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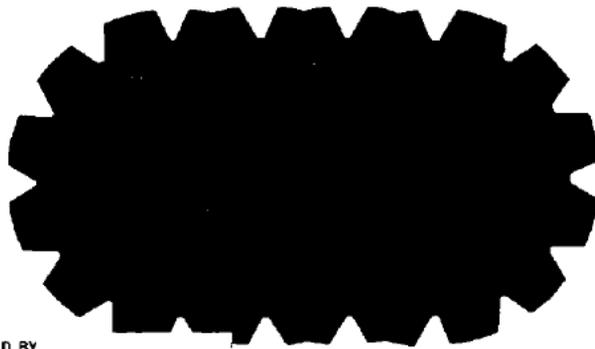
TECHNICAL INFORMATION

An Evaluation of Organic Vapor Respirator Cartridges and Canisters Against Vinyl Chloride

AN EVALUATION OF ORGANIC VAPOR RESPIRATOR

CARTRIDGES AND CANISTERS AGAINST VINYL CHLORIDE

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ABSTRACT

The service lives of four types of approved organic vapor respirator cartridges and four types of approved front or back mounted organic vapor gas mask canisters were determined relative to several concentrations of vinyl chloride. Various mixtures of vinyl chloride gas and air were passed through the cartridges and canisters and the downstream concentration was monitored until breakthrough occurred.

The effect of concentration on breakthrough time conformed to adsorption theory.

Brief investigations indicated service life increased at low humidities and decreased at high humidities.

Recommendations are made concerning the use of organic vapor respirator cartridges and gas mask canisters in atmospheres containing vinyl chloride gas, based on expected service life and facepiece leakage.

INTRODUCTION

Vinyl chloride is a synthetic chemical made by oxy-chlorination of ethylene or by hydrochlorination of acetylene. It is used in the manufacture of containers, wrapping film, electrical insulation, pipe, conduit, and a variety of other products.

In January of 1974, it became known to the National Institute for Occupational Safety and Health(NIOSH) and the Occupational Safety and Health Administration(OSHA) that several employees of the B.F. Goodrich Chemical Company had died from a rare form of liver cancer (angiosarcoma) that may have been occupationally related.

Information presented at a fact-finding hearing to determine the hazards of polyvinyl chloride and vinyl chloride, held by OSHA on February 15, 1974, showed that tumors were produced in animals at concentrations as low as 250 ppm. On the basis of this information an Emergency Temporary Standard was promulgated by OSHA on April 5, 1974. This standard reduced allowable ceiling exposure from 500 ppm to 50 ppm.

On April 15, 1974 information was presented to representatives of OSHA, NIOSH, and EPA by Industrial Bio-Test Laboratories which indicate that angiosarcomas were produced in animals at concentrations of 50 ppm. On this basis, a Proposed Permanent Standard on vinyl chloride was published by OSHA in the Federal Register on May 10, 1974, proposing no detectable level of employee exposure as determined by a method capable of detecting 1 ppm vinyl chloride.

In both the Emergency Temporary Standard and the Proposed Permanent Standard, air-supplied respirators and self-contained breathing apparatus are specified for respiratory protection in atmospheres greater than the ceiling limit.[1,2]

Only limited testing has been done to evaluate organic vapor cartridges and canisters against vinyl chloride. In a study by Lawrence Livermore Labs (A.E.C.) cartridges were evaluated against various classes of organic vapors at concentrations of 1000 ppm. One of these vapors was vinyl chloride. Cartridge life (10% breakthrough) in this test was less than 10 minutes.[3] A 10% breakthrough time occurs when cartridge or canister penetration concentration reaches 10% of the ambient concentration.

In discussing service life of charcoal cartridges or canisters, limitations of facepiece fit must be recognized. Protection factors for various types of respirators are discussed by Hyatt, et al in a paper presented at the 16th Annual Meeting of the Health Physics Society in New York City, July 12 -

16, 1971.[4] A protection factor is defined as the ratio of ambient contamination to contaminant levels within a facepiece. Protection factors for half mask respirators and full-facepiece gas masks are 10 and 100 respectively. Thus, based on fit alone, half mask organic vapor respirators and full-facepiece gas masks could be used in contaminant concentrations of 10 and 100 times the substance ceiling value respectively.

The purpose of this testing program was to gain information on service lives (time a cartridge or canister may be used before breakthrough occurs) of organic vapor cartridges and canisters in concentration ranges consistent with both the Emergency Temporary Standard, the Proposed Permanent Standard for vinyl chloride and established protection factors for half mask organic vapor respirators and full-facepiece gas masks.

In this program, four types of NIOSH/Bureau of Mines approved organic vapor respirator cartridges and four types of NIOSH/BM approved front or back mounted organic vapor gas mask canisters were tested. The weights of charcoal in each of these devices are shown in Table 1. Other than the weight of charcoal in each cartridge or canister, adsorption characteristics were unknown.

Adsorption theory predicts that charcoal is more efficient at higher contaminant vapor pressures. If the equation for service life of various cartridges and canisters versus concentration can be determined for vinyl chloride, then cartridge or canister life can be predicted at concentrations other than test concentrations. An effort was made to establish this relationship for vinyl chloride.

The humidity of ambient air can affect the adsorption capacity of charcoal. This effect was also briefly investigated in relation to vinyl chloride.

TEST SETUP

Generation

The generation system consisted of an air preconditioning subsystem and a vinyl chloride metering subsystem. A schematic diagram of the system is shown in Figure 1. Air was first passed through a solution of 20% NaOH to remove CO_2. The air stream was then divided and passed through either water or concentrated sulfuric acid to condition the air to the desired relative humidity. Air flow was monitored with a dry test meter prior to being mixed with vinyl chloride.

Vinyl chloride gas was taken from one of four tanks of vinyl chloride in nitrogen (0.1%, 1%, 10%, or 20%). The flow

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rate from the appropriate tank was controlled by means of a metering valve and calibrated orifice. The vinyl chloride was then mixed to the desired concentration with the pre-conditioned air and delivered to the cartridge or canister.

Detection

A Wilks Scientific Miran I variable pathlength infrared analyzer was used to monitor ambient and breakthrough concentrations of vinyl chloride. All analyses were done at the 10.9 micron wavelength adsorption band. No interferences were detected. A cartridge or canister penetration sample was pulled through the 5.5 liter analyzer gas sample cell at the flow rate of 6.5 LPM. Breakthrough times were corrected for the resultant 3-minute lag in response. Bags filled with the ambient concentration were periodically analyzed with a gas chromatograph by the Physical and Chemical Analysis Branch of NIOSH to verify test concentrations. Results agreed well within 10%.

TESTS PERFORMED

Preliminary Tests

Preliminary tests were performed on one cartridge type from a single batch to determine the effects of ambient relative humidity on breakthrough time. These tests were run at 600 ppm, 75 + 5°F. Flow rates were based on a moderately heavy work rate of approximately 930 Kg-m/min. This corresponds to a breathing rate of 60 LPM. Cartridges were tested at 30 LPM since they are normally used in pairs. Cartridges were tested at 25, 50, and 85% relative humidity. Tests were run until 50% breakthrough occurred. Breakthrough times for initial, 10% and 50% cartridge penetration were recorded.

