

H

450

~~CX~~ 11-14-78

Corporate Environmental Service
Project 8504-78
October 18, 1978

25-2671

DISTRIBUTION

Akron

R. W. Strassburg

Avon Lake General Chemical

J. M. Whitney
D. G. Desrosiers
M. D. Rider

Avon Lake Technical Center

R. D. Hardesty
J. A. TePas
L. B. Crider

Brecksville R & D Center

C. H. Lufter
J. B. Pausch
R & D Files

Calvert City

C. J. Orsborn
E. E. Atkins

Cleveland

K. J. Kaminski
M. E. Schmiederer
W. C. Becker
W. C. Holbrook
J. A. Klupar
J. W. Lewis

Henry

K. Konter
C. McCrosky

Long Beach

R. W. Birch
E. D. Hancock
W. D. Robb

Louisville

R. R. Taylor
J. W. Robben

Pedricktown

D. P. O'Keefe
J. A. Kiel

THE B. F. GOODRICH CO.

NOV 20 1978

RESEARCH LIBRARY

BFG TECHNICAL DOCUMENT

STATUS REPORT

**A Comparison of Collection Devices
for Vinyl Chloride at Part-per-Billion Levels:
Bendix Flasher Tubes Versus Tedlar Bags**

by

**John W. Born, Paul M. Zakriski
Andrew M. Fairlie, Jr.**

24819001

*Corrected pg. 14 included
11/1/79 NW*

**B F GOODRICH
Research Center**

A Comparison of Collection Devices for Vinyl Chloride
at Part-per-Billion Levels: Bendix Flasher Tubes Versus Tedlar Bags

by

John W. Born, Andrew M. Fairlie, Jr., and Paul M. Zakriski

SUMMARY

Our study involved sampling and measuring VCM concentrations in air at three ppb levels and four relative humidities. We achieved both main purposes of the study. In the process we learned what changes in the current BFG sampling method are necessary to obtain accurate measurements. We also devised the instrumentation and procedure to accomplish such changes.

The current BFG method employs PMCC's (i.e., Bendix Flasher tubes) to sample ambient air for 24 hours at 10 cc per minute. The method does not correct the measurements of VCM concentrations for environmental variables such as relative humidity, air volume sampled, and VCM load. The first purpose of our study was to show whether the current BFG method gives accurate results without such corrections. The study showed that the current results are not accurate. It shows the quantitative effect of the environmental variables on the collection and measurement of VCM concentrations. With corrections for such variables the current BFG method would be capable of measuring ppb concentrations of VCM in air accurately.

Consideration of our findings led us to devise instrumentation and a procedure to correct for such variables. That instrumentation prepares three PMCC calibration samples plus two PMCC monitor samples per 24-hour period. The five PMCC's all sample the same ambient air. They collect the same amount of VCM from the air. However, the three PMCC calibration samples also contain VCM "spikes" from a standard VCM permeation vial. The "spike" weights of VCM permit accurate assignment of the GC peak and concurrent calibration.

The second purpose of our study was to learn whether the California Air Resources Board's method of sampling and measuring such VCM test atmospheres is practicable. It requires the gas chromatographic detection and measurement of only about 0.04 percent as much VCM per sample as the BFG method measures. Our results show that the Board's Tedlar bag method is not practicable. It is not capable of measuring VCM concentrations in the 5.0 cc samples from the bag accurately below 100 ppb. The Tedlar bag method would require concentration of the total sample to compete with the PMCC method.

24813002

CONCLUSIONS

Our conclusions can be briefly summarized. The current BFG method of sampling and measuring property line VCM concentrations gives inaccurate results. The measurements of VCM concentrations at the property line prior to this time are low. They can serve only as a lower limit of the true concentration. It is not possible to correct the data of record to the higher and more accurate VCM concentrations. Our study showed how to correct that PMCC (i.e., Bendix Flasher tube) method to give accurate, reliable results at VCM-air concentrations of 5-40 ppb. We also showed that the California Air Resources Board's Tedlar bag method (with direct injection) is not capable of even detecting ambient VCM concentrations below about 100 ppb reliably without concentration. Our experimental results showed that temperature, humidity, volume of air sampled, and VCM weight critically affect accurate measurements of VCM concentrations.

Simultaneous loadings of four PMCC's and one Tedlar bag from the same VCM-air stream permitted direct comparisons. Loadings for 6 hours at 40 cc per minutes versus 24 hours at 10 cc per minute gave equivalent results. The order of decreasing effect of the environmental variables was humidity, volume of air sampled, and VCM weight. The ambient temperature effect ranks high with the relative humidity of from 44 to 95 percent.

The effects of such variables on the PMCC collection and analysis of VCM can be controlled. In field testing BFG can achieve such control best by concurrently measuring the effect of the variables. That approach is much more feasible than by determining the absolute values of the variables. We have designed a method of simultaneous PMCC sampling and preparation of PMCC calibration samples. The calibration samples would collect the same test atmosphere as the field samples but would also receive a VCM "spike" of known weight. This procedure would provide accurate and reliable measurements of ambient VCM concentrations at property lines. The presence of relatively large concentrations of other organic pollutants in the ambient air could seriously interfere with reliable GC analysis.

RECOMMENDATIONS

1. Display a copy of this report permanently in your file of VCM monitoring reports. It will serve as your first notice that ppb VCM measurements must include corrections for relative humidity, air volume sampled, and apparent weight of VCM collected.
2. Achieve all these corrections plus preparation of VCM calibration samples at the same time you collect the ppb VCM perimeter samples. Use the instrumentation which the BFG Environmental Laboratory will assemble. A vacuum pump will draw ambient air through five cleaned PMCC's at 10.0 cc per minute for 24 hours. An Aalborg five-flowtube flowmeter with NRS needle valves will control the five equal flowrates. A portable calibrator (Analytical Instrument Development, Inc. Model 340) will "spike" the ambient air for three of the five PMCC's at a standard VCM level of 40 ppb. The two remaining PMCC's will collect the "unspiked" ambient air. Thus, all the required corrections will be "built in" during the collection of the five PMCC samples.

24819003

3. As soon as it becomes available, use the latter instrumentation for all future monitoring at ppb levels of VCM.
4. Do not use the CARB direct injection method of measuring VCM-air concentrations below 100 ppb. Its required injection of a 5.0 cc aliquot of ambient air sample from a Tedlar bag does not give adequate GC response for reliable measurement.
5. Avoid confusing a VCM peak with another peak either at or very near the same retention time.
6. Prove out the new instrumentation and sampling procedure at a BFG plant before using it at all BFG plants.
7. Use a Hewlett-Packard 18850A Terminal (or its equivalent) to plot and integrate the GC signal and simultaneously record the results of the measurement. Use the Terminal's "slope sensitivity minus" feature to isolate the VCM peak and insure its quantitative detection.
8. After proving out the new instrumentation and VCM sampling procedure at a PVC plant, use this BFG sampling method to monitor ambient VCM levels at all PVC plant perimeters.

INTRODUCTION

The Los Angeles BFG plant is subject to the State of California Air Resources Board (CARB) ambient air quality standard for vinyl chloride.¹ That regulation details how to collect and analyze ambient VCM-air samples. It requires collection in Tedlar bags. It does not consider the feasibility of using the Bendix Personnel Monitoring Collection Column (PMCC), also termed the "Flasher tube", instead of the Tedlar bag. The regulation sets "a maximum allowable level for ambient concentrations of vinyl chloride within the range of 0.01 to 0.05 parts per million, twenty-four hour average."

The BFGoodrich Company has used and wishes to continue to use activated charcoal monitor tubes (namely, PMCC's) rather than the Tedlar bag. We have conducted this study to learn whether the PMCC method is as effective as the CARB Tedlar bag method. We also wanted to define the reliability of the data already generated by the PMCC method. The study directly compares the reliabilities of the PMCC and the Tedlar bag methods at VCM concentrations of 0.005 to 0.040 parts per million in air. The measurements were made over a range of relative humidities at constant temperature.

24819002

EXPERIMENTATION

The experiment involved simultaneous collection of vinyl chloride monomer (VCM) from the flowing test atmosphere by Bendix Personnel Monitoring Collection Columns (PMCC's) and Tedlar gas bags. The procedure included VCM concentrations of 5.0 to 40 parts per billion (ppb) and relative humidities of 44, 65, 75, and 95%. The temperature of the VCM-"zero air" test atmosphere was $24 \pm 1^\circ\text{C}$ throughout the collections. The constant temperature permitted comparisons on the basis of relative humidity instead of mg of water per m^3 .

