoroughly rinsed with distilled water.

5.2 Collection and Shipping of Samples

5.2.1 Immediately before sampling, the ends of two tubes are broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

5.2.2 The smaller indicator tube is used as a backup and is positioned next to the sampling pump in tandem with the test tube.

5.2.3 The [illegible] is placed in a vertical position with the [illegible] of the [illegible] tube pointing upward. A [illegible] rubber [illegible] is [illegible] to the [illegible] tube [illegible] is to be placed through any hose or other [illegible] prior to sampling.

5.2.4 [illegible] gas, or vapor, must be measured at [illegible] [illegible] at a flow rate of 50 ml/min. The [illegible] [illegible] is placed [illegible] (See Section 2.2.)

8.2.10 Capped tubes are packed tightly before they are shipped to minimize tube breakage during transport to the laboratory. The use of two tubes in series has eliminated the need for cooling during shipping. However, if two tubes are *not* used, *i.e.*, only one tube is used, and if the samples will spend a day or more in transit, then cooling (*e.g.*, with Dry Ice) is necessary to minimize migration of vinyl chloride to the backup section.

8.2.11 Samples received at the laboratory are logged in and immediately stored in a freezer (around - 20°C) until time for analysis. Samples may be stored in this manner for long periods of time with no appreciable loss of vinyl chloride (2 months). Even around -20°C, vinyl chloride will equilibrate between the two sections of activated carbon, *i.e.*, it will migrate to the backup section. This disappearance is observable after 2 weeks and may be confused with sample [illegible] after 2 months.

[illegible] used in the collection [illegible] with a file and [illegible] sections of [illegible] material. It is [illegible] that the sample [illegible]

8.3.3 **Injection.** The first step in the analysis is the injection of [illegible] into the gas chromatograph. To eliminate difficulties arising [illegible] check or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Two microliters of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent and the plunger is pulled back about 0.4 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn to the 7.4 µl mark (2 µl solvent + 0.4 µl air + 5 µl sample = 7.4 µl). After the needle is removed from the sample and prior to injection the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard are made. No more than a 3% difference in area is to be expected. Automatic sampling devices may also be used.

8.3.4 **Measurement of Area.** The area under the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.4 [illegible]

8.4.1 [illegible]

8.4.2 [illegible]

8.4.3 [illegible]

The desorption efficiency equals the amount of vinyl chloride [illegible] from the sorbent divided by the quantity of vinyl chloride contained in the volume of synthetic atmosphere sampled, or

$$\frac{\text{(amount of vinyl chloride from sorbent)}}{\left(\begin{matrix}\text{conc of vinyl chloride} \\ \text{in bag}\end{matrix}\right) \times \left(\begin{matrix}\text{vol of atmosphere} \\ \text{sampled}\end{matrix}\right)}$$

9. **Calibration and Standards**

CAUTION: Laboratory Operations Involving Carcinogens

Vinyl chloride has been identified as a human carcinogen and appropriate precautions must be taken in handling this gas. The Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. They may be found in 29 CFR 1910.93q (Section [illegible]) in Title 29 of the Code of Federal Regulations available in the [illegible] October 4, 1974, [illegible]

[illegible] ... as bag of highly [illegible]

[illegible], standard solutions must be analyzed at the [illegible]. This will minimize the effect of day-to-day [illegible]

2[illegible]

3.1.3 Volumetric Method. A [illegible] gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the valve is closed. The tip of the needle is inserted into a 10-ml volumetric flask containing approximately 5 ml of CS_2. The valve is opened and the plunger is withdrawn slightly to allow the CS_2 to enter the syringe. The action of the vinyl chloride dissolving in the CS_2 creates a vacuum and the syringe becomes filled with the solvent. An air bubble (2%) is present and has been found to be due to the void volume in the needle of the syringe. The solution is returned to the flask and the syringe is rinsed with dioxane CS_2 and the washings added to the volumetric flask. The volumetric flask is then filled to the mark with CS_2. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at -20°C and have been found to be stable at this temperature for 3 days. Tight-fitting plastic caps on the volumetric flasks seem to retain the vinyl chloride better than ground-glass stoppers.