Cartridge Tests

All cartridges in this phase were tested singly at a constant flow rate of 30 LPM. The test atmosphere was controlled at 75 + 5°F, 50 + 5% RH. Test concentrations of vinyl chloride were 250, 500, 750 ppm. At least three cartridges of each of four types were tested at each concentration. In certain circumstances additional tests were run to correlate results obtained from cartridges from different boxes. Also, two cartridges of each of the four types were tested at ambient concentration of 50 ppm. In the tests run at 50 ppm, the test was terminated at 10% breakthrough. In all other tests, cartridges were run until 50% breakthrough occurred. Where possible, initial, 10% and 50% breakthrough times were recorded.

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Canister Tests

All canisters were tested at a constant flow rate of 60 LPM. Again, the test atmosphere was kept at 75 ± 5°F, 50 ± 5% RH. At least two canisters of each of four types were tested at each concentration. Concentrations used were 100, 1000, and 5000 ppm. Canisters were run until 10% breakthrough occurred. Initial and 10% breakthrough times were recorded.

TEST RESULTS

During preliminary testing, a large amount of breakthrough time variability was noticed in cartridges of the same type but from different boxes. These data are shown in Table 2. Variability was also noticed between boxes throughout the testing program, though to a lesser degree.

Figure 2 shows the results of tests to determine the effect of relative humidity on service life of cartridges. From this figure it appears that service life is inversely proportional to ambient relative humidity. A service life decrease of about 16% was seen from tests at 50% RH to tests at 85% RH.

Data from cartridge service life tests is shown in Table 3. These data are shown graphically in Figures 3, 4, 5, and 6. Adsorption theory predicts that charcoal becomes more efficient at higher contaminant concentrations. The graphs of cartridge service life data demonstrate this phenomenon.

It was found that an exponential decay curve was the most appropriate model for service life data. This relationship is defined as:

$$X = Ae^{-BY}$$

where X is vinyl chloride concentration in ppm and Y is 10% breakthrough time in minutes. When the natural logarithm (log e) of the concentration is taken, the relationship becomes:

$$Y = (1/B) \log_e A - (1/B) \log_e X$$

This is the equation of a straight line on semilog graph paper.

Using this model, data for cartridges and canisters were found to be very consistent. Correlation coefficients ranged from 0.981 to 0.994.

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The regression equations for each make of cartridge and canister are shown on Table 5 as well as correlation coefficients and equations for 95% tolerance limits.

Statistical analysis was not performed on initial breakthrough times because of the qualitative nature of the data. The point at which vinyl chloride could be first detected (initial breakthrough) depends not only on instrument settings and baseline drift but on personal judgement as well. However, initial breakthrough times for cartridges were typically 33% lower than the 10% breakthrough times.

Data from canister service life tests are shown in tabular form in Table 4 and in graphical form in Figures 7, 8, 9 and 10. For canisters initial breakthrough times recorded were typically 18% lower than the 10% breakthrough times.

CONCLUSIONS

Conventional activated charcoal of the type used in respirator cartridges and canisters has a very low adsorption capacity for vinyl chloride. This is demonstrated by the short service life of respirator organic vapor cartridges. In tests run at 50 ppm, 50% relative humidity, the lower 95% confidence level for 10% breakthrough time is 40 minutes. A minimum service time must also take into account the time between initial and 10% breakthrough (approximately 33%) and decreased service life due to high humidities (approximately 16%). These factors produce a minimum expected service life for cartridges of 20 minutes.

In canister tests at 100 ppm, 50% relative humidity, the lower 95% confidence level for 10% breakthrough time is 160 minutes. Considering factors for the time difference between initial and 10% breakthrough (18% of the 10% breakthrough time) and decreased in service life due to increased humidity (16%), a minimum service life of 100 minutes can be expected.

Organic vapor respirator cartridges have sufficient life for 20 minutes service at concentrations less than 50 ppm. Organic vapor front or back mounted gas mask canisters have sufficient life for 100 minutes service at concentrations less than 100 ppm.

Protection factors for half-mask organic vapor respirators and for full-facepiece organic vapor gas masks are 10 and 100 respectively. Theoretically, therefore, these devices could be used in contaminant concentrations up to 10 and 100 times

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the exposure limit if facepiece fit were the only consideration. With a 50 ppm ceiling exposure limit, an organic vapor half-mask respirator could be used in concentrations up to 500 ppm and an organic vapor full-facepiece gas mask up to 5000 ppm, without regard to service life.

However, when considering no detectable level of exposure as an exposure limit, both half-mask organic vapor respirators and full-facepiece gas masks would not provide adequate protection.

Another important point of interest when considering use of half-mask organic vapor respirators and full-facepiece gas masks are the warning properties of the contaminant. Vinyl chloride has an odor threshold of approximately 500 to 1000 ppm. A worker wearing these types of devices would have no indication of whether he was being adequately protected in atmospheres with low concentrations of vinyl chloride.

RECOMMENDATIONS

During the course of this testing program, the need for improvement in respirator performance has been demonstrated. Carbon tetrachloride is specified in 30 CFR 11 as the ambient contaminant in the approval of organic vapor cartridges and canisters.[5] Of the 121 solvent vapors and gases tested by Nelson,[3] 51 have lower 10% breakthrough times than carbon tetrachloride. No provisions are made in the NIOSH/BM approval labeling scheme for specifying expected service life. Work needs to be done to assure that devices approved are adequate for gases like vinyl chloride and the 50 other more volatile gases and vapors. A scheme should be developed to test devices against various classes of vapors. In this way, life expectancy could be given for a specific contaminant within one of these classes.

Work should be done to determine the effect of various charcoal characteristics (weight, particle size, pore size, base media, activation method, etc.) on adsorption capacity. For a comprehensive approval program to be meaningful, these characteristics should be defined and assurance must be made that they are adequately controlled in the manufacture of approved devices.

Work should be initiated to find or develop more efficient sorbents for substances which show poor adsorption on conventional respirator charcoal.

Another point of value would be to develop a device to be used integrally with respirator cartridges and canisters

which would enable the user to determine if his cartridge or
canister has reached breakthrough. Such a device might operate
on the same principle as the detector tube.

SUMMARY

    Organic vapor respirator cartridges have sufficient life
for 20 minutes service at concentrations less than 50 ppm.
Organic vapor front or back mounted gas mask canisters have
sufficient life for 100 minutes service at concentrations less
than 100 ppm. Facepiece leakage is expected to be 10% for a
half mask respirator and 1% for a full-facepiece respirator.
A final decision regarding their use against vinyl chloride
must be based on the allowable ceiling exposure for vinyl chloride
adopted in a permanent standard and expected facepiece leakage.

    The approval system for organic vapor respirators and
gas masks should be studied and improved in order to assure
protection against highly volatile gases and to provide the
user with information on service life.

REFERENCES

1. Department of Labor, Occupational Safety and Health Administration. Emergency Temporary Standard for Vinyl Chloride, Title 29 Code of Federal Regulations, Part 1910, Federal Register, Vol. 39, No. 67, Friday, April 5, 1974.

2. Department of Labor, Occupational Safety and Health Administration. Vinyl Chloride - Proposed Standard, Title 29 Code of Federal Regulations, Part 1910. Federal Register, Vol. 39, No. 92, Friday, May 10, 1974.

3. Nelson, G.O., and C. A. Harder. Respirator Cartridge Efficiency Studies: V. Effect of Solvent Vapor. Lawrence Livermore Laboratories Report Number UCRL 75056, August 30, 1973. Livermore, California.