Preparation of the PMCC's and Tedlar Bags for VCM Collection

The PMCC is a stainless steel tube containing 450 mg of a proprietary form of activated charcoal. A Pyrex glass wool filter followed by a stainless steel retainer screen keeps the charcoal in place. The PMCC collects VCM by adsorbing it on charcoal surfaces. The charcoal also adsorbs any water vapor and other organic pollutants in the test atmosphere. Thermal desorption at 250°C removes the adsorbed substances from the charcoal for either cleaning or analysis. A flow of helium gas through the heated PMCC purges the VCM from the tube. Appendix A describes the PMCC further. All desorptions in this study occurred in the Bendix Flasher oven at 250°C . Helium flowed through the PMCC at 30 cc per minute for each 30 minute precollection cleaning cycle. We repeated the cleaning cycles for each PMCC until gas chromatographic (GC) analysis showed no detectable peak at the retention time for VCM. The GC analysis times and temperatures employed during each cleaning cycle were the same as used for the measurement of the VCM from loaded tubes.

Cleaning the Tedlar bags involved filling each one with "zero" air and completely emptying it. We prepared "zero" air for cleaning by flowing compressed air through activated charcoal. Filling and emptying each bag three times cleaned the bag well. GC analysis of 5.0 cc samples from the bag after cleaning verified the absence of detectable VCM.

Thus, each PMCC and Tedlar bag were free of detectable VCM before they were used to collect VCM from the test atmosphere.

Preparation of the VCM Test Atmospheres

Preparation of the required VCM-air test atmospheres began with cleaning the air from the compressed air line. (See Appendix B.) That air stream passed through an oil trap, a silica gel water vapor trap, and an activated charcoal trap for organic vapors in that order at room temperature. The resulting "zero" air was free of water vapor and organic impurities.

The dynamic vapor generator (Appendix B) humidified the "zero" air. Humidification involved bubbling the "zero" air through double-distilled water inside glass reservoirs. Our study included relative humidities of 44, 65, 75, and 95%. We used a Taylor wet-and-dry bulb hygrometer to measure the relative humidity. The purified and humidified air became the diluent in preparing the ppb VCM test atmospheres.

24819005

The VCM for this study came from a Precision Gas Products, Inc. cylinder. The supplier certified that the VCM-air mixture in the cylinder consisted of 48.6 ppm VCM in pure ("zero") air. The National Bureau of Standards essentially verified that certification (Appendix C). The dilution involved mixing the 48.6 ppm VCM-air mixture from the cylinder with the purified and humidified air in the dynamic vapor generator (DVG). The flow rate of the diluent air was 48.6 lpm as controlled and measured with rotameters. We calibrated the two rotameters with a Singer Model 802 dry gas meter. Concentrations of 5.0, 10.0, and 40 ppb resulted from controlling the flow rate of the 48.6 ppm VCM-air mixture at 5.0, 10.0 and 40 cc per minute. An NRS needle control valve, Model No. 8514 (Brooks Instrument Division, Emerson Electric Co.), reproducibly controlled the flow of the 48.6 ppm VCM-air mixtures. We measured the flow rate periodically during the collection with a soap-film bubble meter.

The above procedure produced three different VCM concentrations in air at four different relative humidities. The result was test atmospheres having seven different combinations of VCM concentration and relative humidity.

Collection of VCM Test Atmospheres in PMCC's and Tedlar Bags

After dynamic mixing, the ppb-level VCM-air stream flowed through the five-port glass manifold (see Appendix B). The Tedlar bag collected a 14.4 liter sample of the test atmosphere at the middle port. That sample flowed from inside the supply manifold through a glass L-tube and Teflon tubing into the Tedlar bag. At the same time 14.4 liters of the same test atmosphere flowed through each of four PMCC's in the other four ports of the supply manifold. The flow rate for the PMCC's and the Tedlar bag was 40 cc per minute in all but one set. The corresponding collection period was 6.0 hours. In one set we collected concurrent PMCC and Tedlar bag samples at 10 cc per minute for 24 hours. Past experience assured us that sampling for 6 hours at 40 cc per minute is equivalent to sampling for 24 hours at 10 cc per minute under the same conditions.

We adjusted and monitored the flow rate through each PMCC during the VCM collection with an Aalborg four-flowtube flowmeter. We calibrated the flowrate through each flowtube-plus-PMCC both before and after each collection period. A vacuum pump drew the test atmosphere directly from the supply manifold into each PMCC. The air minus the VCM continued through the flow tube and the vacuum pump. It exited into the exhaust hood.

A specially-fitted 55 gallon steel drum served as the expansion chamber to fill the Tedlar bag.² Appendix D shows a sketch of the drum and associated equipment. We installed a stainless steel quick-connect fitting through the drum lid. A snap-lock ring and a tube gasket made an airtight seal between the lid and the drum. A vacuum pump evacuated the air from the drum through Tygon tubing. We installed a stainless steel tube through the side of the drum with an airtight seal. We connected that tube to the Halkey-Roberts screw-valve of the Tedlar bag in an airtight way. With that connection we could open and close the Tedlar bag valve inside the closed drum. We connected the outer end of the stainless steel tube with Teflon tubing to the glass L-tube inside the supply manifold. The Tedlar bag filled with the test atmosphere as the vacuum pump evacuated the drum. A soap-film bubble meter between drum and vacuum pump measured the evacuation rate.

24819006

A Whitey needle valve adjusted that rate. We measured the rate periodically during the collection. At the end of the collection period we closed the quick-connect fitting in the drum lid. Finally we closed the Tedlar bag valve without opening the drum.

Measurement of the VCM Content of PMCC's and Tedlar Bags

We measured the weight of VCM in each PMCC by thermal desorption followed by GC analysis. The thermal desorption involved heating the PMCC for 2.0 minutes at 250°C in the Bendix Flasher oven with no flow through the tube. Then helium flowed through the PMCC and carried the desorbed VCM through the GC column. The 20 ft x 1/8 inch stainless steel column contained 10% DC-200 on 80/100 mesh Chromosorb PAW (Supelco, Inc.). The Hewlett-Packard 5830A GC detected the VCM by flame ionization. The Hewlett-Packard 18850A Terminal graphed the electronic output from the GC detector, integrated the areas under the peaks, and printed the results. The temperature-time cycle included 2 minutes' desorption, 10 minutes' GC analysis at 70°C, 3 minutes' temperature rise to 150°C, and 10 minutes' thermal cleaning of the column at 150°C. Thus, the measurement equalled all the VCM collected by and recovered from the PMCC.

We measured the VCM content of the air in the Tedlar bag in the manner required by CARB. That involved withdrawing a 5.0 cc sample of the VCM-air mixture from the bag and injecting it from a syringe into the GC column. The 5.0 cc sample represents only (5/14, 400) or 0.00035 of the total VCM-air sample in the bag. The VCM measurements were made with a Hewlett-Packard 5711A GC coupled with a Hewlett-Packard 3380A Integrator.

Measurement of Relative Humidity

The relative humidity measurements came before and after each set of VCM-air loadings. We closed the ports of the supply manifold and attached a glass T-tube to its bottom outlet tube (Appendix B). We stoppered one branch of the T-tube. A Taylor Comfortguide Hygrometer measured the wet bulb and dry bulb temperatures of the emergent air stream. The two temperatures enabled us to calculate the relative humidity. The relative humidity and the temperature of the test atmosphere remained constant throughout each set of measurements.

Calibration of the Gas Chromatographs

The calibration of the Hewlett-Packard 5830A GC involved loading thermally-cleaned PMCC's directly from the 48.6 ppm VCM cylinder. We flowed the VCM-air mixture through the PMCC's at 40 cc per minute. The loading time was 30 minutes for four PMCC's and 3.0 minutes for one PMCC. The loadings thus represented 990 and 99 ppb if the same weights of VCM were collected during a 24-hour period. We analyzed the five PMCC samples in the manner described above.

The calibration of the Hewlett-Packard 5711A GC for the analysis of Tedlar bag samples followed a different procedure. We first injected a measured weight of pure liquid VCM into a measured weight of carbon disulfide in a closed vial. The resulting solution became our primary standard. A series of successive dilutions with carbon disulfide resulted in standard solutions having VCM concentrations of 31.54 ng/μl (i.e., nanograms per microliter) and 0.0282 ng/μl. Syringe injections of from 2.0 to 50 μl of the two solutions resulted in analyses of from 0.0705 ng to 1580 ng. The VCM content of 5 cc of a 10 ppb VCM-air mixture is 0.128 ng.

