



The B. F. Goodrich Company

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DIRECTOR OF ENVIRONMENTAL AFFAIRS

July 12, 1974

FILE COPY

Mr. Julius Jimeno
Docket 36
1726 M Street, N.W., Room 200
Washington, D. C. 20210

Dear Mr. Jimeno:

I am enclosing our laboratory report which fulfills the request by the Office of the Solicitor for further information on the technical details of testing commercially available charcoal filled canister and cartridge protective breathing devices.

The experimental approach is described in detail. The wide range in capacity for absorbing vinyl chloride by commercial absorbants is shown in Table I on page 4 and the clear superiority of activated charcoal is evident. The comparison of cartridge and canister data in Tables 2 and 3 indicates that depth of carbon bed is also a factor in capacity which must be balanced against pressure drop in the design of a respirator for breathing protection. The desorption experiments show that the recharging of cartridges and canisters is feasible.

Laboratory work is continuing. If further pertinent information develops, it will be submitted before August 23, 1974.

Very truly yours,

THE B.F. GOODRICH COMPANY

Roger W. Strassburg, Ph.D.
Director of Environmental Affairs

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TO Dr. P. W. Strassburg	FIELD POINT OR AAFON DEPARTMENT & BULG. NO. Alton; Loc. WFB-4; Dept. 6001	DATE OF LETTER JUN 2, 1974
FROM Dr. W. M. O'Mara	FIELD POINT OR AAFON DEPARTMENT & BULG. NO. Avon Lake Technical Center	

SUBJECT
A. Investigation of the Adsorption Properties of Vinyl Chloride Monomer
on Commercial Carbon Filters

Introduction

This report is a summary of our work on the adsorption characteristics of VCM on carbon filters which are used in conjunction with protective breathing masks. The basic objective of the study was to determine the adsorptive and desorptive characteristics of various, commercially available, carbon filters which are used as protection against inhaled organic vapors. This study involved vinyl chloride monomer only.

Experimental Approach

An experimental flow chamber was constructed so that carbon filter cartridges and canisters could be subjected to a continuous flow of air containing vinyl chloride monomer. A continuous rather than batch monitoring method of analysis was chosen to indicate the presence of vinyl chloride monomer. A photograph of the basic flow chamber is shown in Figure 1. The vinyl chloride-air stream enters the carbon device at A. The scrubbed stream then exits the device at B. Line C is the continuous monitoring system for sensing vinyl chloride monomer in the air stream. Additional experimental data are contained in the Appendix. To demonstrate the type of data that is obtained from the experiment described above, a plot of VCM concentration versus time is shown in Figure 2. The rise in the horizontal baseline indicates incipient vinyl chloride monomer breakthrough.

In our initial experimental design, we used a portable Century Organic Vapor Analyzer to sense vinyl chloride monomer. The major problem with this analyzer was its inherent background which could not be subtracted electronically from the recorder output. To overcome this we replaced this instrument with a Bendix Hydrocarbon Analyzer. Both instruments are flame ionization units; Figure 2 is based on the output of the Bendix instrument. The Bendix instrument is well suited for the type of measurement carried out because of the following unique characteristics:

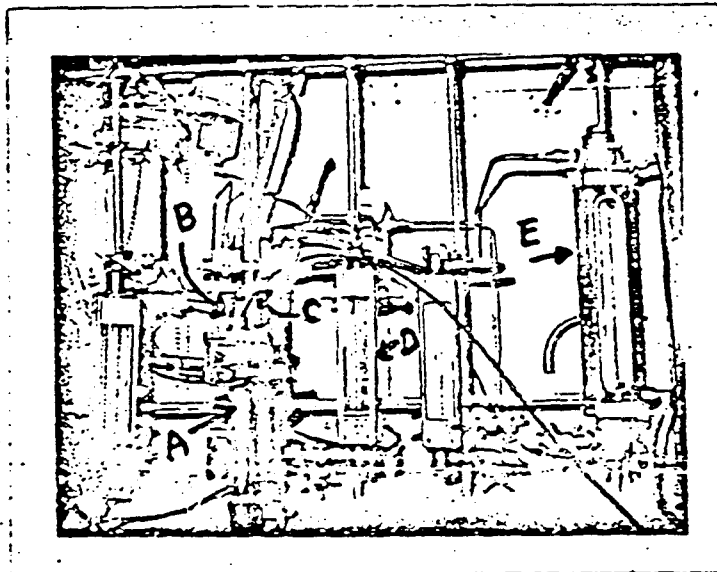
- (1) low drift
- (2) linear (vs. logarithmic) amplification
- (3) background zero suppression
- (4) excellent stability

