B.F.GOODRICH CHEMICAL COMPANY TECHNICAL REPORT

TITLE		
An Analytical System for Measuring the Adsorption of VCM on Charcoal		
AUTHOR	LOCATION	DATE
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SUMMARY

An analytical VCM flow chamber has been designed to measure continuously the adsorption of VCM on charcoal. The method involves flowing a stream of VCM in air (variable VCM concentrations and flow rates) into a specially designed charcoal cartridge holder and monitoring the air stream downfield from the cartridge with a Century Organic Vapor Analyzer. Breakthrough time (T_5) is defined as the time in minutes at which this air stream reaches a VCM concentration of 5ppm. A comparison of selected T_5 values obtained in our apparatus has been made with recent data generated at Harvard (for the Welsh Co.) on the adsorption of VCM in Welsh cartridge 7500-1:

BFG Data	Harvard Data
30 l/min., 100ppm: T_5 = 41	32 l/min., 97ppm: T_5 = 45
30 l/min., 81ppm: T_5 = 50	32 l/min., 85ppm: T_5 = 50

The above data shows good agreement between the two laboratories even though the testing procedures used are quite different.

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Introduction

The use of adsorptive carbon in personal masks to decrease the intake of hydrocarbons is well known. A program has been set up within the company for production workers, exposed to vinyl chloride monomer, to use these masks. A number of questions arose as to the efficiency of the carbon cartridges used in these masks to adsorb vinyl chloride monomer. To fill this need, we set up a laboratory scale apparatus in which we could:

(1) generate various levels of VCM in air,

(2) produce a variety of flow rates which simulate typical respiration rates, and

(3) measure the adsorption of VCM in commercial carbon filters.

Approach

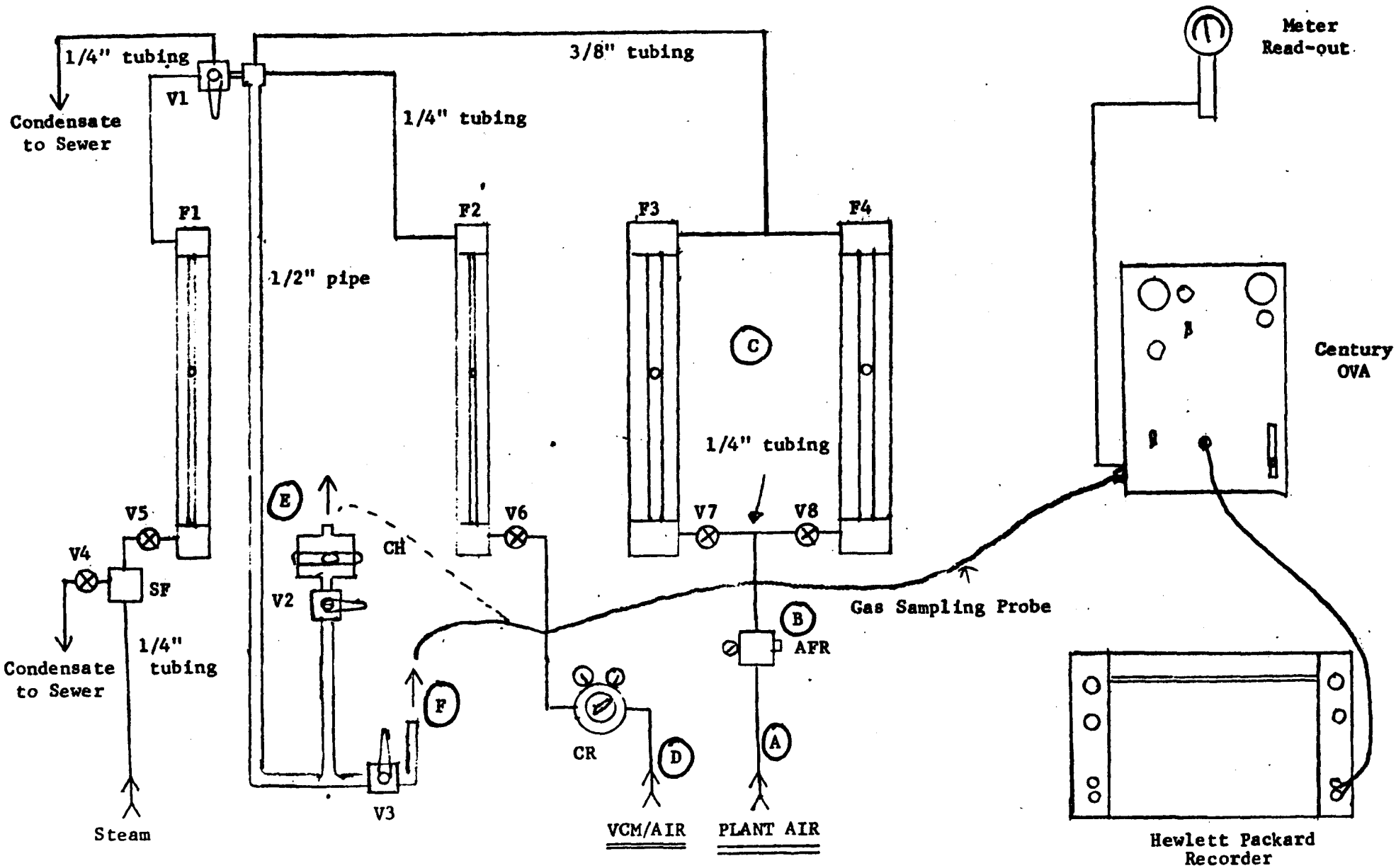
Although OSHA requires those selling these types of masks and cartridges to test the complete assembly, we saw no reason why the basic phenomenon of adsorption on carbon could not be modelled in a simple flow chamber device. Basically our system consists of four calibrated flowmeters (two air lines, VCM line and steam line), a mechanical device for holding a carbon cartridge in such a way that no leakage occurs around the cartridge, and a continuous VCM monitoring device. With respect to the last requirement, we could have used either the Bendix Hydrocarbon Analyzer or the Century Analyzer. We chose not to use the Bendix Analyzer because this would have required the installation of our flow chamber on the third floor of Bldg. 451. Our main objection to this location was the lack of temperature control. Since the adsorption process is strongly influenced by temperature, we felt a more controlled atmosphere was necessary.

In this first report, results on the adsorptive efficiency of the Welsh cartridge at two flow rates and a variety of VCM concentrations are summarized. Two other types of cartridges have also been evaluated under one set of experimental conditions. In addition, recent VCM adsorption data collected by Bill Burgess at Harvard using the OSHA required technique are also summarized.

VCM Flow Chamber

The apparatus constructed by us to measure the adsorptivity of VCM on carbon is shown in Figure 1A. The location and types of air filters, flow meters and metering valves are also included in this drawing. All flow meters were calibrated with a bubble meter. Final check-out of the system was accomplished by comparing the theoretical VCM content (via flowmeters) against the actual VCM content (via Century Analyzer). In all cases these values are within 1% of each other.

Figure 1A: VCM Flow Chamber



The system operates in the following manner. Referring to Figure 1A, plant air enters the system (A), is filtered (B) and then enters the flow-meter bank (C). VCM enters the system (D) and the combined mixture can be directed to either the cartridge holder (E) or the by-pass (F). Other experimental information relating to other specifics of the flow chamber are included in Appendix 1.

A typical run is shown in Figure 1. In this experiment, Welsh cartridge 7500-1 was exposed to 81ppm of VCM at a total flow rate of 15 liters/min. Initially the VCM flow chamber is placed on "by-pass" in order to check the VCM concentration with the Century analyzer. This concentration is shown on the recording chart as "VCM level w/o filter". At this point, the valve to the "by-pass" is closed and the valve to the cartridge holder (E, Figure 1A) is opened. In Figure 1A, this is designated "w filter" and arbitrarily chosen as time equal to zero. It can be seen that there is an immediate response of the recorder from 81ppm to ~8ppm. The one drawback of the Century analyzer is the presence of a 5-10ppm background. Thus the recorder response at 8ppm in the above experiment represents a zero VCM response. It should be noted that this same background exists with no VCM in the system. We have also analyzed purified breathing air and obtained the same background results. At this time we feel (but cannot prove conclusively) that this background is internally generated within the Century Analyzer. Nevertheless, this background does not seriously hamper the type of data desired from the experiment. Returning to Figure 1, the output of the recorder indicates that the Welsh cartridge completely stops VCM from entering the system, assuming that the 8ppm background contains zero VCM. Since there is variability in the background (5-10ppm) we cannot say unequivocably that there is not 1-2ppm of VCM leaking through the carbon filter. However in terms of the definition of the problem, we do not consider this a serious drawback. It can be seen (Figure 1) that the background actually decreases as time progresses. This background reaches a minimum at ~50 minutes, then begins to increase at ~60 minutes. We interpret this response at 60 minutes to be incipient VCM breakthrough. It can be seen that there is a steady upward response of the recorder from the point to about 140-150 minutes when the 81ppm level is reached.