24819007

RESULTS AND DISCUSSION

From the start our purpose became threefold. First was to learn whether the Tedlar bag method of collection and analysis is practicable. Second was to compare the results of the PMCC method with the results of the Tedlar bag method. Concurrent collection of identical VCM-air samples in the PMCC's and Tedlar bag achieved both of these purposes. Our third purpose was to determine if the historical VCM ambient data, which were collected without regard to relative humidity and temperature, are reliable. This also has been accomplished by the sampling and analysis of test atmospheres of constant composition.

Calibrations of the Gas Chromatographs

Calibrations of the two gas chromatographs were the necessary first step of analysis. Table I and Figure 1 show that the calibration curve for the PMCC analyses was a straight line. The VCM calibration factor within the 95% confidence limits was 110 ± 4.0 au/ng. Tables II and III give the data for two separate GC calibrations for the Tedlar bag analyses. The first calibration (Table II) gave the wider spread of data. Its calibration factor within 95% confidence limits was $1,523 \pm 1,157$ au/ng. The second calibration gave a factor of $1,930 \pm 260$ au/ng (95% limits). Loss of small amounts of VCM is difficult to avoid during the repeated dilutions in preparing standard ppb solutions of VCM in carbon disulfide. Even a small loss is critical in the 0.0135 - 0.108 ng/ μ l range. Therefore, we used greater skill from practice and a higher range of VCM concentrations in preparing the second series of standard solutions. Figure 2 shows that the calibration curve for the data in Table III is a straight line through the origin. We have used the calibration factor of 1,930 au/ng throughout our subsequent calculations.

The response factors for the Tedlar bag samples involved measurements at the 0.06 ng VCM level. That level is virtually the GC detection limit. In sharp contrast the PMCC response factor involved measurements at the 60,000 ng VCM level. The range of 10^6 ng between the two VCM levels is very wide. It partially explains the difference in calibration factors. Figure 3 illustrates how that difference is consistent with the nature of the calibration curve. The chief reason for the difference is the usual negative inflection in the calibration curve in the vicinity of the limit of GC detection (i.e., "zero"). The inflection is probably due to a combination of instrument "noise" and physical interactions of the VCM with the trapping charcoal, the column, and the detector. In short, the GC becomes proportionately less sensitive as the VCM weight approaches zero. Thus the rate of decrease of the ratio (au/ng) speeds up in the vicinity of zero VCM.

Collection of VCM from Air Samples in PMCC's

The relative humidity will certainly vary during 24-hour collections of VCM-air samples. In fact, both the relative humidity and the ambient temperature will probably vary during a single 24-hour collection. The concentration of water vapor varies with the ambient temperature at any fixed relative humidity. In an earlier study of VCM analyses at 1.0 ppm concentration³, we found that relative humidity had a profound effect on VCM detected by the PMCC tube. The effect becomes more pronounced as sampling volume increases. We evaluated the data from the present study in terms of both relative humidity and the weight of water charged to the tube.

24819008

Table IV summarizes the experimental data from the collection of VCM-air samples in PMCC's. The values on each line of the table are for several simultaneous PMCC collections. Table VIII states the number of PMCC's per corresponding line in Table IV. Table IV shows the following in order:

- (a) the VCM-air concentration in parts per billion,
- (b) the percent relative humidity,
- (c) the GC response in area units,
- (d) the calculated weight of VCM recovered from the PMCC,
- (e) the GC response factor in au/ng, and
- (f) the percent recovery of VCM.

We calculated the weight of VCM in each PMCC by multiplying the measured VCM-air volume by the VCM-air concentration. The GC response factor was the GC response divided by the charged weight of VCM. We calculated the percent recovery by dividing the sample response (in au/ng) by the calibration factor (110 au/ng).

We needed to know how the experimental variables affected the GC peak area. Interpreting the actual GC area is difficult. It must change with variations in either the VCM concentration or the volume of "contaminated" air passing through the PMCC. Therefore, we calculated an "adjusted GC response". The "adjusted GC response" is defined as the response per 15 liters of sampled test atmosphere $\times 10^{-3}$. The 15-liter standard volume was selected because it approximates many of the actual volumes in the sampling program. That is, Equation (1) is

$$\text{adjusted PMCC peak area} = \left(\frac{\text{actual GC peak area}}{\text{actual sampled volume (l)}} \right) (15 \text{ l} \times 10^{-3})$$

Mathematical modeling was used to show the effect of the experimental variables on the GC response. We employed multiple regression analysis using adjusted GC area versus ppb VCM, total sampled volume (liters), and either relative humidity or total mg of water vapor. Looking at the GC area per unit volume then enabled us to look at and graph the varying efficiencies of detecting VCM. We thus evaluated the effects of different levels of humidity and total volume for the range of VCM levels. The mathematical levels based on mg of water vapor were consistently inferior to those using relative humidity. We therefore dropped the mg H₂O models from further consideration. Models based on VCM percent recovery did not show the effect of varying VCM levels as did models based on adjusted GC response. We required a model which passes through the origin of the graph. The model based on VCM recovery did not do so.

Table V shows the adjusted GC peak areas, volumes of test atmosphere, ppb VCM, and % R.H. data. The fifth set of data in Table V had an abnormally low adjusted GC area relative to the corresponding sample volume, ppb VCM, and % R.H. The value shown is 41.1 compared to a predicted 84.2 au. We deleted that row of data and chose Equation (2) as our final mathematical model:

24819009

$$\begin{aligned} \text{adjusted GC peak area/15 liters} = & (1.3683) [(\text{volume}) (\text{ppb VCM})] + \\ & (0.001044) [(\text{ppb VCM}) (\% \text{ R.H.})^2] - (0.02100) [(\text{volume}) (\text{ppb VCM}) (\% \text{ R.H.})] \end{aligned}$$

This model explains 97.2% of the observed variation in adjusted GC areas (i.e., $R^2 = 0.972$). The 95% confidence limits are $\pm 40 \text{ au} \times 10^{-3}$.

Using Equation (2) we generated Table VI. It predicts the adjusted GC area/15 liters covering the range of ppb VCM and % R.H. Predictions were made only at the total volumes of 12 and 15 liters of test atmosphere. Only two volumes were lower, and the risk of extrapolation is too great. Figures 4 and 5 illustrate the results via a plot of the data in Table V. To clarify the reader's examination of Figures 4 and 5, we remind that a change in adjusted GC peak area with a change in total air flow reflects a change in the efficiency of detecting VCM. The following Equation (3) permits calculating the predicted actual GC peak area:

$$\text{predicted actual GC area} = \frac{(\text{adjusted GC area}) (\text{actual volume, l}) (1,000)}{(15 \text{ l})}$$

The plots in Figures 4 and 5 illustrate how well Equation (2) fits the data. The curves show that % R.H. has a dominant influence on the adjusted GC area (and therefore on the actual GC area). For example (Figure 5), at 15 liters and 40 ppb the adjusted peak area is 340,000 au at 45% R.H. but almost 0 at 95% R.H. Above an average 75% R.H. taking a PMCC ppb VCM sample is hardly worth while. Some compensation for % R.H. is needed at all humidity levels. Increasing the ppb VCM concentration increases the adjusted peak area as expected. Finally, comparing Figures 4 and 5 shows the effect of changing the volume of test atmosphere through the PMCC. The plots indicate that a lower total flow reduces the effect of high humidity. This reduction is expected on a theoretical basis since less air volume means less total water to interfere with VCM adsorption and desorption during collection and analysis.

Collection of VCM-Air Samples in Tedlar Bags

Table VII summarizes the experimental data from the collection of VCM-air samples in Tedlar bags and the subsequent analyses. The column headings were described before in this report for Table III.

Multiple regression analysis was attempted again. As before it was based on actual GC response versus ppb VCM and % R.H. (or ng of H_2O). Constant sample volume (5.0 cc GC injections) made adjustment of GC response unnecessary. We were not able to find a significant relationship among the variables for the Tedlar bag samples. The apparent sampling and testing error was essentially the same as the total observed variation in GC response. Figure 6 helps to show this almost total lack of significant relationships. Note that the scatter of results within a particular VCM-humidity combination is about equal to the total scatter of data points. The regression analysis does not seem to respond at these extremely low VCM levels.

Number of "Hits" in PMCC and Tedlar Bag Analyses

It is time now to compare "hits and misses" for individual ppb VCM samples from PMCC's versus Tedlar bags. Tables IV and VII show our estimates of GC peak areas for PMCC and Tedlar bag analyses. However, they don't tell the whole story. As the VCM concentration drops to extremely low values, reliable results become

24819010

more and more difficult to obtain. Frequently VCM cannot be detected at all in a VCM-air sample at such levels. The following results from Table VIII illustrate the number of "hits" for PMCC and Tedlar bag analyses versus ppb VCM.

