

CHEMICALS
RESEARCH

JUN 3 1974

Interoffice Communication

To Flynt Kennedy

From R. E. Laramy

Date May 31, 1974

Subject Personnel Monitoring for Vinyl Chloride Monomer

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With the advent of the vinyl chloride monomer (VCM) problem early in 1974, a considerable amount of time and effort have been expended in acquiring, using and evaluating techniques to monitor personnel exposure to VCM. The majority of this effort has been carried on by the Aberdeen, Miss., plant and the Lake Charles, La., plant. Initially our concern was to monitor levels of VCM which would not exceed 500 ppm over an eight-hour period based on a time-weighted average. Other producers of VCM and/or polyvinyl chloride (PVC) had already adopted a charcoal adsorption dosimeter. Government agencies, e.g. The Occupational Safety and Health Administration (OSHA) and the National Institute of Occupational Safety and Health (NIOSH), had also adopted the charcoal adsorption dosimeter technique. With the advent of the Emergency Temporary Standard (ETS) which prescribed personnel monitoring and a maximum level of 50 ppm VCM, Continental Oil Company opted to be in compliance with government regulations. All three of our plants--Lake Charles, Aberdeen and Oklahoma City--were in compliance using the charcoal dosimeters by the deadline specified in the Federal Register (22 April 1974). Both Aberdeen and Lake Charles were in compliance much before this deadline.

Basically, the charcoal adsorption technique requires a suitable pump to pull air through a tube packed with charcoal. The VCM adsorbs on the charcoal. After a prescribed time period the charcoal tube is taken to the laboratory, eluted with carbon disulfide and the resultant eluate, containing the VCM, is analyzed by gas chromatography and detected with a flame ionization detector. The assumptions inherent in this method are: (1) the VCM is quantitatively adsorbed on the charcoal; (2) the VCM is quantitatively desorbed by CS₂; (3) pumping rates are precisely known; and (4) the analytical procedure is accurate, precise and reproducible. Our first problem was locating a source of charcoal that would, presumably, quantitatively adsorb the VCM without breakthrough over the time periods specified by the various plants. A source of charcoal was located by Paul Fetzer, of the Lake Charles plant, which appeared to do the job. The next problem was locating a suitable pump and devising a suitable experimental configuration that could be worn by individuals. A pump was located from the Bendix Company and several were purchased for the various plants. A suitable device to hold the pump and charcoal adsorption tubes was devised by Paul Fetzer and adopted by the other two plants. Both the Aberdeen plant and the Lake Charles plant did experimental studies to determine adsorption and desorption efficiencies. Lake Charles claims greater than 90% efficiency while Aberdeen claims only about 65% recovery. Based on this, Ponca City did a rapid study on the adsorption efficiencies and obtained results varying from less than 90% to greater than 400%. This immediately pointed to a problem, and further work was initiated at Ponca City. Prior to our further study a meeting was held in Houston with Frank Scott,

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Dave Porchey and myself to establish uniform procedures for all four locations, i.e. Aberdeen, Lake Charles, Oklahoma City and Ponca City. The results of this meeting are summarized in my letter to Leon Vernon, dated 24 April 1974. It was decided in this meeting to continue with carbon adsorption, to use two- and four-hour time intervals, to explore new techniques for monitoring, and to re-evaluate the carbon adsorption technique.

The carbon adsorption technique is fraught with numerous problems. First, the adsorption efficiency of charcoal is highly dependent on activation, supplier and batch. Some charcoals work reasonably well while others have little affinity for VCM. Second, desorption of the VCM from the charcoal with carbon disulfide must be done with care to prevent loss of the monomer. All solutions must be handled at dry ice temperature and in closed containers to achieve any resemblance of analytical accuracy. Carbon disulfide appears to be a good solvent for desorption, but in itself has a very unpleasant odor, is highly volatile and extremely toxic (OSHA limit is concentration of 20 ppm over an eight-hour TWA). Third, pumps suitable for pulling air through the charcoal must have a constant pumping rate. Such pumps are costly, averaging \$300-350 per pump. Fourth, the time the air is pumped through the charcoal must be accurately known since this figure becomes an integral part of the final calculation. This, in turn, requires either a digital readout showing the volume pumped or careful monitoring by the individual wearing the pump to record both the start and stop time of the pump and the pumping rate. Each pump must be calibrated to assure constant and known pump rate. Both variables are extremely difficult to control since it must be the operator who verifies both. Fifth, repeatable injections of disulfide mixtures are difficult to obtain because of the high volatility of the solvent. Experienced analysts are generally required to obtain accurate and meaningful data. Sixth, calculation of the final VCM concentration is relatively complex and has many places for error. Seventh, copious quantities of both charcoal and carbon disulfide are consumed, at least in our present mode of operation. Eighth, analysis time of the charcoal, once received in the laboratory, is inordinately long, which, in turn, limits the amount of surveillance that can be accomplished. In addition, since publication of the Proposed Permanent Standard (PPS) which set the level of VCM at "no detectable limit," implying 1.0 ppm as the limit, it is extremely doubtful that the disulfide extraction will work with the specified precision of $\pm 50\%$. Even if this level goes as high as 20 ppm, it is still doubtful if the precision could be obtained.