This Study

Using the above VCM flow chamber, the Welsh cartridge (7500-1) was subjected to a number of exposures where both flow and VCM concentration were varied. All recorder outputs from these various experiments are presented in Appendix 2. A summary of all experiments, including breakthrough times, is included in Table 1. The Harvard data is also included in the table. It is obvious that different interpretations can be given to "breakthrough time". It can be taken as the time at which incipient breakthrough occurs. Initially we determined this time by intersecting two lines (one through the baseline, one through the upward curve). We

Table 1

Summary of VCM Adsorption Date Obtained on the VCM Flow Chamber[1]

Experiment	Carbon Cartridge	Flow Rate l/minutes	VCM Concentration ppm	T_s, Minutes[2]	Reference Figure[3]
1	Welsh 7500-1[4]	15	81	95	1
2	Welsh 7500-1	30	81	49	2
3	Welsh 7500-1	15	160	84	3
4	Welsh 7500-1	30	160	30	4
5	Welsh 7500-1	15	500	44	5
6	Welsh 7500-1	30	500	22	6
7	Welsh 7500-1	15	100	87 ± 10[8]	7
8	Welsh 7500-1	30	100	41	8
9	American Optical AO R55	30	100	21	9
10	Welsh, 7500-3[5]	30	100	36 ± 4[9]	10
11	PVC[6]	30	100	0	--
12	Welsh 7500-1	30	50	51	--
13	Welsh 7500-1	30	275	23	--
14A	Westvaco Nuchar WV-H8X30	30	100	15	11
16	Willson (R-25)	15	100	34	--
17	Willson (R-11)	30	100	0	--
Harvard Study[7]	Welsh 7500-1	32	85	50	--
Harvard Study[7]	Welsh 7500-1	32	97	45	--

(1) see Figure 1A and text

(2) defined at the time at which the concentration of VCM downstream from the filter reaches 5ppm

(3) see Appendix 2

(4) this cartridge contains 70cc of charcoal, surface area 1100 sq. meters/gram

(5) this cartridge was designed to stop hydrocarbons and acid gases

(6) high porosity PVC used as filter

(7) data obtained by Bill Burgess of Harvard in which the entire mask is tested under OSHA requirements. Burgess is a Welsh consultant.

(8) average of 3 runs

(9) average of 4 runs

called "breakthrough time" the point at which these two lines intersected. This approach has been abandoned because of the arbitrary nature in which the line through the upward curve can be drawn. The definition of breakthrough time that we now use and will use in reporting all data, is the time in which a concentration of 5ppm VCM is reached. This is designated T_5.

Discussion

In very general terms, it can be seen from the data in Table 1 that the Welsh cartridge (7500-1) will retain VCM from 22 minutes (30 l/min. at 500ppm) to 95 minutes (15 l/min. at 81ppm). From the limited data in Table 1, the effect of VCM concentration on T_5 at a constant flow and the effect of flow on T_5 at a constant VCM conc entration can be demonstrated. Plots of these data are shown in Figures 2A and 3A respectively. With respect to the effect of VCM concentration on T_5 at a constant flow rate (30 l/min.), Figure 2A indicates a gradual, almost linear decrease in efficiency, (i.e., T_5) as the VCM concentration increases from 50 to ~150ppm. Above 150ppm VCM and up to 500ppm, the efficiency of the charcoal in absorbing VCM is not significantly changed. In other words, from 50ppm to 150ppm there is a 62% decrease in efficiency (T_5) but from 150ppm to 500ppm there is only a 9% further decrease in efficiency. If this phenomenon is important in setting requirements pertaining to the use of the Welsh mask, then additional studies should be carried out over a range of flow rates.

The effect of flow rate on the efficiency of the Welsh cartridge to adsorb VCM monomer is shown in Figure 3A. It should be noted that the data for each line is limited to two data points but the trend which is demonstrated is of interest. For all exposure levels (81, 100, 160, 500ppm) of VCM, there is an approximate 50-60% reduction in adsorption efficiency as the rate is increased from 15 l/min. to 30 l/min. Again if an extension of this data is important in setting requirements for the use of the Welsh mask, more data will be collected.

The Harvard Study

Jim Matheson of Welsh revealed to me the data that was collected by Prof. Burgess of Harvard University. In these experiments, Burgess tested according to the OSHA requirements in which the entire mask is used. He used gas chromatography to "batch monitor" the air going through the charcoal. The data for two exposures are included in Table 1. Comparing that data to similar data generated by us (entries #2 and #30, Table 1) indicates an excellent correlation in light of the differences in the two experiments. By extrapolating and interpolating the data in Figure 2A and 3A, our data appears to be biased on the low side (i.e. shorter breakthrough times) by 5-10% when our data is compared to the Harvard data. At some future time, we will repeat the Harvard experiment in terms of flow rate and concentration to verify the presence of any bias.