4. Hyatt, E.C., J. A. Pritchard, and C.P. Richards. Protection Factors for Respirators. Presented at 16th Annual Meeting of the Health Physics Society, New York City, New York, July 12-16, 1974. Los Alamos Scientific Laboratory Document No. LA-DC-12318.

5. Department of the Interior, Bureau of Mines. Respiratory Protective Devices; Tests for Permissibility; Fees; Title 30 Code of Federal Regulations, Part 11. Federal Register, Vol. 37, No. 59, Saturday, March 25, 1972.

Table 1. Cartridge and Canister
Charcoal Weights

Cartridges

Manufacturer	Charcoal Weight (GMS)
1	49.7
2	35.7
3	35.0
4	36.1

Canisters

Manufacturer	Charcoal Weight (GMS)
1	436.8
2	318.4
3	463.8
4	312.2

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Wet & Dry Bulb
Temperatures

Compressed
Air

Regulator

Flow Control

H_2O

20% NaOH

Flowmeters

Conc. H_2SO_4

Mixing Bottle

Orifice &
Manometer

N.C. Flow Control

.1%, 1%, 10% or 20%
Vinyl Chloride

Mixing
Bottle

Switching
Valve

Cartridge or Canister

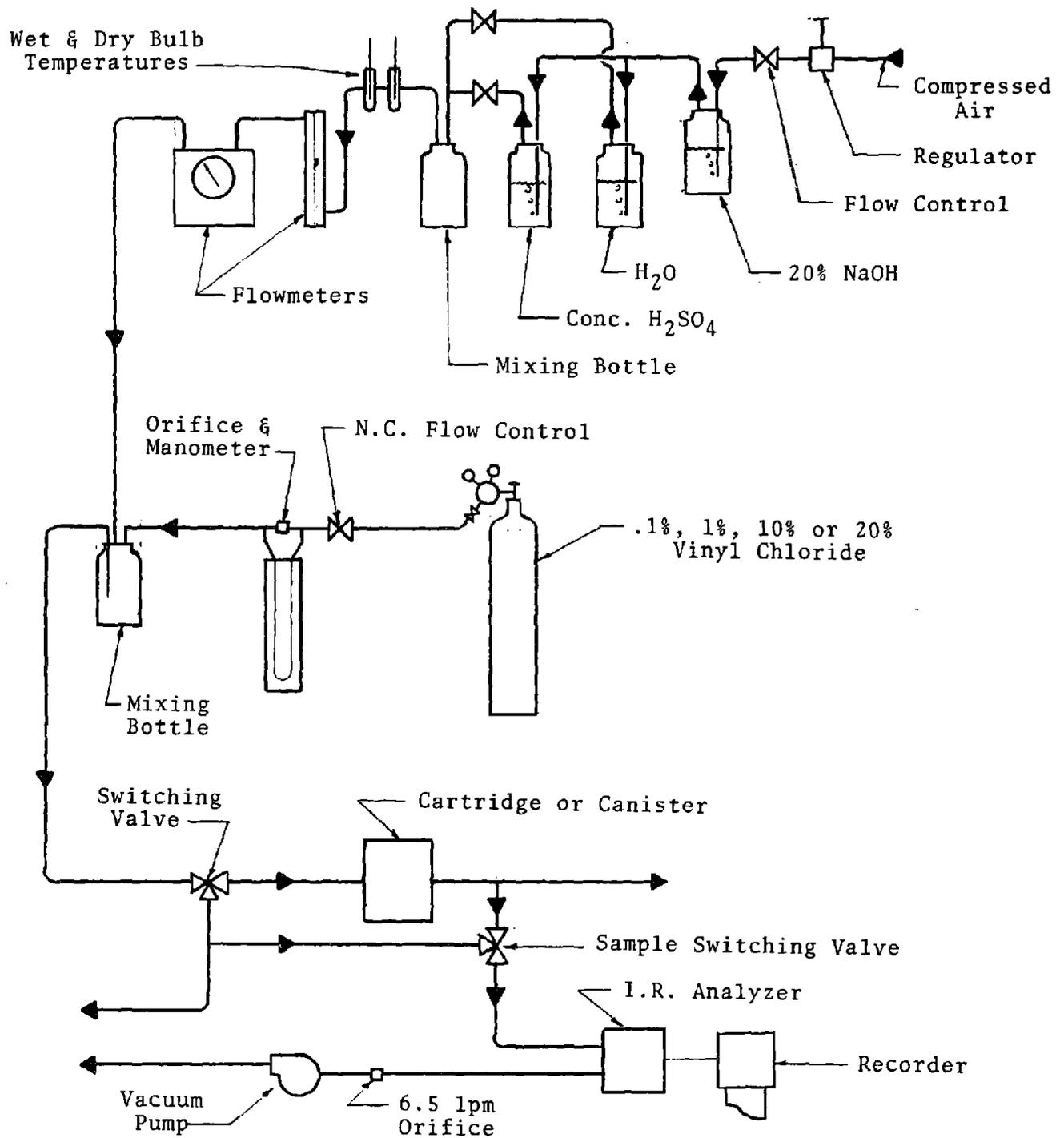Sample Switching Valve

I.R. Analyzer

Recorder

Vacuum
Pump

6.5 lpm
Orifice

Figure 1.   VINYL CHLORIDE CARTRIDGE AND
CANISTER TESTING SYSTEM

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Table 2. Cartridge Variability
Between Boxes

Box Number	Number of Tests	Breakthrough Times (minutes)					
		Initial		10%		50%	
		$\overline{x}$	σ	$\overline{x}$	σ	$\overline{x}$	σ
1	3	4.98	0.65	9.87	0.76	15.4	0.7
2	5	12.1	0.47	17.24	0.77	22.15	0.71

