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James Summers, Ashok Shah	ALTC, Oaktree	July 3, 1992

SUBJECT

REVIEW OF BFG DATA ON VCM EXPOSURE.

We have reviewed previous BFGoodrich work which validated ambient vinyl chloride monomer (AVCM) measurement procedures, reviewed work on mathematical models which set a requirement on residual vinyl chloride monomer, and reviewed work which measured worker exposure to AVCM in customer plants and BFG plants.

MEASUREMENT PROCEDURES

A method which collects 250 ml air samples, absorbs the VCM in these samples onto activated charcoal, then uses a gas chromatograph and flame ionization detection to measure vinyl chloride is a reliable method, validated by O'Mara and Quisenberry [1].

A method which collects VCM from air over a period of time by pumping air through activated carbon is a good method, developed by Dow and quickly used by the rest of the industry. However it was not validated at BFG by Zakriski until the late 1970s or early 1980s [2].

MODELS

A mathematical model was developed by Ahmed & Haller for AVCM concentrations during thermal processing of PVC [3].

$$AVCM = \frac{(RVCM)(\text{weight of PVC in 8 hrs})(\text{fraction of VCM lost})\ R\ T}{28.8\ (\text{number of air turnovers/hr})(\text{air volume in building})}$$

This model assumed but did not verify that VCM was instantly distributed uniformly into the whole room. There were also two unknown factors in the equation. RVCM was not measured at the time AVCM was measured, thus requiring a probability calculation of RVCM based on an average for the year and a distribution measured seven years later. And the number of air turnovers per hour was not known at the time of the AVCM measurements, thus requiring a calculation based on the above calculated probability of RVCM.

The conclusion that resin must be at or below 8.5 ppm to assure that AVCM < 0.5 ppm is weak.

Another mathematical model was developed by O'Mara, et al, for AVCM under various conditions of storage [4,5].

$$AVCM = (1.97X10^{-7})\ (Temp)^{2.96}\ (Ventilation)^{-1.29}\ (Loading)^{1.02}\ (RVCM)^{1.2}$$

$$(time)^{3.3} - 0.66\ Ln\ time \qquad \text{for } 5 < time < 170 \text{ hours}$$

and

$$AVCM = (0.553)\ (Ventilation)^{-1.29}\ (Loading)^{1.02}\ \ (RVCM)^{1.2}\ (time)^{-0.382}$$

for time > 170 hours

where porosity is 0.2. The model is good only for suspension PVC. Experimental data showed that fans were needed to assure the assumed uniform distribution in the building. Air turnover was assumed to be 0.5-0.6/hour, without verification. Verification showed actual AVCM 2-4 times the AVCM expected from the model.

The conclusion that resin must be at or below 8.5 ppm to assure that AVCM < 0.5 ppm is weak.

WORKER EXPOSURE

Personal monitoring of AVCM, where RVCM is also known, indicates in several instances that, if the PVC contained 8.5 ppm, then the worker would have been exposed to greater than 0.5 ppm AVCM [6].

Data	RVCM, ppm	AVCM	From model; If RVCM = 8.5; Calculated AVCM
Johnson Plastics			
Mixer operator	<1	0.4	>3.4
Mixer operator helper	<1	0.06	>0.5
Extruder operator feeder	<1	0.1	>0.9
Andersen Window			
forman opening rail car	0.55	0.46	7.1
mixer operator	0.55	0.23	3.6
Cooley Inc.			
Materials handler	<1	0.06	>0.5
Hopper feeder	<1	0.12	>1.0
Extruder forman	<1	0.31	>2.6
Extruder operator	<1	0.2	>1.7

The problem VCM levels are concentrated on powder mixing operations and calendering, where large surface areas of melt are exposed.

INFORMATION NEEDED

This review points to a need to better understand the range of ventilation rates in powder mixing and melt mixing (at BFG customers), and a need to better understand local AVCM levels in relation to RVCM in operations where ventilation rates are known (in BFG powder mixing and melt compounding operations). The range of warehouse ventilation rates needs to be better known. And the warehouse (storage) model needs to be expanded to other PVC resins such as dispersion resins.

REFERENCES

1. M. M. O'Mara, J. C. Quisenberry, "A Method for Analyzing VCM at the Part-Per-Billion Level", BFG Staff Technical Service Report, June 7, 1974.