Figure 2A

Effect of VCM Concentration on T_5 at Constant Flow Rate

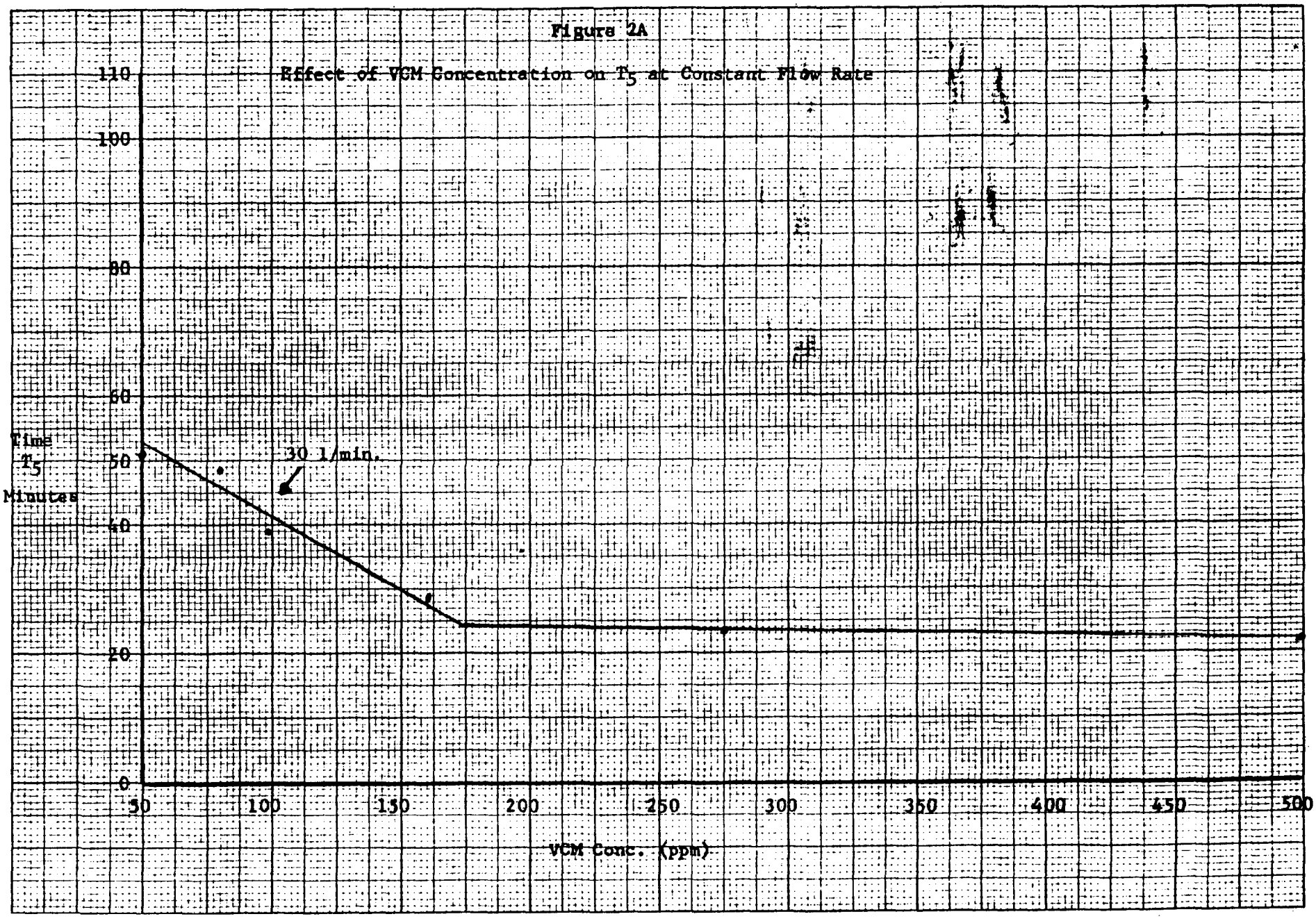


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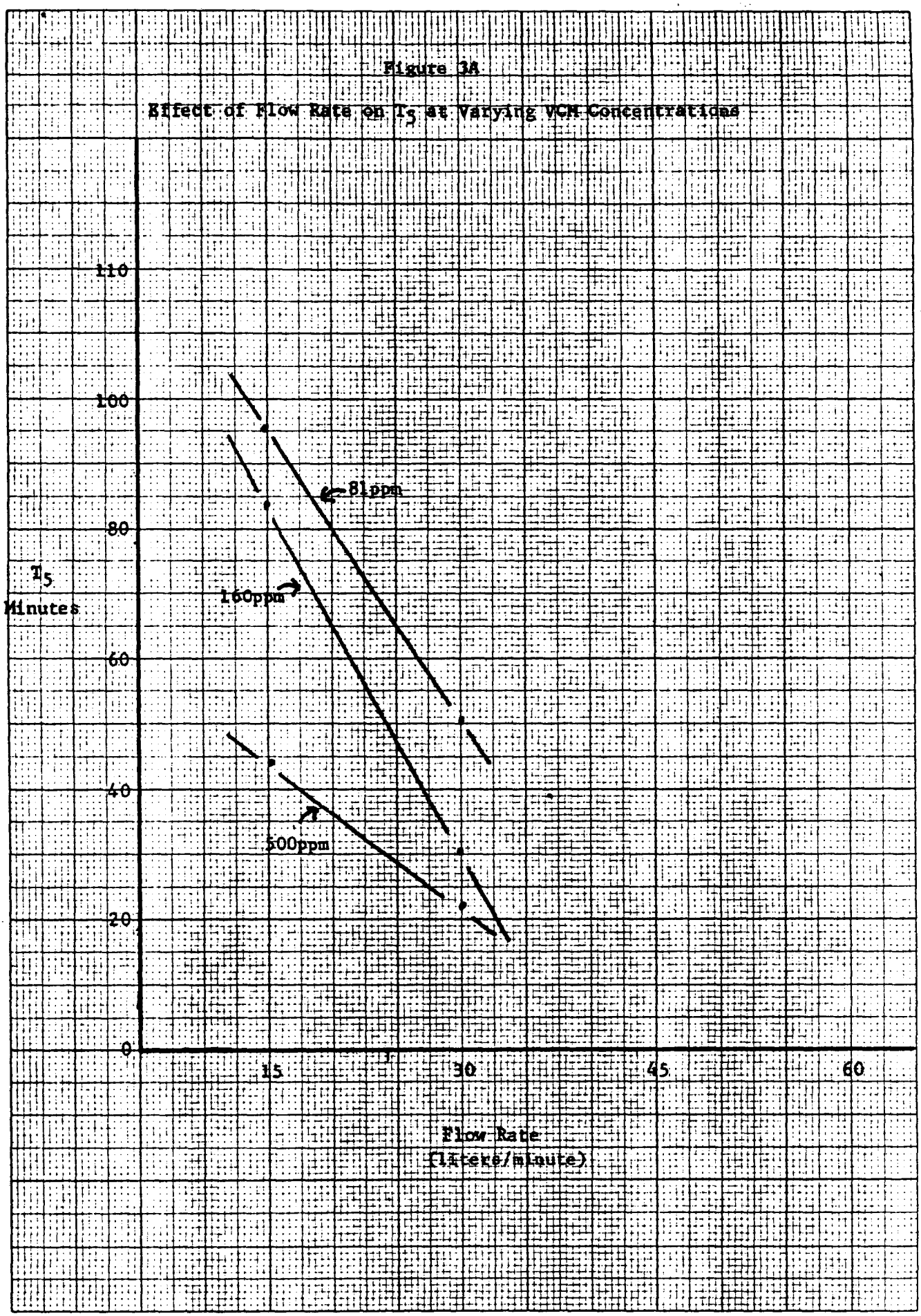
Figure 3A

Effect of Flow Rate on T_5 at Varying VCM Concentrations



Evaluation of Other Cartridges

It was desirable to pick one set of experimental conditions in order to rapidly evaluate other charcoal filters. For a number of reasons we felt that a flow rate of 30 l/min. and a VCM concentration of 100ppm filled this need. Using these conditions we have evaluated the following cartridges:

(1) American Opticals AO R55
(2) Welsh 7500-3
(3) a PVC compound designed for use as a cigarette filter
(4) Westvaco WV-H8X30
(5) Willson, R-25
(6) Willson, R-11

The data from these experiments are also summarized in Table 1. It is obvious that the American Optical filter is only about as 50% as effective as the Welsh cartridge (7500-1), that the Welsh 7500-3 cartridge is about as effective as the Welsh 7500-1 cartridge, and that both the PVC filter and the Willson R-11 cartridge are ineffective adsorbants for vinyl chloride monomer. Other evaluations are included in Table 1.

We do not understand the difference in efficiency between the Welsh 7500-1 cartridge and the American Optical (A.O.) cartridge. The A.O. filter contained 70cc. of charcoal which seemed to be of a finer mesh than the Welsh charcoal. We do not as yet know what the surface area of the A.O. charcoal is but suspect that this may be the reason for the differences in activity. We plan to investigate this aspect further.

Reproducibility

We have not been able to measure the reproducibility of the test described in this paper to any great extent. However, we have generated some data for three of the cartridges tested. These data are also included in Table 1. From these limited repetitive runs (see Experiments 7, 8, 10, Table 1), there appears to be an average deviation of about 12%. We have checked for flowmeter drift and for other potential causes of this deviation. At this time we believe the data deviation is due to the cartridges (i.e. heterogeneity of packing). When we have time, this will be investigated more thoroughly.

Future Work

(1) Much of our future work depends on how well the limited data provided in this study can be used in setting standards pertaining to the use of the Welsh masks,

(2) we will continue to monitor other carbon filters in order to determine the variability in efficiency from supplier to supplier,

(3) Welsh has sampled us with one of their charcoal cannisters; this will be tested in the near future,

(4) Welsh is preparing for us a cartridge containing coconut shell charcoal. The surface area of this carbon is 1500 sq. meters/g or 36% higher than the "petro-carbon" normally supplied by Welsh;

(5) we will also measure the efficiency of another Welsh cartridge which contains twice the amount of charcoal that 7500-1 contains.

(6) we will be investigating different types of chemical adsorbants in an attempt to find a candidate which will significantly outperform the Welsh cartridge.

APPENDIX 1

Additional Experimental Information

OVA Calibration

We initially calibrated the Century Analyzer against two independent standards (between 0-500ppm) then tested the accuracy of our calibrated flowmeters. As previously mentioned, these two values (theoretical and actual) were within 1% of each other. This was rerun a number of times throughout the 0-500ppm range.

Flow Chamber Air

The air used in these experiments was filtered. It contained 350ppm CO_2 and 25% relative humidity. In our initial design we added a steam line for generating higher humidities if necessary. All data reported in this report is for the 25% relative humidity situation.

VCM Flow Chamber

The following designations refer to Figure 1A and provide a more complete description of the equipment.

V1 - 3-Way plug valve - Hoke 7165F4B

V2, V3 - Plug valves - Jamesbury 1/2" 316SS

V4, V7, V8 - Control valves, coarse - Hoke 2215F4Y

V5, V6 - Control valves, fine - Hoke 2235F4Y

AFR - Air filter-pressure regulator - Conoflow FH-60XT

CH - Cartridge holder

CR - Harris Cylinder Regulator

F1, F2 - F. & P. Co. Flowmeter - No. FP-1/8-12-G-5

F3, F4 - F. & P. Co. Flowmeter - No. 2F-1/4-20-G-5

SF - Steam strainer - 1/4" Leslie 300

Recorder Output

We used a Hewlett-Packard Model recorder for monitoring the output of the Century Analyzer. Full scale output was 2 volts. The recorder traced the meter on the Century exactly. The chart speed for all runs was 0.1 inch/minute.

VCM Standard

Our source of VCM was an air standard (Matheson Gas Products) containing .99% VCM. A gas chromatographic analysis on a Porapak QS column (R_f air = 1.000, R_f VCM = 0.610) indicated a VCM concentration of .97%. We believe there is some error in this value since R_f VCM was determined from the pure monomer. All theoretical calculations of VCM in air have been based on the 0.99% VCM analysis.