Note: Above tests run at 30 LPM total flow, 500 ppm 50% RH

$\overline{x}$ = mean

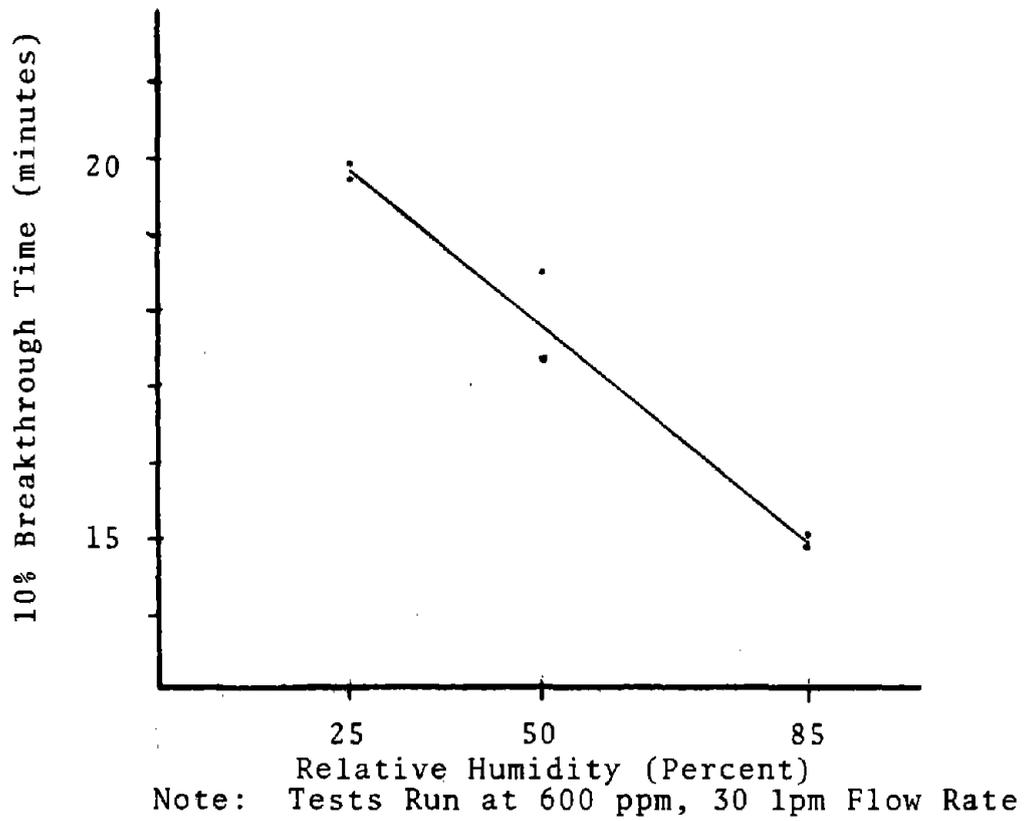σ = standard deviation

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Figure 2. EFFECT OF RELATIVE HUMIDITY ON
CARTRIDGE BREAKTHROUGH TIME

Table 3

Cartridge Test Data

Concentration (ppm)	Manufacturer	Number of Tests	Breakthrough Times (minutes)					
			Initial		10%		50%	
			$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
750	1	3	17.27	1.17	25.28	1.16	32.63	1.33
750	2	3	9	0	16.73	0.35	23.53	0.32
750	3	3	7.2	0.26	13.37	0.32	19.72	0.94
750	4	3	10.9	0.1	16.58	0.43	22.4	0.3
500	1	4	22.65	6.3	33	4.81	42.73	4.85
500	2	3	11.55	0.71	20.7	0.7	30.02	0.73
500	3	5	11.42	1.18	18.6	1.71	26.66	2.01
500	4	3	13.37	0.32	10.75	1.02	26.62	1.42
250	1	3	41.77	1.46	51.37	0.7	67.2	0.8
250	2	3	20.27	2.12	29.7	1.03	42.93	0.91
250	3	3	21.13	2.26	28.8	2.36	41.3	2.84
250	4	3	21.2	1.04	28.13	0.85	39.07	0.93
50	1	2	54.38	0.53	74.06	3.45	-	-
50	2	2	28.13	2.65	43.5	1.06	-	-
50	3	2	29.25	3.18	48.	0	-	-
50	4	2	32.63	2.65	48	3.18	-	-

Note: Above tests run at 30 LPM total flow and 50% RH

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Table 4. Canister Test Data

Concentration ppm	Manufacturer	Number of Tests	Breakthrough Times (Min)			
			Initial		10%	
			$\bar{x}$	σ	$\bar{x}$	σ
5000	1	2	54.5	0.71	53.24	1.06
5000	2	2	33	1.41	43.25	1.06
5000	3	2	31	1.41	43.0	1.41
5000	4	2	25.5	0.71	33.0	0
1000	1	3	144.3	5.51	158.0	3.61
1000	2	3	95.67	10.97	111.0	4.58
1000	3	3	90.67	4.04	108.3	5.51
1000	4	3	72.3	2.52	84	2.0
100	1	2	312	0	356	5.66
100	2	2	218.5	3.54	284	4.24
100	3	2	217	5.66	276.5	7.78
100	4	2	169.5	6.36	208.5	6.36