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Figure 1: Experimental VCM Flow Chamber



- (A) vinyl chloride/air stream into cartridge holder
- (B) cleaned air stream exit
- (C) analyzer sampling line
- (D) vinyl chloride flowmeter
- (E) high capacity air flowmeter

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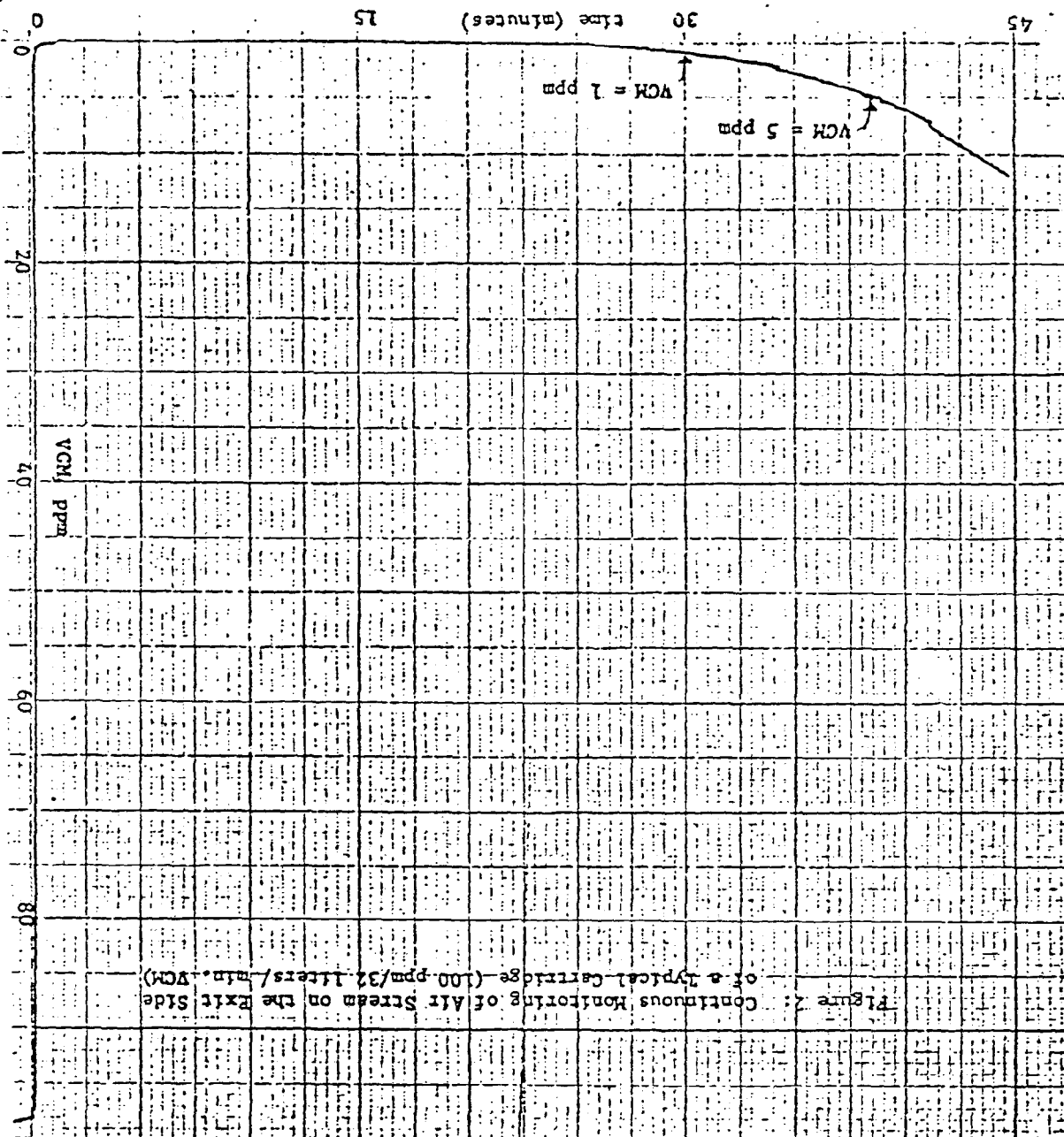