2. Conversation with Paul Zakriski, 6/9/92.

3. M. J. Ahmed, H. S. Haller, "Modeling of VCM Concentrations During Thermal Processing of PVC", BFG Technical Document, 3/31/83.

4. M. M. O'Mara, L. B. Crider, R. L. Bowles, C. J. Tomanek, "A Physical Model for the Diffusion of Vinyl Chloride Monomer from PVC Under Various Conditions of Storage", BFG Technical Document, August 25, 1975.

5. Linwood B. Crider, Michael M. O'Mara, Robert L. Bowles, "A Model for the Diffusion of Vinyl Chloride Monomer from PVC Under Various Conditions of Storage", Society of Plastics Engineers, "Safety and Health with Plastics", National Technical Conference, Denver, page 195, Nov. 8-10 1977.

6. Richard J. Kruszynski, "OSHA - NIOSH - EPA, 2nd Quarter, 1975 Update", BFG Inter-Organization Correspondence, 7/8/75.

PVC PROCESSING VENTILATION SURVEY

Company Name	Contact:	Phone:
PVC Processing		
Powder mixing		
Separate room?		
Size of room, ft^3		
Local ventilation, ft^3/min		
Area ventilation, ft^3/min or turn over/hr		
Rate of mixing, lbs/hr		
Flexible or rigid		
Extrusion		
Separate room?		
Size of room, ft^3		
Local ventilation, ft^3/min		
Location		
Area Ventilation, ft^3/min or turn over/hr		
Rate of PVC extrusion (total), lbs/Hr		
Flexible or rigid		
Injection Molding		
Separate room?		
Size of room, ft^3		
Local ventilation, ft^3/min		
Location		
Area ventilation, ft^3/min or turn over/hr		

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BFG PLANT VENTILATION DATA AND MONITORED EFFECTIVENESS

Resin Plant	
Resin Type	
Lot No.	
RVCM as manufactured Date	
ppm by weight	
RVCM as loaded Date	
ppm by weight	
Rail, Truck, Bags, or Silo	
Compounding Plant	
Powder Mixing Stage	
Compound No.	
Lot No.	
Rigid or Flexible	
Powder Rate, lbs/hr. (total lines)	
Personal Monitoring in Pwd. Mixing Date	
ppm (AVCM) by weight	
Worker & Location	
Size of powder mixing room, ft^3	
Separate from melt mixing room?	
How many lines?	
Ventilation, list all local & area Location	

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BFG52518

REFERENCES

STAFF TECHNICAL SERVICE REPORT NO. 308

D

B. F. Goodrich Chemical Company

A DIVISION OF THE B. F. GOODRICH COMPANY

DEVELOPMENT CENTER

A METHOD FOR ANALYZING VCM AT THE PART-PER-BILLION LEVEL

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COMPANY CONFIDENTIAL

M. M. O'Mara and J. G. Quisenberry

Date Completed: June 5, 1974 Date Issued: June 7, 1974

Project No.: 3690 Department No.: 5026

Abstract:

A gas chromatographic method based on flame ionization detection and coconut charcoal adsorption has been developed for detecting VCM in the atmosphere at the 1 part per billion (ppb) level. The basic principle involves the adsorption of a 250cc air sample on activated charcoal contained in the sample loop of a gas chromatograph. The loop is heated to 200°C. to desorb VCM and the VCM is then analyzed chromatographically. A calibration curve ranging from 5 ppb to 280 ppb was experimentally determined. The curve was linear and a linear regression analysis of the data revealed a ± 3.0% deviation in the slope of the calibration curve. At the 20 ppb level, a 9% deviation in reproducibility (5 runs) exists.

A complete description of the method is provided. The general method is potentially applicable at the parts-per-trillion level and lower.