Note: Above tests run at 60 LFM total flow and 50% RH

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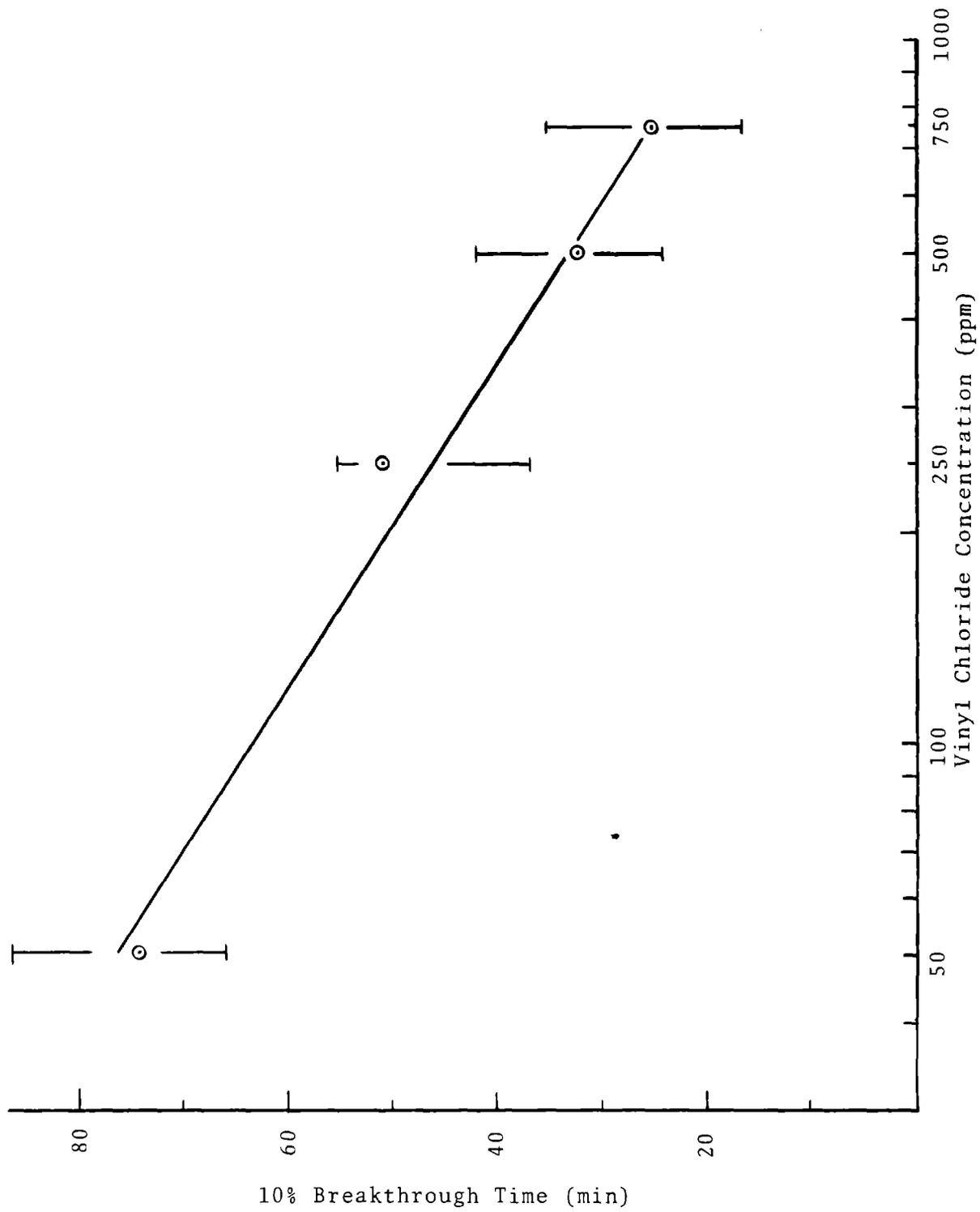
Figure 3.   Effect of Concentration on Breakthrough Time - Cartridge Make #1
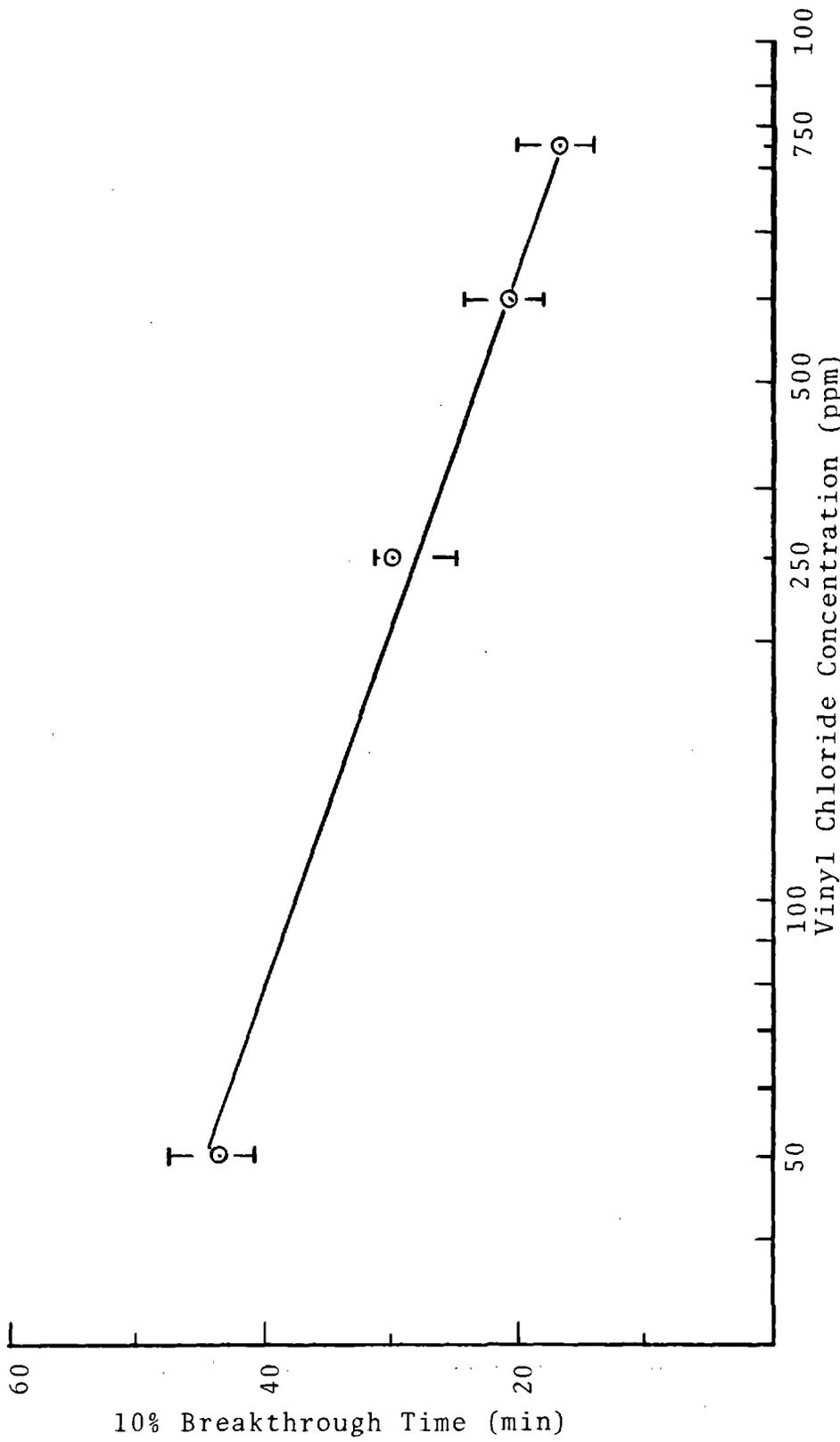
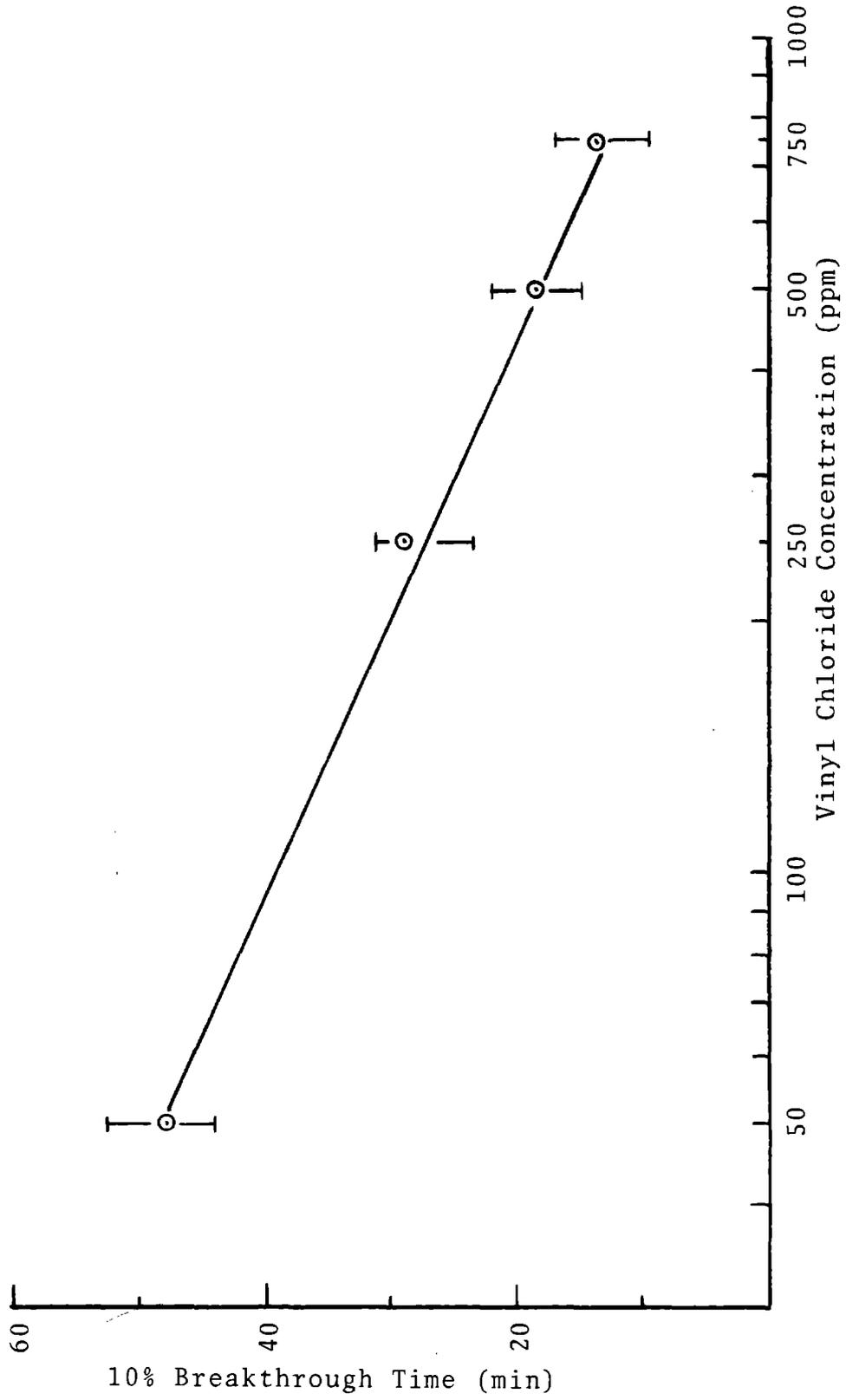Figure 4. Effect of Concentration on Breakthrough Time
Cartridge Make #2