Figure 2

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Experimental Results

(1) Initial Evaluation of Commercial Cartridges

A variety of commercial cartridges were evaluated with the Century analyzer in order to obtain a profile of their ability to retain vinyl chloride monomer. All evaluations were carried out at a flow of 30 liters per minute and a vinyl chloride concentration (volume/volume) of 100 parts-per-million. In these early evaluations, the time to 5 parts per million of vinyl chloride at the exit side of the carbon matrix was determined. This value is referred to as T_5 (in minutes). Table 1 contains a summary of the various cartridges evaluated and the corresponding T_5 values obtained.

Table 1

T_5 ⁽¹⁾ Values for Various Carbon Cartridges
When Tested at 30 liters/minutes and 100 ppm of Vinyl Chloride Monomer

<u>Cartridge</u>	<u>T_5 ⁽¹⁾, minutes</u>
Welsh 7500-1	41, 34, 39, 44, 33
American Optical AOR55	21
Westvaco Nuchar WV-H 8X30	15
Willson R-25	34
Willson R-11	0
American Optical R-51	29
Willson R-21	42 ± 13
Welsh 7400-1L (cart st ridge)	93
Welsh (Canister) 7800-1M	678
MSA Cartridge 44-35	13

(1) T_5 refers to the time in minutes for the concentration of VCM at the exit end of the cartridge to reach 5 ppm.

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It can be seen from these data that the commercial cartridges and canisters chosen for this study exhibit a broad range in ability to absorb vinyl chloride monomer. All of the 3-inch cartridges were effective from zero minutes (no VCM adsorption) to about 40 minutes. After initial vinyl chloride breakthrough there is a gradual rise to a value corresponding to the concentration of vinyl chloride in the air stream.

As expected, the 4-inch cartridge (Welsh 7400-1L) and the canister outperformed the 3-inch cartridges under these test conditions. It should be noted that in the end-use mask construction, two of the 3-inch cartridges are used. On the other hand, a single 4-inch cartridge or canister is used in masks employing these carbon devices. Thus to obtain a true evaluation of the 4-inch cartridge and canister, they must be exposed to an air flow that is double that used for the 3-inch cartridge evaluation. This type of evaluation is described below.

(11) Detailed Evaluations of the Welsh Canister, 3-inch Cartridge and 4-inch Cartridge

The NIOSH requirement for testing protective masks calls for evaluations at the following atmospheric flow rates: 32 liters/minute and 64 liters/minute. The Welsh canister (7800-1M), the Welsh 4-inch cartridge (7400-1L) and the Welsh 3-inch cartridge (7400-1) were evaluated within these guidelines. Testing with the 3-inch cartridge was restricted to a flow rate of 32 liters/minute while that for the 4-inch cartridge and canister was limited to a flow rate of 64 liters/minute. In order to improve the accuracy of the measurement, a Bendix Total Hydrocarbon Analyzer was obtained for monitoring vinyl chloride monomer. Using this instrument in the experiment approach described above, measurements at 1 ppm VCM breakthrough (T_1) could be accurately obtained. Table 2 contains a summary of T_1 values obtained for the three Welsh cartridges and canisters. These data show that vinyl chloride breakthrough (T_1) is essentially the same for the 3-inch and 4-inch cartridges when tested at the two required flow rates. It is also obvious that breakthrough is quite dependent upon concentration. For the two cartridges, a 4-fold increase in VCM concentration caused a 50% increase in breakthrough time. The stronger dependence of VCM/air rate on breakthrough time is demonstrated by comparing data in Table 1 with that in Table 2. For example, comparing T_5 data (accurate T_1 data is not available in Table 1) it is seen that for the 4-inch cartridge there is a 50% increase in breakthrough (T_5) when the rate is increased from 30 liters/minute ($T_5 = 93$ minutes) to 64 liters/minute ($T_5 = 48$ minutes) at a VCM concentration of 100 ppm.