In view of the listed problems with charcoal dosimeters, we (Ponca City) did an investigation of adsorption efficiencies and breakthrough. Figure I shows a plot of breakthrough using a 15-ppm VCM sample flowing through 17 grams of charcoal at a flow rate of 1.7 liters/minute. At the end of two hours, 2 ppm of VCM is coming through; and at the end of four hours, 6 ppm VCM is breaking through. Even at the end of one hour there is breakthrough beginning (0.3 ppm VCM). The efficiency of adsorption was calculated by weighing the permeation tube before and after the four hours. This calculated to be slightly over 100%.

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Obviously this cannot be correct since we show breakthrough of 6 ppm after four hours. The error may be in weighing; i.e., the weight of the permeation tube may have to be more precisely determined than our balance is capable of. In any event, it does indicate the care required when trying to determine these variables. This experiment was run twice with the same results. The entire experiment was conducted under close control of all experimental conditions and using a rather elaborate laboratory setup, i.e., several sampling areas to determine concentration at various points, carefully controlled flow rate, and a mostly all-glass system. Two other efficiency studies were conducted using a setup identical to that used at Lake Charles. Using a 9.0-ppm VCM concentration (based on a permeation tube) and a Bendix pump, recoveries of 305% and 432% were obtained. The charcoal tube and permeation tube were removed and the apparatus sampled with just air being pulled through. A concentration of ~9 ppm VCM was detected. This was probably due to VCM lingering in the tube which was used to hold the permeation tube or adsorption on the Tygon tubing; later experiments exonerated the Tygon; and the literature states that VCM can be retained in glass for several hours. An additional experiment was run using a fresh holder for the VCM and a different pump (the Century OVA), and a recovery of 90% was obtained. These results mainly indicate that use of charcoal tubes and disulfide extraction must be very carefully controlled if reliable results are to be expected. All this was done in a laboratory environment, which would indicate that in plants the problems may be even greater.

In addition to the charcoal work, we have also completed a study of air bag sampling. Attached are three tables giving the statistical evaluation of our results using a 1.0-, 5.0- and 10.0-ppm VCM-in-air standard. The data speak for themselves. The analytical precision is excellent for all four analysts, and even when combining the results of all four together, the precision is still within ± 10 percent--this at the 99% confidence level. The samples were run over an eight-day period and these indicate no loss of VCM or any trend signifying reduction in VCM concentration. In fact, even in the most extreme cases the difference in results is only 17%, well within the 50% specified in the Federal Register. Even this difference is probably due to instrumental changes rather than operator difference. No attempt was made at this point to correct for instrument variance.

Sampling using air bags is very simple. A low cost pump can be employed, e.g., aquarium pumps at a cost of \$4-7 per pump. The bags themselves are relatively inexpensive, costing only \$7-8 bag, and they can be used over and over until actual material failure. There is no need to know pumping rate since the sample is analyzed by gas chromatography and concentration is calculated based on standard gas blends. The time to acquire a sample can be easily regulated from ~4 minutes to over two hours when using a 7-liter bag. This can be varied by using a simple check valve and a Tee splitter. Any analyst with the ability to inject samples into a chromatograph with a syringe can do the analysis. In fact, in our study, three of the four individuals doing the analysis had less than one week's experience in running gas chromatographs.