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Figure 5. Effect of Concentration on Breakthrough Time
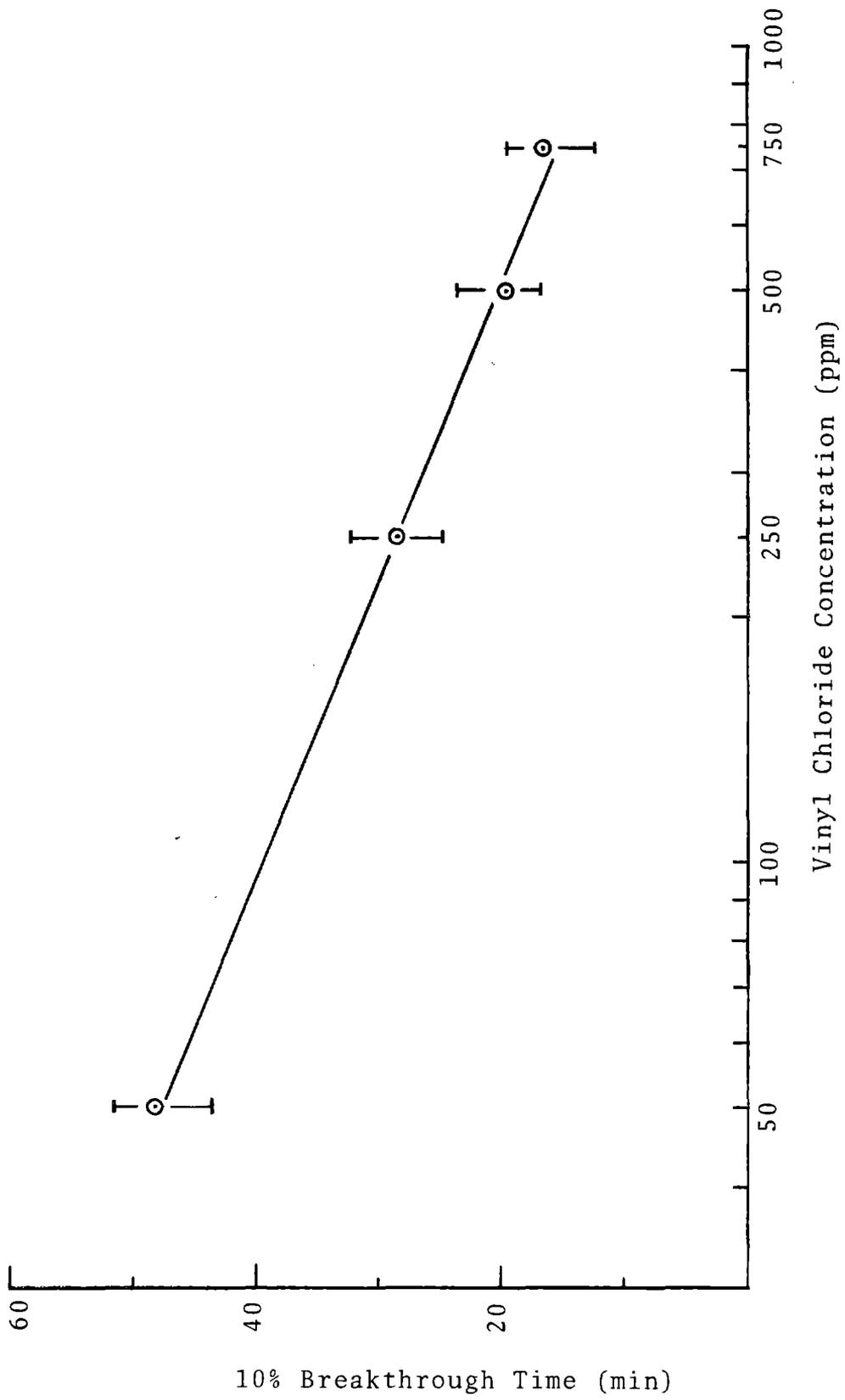Cartridge Make #3

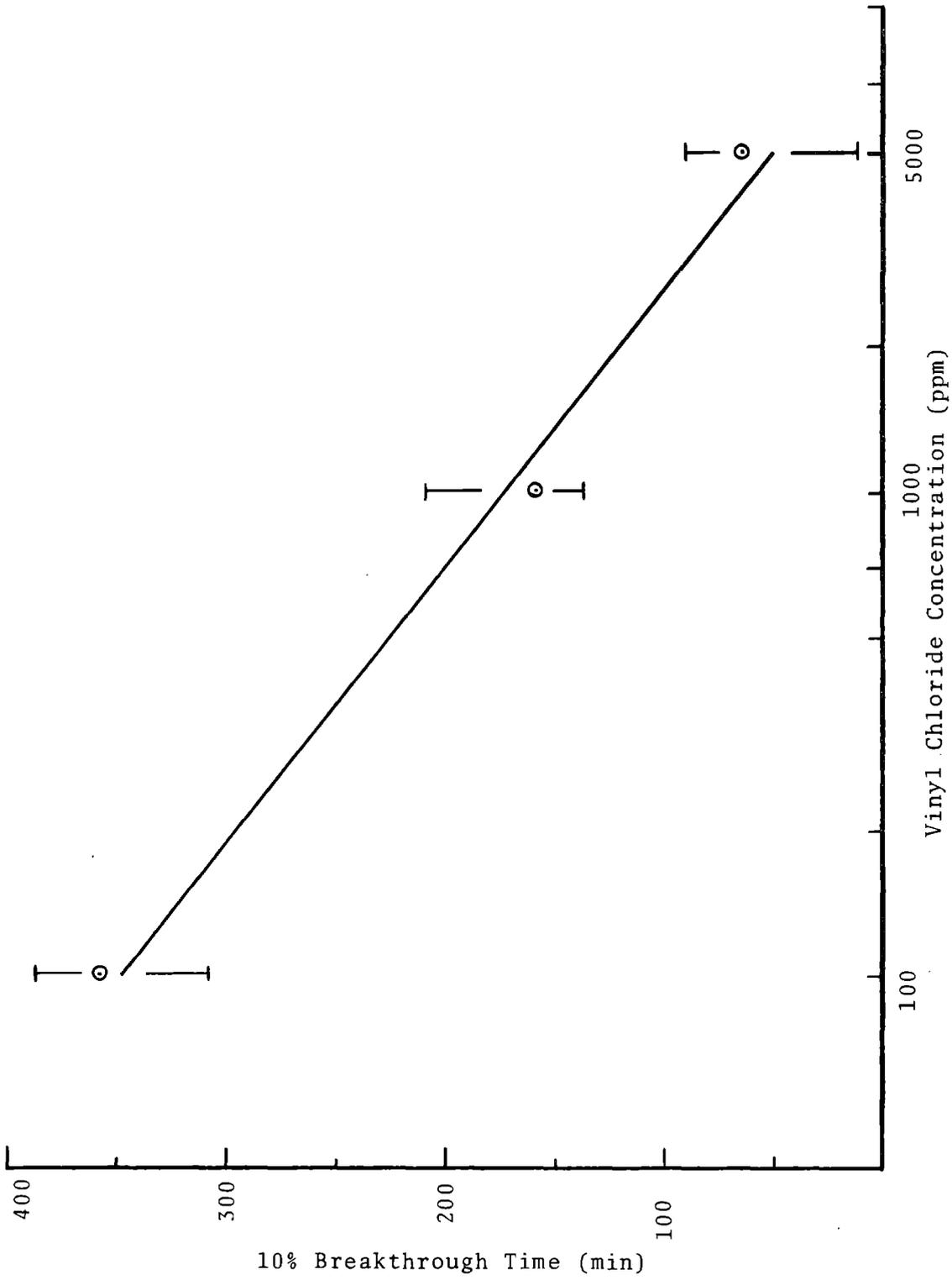Figure 6. Effect of Concentration on Breakthrough Time
Cartridge Make #4