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Table 2

T₁ (1) Values for the Welsh 3-inch, 4-inch Cartridges
and Canister at Various Concentrations of Vinyl Chloride Monomer

I. Welsh 7500-1 (3-inch)

32 liters/minute

<u>VCM, ppm</u>	<u>T₁, minutes</u>
25	60
50	60
100	35 (T ₅ = 44 minutes)

II. Welsh 7400-1L (4-inch)

64 liters/minute

<u>VCM, ppm</u>	<u>T₁, minutes</u>
25	70
50	60
100	40 (T ₅ = 48 minutes)

III. Welsh 7800-1M (Canister)

64 liters/minute

<u>VCM, ppm</u>	<u>T₁, minutes</u>
25	522 (8.7 hrs.)
100	342 (5.7 hrs.)
1000	102 (1.7 hrs.)

(1) T₁ refers to the time in minutes for VCM concentration to reach 1 ppm.

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Considering only those data in Table 2 it can be shown that the amount of vinyl chloride adsorbed increases with increasing concentration of vinyl chloride in the air stream. The absolute amount of vinyl chloride adsorbed by the carbon in each of the experiments can be obtained from the following equation:

$$VCM, cc = \text{total rate (cc/min.)} \times \text{concentration VCM} \left(\frac{P_{VCM}}{P_{OG}} \right) \times T_0$$

where T_0 is initial breakthrough at "zero" parts per million.

Once obtained, relative VCM adsorption efficiencies can be calculated by dividing these values by the weight of the carbon in the cartridge. A summary of these data are contained in Table 3. It is evident that the efficiency of carbon to absorb vinyl chloride monomer is not constant but rather increases as the concentration of vinyl chloride monomer increases in the air. It is significant to note that the efficiency of carbon to adsorb vinyl chloride monomer is nearly constant for the two cartridges when compared at the same vinyl chloride concentration, even though the flow rates are significantly different. This sameness in efficiency, of course, relates back to the previous statement that these two cartridges offer the same degree of protection. As a final comment the very high efficiency of the carbon bed in the canister is responsible for the excellent (relative) protection this device provides.

It appears that empirical mathematical equations describing breakthrough times for the two types of cartridges could be readily developed since the adsorption efficiency at a given VCM concentration is constant. However, before this is attempted more data would be necessary at different flow rates and over a broader concentration range.

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Table 3

Calculation of Absolute Adsorption of VCM (cc)
on Carbon and Efficiencies (cc VCM/g Carbon)

• I. Welsh 7500-1 (3-inch)

32 liters/minute

<u>VCM, ppm</u>	<u>VCM Adsorbed, cc</u>	<u>Efficiency⁽¹⁾, cc/g</u>
25	48.0	1.34
50	82.4	2.29
100	108.8	3.03

II. Welsh 7400-1L (4-inch)

64 liters/minute

<u>VCM, ppm</u>	<u>VCM Adsorbed, cc</u>	<u>Efficiency⁽²⁾, cc/g</u>
25	88.0	1.31
50	160.0	2.38
100	227.0	3.39