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One of the individuals was a new employee with only one week's experience in a laboratory. His results are equally as good as those obtained by the experienced analyst. Analytical time for an analysis is only five minutes at the most; and if, through some cause, an analysis is ruined, another sample can be run from the same bag and the results salvaged. This is not true with the charcoal dosimeter. The bags can be easily attached to individuals, are of light weight, and the pumps used are small, light and convenient. The low initial cost of the entire apparatus coupled with the speed of analysis will permit significantly more monitoring to be accomplished than can now be done with charcoal dosimeters. Finally, the results obtained are much more reliable, easier to produce and should instill greater confidence in the actual levels of exposure being encountered.

Based on all of the facts listed, continued use of charcoal dosimeters would seem wasteful of time and talent. The varied results we have obtained on recovery experiments, if nothing else, indicate considerable care must be exercised if reliable results are to be obtained. It seems a logical extension that if we have these problems in an environment of carefully controlled conditions, the plants would probably experience at least these problems and conceivably several more. In addition, in our work at the Oklahoma City plant we have observed that the pumping rate on the Bendix pump varies from 1.8 liters/minute to 1.2 liters/minute over a two-hour period. We readily acknowledge that our experiments are not thorough or adequately sufficient to unequivocally say charcoal dosimetry is not valid. However, they are adequate to imply that without extreme care and calibration, results will probably be erroneous. This coupled with the cost, lack of convenience, inordinate analytical time and inconsistencies of results makes this technique of personnel monitoring the least palatable. Comparison with air bag sampling makes it even less inviting.

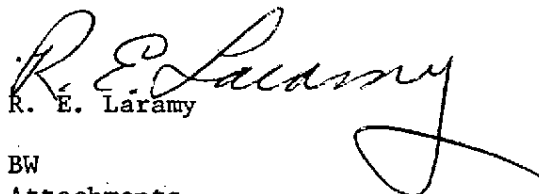
In view of this it seems wasteful of time, energy and money to pursue charcoal dosimetry any further. Our method of choice for personnel monitoring is to use air bags. As of this date, my Group is stopping all further evaluation of charcoal dosimetry in favor of air bag sampling. It is our feeling that the plants should do likewise, and I put this forth as a recommendation. The air bags we are now using can be purchased from Calibrated Instruments, Inc., 731 Saw Mill River Road, Ardsley, New York 10502 [Tel. (914) 693-9232]. The bags come in various sizes and are made from a seven-layer laminated polyester with an aluminum outer cover. They are equipped with a sampling valve. Currently we are using the 7-liter size at a cost of \$7.95/bag. We use an aquarium pump--Lews air pump for \$7.95 or a NAPCO pump for \$3.95. Either pump can be purchased at most sporting goods stores as they are used to aerate minnow buckets. The Lews air pump is also sold by Calibrated Instruments, Inc., equipped with a simple timer circuit and is priced at \$68. I do not recommend purchasing this pump. Another supplier of a Mylar-Teflon bag is Giangario Scientific Company in Pittsburgh, Pa. [Tel. (412) 687-6415]. Their cost is approximately \$40/bag.

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Currently, Mr. E. L. Sones, of my group, is assisting Oklahoma City in Their monitoring program. I have advised him for the week of 3 June to use air bag sampling exclusively. I am confident the results of his work will confirm our choice of air bag sampling and that it will work in the plants. He is currently using charcoal dosimetry and is experiencing several problems, e.g., varying pump rates, operator resistance, and failure to validate times of pumping, long sample preparation times, approximately 0.7 ppm VCM on fresh charcoal before use, variable results and questionable accuracy.

If there are any questions as to my decision and/or recommendation, feel free to contact me.


R. E. Laramy

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Attachments

Copies to:

DBB-GP-LNV-DVP-MS-FS-RW

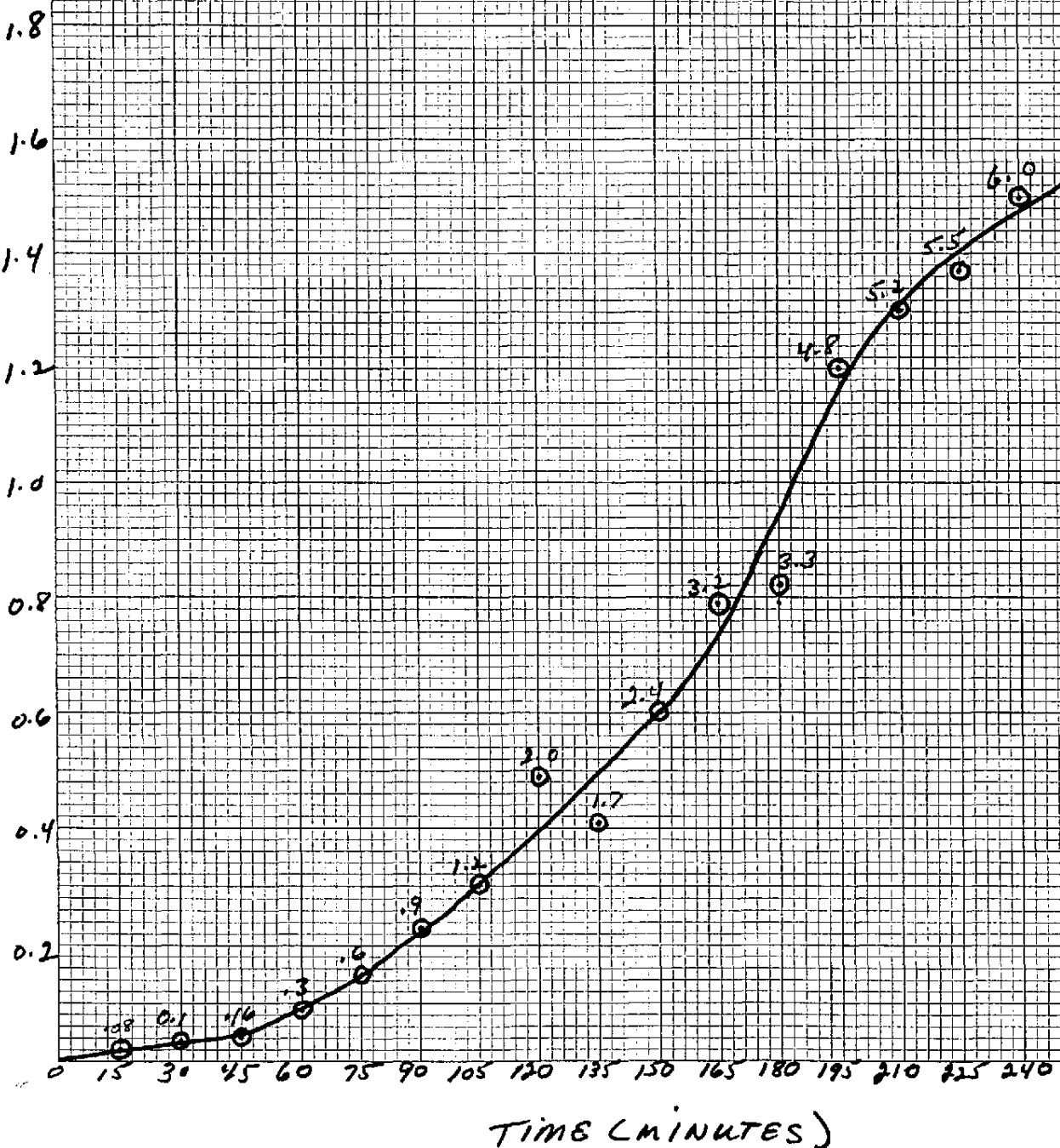
PLF-CP-REG-WDL-CBH-ELS

SATURATION STUDY - VCM ON CHARCOAL

VCM CONCENTRATION = 15 ppm
 WEIGHT OF CHARCOAL = 16.9 grams
 FLOW RATE OF AIR = 1.7 LITERS/MIN
 TIME OF RUN = 4 HOURS
 RECOVERY ~ 100%

FIGURES IN RED = ppm VCM

PEAK AREA (ARBITRARY UNITS)



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TABLE I

STATISTICAL DATA FOR 1.0 PPM VCM IN AIR

1.0 ppm on 5/21/74

Person	No. of Runs	Mean	Standard Deviation	Var	Confidence Levels				Error			
					50	90	95	99	50	90	95	99
1	5	.2746	8.75×10^{-3}	7.65×10^{-5}	2.99×10^{-3}	8.34×10^{-3}	1.08×10^{-2}	1.80×10^{-2}	1.06	3.04	3.95	6.56
2	5	.2959	2.06×10^{-2}	4.28×10^{-4}	6.85×10^{-3}	1.97×10^{-2}	2.57×10^{-2}	4.26×10^{-2}	2.32	6.66	8.67	14.40
3	5	.3142	1.50×10^{-2}	2.25×10^{-4}	4.97×10^{-3}	1.43×10^{-2}	1.86×10^{-2}	3.09×10^{-2}	1.58	4.55	5.92	9.82
4	5	.3055	8.32×10^{-3}	6.92×10^{-5}	2.76×10^{-3}	7.93×10^{-3}	1.03×10^{-2}	1.72×10^{-2}	.903	2.60	3.38	5.61