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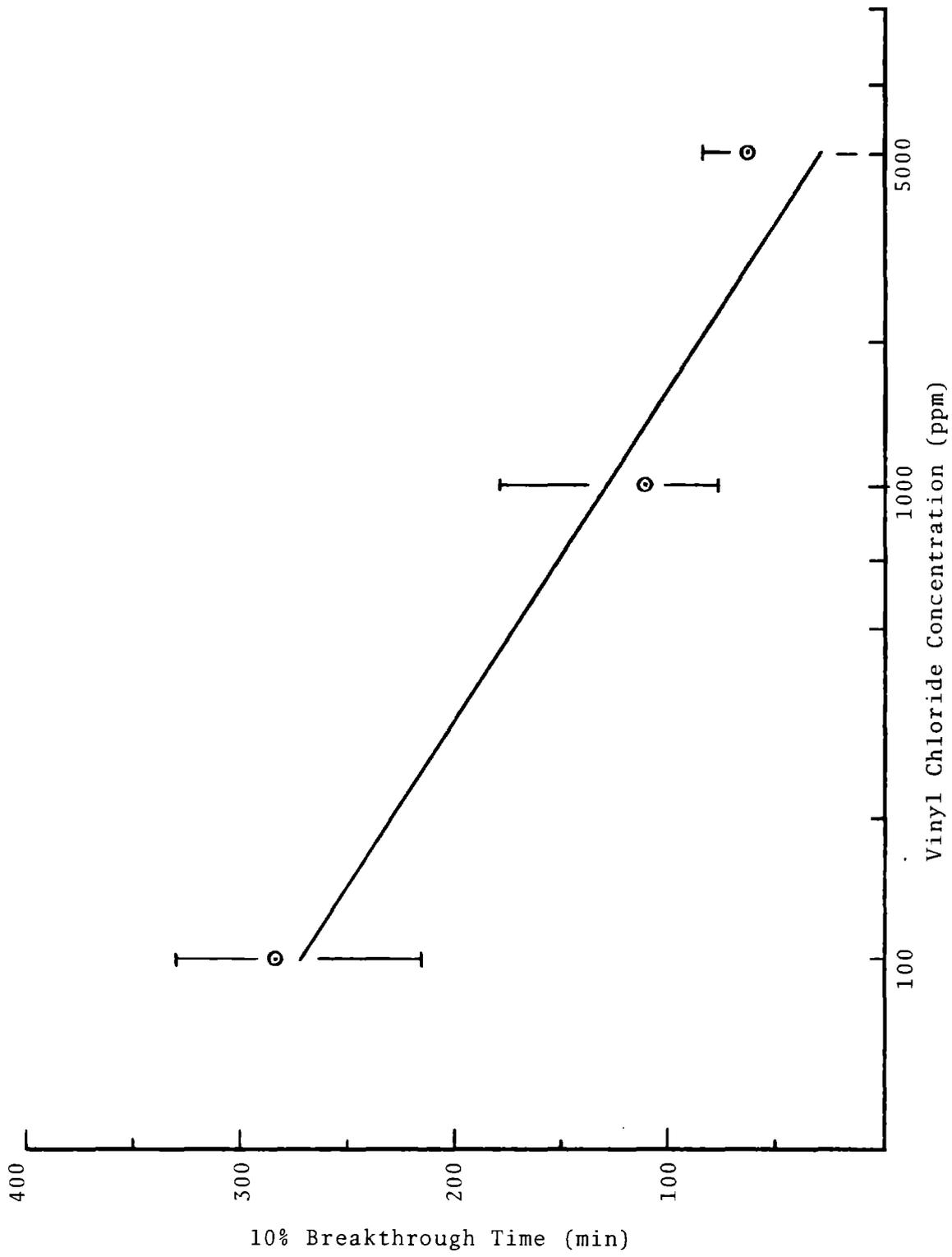Figure 7. Effect of Concentration on Breakthrough Time - Canister Make #1

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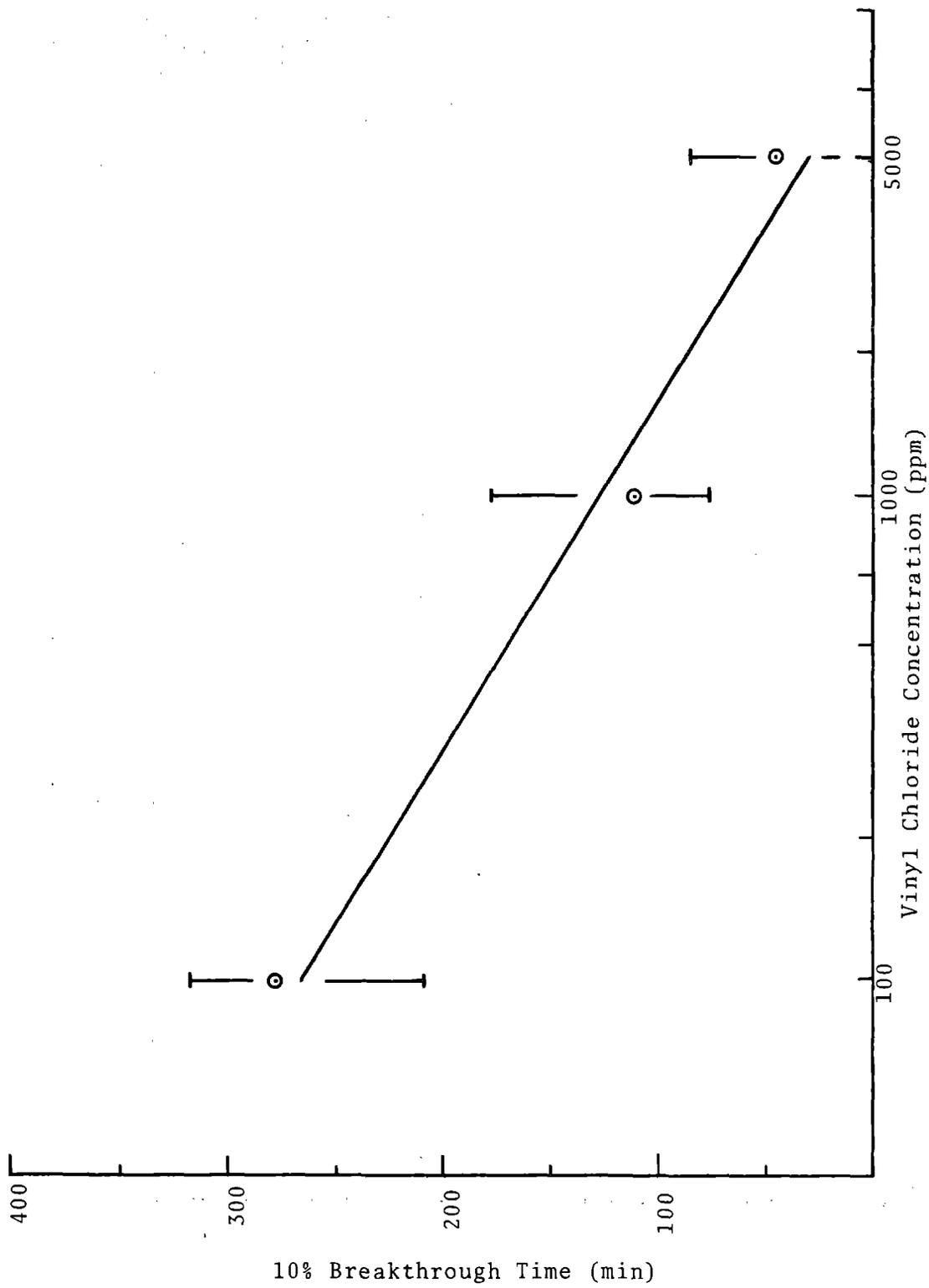Figure 8. Effect of Concentration on Breakthrough Time - Canister Make #2