[illegible] cap is used from the standard [illegible] between the [illegible] and the volumetric [illegible]

10.5 The concentration of vinyl chloride in air may be expressed in mg/m³:

$$mg/m^3 = \frac{\text{corrected weight (in mg)}}{\text{volume of air sampled (in l)}} \times$$

10.6 The concentration may also be expressed in terms of parts per million (ppm) by volume:

$$ppm = mg/m^3 \times \frac{24.45}{M.W.} \times \frac{760}{P} \times \frac{T+273}{298}$$

where: 24.45 = molar volume (l/mole) at 25°C and 760 mmHg.

M.W. = molecular weight.

P = pressure (mmHg) of air sampled.

T = temperature (°C) of air sampled.

[illegible], A.W. Tracy, and W.J.Wendle,

[illegible]

The Standard Oil Company
Chemical Group
[illegible] Oak Tree Boulevard
[illegible], Ohio 44131
[illegible]

August 28, 1980
XOE-92-80

Mr. Ray Novak - Tech. Dir.
Rhinelander Paper Company
Rhinelander, WISC. 54501

Dear Mr. Novak:

RE: RESULTS OF AREA MONITORING AT RHINELANDER PAPER COMPANY

On August 7, 1980, Bill Potter and T. S. Bialka visited Rhinelander to monitor the Cabin 976 papercoating line for VCM emissions.

[illegible] Method

[illegible] used in this report was adsorption of VCM onto [illegible] using SKC charcoal tube at 30-60 cc/min; analysis [illegible] gas chromatography.

[illegible] from the breathing zone of all employees [illegible] sampling. General area samples were also [illegible] of VCM release. Analysis of the [illegible] Monsanto Corporate Environmental [illegible] Ohio. The laboratory is

[illegible] published in the Federal Register [illegible] 1 ppm is as follows:

[illegible] ceiling of 5 ppm

[illegible] ppm TWA.

[illegible]

The results above are based on limited testing and actual continuing factory exposure may be different. The test results are believed to be representative of conditions found under the particular and peculiar operating conditions existing at the time and place where the tests were made and no representations are made concerning other times, conditions or production levels. Submission of the test results is not intended to determine or insure compliance with any standard, specification, governmental regulation or policy, although such results can be useful in establishing the elements necessary for a program of compliance. We hope that the data presented will assist you in continuing to provide a safe workplace for your employees.

The responsibility of maintaining an environment in compliance with [illegible] rests with the individual manufacturer.