APPENDIX 2

Century OVA Recorder Outputs

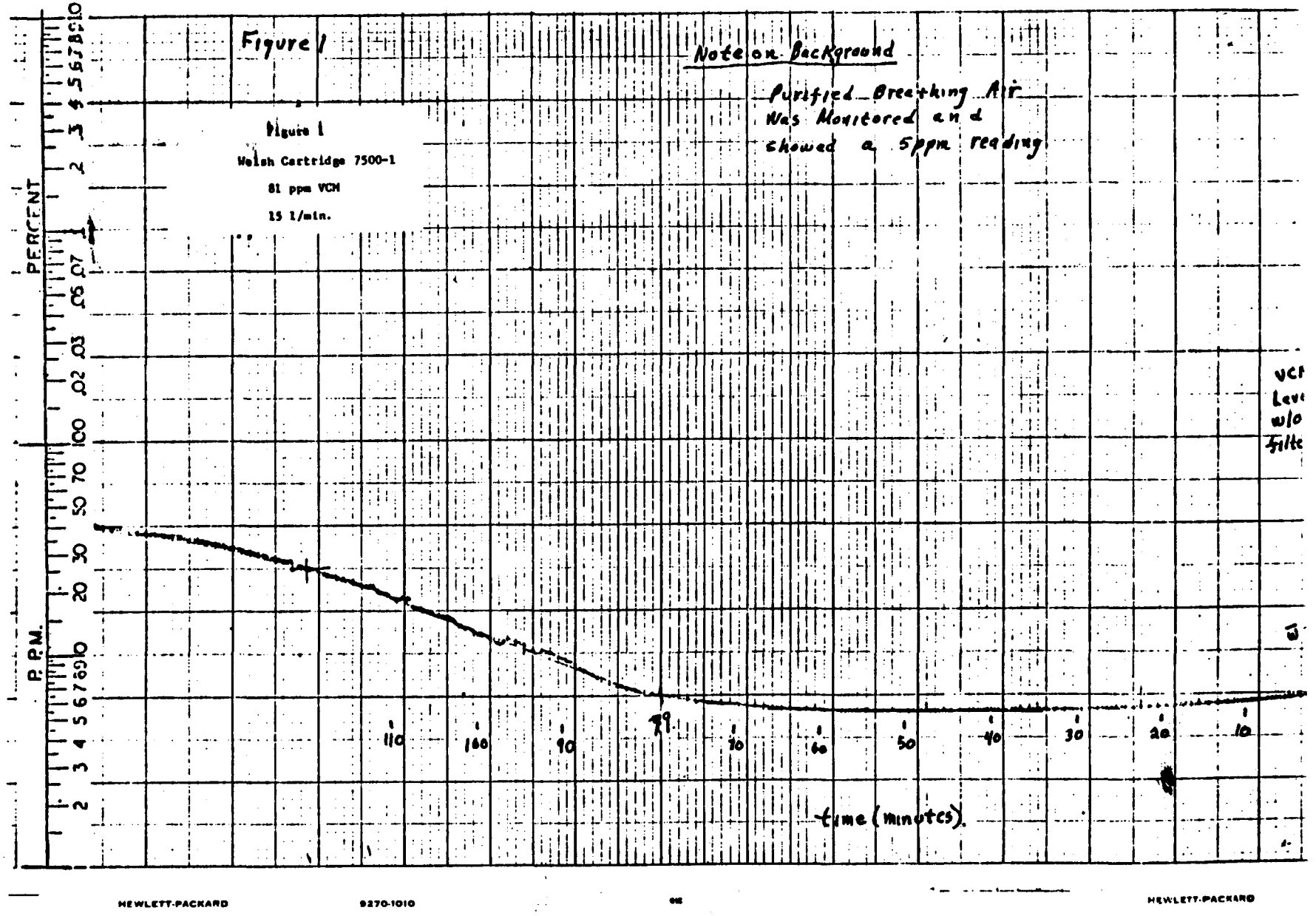


Figure 1
Figure 1
Welsh Cartridge 7500-1
81 ppm VCM
15 l/min.
Note on Background
Purified Breathing Air
Was Monitored and
showed a 5ppm reading
PERCENT
P.P.M.
time (minutes)
110
100
90
80
70
60
50
40
30
20
10
HEWLETT-PACKARD
9270-1010
HEWLETT-PACKARD

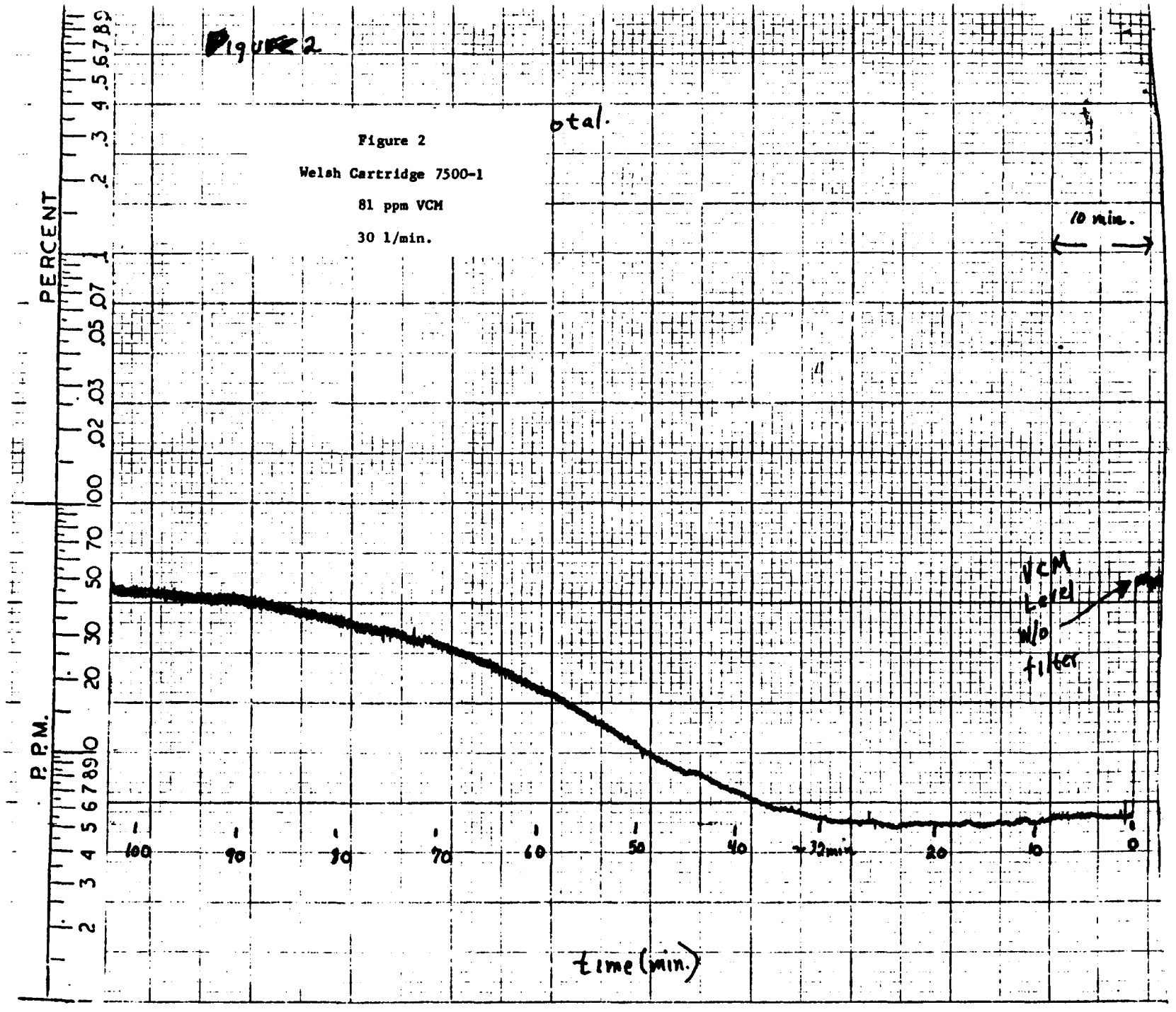


Figure 2
Figure 2
Welsh Cartridge 7500-1
81 ppm VCM
30 l/min.
total
10 min.
PERCENT
P.P.M.
time (min.)
VCM Level w/o filter
100
90
80
70
60
50
40
~32 min
20
10
0