VCM Concn. (ppb)	PMCC Samples			Tedlar Bag Samples		
	Analyses Attempted	No. of "Hits"	Successes (%)	Analyses Attempted	No. of "Hits"	Successes (%)
5	12	11	92	15	2	13
10	39	29	74	120	47	39
40	19	19	100	43	28	65
Total:	70	59	84	178	77	43
At ≤ 10 ppb:	51	40	78	135	49	36

The results show how questionable the Tedlar bag method of analysis really is. They suggest that this type of analysis should not be attempted at VCM levels much below 100 parts per billion with 5.0 cc samples at the present state of technology. In contrast the PMCC method of collection and analysis is practicable under the conditions of this experiment.

Relationship of Tedlar Bag Samples to Adjusted GC Peak Areas

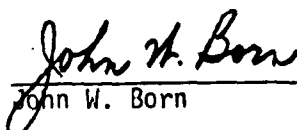
We used multiple regression analysis to learn whether adjusted GC peak areas of PMCC VCM samples could be predicted from measurements of Tedlar bag samples and % R.H. Table IX lists the data used and shows the ppb VCM in each test atmosphere. We obtained a significant relationship by using the following model (Equation 4):

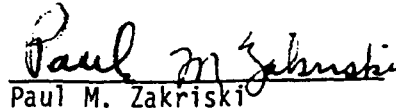
$$\begin{aligned} \text{Adjusted PMCC GC peak area} &= \\ &= 94.19 + (0.3085) (\text{Tedlar GC peak area}) - (1.2421) (\% \text{ R.H.}) \end{aligned}$$

This model explains 74.7% of the observed variation in adjusted GC peak area (i.e., $R^2 = 0.747$). The 95% confidence limits are $\pm 44 \text{ au} \times 10^{-3}$. We dropped the ninth set of data in Table IX from the analysis as an outlier. Its predicted value was 45.5 au compared with an observed value of 170 au. (see Table X).

We used Equation 4 to develop Table X. That table predicts the adjusted PMCC GC peak area for a variety of Tedlar bag GC peak area - % R.H. combinations within our general experimental range. Figure 7 displays curves based on Equation (4) and plots the data used in developing that equation.

The preceding section of this report shows how the difficulty of detecting VCM in test atmospheres by the Tedlar bag method increases as the concentration goes from 40 to 10 to 5 ppb. Figure 6 suggests the same trend. That is, for 75% R.H. or less the PMCC gives measurable VCM. However, comparable Tedlar bag samples give an estimate of zero PMCC VCM by Equation 4. Figure 6 shows 3 to 5 ppb VCM by the PMCC method when the Tedlar bag shows 0 ppb VCM. Table XI gives the data which were calculated from Equation 4 and used to plot the curves in Figure 7.


John W. Born


Paul M. Zakriski


Andrew M. Fairlie

24813011

REFERENCES

1. State of California Administrative Code, Title 17, Health and Safety Code, Section 39606(b).
2. Code of Federal Regulations, Title 40, Chapter I, Part 61, Subpart I - "National Emission Standard for Benzene Emissions from Maleic Anhydride Plants", Figure 111-1: Integrated-bag sampling train, page 48.
3. Born, J. W.; Zakriski, P. M.; and Hardesty, R. D.; Evaluations of Bendix Flasher Tubes and MSA Tubes as VCM Monitors, Status Report, 8504-76, August 24, 1978.

24819612

TABLE I

Calibration of the Gas Chromatograph for PMCC Sample Analyses

PMCC No.	VCM Concentration in Air (ppb)	Weight of VCM in PMCC (μ g)	GC Peak Area (au)	Peak Area/VCM Wt. (au/ng)
J1	486.	89.58	9,870,000	110.
J2	486.	92.57	10,040,000	108.
J3	486.	89.58	9,866,000	110.
J4	48.6	8.958	993,600	111.

Average (Peak Area/VCM Weight) = 109.8 au/ng

Standard deviation = 1.26 au/ng

95% confidence limits = ± 4.0 au/ng

Coefficient of variation = 1.15%

TABLE II

Calibration of the Gas Chromatograph for Tedlar Bag Sample Analyses

Std. Solution C Volume (μ l)	Weight of VCM (ng)	GC Response (area units)	Factor (au/ng)
2.5	0.0675	150	2,222.
2.5	0.0675	131	1,941.
2.5	0.0675	81	1,200.
2.5	0.0675	112	1,659.
			[1,756.]
5.0	0.135	142	1,052.
5.0	0.135	297	2,200.
5.0	0.135	253	1,874.
			[1,709.]
20.0	0.540	804	1,489.
20.0	0.540	697	1,291.
20.0	0.540	700	1,296.
20.0	0.540	284	526.
			[1,150.]

Standard Sol'n. C (μ l)	VCM Weight (ng)	Calibration Factor (au/ng)	Standard Deviation (au/ng)	Coefficient of Variation (%)	95% Confidence Limits (au/ng)
2.5	0.0675	1,756	436	24.9	$\pm 1,386$
5.0	0.135	1,709	592	34.6	$\pm 2,545$
20.	0.540	1,150	426	37.0	$\pm 1,357$
Overall Average:		1,523	519	34.1	$\pm 1,157$

24819013

TABLE III

Calibration of the Gas Chromatograph for Tedlar Bag Sample Analyses

<u>Standard Solution B Volume (μl)</u>	<u>Weight of VCM (ng)</u>	<u>GC Response (area units)</u>	<u>Calibration Factor (au/ng)</u>
10.0	315.	642,679	2,040.
15.0	473.	944,632	2,000.
25.0	788.	1,440,660	1,830.
30.0	946.	1,738,106	1,840.
50.0	1,577.	3,055,728	1,940.

Average Calibration Factor = 1,930 au/ng
Standard Deviation = 94 au/ng
Coefficient of Variation = 4.9%
95% Confidence Limits = ±260 au/ng

TABLE IV

Summary of Data from the Collections of VCM in PMCC's

<u>VCM (ppb)</u>	<u>R.H. (%)</u>	<u>GC Response (area units)</u>	<u>VCM Wt. (mg)</u>	<u>Factor (au/ng)</u>	<u>VCM Recovery (%)</u>
5.0	44	8,096	73.6	110 ±16	100.
5.0	44	54,540	202.	270 ±75	245.
5.0	44	25,564	166.	154 ±21	140.
10.0	44	4,648	43.2	108.	98.
10.0	44	39,483	369.	107 ±32	97.
10.0	44	63,491	367.	173 ±30	157.
10.0	65	29,117	371.	68.8±18	62.5
10.0	65	51,078	382.	154 ±29	140.
10.0	75	57,222	374.	153 ±10	139.
10.0	74	35,980	378.	84.6±27.4	86.7
10.0	74	19,810	308.	64.3±23.1	58.4
10.0	95	11,279	398.	37.0±13.0	33.6
10.0	95	38,237	368.	104 ±12	94.5
40.0	44	35,535	1,545.	230 ±12	209.
40.0	67	146,135	1,457.	100 ± 7.8	90.9
40.0	67	143,573	1,267.	100 ±29	90.9
40.0	95	33,697	1,398.	24.5± 5.3	22.2
40.0	95	11,180	1,480.	4.64±2.92	4.22

24819014

TABLE V

PMCC Volumes Sampled, Water Charged, and Adjusted GC Peak Areas

<u>VCM (ppb)</u>	<u>R.H. (%)</u>	<u>Water (mg)</u>	<u>GC Response (au)</u>	<u>VCM-Air Volume Sampled (l)</u>	<u>Adjusted GC Response (au x 10⁻³/15 l)</u>
5.0	44	57.3	8,096	5.74	21.16
5.0	44	160.	54,540	15.8	51.78
5.0	44	251.	25,564	13.0	29.59
10.0	44	17.7	4,648	1.74	40.07
10.0	44	146.	39,483	14.4	41.13
10.0	44	133.	63,491	13.1	72.76
10.0	65	200.	29,117	14.4	30.29
10.0	65	221.	58,623	15.5	56.66
10.0	75	251.	57,222	14.5	59.36
10.0	74	239.	35,980	14.5	37.30
10.0	74	206.	19,810	13.4	22.24
10.0	95	330.	11,279	15.0	11.24
10.0	95	310.	38,237	14.2	40.51
40.0	44	153.	355,350	15.1	349.2
40.0	67	221.	146,135	14.3	153.5
40.0	67	200.	143,573	12.6	170.4
40.0	95	297.	33,697	13.3	38.12
40.0	95	309.	11,180	14.4	11.67