III. Welsh 7800-1M (Canister)

64 liters/minute

<u>VCM, ppm</u>	<u>VCM Adsorbed, cc</u>	<u>Efficiency⁽³⁾, cc/g</u>
25	777.6	2.51
100	1958.4	6.31
1000	6336	20.4

- (1) cartridge contained 35.9g carbon
- (2) cartridge contained 67.0g carbon
- (3) canister contained 310.3g carbon

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(iii) Desorption of Vinyl Chloride Monomer

It was of interest to study the desorption characteristics of vinyl chloride monomer from the cartridges. To accomplish this objective, the 3-inch Welsh cartridge was exposed to vinyl chloride monomer at 100 ppm and 32 liters/minute until initial breakthrough at 1 ppm (i.e. T_1) was achieved. At this point the vinyl chloride feed stream was shut off and the cartridge was exposed to clean air at 32 liters/minute. A skewed bell-shaped curve developed which maximized at 33 ppm (time = 84 minutes) and decreased to 0 ppm (time = 330 minutes). In actuality we were producing a gas chromatogram in which the carbon canister was a crude chromatographic column, the air was the carrier gas, the vinyl chloride was the sample and the Bendix analyzer was the detector. It is well known that one way to decrease the retention time in gas chromatography is to increase the flow rate. To demonstrate this phenomenon with the present system, we repeated the above experiment (3-inch cartridge, 100 ppm VCM, 32 liters/minute) except once initial VCM breakthrough occurred the vinyl chloride feed was discontinued and the clean air rate was increased to 64 liters/minute. At this increased flow rate, the bell shaped "chromatographic" curve was less skewed. The maximum now occurred at 36 ppm (time = 49 minutes) and decreased to 0 ppm (time = 194 minutes). This trace is shown in Figure 3. Thus by doubling the "carrier gas" flow rate from 32 liters/minute to 64 liters/minute, the "retention time" decreased by 42%.

It is obvious that other chromatographic principles can be used to further decrease the desorption time of VCM on carbon. For example, higher flows in combination with heat could potentially lead to very rapid removal of the VCM from the carbon.

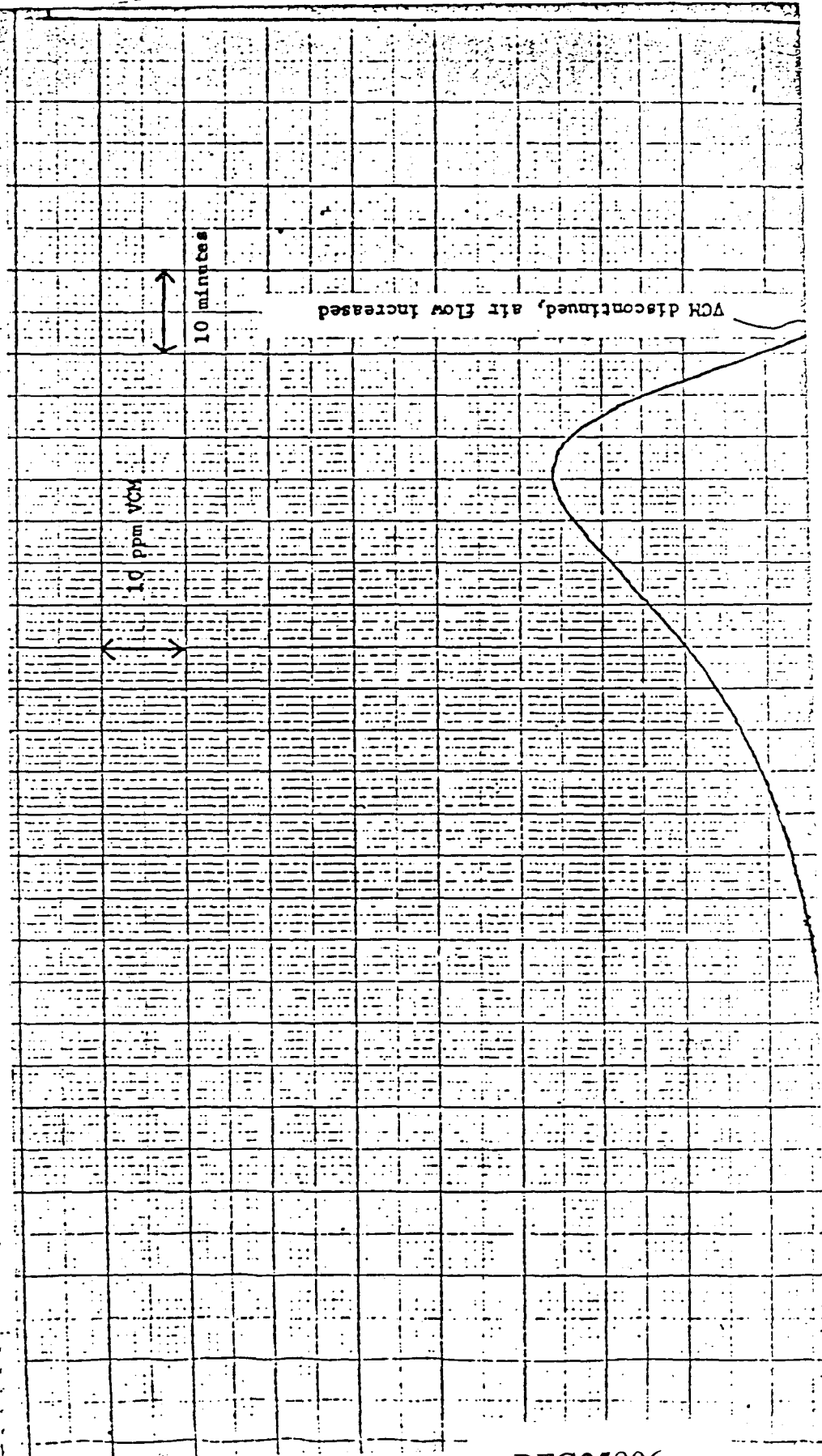
(iv) Performance of Cartridge after Repeated Adsorption-Desorption of Vinyl Chloride