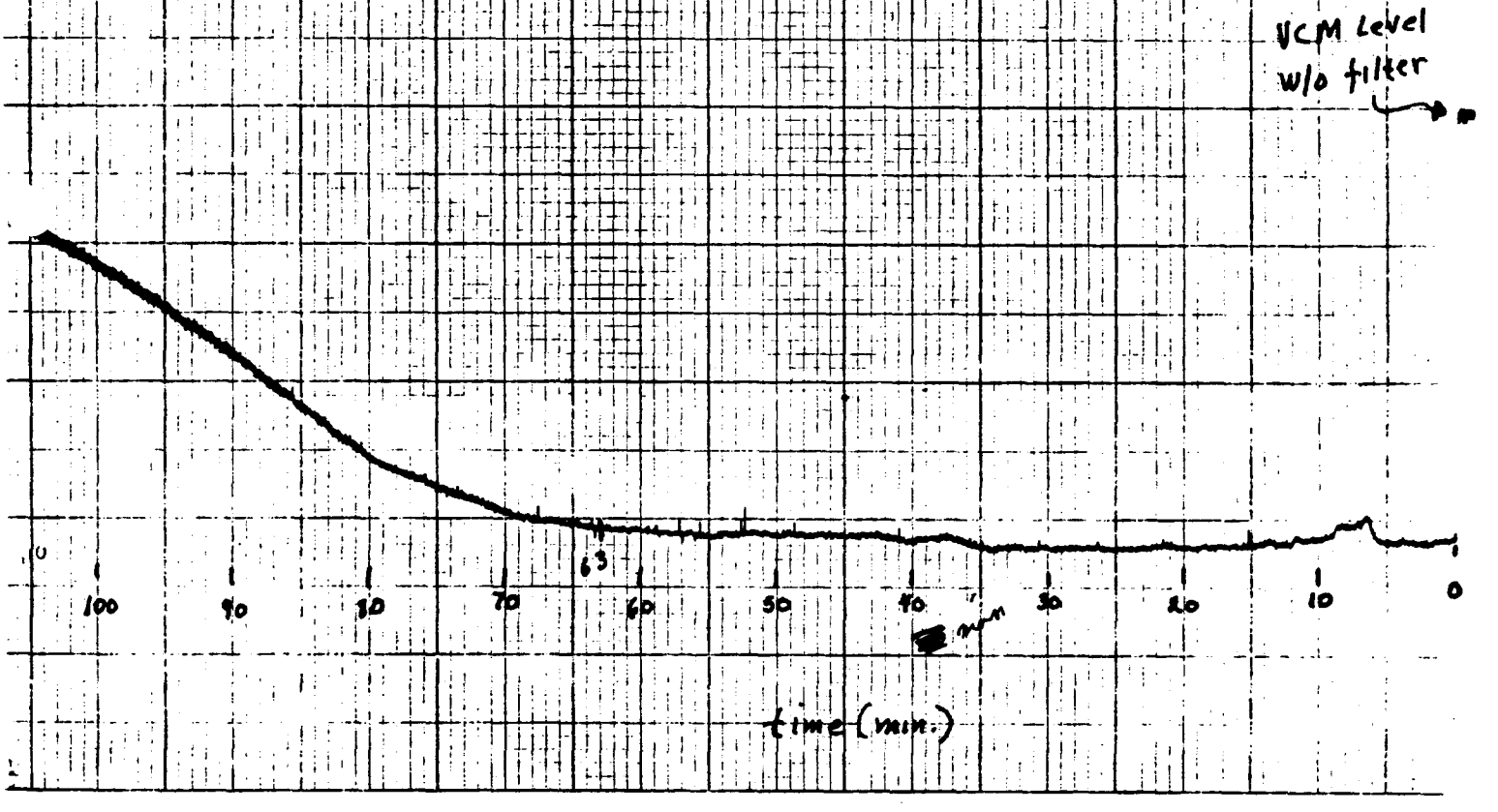
Figure 3

Figure 3

Welsh Cartridge 7500-1

160 ppm VCM

15 l/min.



HEWLETT-PACKARD 9270-1010

24591017

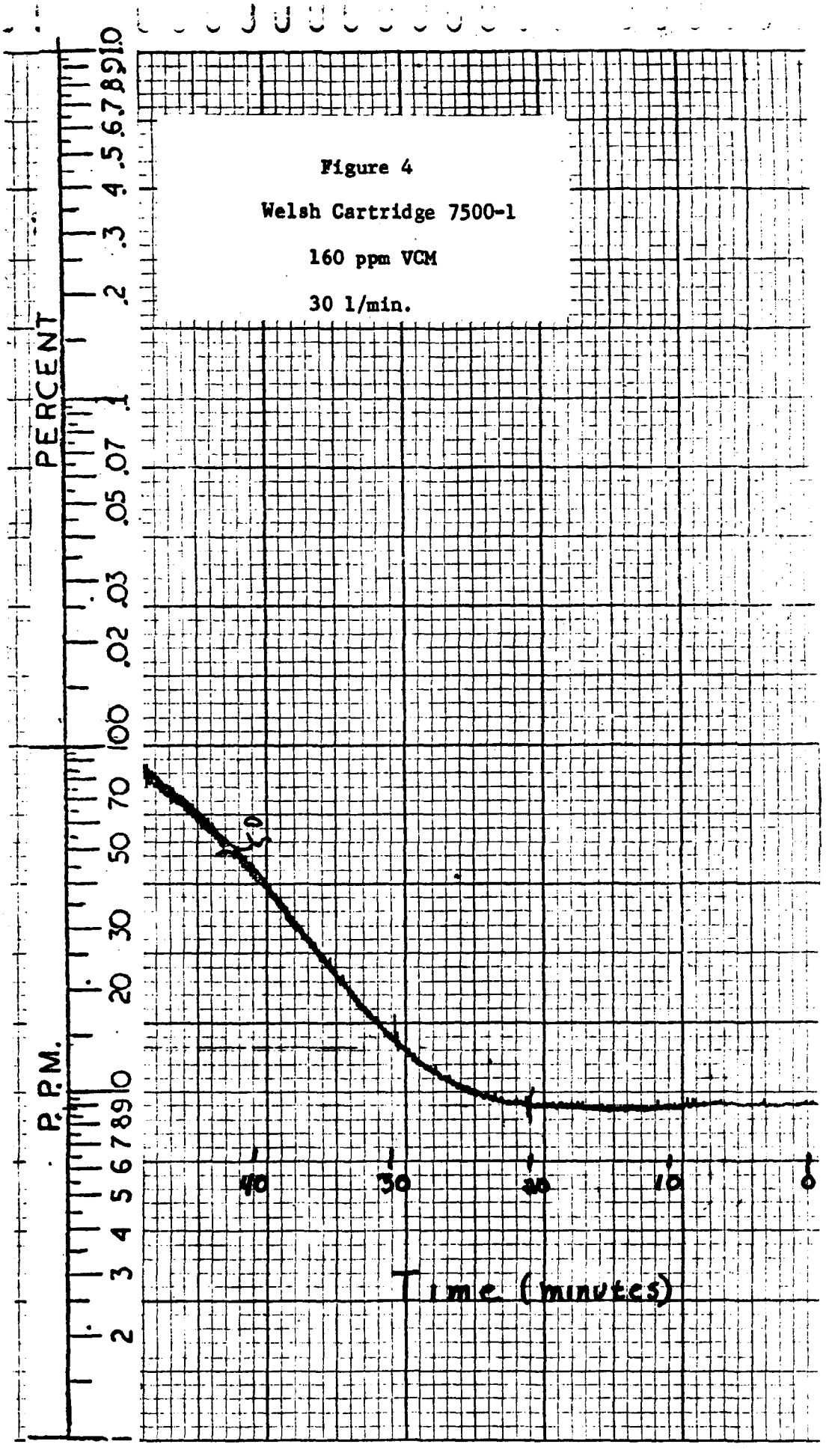


Figure 4

Welsh Cartridge 7500-1

160 ppm VCM

30 l/min.