24819015

TABLE VI

Predictions of Adjusted PMCC GC Peak Areas for 12 and 15 Liters

VCM (ppb)	R.H. (%)	VCM-Air Volume Sampled (l)	Adjusted GC Peak Area (au)*	
			Minus the 5th Set	Including All Sets
10	30	12	98	83
10	45	12	72	65
10	65	12	45	41
10	75	12	34	29
10	95	12	19	5
20	30	12	196	165
20	45	12	144	130
20	65	12	89	82
20	75	12	68	58
20	95	12	38	10
30	30	12	294	248
30	45	12	215	195
30	65	12	134	123
30	75	12	102	87
30	95	12	57	16
40	30	12	392	331
40	45	12	287	259
40	65	12	178	164
40	75	12	135	116
40	95	12	76	21
10	30	15	120	103
10	45	15	85	81
10	65	15	45	51
10	75	15	28	36
10	95	15	0	7
20	30	15	240	206
20	45	15	169	162
20	65	15	89	103
20	75	15	56	73
20	95	15	1	13
30	30	15	360	310
30	45	15	253	243
30	65	15	134	154
30	75	15	83	109
30	95	15	1	20
40	30	15	480	413
40	45	15	338	324
40	65	15	178	205
40	75	15	111	146
40	95	15	1	26

*These values were calculated using Equation 2.

24819016

TABLE VII

Summary of Data from the Collections of VCM in Tedlar Bags

<u>VCM (ppb)</u>	<u>R.H. (%)</u>	<u>GC Response (area units)</u>	<u>VCM Wt. (ng)</u>	<u>Factor (au/ng)</u>	<u>VCM Recovery (%)</u>
5	44	0	0.129	0	0
10	65	109.	0.130	838 ± 277	43.5
10	65	189.	0.128	1,480 ± 109	76.6
10	74	0	0.128	0	0
10	74	56.4	0.128	441 ± 134	22.9
10	75	254.	0.129	1,968 ± 1,271	102.
40	67	340.	0.510	667 ± 231	34.6
40	67	112.	0.510	220 ± 86	11.4
10	95	131.	0.132	992 ± 167	51.4
10	95	252.	0.130	1,938 ± 148	101.
40	95	183.	0.517	354 ± 217	18.3
40	95	119.	0.517	230 ± 85	11.9

24819017

TABLE VIII

Comparison of GC Responses vs. Injections for Tedlar Bags and PMCC's

VCM Concentration (ppb)	Relative Humidity (%)	Tedlar Bag		PMCC	
		Number of Injections	Number of Responses	Number of Injections	Number of Responses
5.0	44	-	-	4	4
5.0	44	-	-	4	4
5.0	44	15	2	4	3
10.0	44	-	-	4	1
10.0	44	-	-	4	3
10.0	44	-	-	4	3
10.0	65	27	12	4	4
10.0	65	13	7	4	3
10.0	75	22	3	3	3
10.0	74	15	0	4	3
10.0	74	11	5	4	2
10.0	95	12	5	4	4
10.0	95	20	15	4	3
40.0	44	-	-	4	4
40.0	67	10	7	4	4
40.0	67	15	11	4	4
40.0	95	12	6	3	3
40.0	95	<u>6</u>	<u>4</u>	<u>4</u>	<u>4</u>
Totals:		178	77	70	59

Responses/Injections: (77/178) = 43%; (59/70) = 84%
 Analysis Time per Set: Tedlar bag = 1.0 hour; PMCC = 2.0 hours.
 Comparative Analysis Times: Tedlar bag = 178 hours; PMCC = 100 hours.

24819018

TABLE IX

Data Used to Develop Equation 4 to Relate Tedlar and PMCC GC Peak Areas

<u>VCM Concentration (ppb)</u>	<u>R.H. (%)</u>	<u>Observed Tedlar Peak Area (au)</u>	<u>Predicted Adjusted PMCC Peak Area (au)</u>
5.0	44	0	29.59
10.0	65	109.0	30.29
10.0	65	189.0	56.66
10.0	74	0	37.30
10.0	75	56.40	22.24
10.0	75	254.0	59.36
10.0	95	131.0	11.24
10.0	95	252.0	40.51
40.0	67	112.0	170.4
40.0	67	340.0	153.5
40.0	95	119.0	11.67
40.0	95	183.0	38.12

TABLE XComparison of Adjusted PMCC Peak Areas: Observed vs. Predicted^a

<u>Adjusted PMCC VCM GC Peak Areas (au)</u>		<u>Difference</u>	
<u>Observed^b</u>	<u>Predicted^c</u>	<u>(au)</u>	<u>(%)</u>
59.3589	79.3980	-20.0391	-33.7592
29.5880	39.5395	-9.9515	-33.6337
37.2979	2.2769	35.0209	93.8953
11.2415	16.6088	-5.3673	-47.7450
40.5053	53.9393	-13.4340	-33.1660
38.1188	32.6517	5.4671	14.3423
11.6701	12.9066	-1.2364	-10.5950
22.2418	18.4352	3.8066	17.1146
30.2881	47.0840	-16.7959	-55.4536
153.5032	115.8671	37.6360	24.5181
170.3794	45.5254	124.8540	73.2800
56.6588	71.7653	-15.1065	-26.6622

^a The predicted values are based on the observed Tedlar bag VCM GC peak areas. They were calculated to show the relationship between the observed Tedlar peak areas and the corresponding PMCC peak areas.

^b The observed adjusted PMCC GC peak areas come from Table V as calculated by Equation 1.

^c The predicted adjusted PMCC GC peak areas were calculated from the observed Tedlar bag GC peak areas by Equation 4.

24819019

TABLE XI

Data Derived from Equation 4 and Used to Plot Figure 7

<u>Assigned Tedlar Peak Area (au)</u>	<u>R.H. (%)</u>	<u>Predicted Adjusted PMCC Peak Area (au)</u>
0	45	38
150	45	85
300	45	131
0	65	13
150	65	60
300	65	106
0	75	1
150	75	47
300	75	94
0	95	-24
150	95	23
300	95	69