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*Modified Report

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Table of Contents

I. Introduction

The need to analyze vinyl chloride monomer (VCM) in the low parts per billion (ppb) range is obvious as monitoring proceeds away from the point source. A number of approaches can be used to monitor at this level but the most obvious and best developed method is based on the use of gas chromatography. Since neither flame ionization nor electron capture are sensitive enough to measure at this level (recent advances in microcoulometric detectors might make this a viable approach) a pre-chromatographic concentrating step is called for. The literature contains a number of publications in this area but the articles by West[1] and Scheel[2] provide an adequate background to this type of approach. About 3 years ago, Scheel personally described to me his work in this area. His studies on the thermal desorption rather than the solvent desorption of coconut charcoal were of interest to our pyrolysis work at that time. In fact, we have previously studied the thermal desorption of materials from molecular sieves.[3] West, in his work, described the use of gas chromatography to analyze air pollutants which were thermally desorbed from activated alumina, silica gel and charcoal.[1] The work described in our report is an extension of West's method, optimized to the analysis of VCM in air and modified for part per billion analysis.

II. Analytical Approach

In essence, the sample loop of an 8-port gas chromatographic sampling valve is replaced with a 6" x $\frac{1}{4}$" stainless steel tube which contains ~0.2g of coconut charcoal. Two of the sample ports are used to flush a 250 ml gas sample container with helium through the charcoal bed. Once this flushing operation is complete, the charcoal bed is heated to 200°C. At that point, the gas sampling valve is actuated thereby diverting the chromatographic carrier gas through the carbon bed and onto the chromatographic column. In this way, the VCM is removed from the carbon bed and deposited on the chromatographic column. A typical analysis is then carried out. The limiting factor in terms of sensitivity in this analysis is the 250 ml sample container. With this constraint, analysis is limited to ~1 part-per-billion.

III. Problems

Although the approach was rather straightforward, two problems arose which should be recognized by those attempting to duplicate the procedure. The carbon bed contains glass wool to prevent carbon movement and loss inside the sampling loop. We found that unless the glass wool is thermally conditioned, ghost peaks occur in the chromatographic analysis (see Appendix). The second problem occurred in making up standards at the low part-per-billion level. Our previous work in preparing standards involved the part-per-million level and at that time no problems developed in those analyses.[4] However, in the part-per-billion range we noticed that initially it was very difficult to reproduce our standards especially in the 5 - 20 ppb region. The problem was finally traced to residual VCM in

our make-up air. An analysis of the air near the air compressors inlet (roof of boiler house) revealed 100 ppb of residual VCM. We solved this problem, by putting an activated carbon bed on our air stream. However, to assure ourselves of true zero VCM grade air, all standards were prepared from cylinder air which was tested for VCM before use. Once these two problems were recognized, the analytical development of the method was relatively simple.

IV. VCM Calibration Curve

All standards were prepared by mixing a 19 ppm VCM standard with air and flowing this mixture into the 250 ml sample container. With our flow-meter ranges, we are limited (lowest) to a 2 ppb calibration standard. A 1 ppm VCM standard will be ordered. This will allow us to prepare standards at the 0.1 p.p.b. level if this becomes necessary.

Table 1 contains a summary of the calibration data [illegible] gas chromatographic peak areas for those standards. [illegible] calibration data are also shown in Figure 1. A typical chromatographic analysis at the 5 ppb level is shown in Figure 2. It is important to note that the chromatograph was not at the most sensitive setting during this 5 ppb analysis. If it were, the peak would be 4 times the size shown in Figure 2. Thus with a steady baseline at maximum sensitivity, an analysis of 1 part-per-billion of VCM is quite reasonable.

The gas chromatographic data in Table 1 was hand calculated because of a malfunction in PACE (off-line computer). PACE-obtained data (see Appendix) was reliable above 20 ppb but for VCM concentrations below this, the data was not self-consistent.

A linear regression analysis of the expanded calibration data in Table 2 (see Appendix) yielded the following equation:

$$[\text{VCM}]\ \text{ppb} = 1.99\ (\text{G.C. Area}) - 4.81\ \text{ppb}$$

The slope was 1.99 ± .06 ppb/area with a correlation coefficient of 0.990. The excellent linearity of the calibration curve is indicative of a number of important phenomena. If there is any loss of VCM during the purging operation, it is independent of the concentration of VCM. Also if any VCM remains on the charcoal, this too is concentration independent. We were concerned about this latter possibility in that we might be building a "memory" on the charcoal bed. However, repeated blank runs have been carried out and to date this does not appear to be a problem. If very high levels of VCM are deposited on the charcoal subsequent analyses could shown a "memory" to this initial deposition.