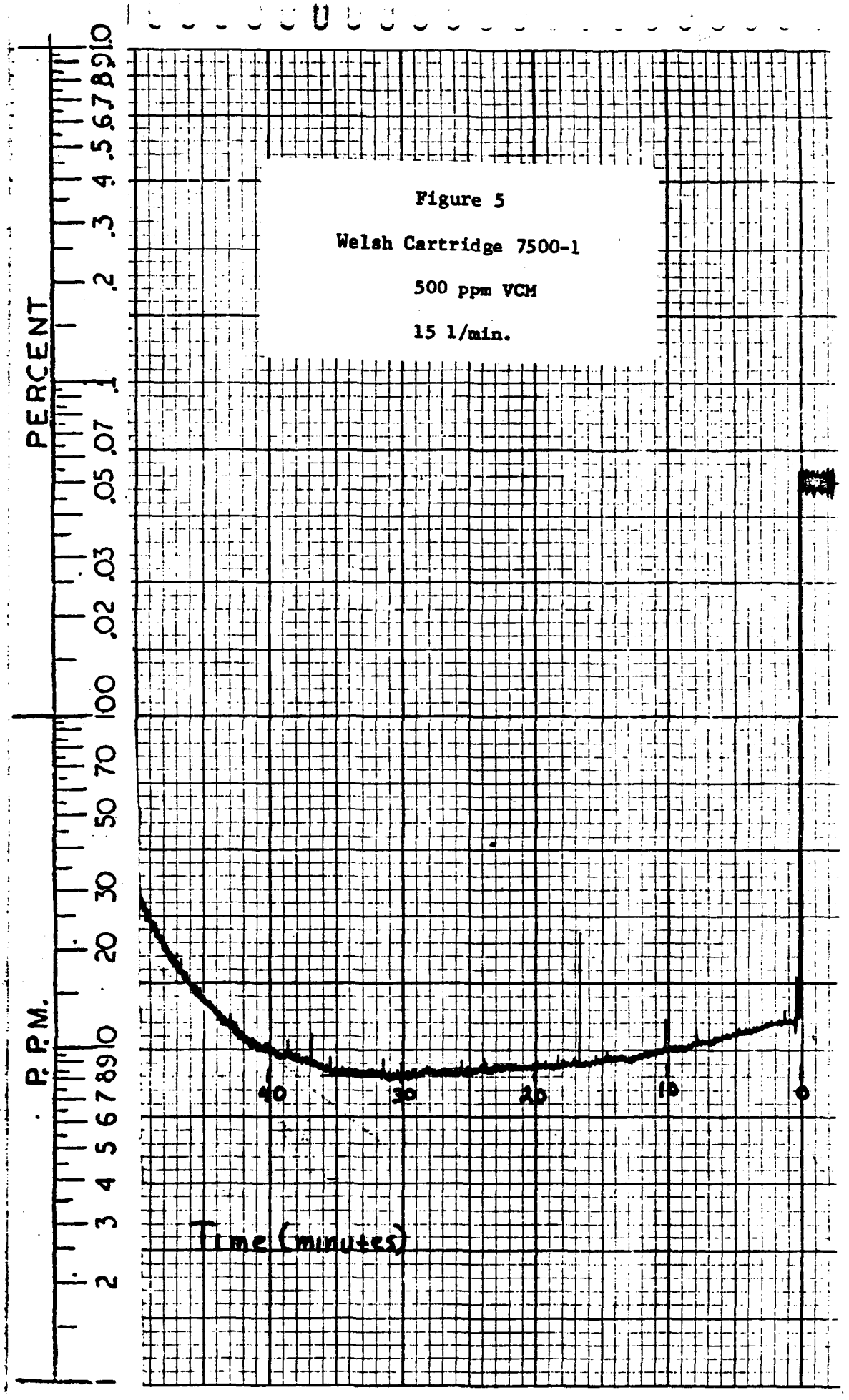


Figure 5

Welsh Cartridge 7500-1

500 ppm VCM

15 l/min.

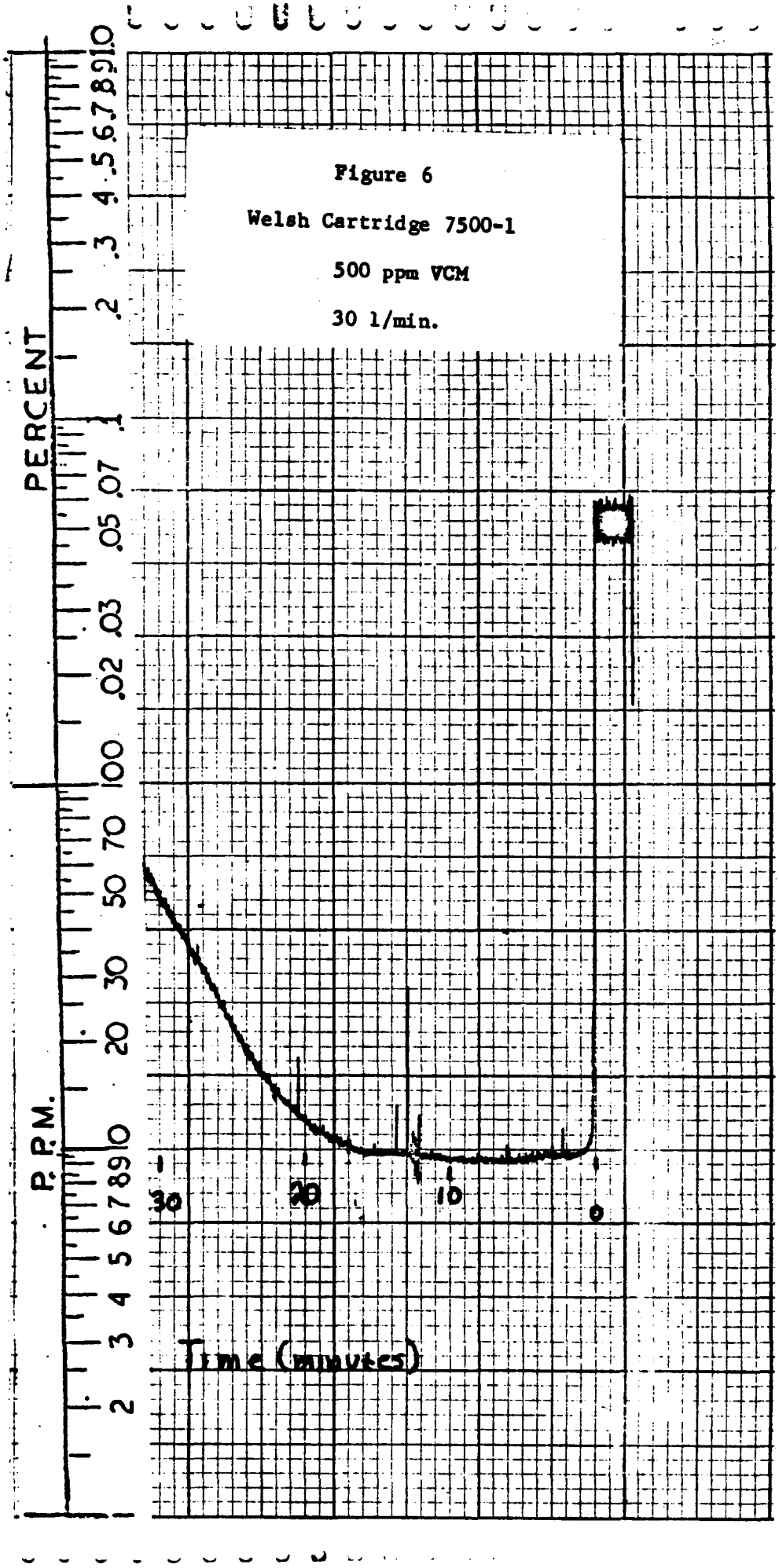


Figure 6

Welsh Cartridge 7500-1

500 ppm VCM

30 l/min.