1.0 ppm on 5/22/74

1	5	.2964	1.13×10^{-2}	1.29×10^{-4}	3.76×10^{-3}	1.08×10^{-2}	1.41×10^{-2}	2.34×10^{-2}	1.27	3.65	4.75	7.88
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1.0 ppm on 5/23/64

1	5	.3278	1.06×10^{-2}	1.12×10^{-4}	3.52×10^{-3}	1.01×10^{-2}	1.32×10^{-2}	2.18×10^{-2}	1.07	3.08	4.02	6.66
2	5	.3165	1.33×10^{-2}	1.78×10^{-4}	4.42×10^{-3}	1.27×10^{-2}	1.66×10^{-2}	2.74×10^{-2}	1.40	4.02	5.23	8.68

1.0 ppm on 5/24/74

1	5	.3219	1.48×10^{-2}	2.21×10^{-4}	4.92×10^{-3}	1.42×10^{-2}	1.84×10^{-2}	3.06×10^{-2}	1.53	4.40	5.73	9.50
2	5	.3307	1.00×10^{-2}	1.01×10^{-4}	3.33×10^{-3}	9.57×10^{-3}	1.25×10^{-2}	2.07×10^{-2}	1.01	2.89	3.77	6.25

1.0 ppm on 5/25/74

1	5	.3312	1.11×10^{-2}	1.23×10^{-4}	3.68×10^{-3}	1.06×10^{-2}	1.38×10^{-2}	2.29×10^{-2}	1.11	3.20	4.16	6.91
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1.0 ppm (5 runs/day for 5 days)

1	25	.3104	2.45×10^{-2}	5.98×10^{-4}	3.35×10^{-3}	8.37×10^{-3}	1.01×10^{-2}	1.37×10^{-2}	1.08	2.70	3.25	4.41
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1.0 ppm (4 operators - 5 times each for one day)

1,2,3,4	20	.2975	1.99×10^{-2}	3.96×10^{-4}	3.06×10^{-3}	7.69×10^{-3}	9.32×10^{-3}	1.27×10^{-2}	1.03	2.59	3.13	4.28
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TABLE

STATISTICAL DATA FOR 5.0 PPM VCM IN AIR

5.0 ppm on 5/21/74

Person	No. of Runs	Mean	Standard Deviation	Variance	Confidence Levels				Error			
					50	90	95	99	50	90	95	99
1	5	1.4754	2.64×10^{-2}	6.95×10^{-4}	8.74×10^{-3}	2.51×10^{-2}	3.27×10^{-2}	5.43×10^{-2}	0.59	1.70	2.22	3.68
2	5	1.4547	2.20×10^{-2}	4.86×10^{-4}	7.3×10^{-3}	2.10×10^{-2}	2.74×10^{-2}	4.5×10^{-2}	0.50	1.44	1.88	3.12
3	5	1.5255	2.14×10^{-2}	4.59×10^{-4}	7.1×10^{-3}	2.04×10^{-2}	2.68×10^{-2}	4.4×10^{-2}	0.46	1.34	1.74	2.89
4	5	1.4989	4.44×10^{-2}	1.97×10^{-3}	1.5×10^{-2}	4.2×10^{-2}	5.5×10^{-2}	9.2×10^{-2}	0.97	2.74	3.71	6.15

5.0 ppm on 5/22/74

1	5	1.4388	2.21×10^{-2}	4.87×10^{-4}	7.3×10^{-3}	2.10×10^{-2}	2.74×10^{-2}	4.54×10^{-2}	0.51	1.46	1.90	3.16
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5.0 ppm on 5/23/74

1	5	1.5184	1.06×10^{-2}	1.12×10^{-4}	3.5×10^{-3}	1.01×10^{-2}	1.31×10^{-2}	2.18×10^{-2}	0.23	0.66	0.86	1.43
2	5	1.5414	2.75×10^{-2}	7.57×10^{-4}	9.1×10^{-3}	2.62×10^{-2}	3.42×10^{-2}	5.66×10^{-2}	0.59	1.70	2.22	3.68