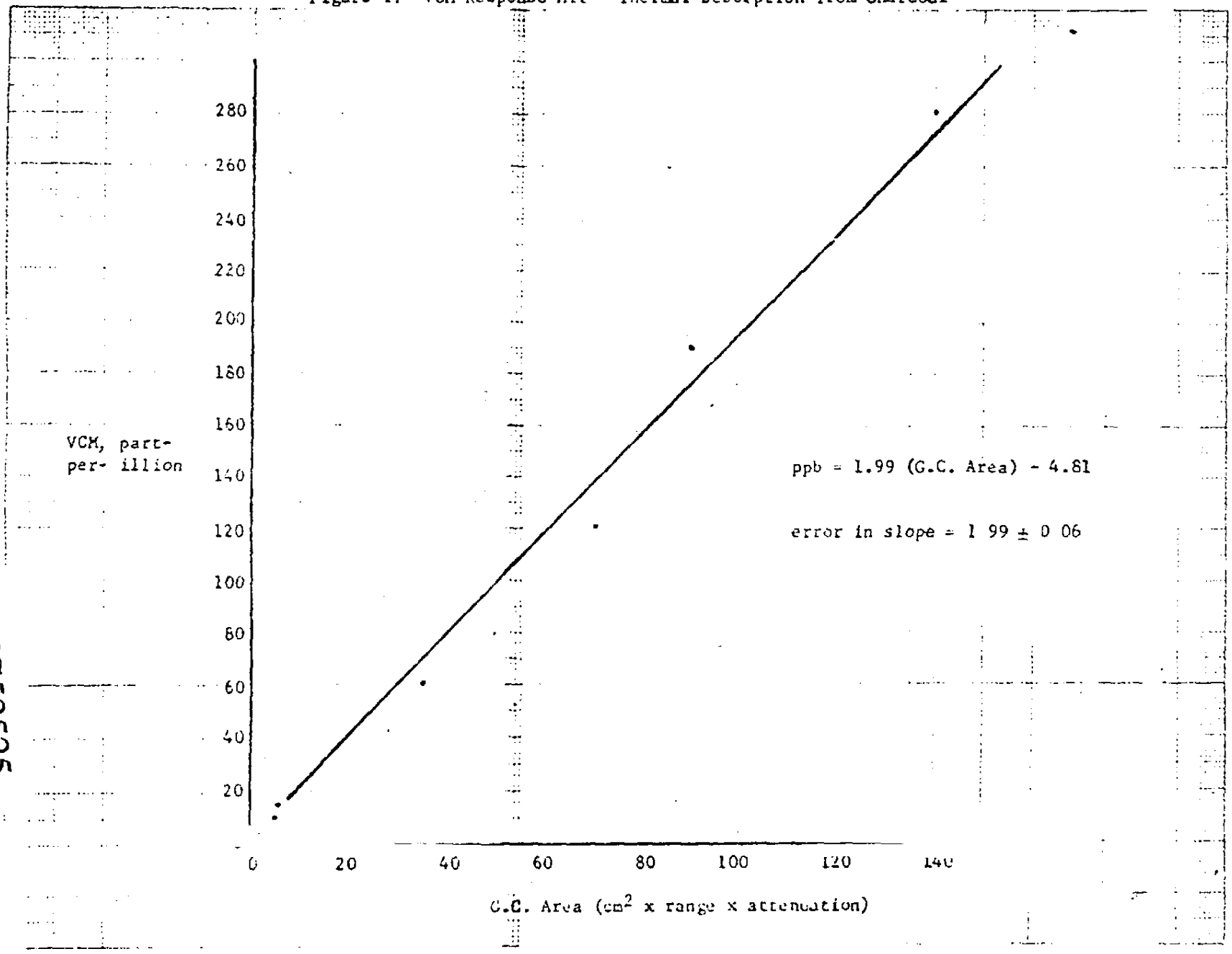
Table 1

Calibration Data for VCM Adsorbed On Carbon and Chromatographically Analyzed After Thermal Desorption

VCM Concentration (ppb)	Peak Area[(a)]
5	2.5
10	5.0
15	6.2
20	14.9
40	22.4
60	35.1
120	69.7
190	90.0
280	140.4

(a) Defined as "the peak height times the peak width at half height times the range times the attenuation". PACE data was not reliable in the 5 to 20 ppb region; the PACE problem is correctable. These values are average values of 2 or more determinations.