Very truly yours,

[illegible] CHEMICAL GROUP
[illegible] Division

[illegible] Schave
[illegible]ct Manager

K. Schneider — Cleveland Chemical

T. S. Wialka — Akron - D/0020, 5-H — 8-25-80

RHINELANDER PAPER CO. - VCM

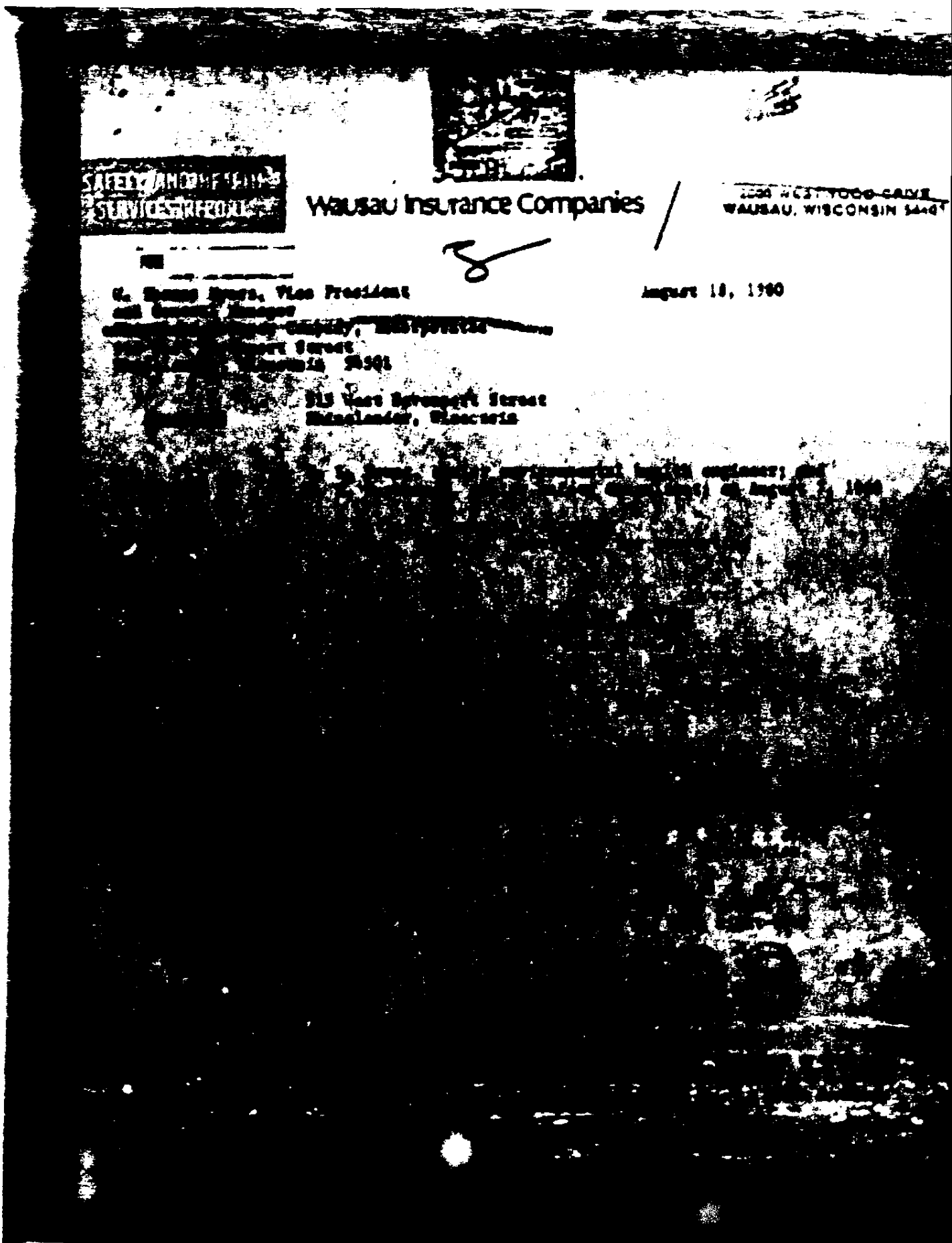
On August 7, 1980 the Rhinelander Paper Company, Rhinelander, Wisconsin was visited to monitor the workplace for VCM. The visit was made at the request of the customer, since they were using a SBR latex in their operations. Samples were collected on SKC charcoal tubes at 30-60 cc/min.; analysis was by gas chromatography.

[illegible] were collected from the breathing zone of all employees [illegible] operation. General area samples were [illegible] of VCM release. Analysis of [illegible] Enviro-Tech Laboratories. The laboratory is [illegible] ng/sq cm [illegible] ppm [illegible] ppm [illegible] city.

RHINELANDER PAPER COMPANY

CH MONITORING RESULTS - 8/7/80

Sample/Location/ Operation	Sample Time (min.)	Sample Volume (liters)	Concentration (ppm)
R. Fisher Coating/Mixing	200 223	10.2 10.2	0.2 0.3
R. Craig, Foreman	426	10.1	0.2
J. [illegible]	[illegible] [illegible]	10.0 11.3	0.1 0.1
[illegible]	[illegible]	[illegible]	0.3 0.2



Wausau Insurance Companies

WAUSAU, WISCONSIN

August 18, 1980

315 West Sycamore Street

Rhinelander Paper Company
Incorporated

time-weighted average permissible exposure level of one part per million (1 p.p.m.) and also below the OSHA action level of 0.5 p.p.m.

4582

211.12094