5.0 ppm on 5/24/74

1	5	1.5613	2.97×10^{-2}	8.82×10^{-4}	9.84×10^{-3}	2.83×10^{-2}	3.69×10^{-2}	6.11×10^{-2}	0.63	1.81	2.36	3.92
2	5	1.5446	1.97×10^{-2}	3.89×10^{-4}	6.53×10^{-3}	1.88×10^{-2}	2.45×10^{-2}	4.06×10^{-2}	0.42	1.22	1.58	2.63

5.0 ppm on 5/28/74

1	5	1.4719	4.01×10^{-2}	1.61×10^{-3}	1.33×10^{-2}	3.83×10^{-3}	4.98×10^{-2}	8.27×10^{-2}	0.94	2.60	3.39	5.62
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5.0 ppm (5 runs/day for 5 days)

1	25	1.4953	4.74×10^{-2}	2.24×10^{-3}	6.49×10^{-3}	1.62×10^{-2}	1.96×10^{-2}	2.65×10^{-2}	0.43	1.08	1.31	1.77
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5.0 ppm (4 operators - 5 times each for one day)

1,2,3,4	20	1.4862	3.83×10^{-3}	1.47×10^{-3}	5.90×10^{-3}	1.48×10^{-2}	1.79×10^{-2}	2.45×10^{-2}	0.40	1.00	1.21	1.65
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TABLE III

STATISTICAL DATA FOR 10.0 PPM VCM IN AIR

10.0 ppm on 5/21/74

Person	No. of Runs	Mean	Standard Deviation	Variance	Confidence Levels				Error			
					50	90	95	99	50	90	95	99
1	5	2.3576	6.94×10^{-2}	4.82×10^{-3}	2.3×10^{-2}	6.62×10^{-2}	8.62×10^{-2}	0.143	0.98	2.81	3.66	6.06
2	5	2.3861	7.19×10^{-2}	5.16×10^{-3}	2.4×10^{-2}	6.85×10^{-2}	8.92×10^{-2}	0.148	1.00	2.87	3.74	6.20
3	5	2.4967	1.62×10^{-2}	2.63×10^{-4}	5.4×10^{-3}	1.55×10^{-2}	2.01×10^{-2}	3.34×10^{-2}	0.21	0.62	0.80	1.34
4	5	2.2783	6.42×10^{-2}	4.12×10^{-3}	2.13×10^{-2}	6.12×10^{-2}	7.97×10^{-2}	0.132	0.93	2.69	3.50	5.80

10.0 ppm on 5/22/74

1	5	2.3416	4.65×10^{-2}	2.16×10^{-3}	1.54×10^{-2}	4.43×10^{-2}	5.77×10^{-2}	9.57×10^{-2}	0.66	1.89	2.46	4.08
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10.0 ppm on 5/23/74

1	5	2.6801	1.32×10^{-2}	1.75×10^{-4}	4.39×10^{-3}	1.26×10^{-2}	1.64×10^{-2}	2.73×10^{-2}	0.16	0.47	0.61	1.02
2	5	2.6331	3.14×10^{-2}	9.88×10^{-4}	1.04×10^{-2}	3.00×10^{-2}	3.90×10^{-2}	6.47×10^{-2}	0.39	1.14	1.48	2.46

10.0 ppm on 5/24/74

1	5	2.4999	3.55×10^{-2}	1.26×10^{-3}	1.18×10^{-2}	3.38×10^{-2}	4.40×10^{-2}	7.31×10^{-2}	0.47	1.35	1.76	2.92
2	5	2.4489	0.2834	8.03×10^{-2}	9.39×10^{-2}	0.270	0.352	0.583	3.83	11.03	14.37	23.83

10.0 ppm on 5/28/74

1	5	2.4522	6.01×10^{-2}	3.62×10^{-3}	1.99×10^{-2}	5.73×10^{-2}	7.46×10^{-2}	0.124	0.81	2.34	3.04	5.05
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10.0 ppm (5 runs/day for 5 days)

1	25	2.4627	0.13458	1.81×10^{-2}	1.84×10^{-2}	4.60×10^{-2}	5.56×10^{-2}	7.53×10^{-2}	0.75	1.87	2.26	3.06
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10.0 ppm (4 operators - 5 times each for one day)

1,2,3,4	20	2.3797	9.74×10^{-2}	9.49×10^{-3}	1.50×10^{-2}	3.77×10^{-2}	4.56×10^{-2}	6.23×10^{-2}	0.63	1.58	1.92	2.62
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