Figure 1: VCM Response Aft Thermal Desorption from Charcoal



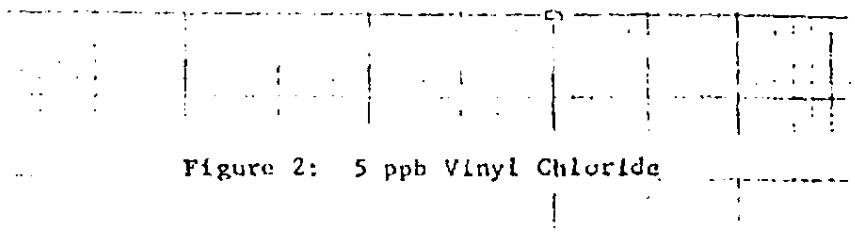
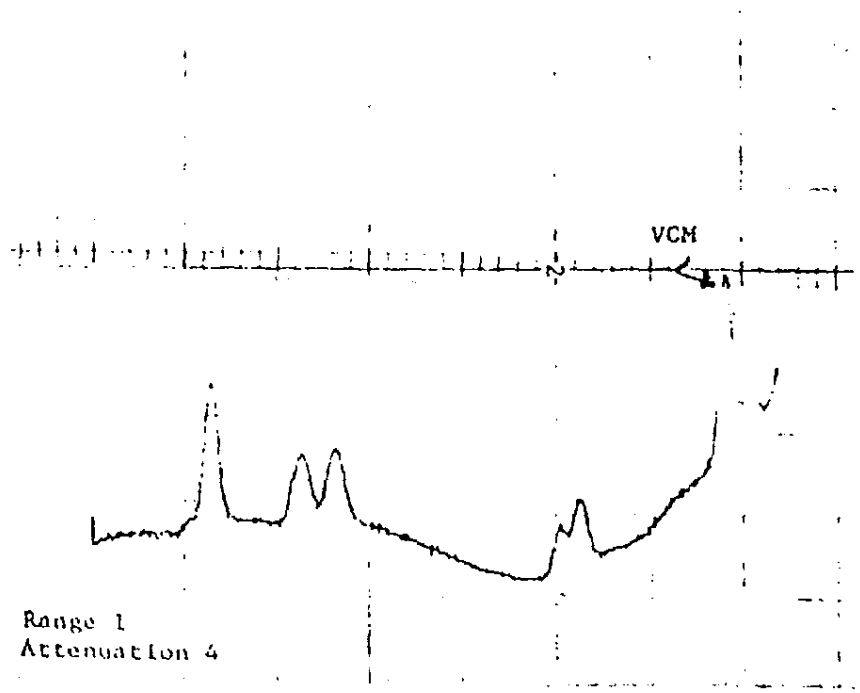


Figure 2: 5 ppb Vinyl Chloride



V. Discussion

Two approaches were possible with this technique. One (that chosen) involved making one carbon adsorption bed for the gas chromatograph and sampling with the 250 ml glass containers. The other approach involved making a series of carbon beds and sampling directly with these. We chose the former method for a number of reasons. Ultimately we had control over the adsorption experiment. In the field, sampling with the sampling container, neither the sampling rate or the sampling time are especially critical. For example, sampling at a rate of 1 or 2 liters/min. for any period of time over a few minutes is adequate. However, much tighter control over both the sampling rate and the time would be absolutely critical if sampling was done with the carbon bed directly. We also checked the flowmeter on one of the portable pumps with a precision flowmeter and found it to be out of calibration by 11%. In terms of sampling with the glass vessels, this deviation is unimportant. However, it is not unimportant in sampling with the carbon bed. Before any analysis is attempted, a 11% error is introduced immediately.