Based on chromatographic principles, the cartridges used to adsorb vinyl chloride should be reusable once desorption has been carried out. To verify this, a 3-inch cartridge was exposed to vinyl chloride and desorbed at 64 liters/minute. This was repeated twice. This "regenerated" cartridge was then exposed to VCM at 100 ppm and 32 liters/minute. It was found that the efficiency to absorb vinyl chloride monomer was the same as found for a new cartridge. The breakthrough times for the regenerated cartridge were $T_1 = 35$ minutes and $T_2 = 45$ minutes. These values are identical to those values reported in Table 2 for a new 3-inch cartridge.

Figure 3

Desorption of VCM from 3-inch Welsh Cartridge at 64 liters/minute Clean Air

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Appendix I

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Appendix I

Experimental

Vinyl Chloride Standards

Vinyl chloride monomer in air standards (19, 900, 9990 ppm) were obtained commercially from Precision Gas Products, Inc., Rahway, New Jersey 07065.

Cartridges-Canisters

All cartridges and canisters were obtained commercially from the suppliers already mentioned. All devices were tested as received.

Make-Up Air

In order to attain the high flow rates necessary, in-plant compressed air was used to dilute the vinyl chloride standards. This air stream was purified by means of an oil filter and a 9-inch (length) by 5-inch (diameter) carbon bed. *The relative humidity of make up air after passage through the carbon was 25% at 74°F. Incoming air probably had relative humidity of ca. 60%.*

Flowmeters

All streams were metered with F. & P. Co. precision bore flowmeters.

Vinyl Chloride Analyzers/Recorder

The Century Organic Vapor Analyzer used in the initial phases of this work was purchased from Century Systems Corp., Arkansas City, Kansas 67005. The Bendix Total Hydrocarbon Analyzer (Model 8401) was purchased from Bendix, Ronceverte, W. Va. 24970. A Hewlett-Packard Model 7101B Strip Chart recorder was used to display the outputs from the Century and Bendix instruments.

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