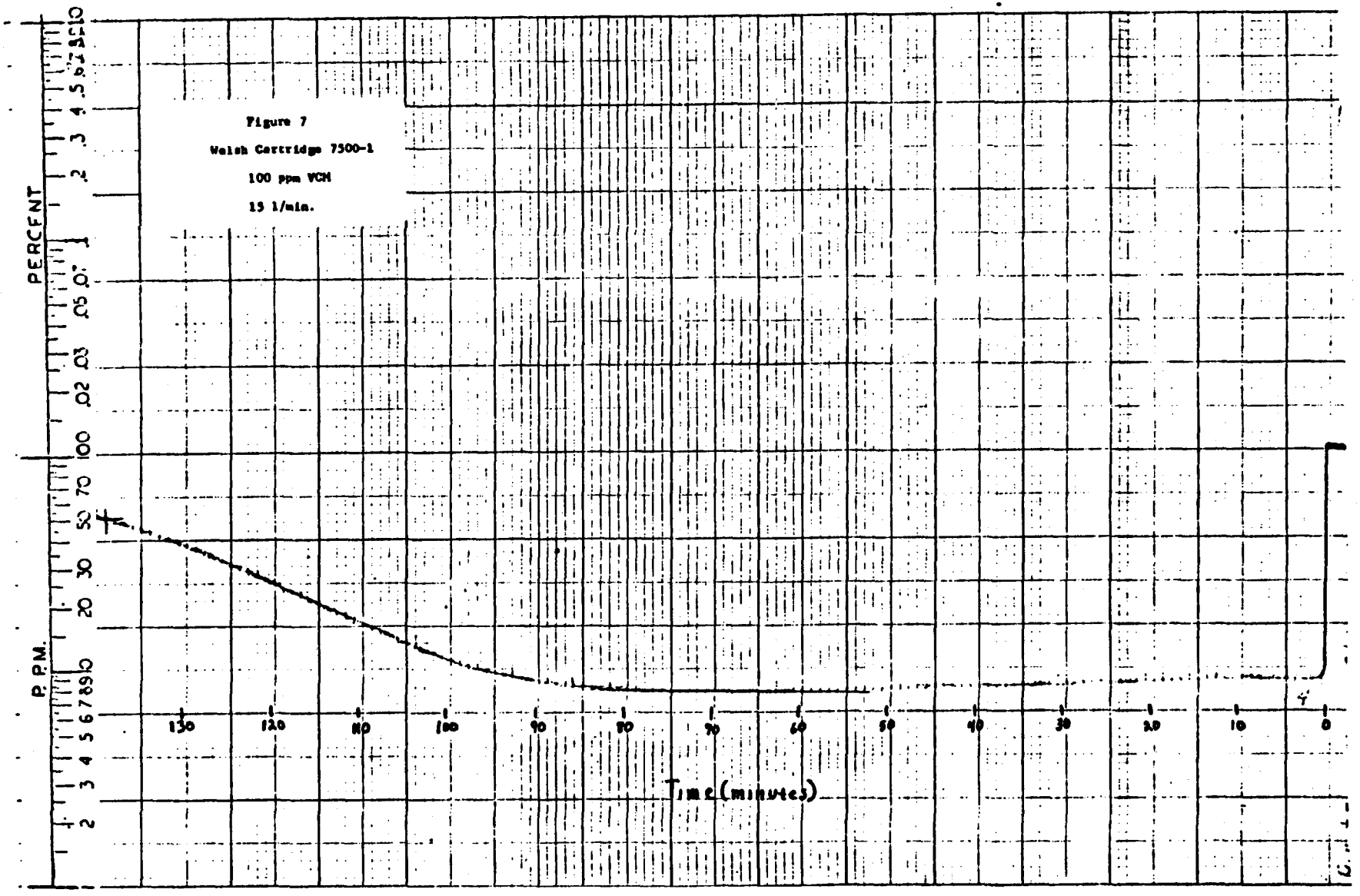


Figure 7
Welsh Cartridge 7500-1
100 ppm VCM
15 l/min.
PERCENT
P.P.M.
Time (minutes)
150
120
110
100
90
80
70
60
50
40
30
20
10
0
HEWLETT PACKARD
9270-1010

2459102I

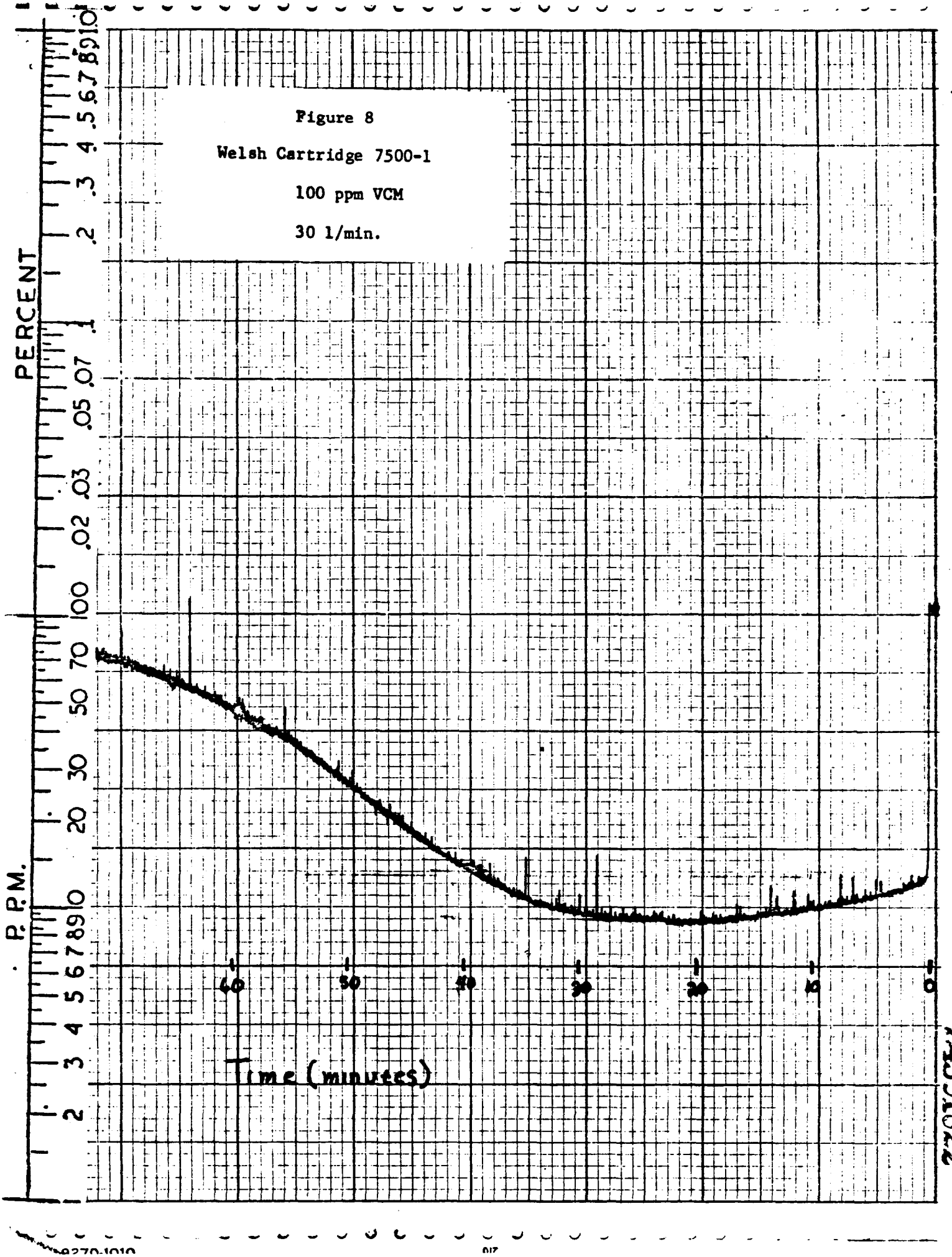


Figure 8
Welsh Cartridge 7500-1
100 ppm VCM
30 l/min.
PERCENT
P.P.M.
Time (minutes)

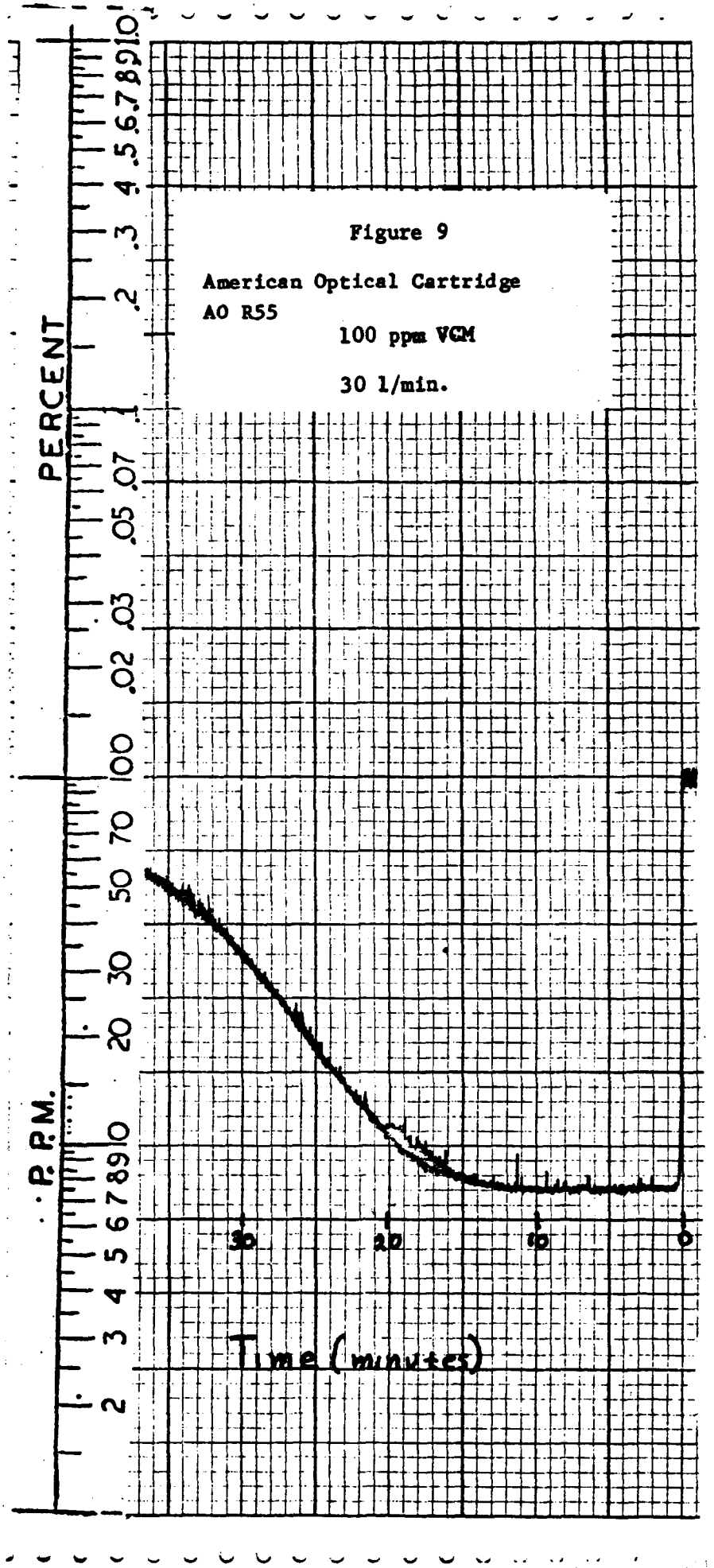


Figure 9

American Optical Cartridge
AO R55

100 ppm VCM

30 l/min.