Another demand we placed on the analysis was rapid turnover. A recent analysis of automobile exhaust demonstrated the problem if too much material is adsorbed on the charcoal. The chromatograph must be baked out after every run. With the automobile exhaust samples, it took an hour to clean the chromatograph of the high boiling components that were trapped out of the exhaust. This, of course, would be no problem if we had a number of chromatographs available for the analysis. In light of the number of samples that need to be run, rapid turnover was a necessary constraint. This seemed to eliminate direct use of the carbon bed because of the other components that would be deposited in relatively high yields. Finally, the sampling rate was a potential problem from another standpoint besides control. Very little carbon (~0.2g) is involved in the adsorption. We initially started out with ~.5g of carbon but this had to be abandoned because it led to a rather diffuse VCM chromatographic peak. To keep the adsorption efficiency high, the sample containers are purged at a flow rate of 100 cc/min. or 1/10th the sampling rate that would be used in the field. Efficiency might be quite low at this field rate especially in light of the small amount of carbon that must be used to obtain acceptable chromatographic results.

Needless to say all of these problems can be overcome if analysis below a part-per-billion is important. Efficiency studies can be carried out, the portable pumps can be fitted with high precision flowmeters, and the chromatographic analysis time can be lengthened, for example. In terms of developing a rapid, reliable method for analyzing VCM in the 1 ppb region, we feel the method chosen was the best compromise.

Appendix I

Procedural Information Relating

To The Analysis of VCM at the 1 ppb Level

I. Chromatograph

Model: Hewlett-Packard Model 5710A
He: 37.5 cc/min.
H_2: } factory specifications
Air: }
Column Temperature: initial - 80°C. for 2 minutes
program - 16°C./minute
final - 200°C. for 2 minutes
Injection Port Temperature: 150°C.
Detector Temperature: 250°C.

II. Column

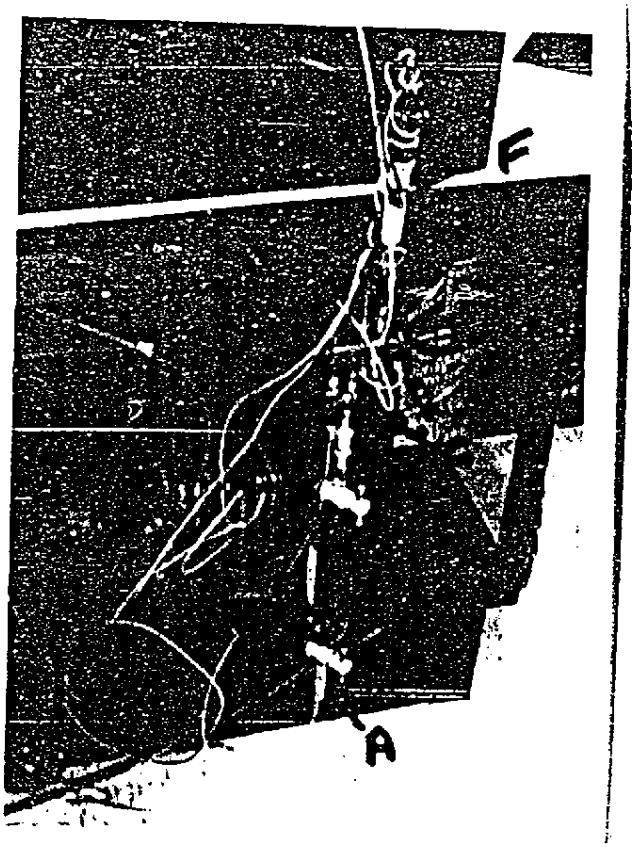
8' X 1/8" Porapak QS, 50/80 mesh

III. Carbon Adsorption Bed

A 6" X 14" stainless steel column containing 0.2306g of Fisher Scientific activated coconut charcoal (Catalog Number 5-685-B), mesh size 6-14, was prepared. Glass wool was placed at both ends of the bed to prevent movement. It is important that the glass wool be heated to 250°C. overnight to avoid ghost peaks during analysis. The 1/4" column is then placed in a vertical position, interfaced at both ends with 1/8" stainless steel tubing and connected to a gas sampling valve in the position occupied by the gas sampling loop. The photograph below (Part IV) shows the gas sampling valve and carbon bed. The carbon bed was wrapped with a heating element and a thermocouple was inserted to monitor temperature. Adsorption is carried out at 25°C. and desorption at 200°C.