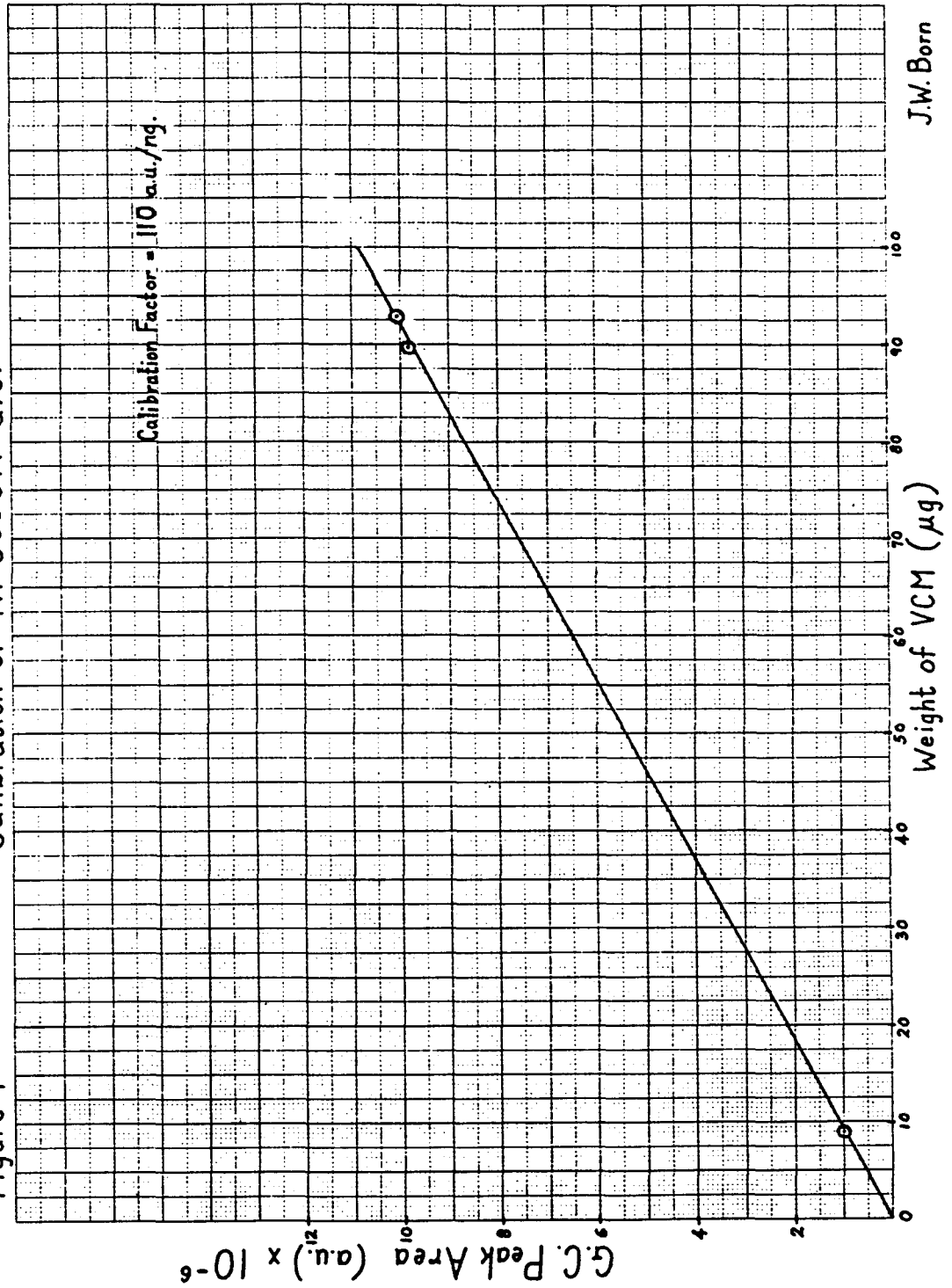
24819620

461510

K-E 10 X 10 TO THE CENTIMETER
KUMFEL & SONS CO. NEW YORK, N.Y.

Calibration of HP5830A G.C.

Figure 1

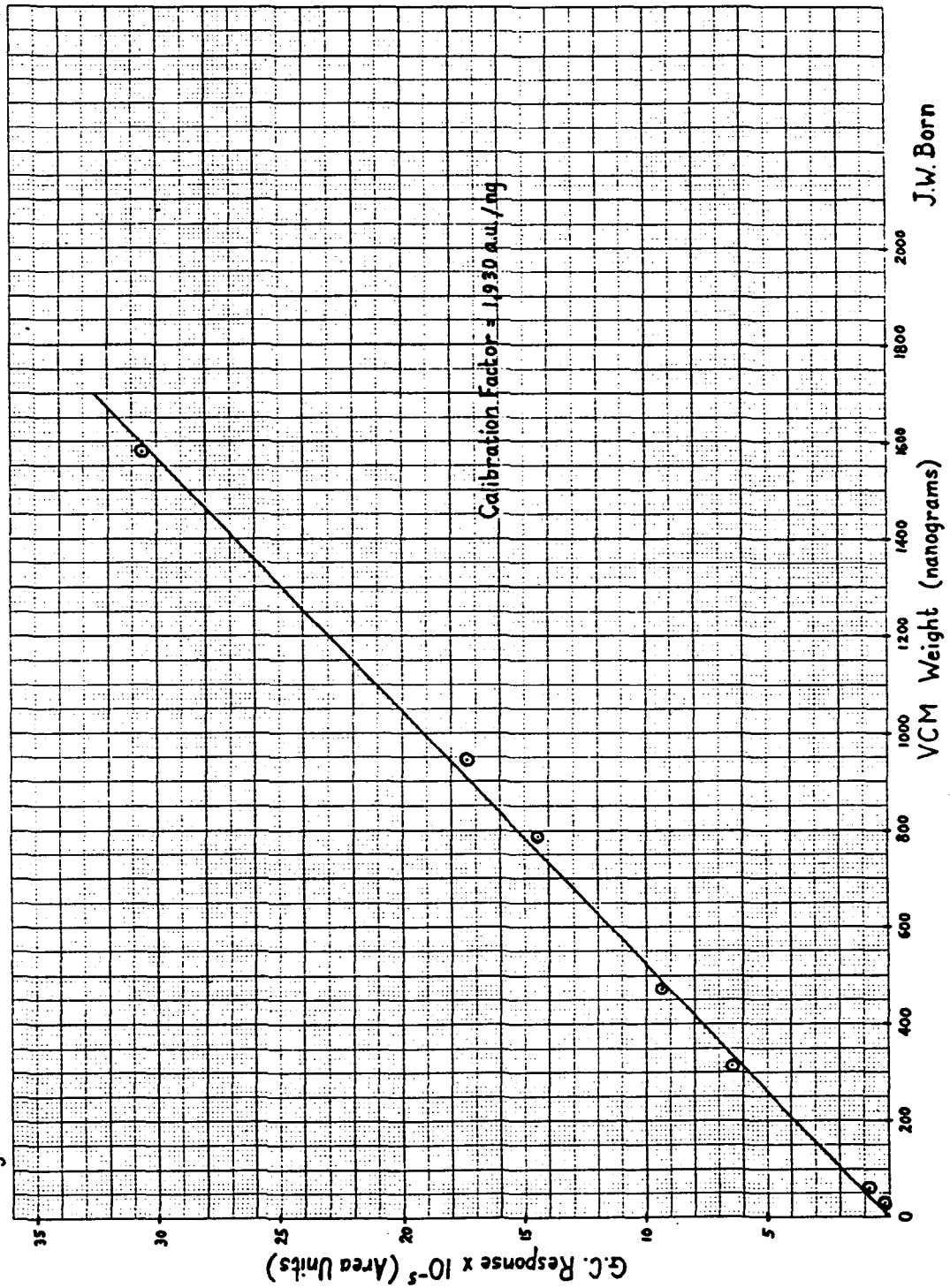


J.W. Born

24819021

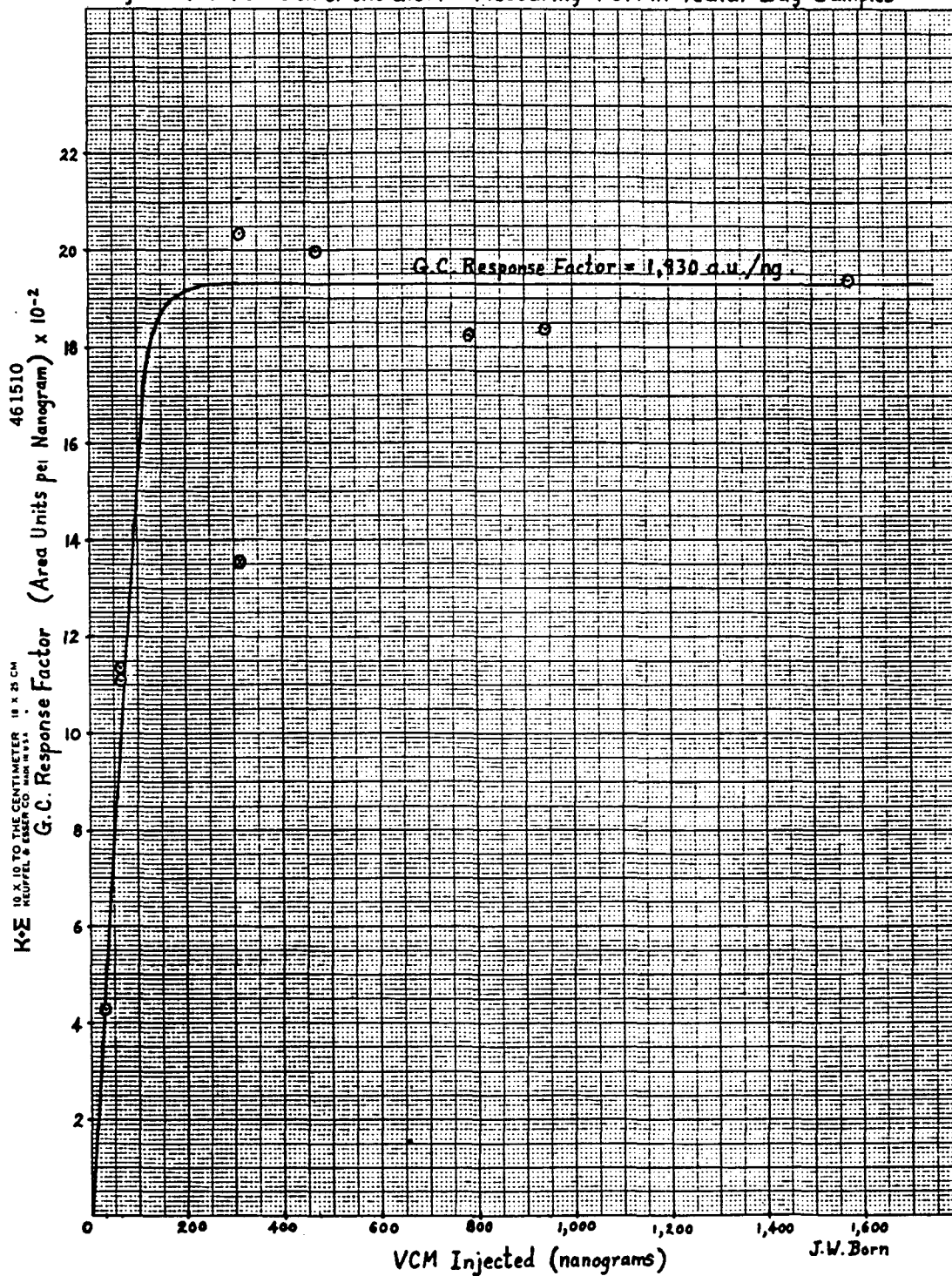
K-E 461510
10 X 10 TO THE CENTIMETER IN X 10⁻¹ M
NEUPTEL & CASER CO. MADE IN U.S.A.
Calibration of HP5711A-16A: Column #48

Figure 2.