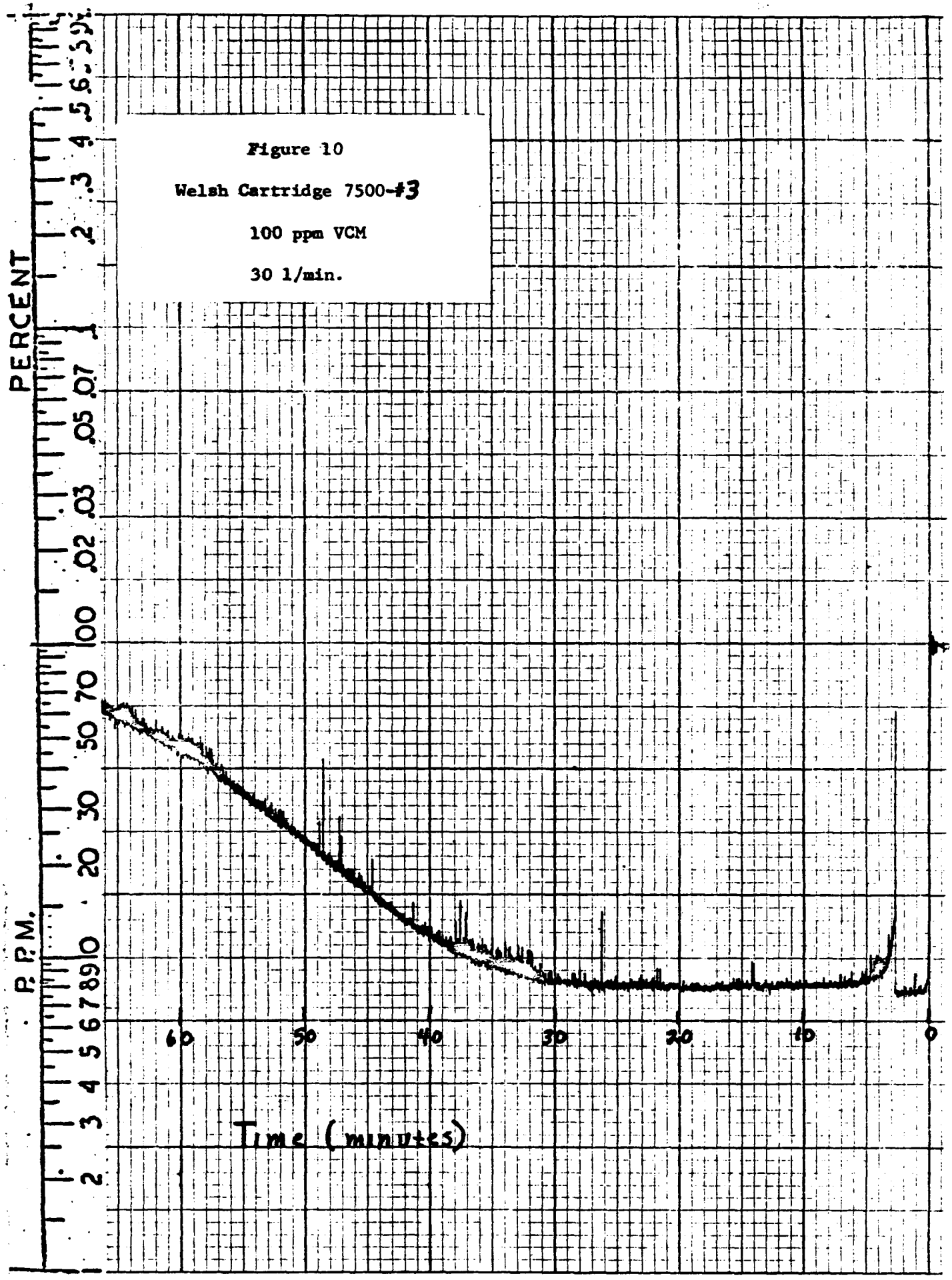


Figure 10
Welsh Cartridge 7500-#3
100 ppm VCM
30 l/min.
PERCENT
.1 .2 .3 .4 .5 .6 .7 1 2 3 4 5 6 7 8 9 10 20 30 50 70 100
R.P.M.
2 3 4 5 6 7 8 9 10 20 30 40 50 60
Time (minutes)
60 50 40 30 20 10 0

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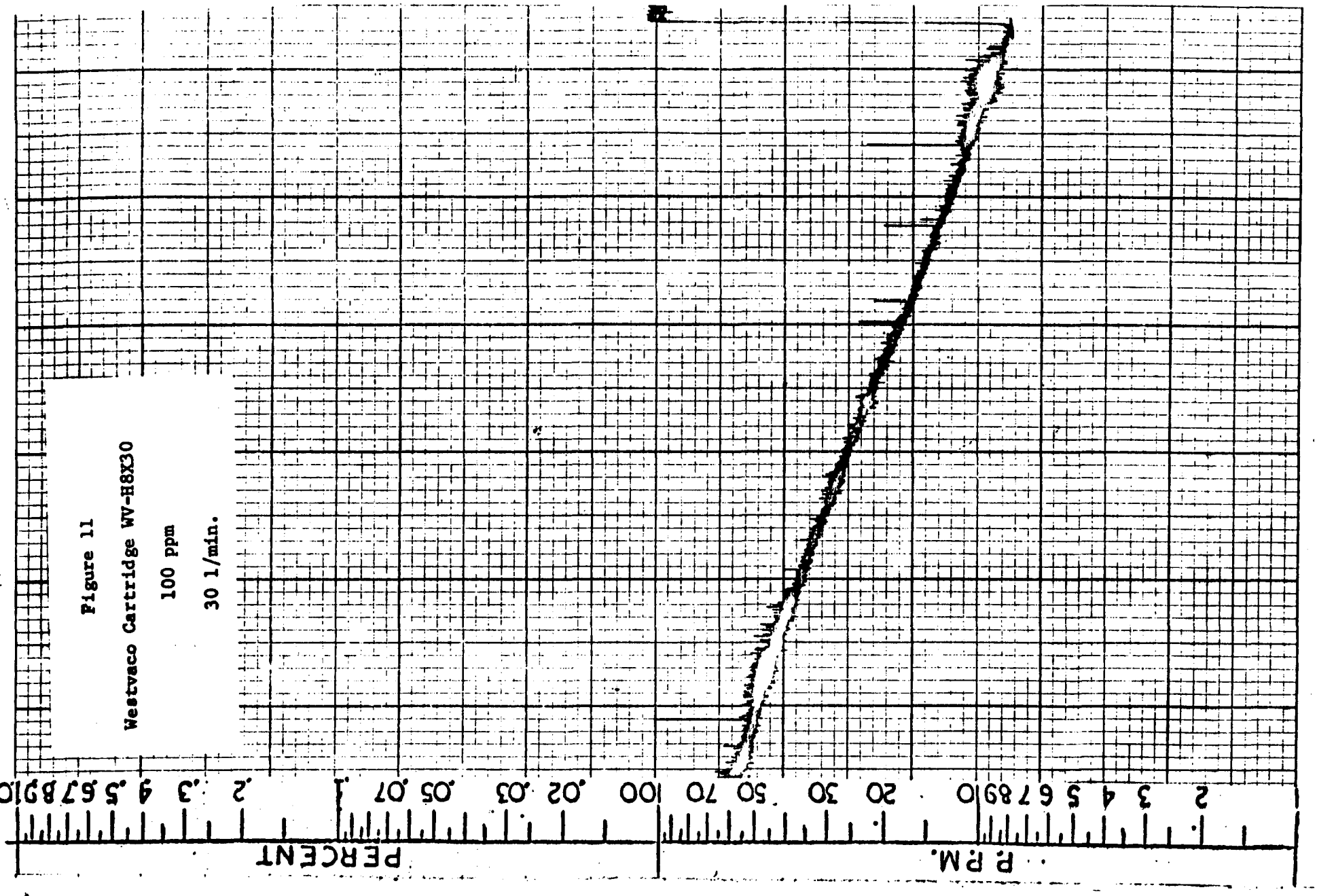
Figure 11
Westvaco Cartridge WV-H8X30
100 ppm
30 l/min.
PERCENT
RPM.