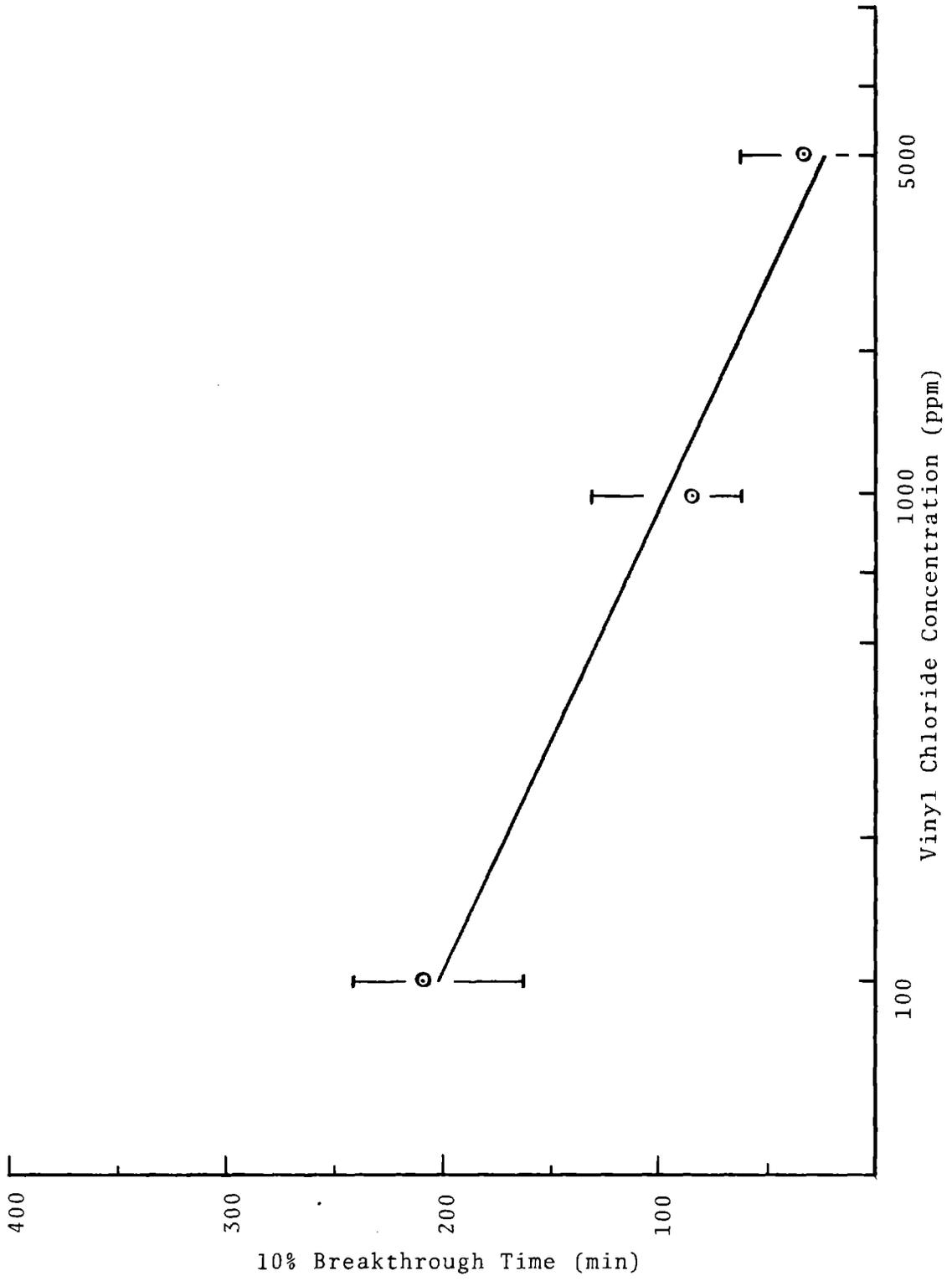Figure 9. Effect of Concentration on Breakthrough Time - Canister Make #3

Figure 10. Effect of Concentration on Breakthrough Time - Canister Make #4

Table 5. Statistical Models of Breakthrough Data

Cartridges

	Linear Equation*	Correlation Coefficient	95% Tolerance Limits
Make #1	$Y = 149.5 - 18.68\ X$	0.9814	$Y \pm 8.63 \sqrt{1.09 + (.10)(X - 5.72)^2}$
Make #2	$Y = 83.49 - 10.02\ X$	0.9929	$Y \pm 2.85 \sqrt{1.09 + (.10)(X - 5.72)^2}$
Make #3	$Y = 99.55 - 13.04\ X$	0.9938	$Y \pm 3.53 \sqrt{1.09 + (.10)(X - 5.72)^2}$
Make #4	$Y = 93.56 - 11.76\ X$	0.9931	$Y \pm 3.30 \sqrt{1.09 + (.10)(X - 5.72)^2}$

Canisters

	Linear Equation*	Correlation Coefficient	95% Tolerance Limits
Make #1	$Y = 696.2 - 75.82\ X$	0.9935	$Y \pm 33.3 \sqrt{1.14 + (.064)(X - 6.7)^2}$
Make #2	$Y = 562.0 - 62.74\ X$	0.9862	$Y \pm 47.6 \sqrt{1.14 + (.064)(X - 6.7)^2}$
Make #3	$Y = 546.1 - 60.86\ X$	0.9853	$Y \pm 47.7 \sqrt{1.14 + (.064)(X - 6.7)^2}$
Make #4	$Y = 411.5 - 45.67\ X$	0.9877	$Y \pm 32.7 \sqrt{1.14 + (.064)(X - 6.7)^2}$

*Y = 10% Breakthrough time in minutes

X = $\log_e$ (Vinyl chloride concentration in ppm)