J.W. Born

Figure 3. Calibration of the G.C. for Measuring VCM in Tedlar Bag Samples



24819023

Figure 4. Adjusted PMCC Area vs. ppb VCM, % R.H., and Air Volume

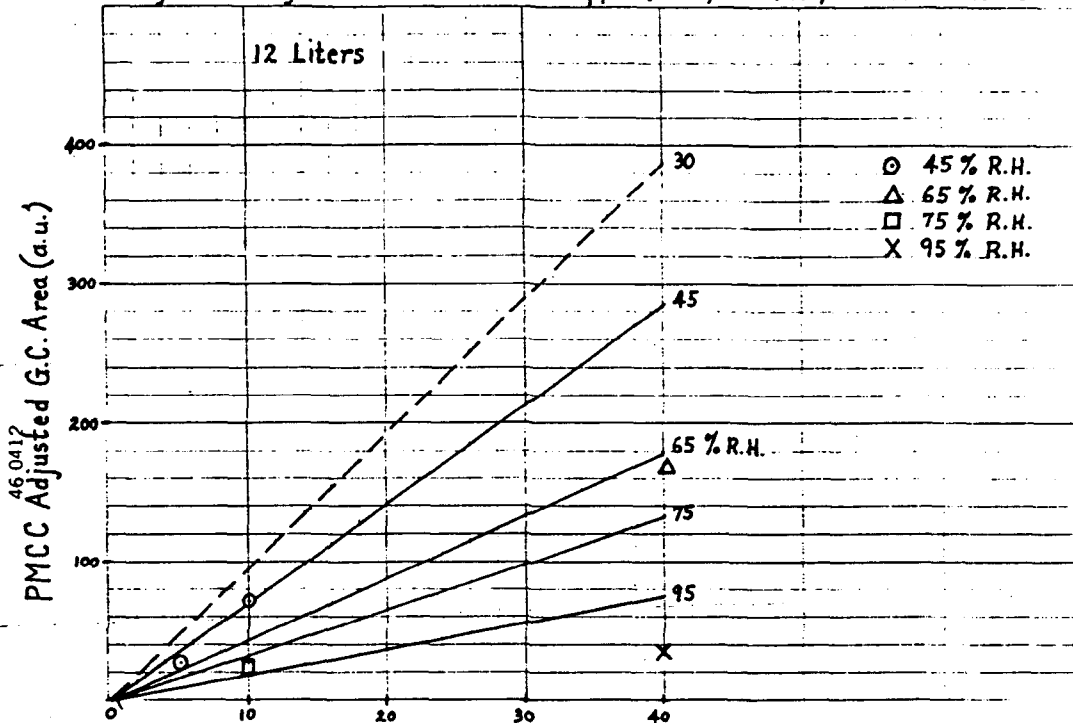
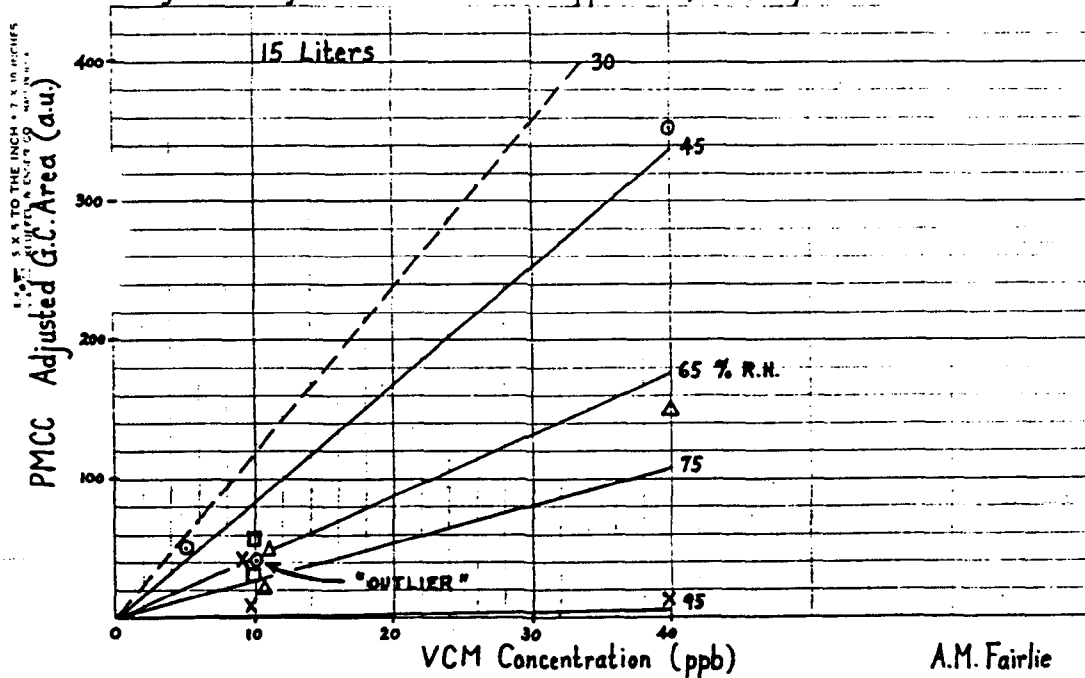