IV. Gas Sampling Valve

Any 8-port gas sampling valve can be used to interface the carbon bed to the chromatograph. Two of the ports are used for the carbon bed, two of the ports are used to purge the sample vessel through the carbon bed and two of the ports are used to flush the carbon bed onto the chromatographic column. The two remaining ports are "looped" together to provide a by-pass for purging. The location of the helium line, gas sampling container, effluent line, etc. are shown below and labeled accordingly. Two metering valves are also shown in the photograph. These are necessary to close off the carbon bed during the heat up procedure.



A - helium purge line to bottom of sampling vessel

B - sampling vessel

C - metering valves for isolating carbon bed

D - 8-port gas sampling valve

E - carbon bed

F - thermocouple on carbon bed

V. Procedure

The following description covers the procedural aspects of analyzing VCM with the carbon bed.

The 250 ml sampling vessel containing vinyl chloride monomer is interfaced to the sampling valve (see photograph) the helium purge line, teed from the main line through a metering valve, is connected to the bottom of the sampling vessel. The two metering valves on the gas sampling valve are opened, the stopcock at the top of the sampling vessel is opened, followed by the stopcock at the bottom. The helium flow through the vessel onto the carbon bed (at 25°C.) is maintained between 100 - 110 cc/min. for 7.0 minutes. At the end of this purge time, the bottom stopcock, top stopcock and the two metering valves on the sampling valve are closed (in the order described). At this point, the heater on the carbon bed is turned on. In our system, it takes approximately 3 minutes to reach 200°C. Once the thermocouple on the carbon bed indicates 200°C., the valve is "pulled" or "pushed" to bring the carbon bed on stream with the chromatographic column.

The temperature on the bed is allowed to rise to 225°C. (about 1 minute after the valve is actuated). We believe this may be necessary to avoid memory on the carbon bed. The heater on the bed is then turned off. Once the valve is actuated, the chromatographic process is initiated [(1) 2 minute delay at 80°C., (2) program to 200°C. at 16°C./minute, (3) hold at 200°C. for 2 minutes].

VI. Complete Calibration Data

In this section, the average data contained in Table 1 will be expanded to include all data.

As mentioned above, the PACE data was not self-consistent. A summary of all data including all standards with PACE and hand calculated analyses are contained in Table 2. We discovered the error in PACE while running the 10 ppb standards. These were repetitive runs and the two peaks were visually superimposable on an area basis. The two areas calculated by hand showed a difference of about 3% which correlated well with the visual observation. However, PACE data indicated a difference of ~40%. From 20 ppb to 280 ppb, PACE data correlates well with the hand calculated data. In these cases, the VCM is 90% of the chromatograph and this may relate to the current PACE problem.

The 9% deviation in reproducibility previously mentioned was determined from the 20 ppb data. While the 120 ppb data shows a greater spread, this data may be in error because of VCM contamination in the make-up air of the calibration gas.

VII. Linear Regression Analysis

The linear regression analysis was carried out on all the data in Table 2. The following data relate to the regression analysis:

(1) slope: 1.99
(2) y-intercept: -4.81

Other Applications

The general technique described in this paper can be used in a number of other applications. For example, it can be used for analyzing pollutants on a thermal conductivity gas chromatograph where increased amounts of sample are required. For the analysis of compounds that are not sensitive to flame ionization, this technique coupled to thermal conductivity gas chromatography may be very adequate.

The true potential of the technique has not been evaluated. It offers the potential to analyze quantitatively at almost any level.

Table 2

PACE and Hand Calculated Data for VCM Standards

VCM Standard, ppb	G.C. Area	
	PACE	Hand-Calculated(1)
5	.000993	2.60
5	.000393	2.34
10	.00904	5.10
10	.01616	4.95
20	.00645	14.0
20	.00655	13.5
20	.00731	13.8
20	.00796	17.8
20	.00767	15.2
40	.0111	22.4
15	.0198	6.50
15	.0082	6.00
60	.0187	34.9
60	.0174	35.3
120	.0410	81.9
120	.0347	69.8
120	.0292	57.7
190	.0448	93.3
190	.0438	86.6
280	.0643	134.2
280	.0711	146.6

(1) Peak height x peak width x attenuation x range. These values are based on a 1.198 MV full scale G.C. recorder.

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3. M. M. O'Mara, J. A. Nikora, "A Pyrolysis-Gas Chromatographic Technique For Identifying Adsorbed Materials", I.O.C., 9/14/69.

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