Figure 5. Adjusted PMCC Area vs. ppb VCM, % R.H., and Air Volume

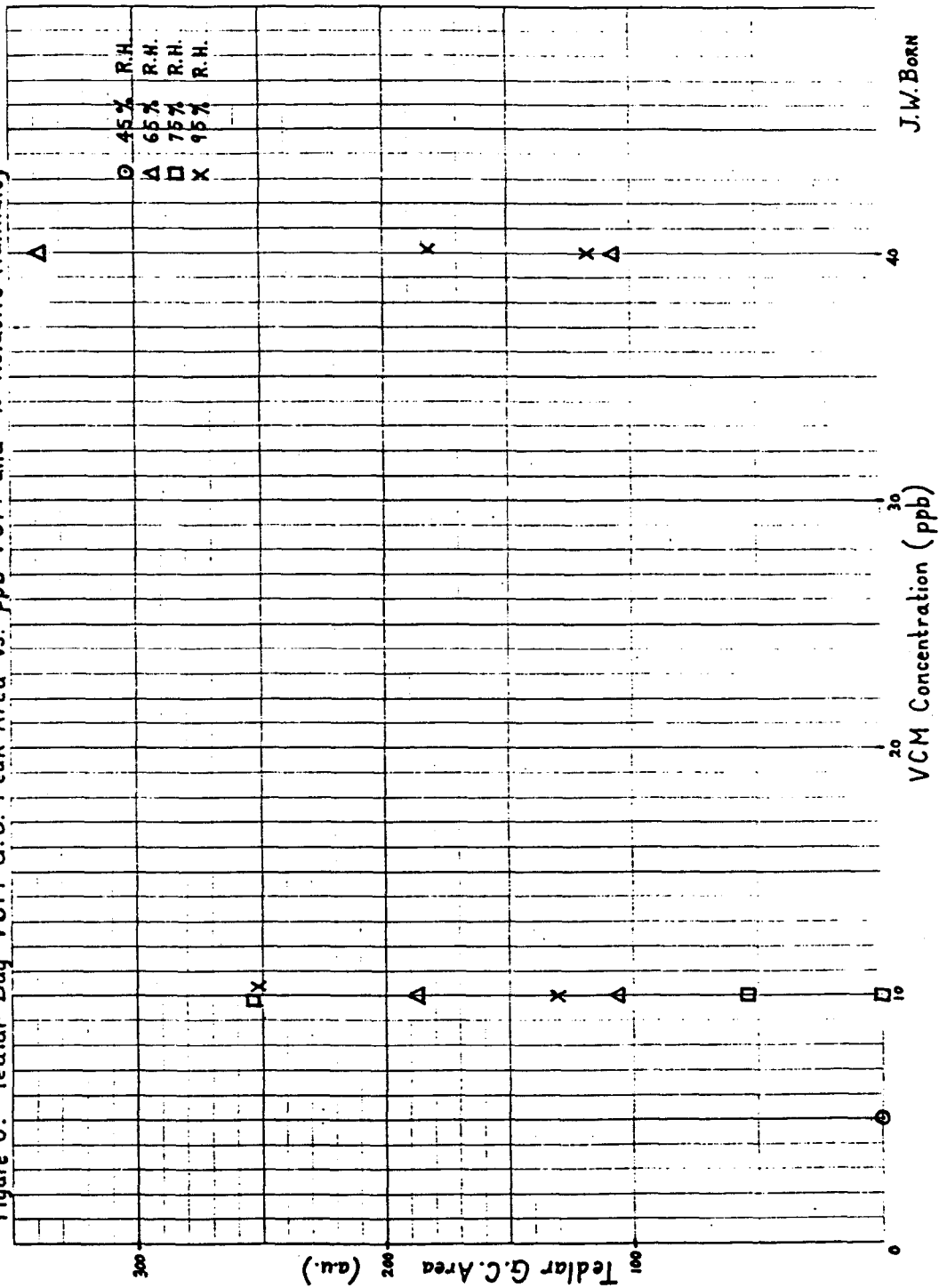


24819024

KOE 3 X 5 TO THE INCH • 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

46 0412

Figure 6. Tedlar Bag VCM G.C. Peak Area vs. ppb VCM and % Relative Humidity



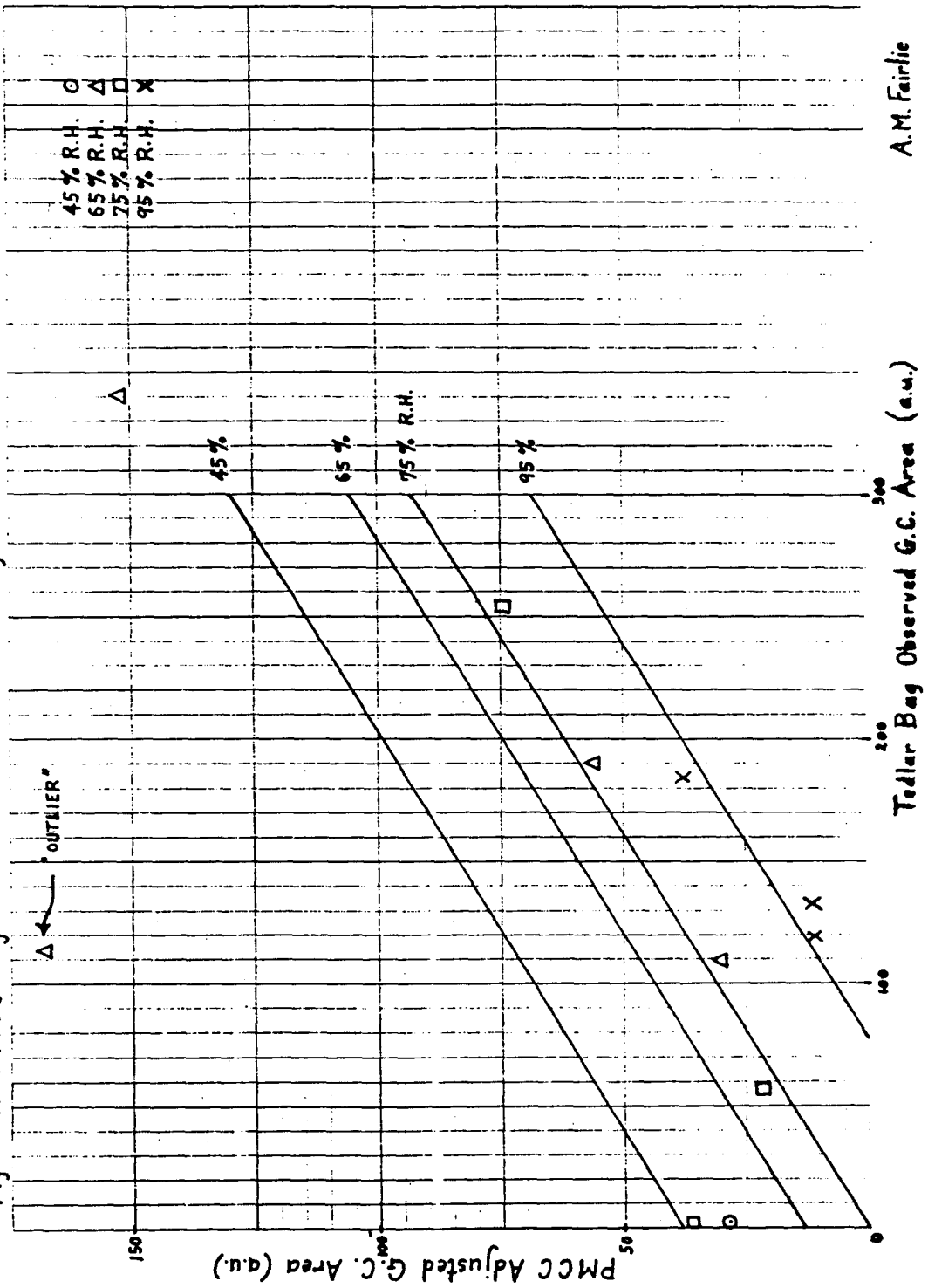
J.W. Bost

24819025

46 0412

REF. 5.5.5 TO THE INCH

Figure 7. PMCC Adjusted G.C. Area vs. Tedlar Bag Observed G.C. Area and % Relative Humidity



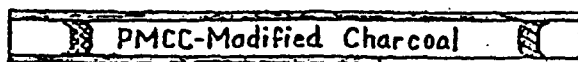
A.M. Fairlie

24819026

Descriptions of the Bendix Flasher & Flasher Tube

Bendix PMCC

Bendix Flasher Tube



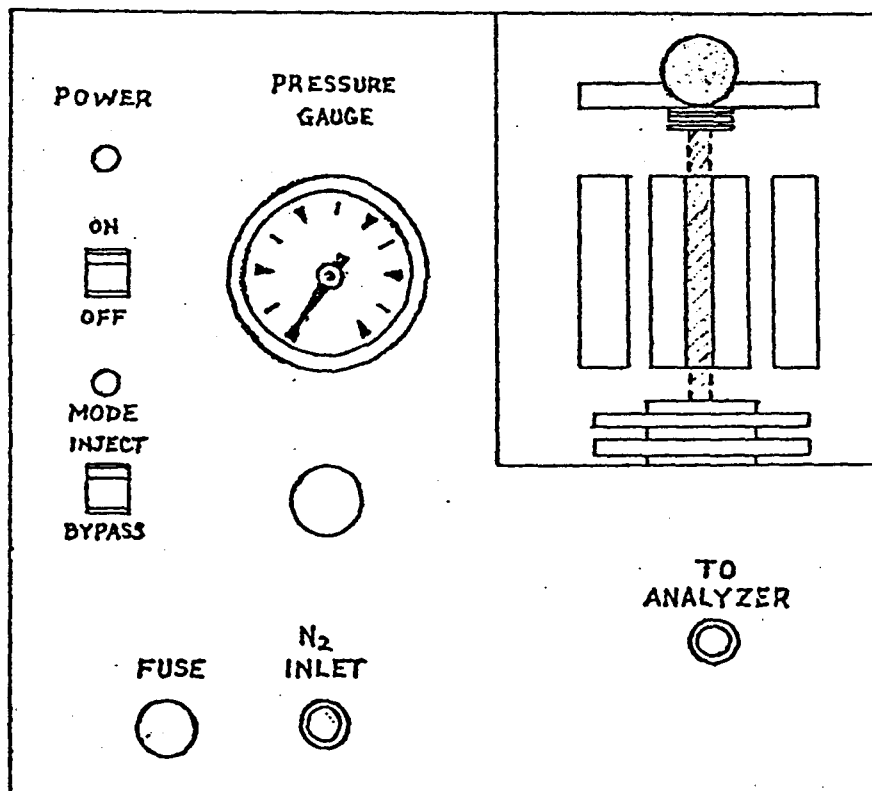
Length : 76 mm

O.D. : 6 mm

I.D. : 4 mm

Activated Charcoal : ~ 450 mg.

Bendix Flasher



24819027