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RESEARCH NOTE

Evaluations of Charcoal Badges as Monitors for Vinyl Chloride Monomer

by

John W. Born

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SUMMARY

Two activated charcoal badges have proved to be effective VCM monitors under laboratory conditions. The conditions included exposure to 1, 5, and 10 ppm concentrations of VCM in air for 6 hours at 50% relative humidity. The two badges' calibration factors were 6.0 and 7.8 ppm per 0.10 mg of vinyl chloride monomer.

The calibration curves were straight lines through measured weights of adsorbed VCM up to 0.16 mg. The 0.16 mg of VCM corresponded to a 360-minute exposure to a 10 ppm VCM concentration. It is reasonable to assume that exposing a badge for 40 hours to a 1.6 ppm VCM concentration would give satisfactory results. Such week-long exposures to higher VCM concentrations may prove feasible. Further evaluations are needed to prove that.

CONCLUSIONS

1. The Louisiana State University (LSU) charcoal badge served well as a VCM monitor for 360-minute exposures to 1, 5, and 10 ppm concentrations of VCM in air at 50% relative humidity.

2. The calibration curves for the two LSU badges suggest that an LSU badge might serve continuously for five days before analysis.

3. The LSU badge appears promising as an area VCM monitor both inside and outside B.F.Goodrich plants.

4. The LSU badge may prove to be an effective monitor for other volatile pollutants.

RECOMMENDATIONS

1. Evaluate the LSU badges as VCM monitors under BFG plant operating conditions compared with present monitors.

2. Continue to evaluate the LSU badges in the laboratory as interest warrants; for example:

   a. study the effect of humidity,
   b. study the effect of longer-term VCM exposures such as five days,
   c. study the concurrent effect of other vapors in the air on the VCM monitoring, and
   d. study the LSU badges as monitors for other volatile pollutants.

3. Extend all such laboratory evaluations to the interested B.F.Goodrich plants if the badges prove to be effective.

4. Arrange the assembly of the LSU badge to permit filling with charcoal through the open face before placing the diffusion membrane.

INTRODUCTION

With proper calibration and use, personal monitor tubes meet many air sampling requirements. Such tubes include the Bendix Personnel Monitoring Collection Column (PMCC) and the Mine Safety Appliances Company Organic Vapor Sampling Tube (MSA tube). However, these tubes require the use of a battery-operated air sampling pump. The pump battery requires recharging after 6 hours or less of use. The pumping rate usually varies during the sampling period. The inability to measure the flow rate through the tube continuously makes the sampled air volume somewhat uncertain. The concentration of the pollutant in the air is therefore also uncertain. There is thus a need for a safe solid-state monitor which does not require a vacuum pump. Paul M. Zakriski has obtained two such monitors from Louisiana State University (LSU).

Description of the LSU Monitor Badges

The Ethyl Corporation and LSU have developed a vinyl chloride monitor badge. The badge consists of a cylindrical case containing about one gram of activated charcoal granules. See Figure 1. The LSU badge has 11 essential parts. The shell which

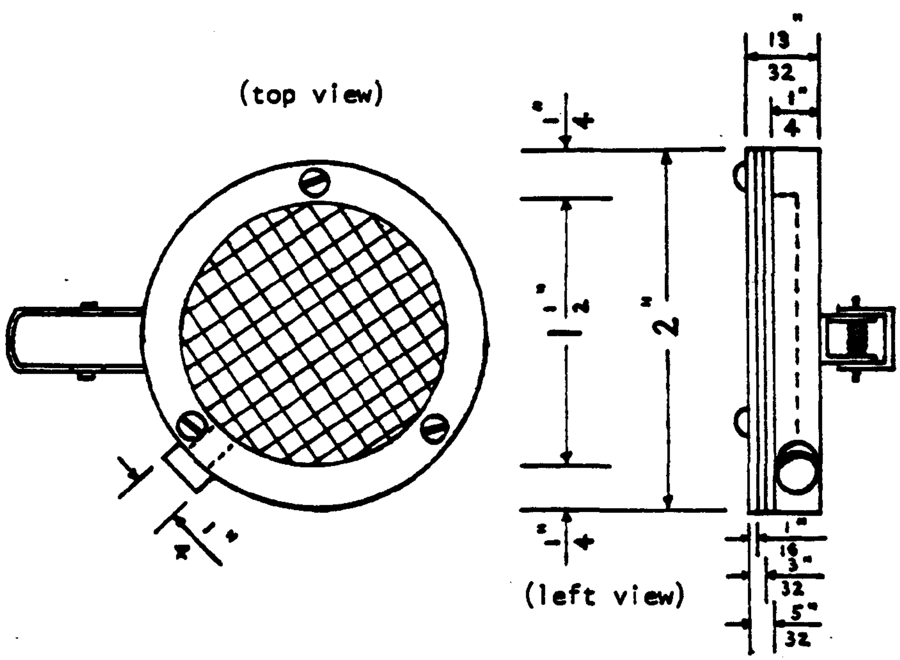

FIGURE 1

LSU Monitor Badge for Vinyl Chloride

contains the activated charcoal granules has eight parts. They are the base, the diffusion membrane, the protective ring, the screen, and the cover ring. Three screws secure the latter five parts together in that order. A Teflon plug closes the filler hole in the base. A spring clamp attaches the badge to a person's clothing or to some area fixture.

Charging the Badges with VCM

The dynamic vapor generator (see Reference 1) supplied the VCM-air stream for charging the activated charcoal (Nuchar WV-H, 8x30 mesh) in each badge. We added an in-line chamber between the dilution chamber and the supply manifold to contain the badge. The badge chamber is Pyrex glass with spherical ground-glass joints. The connections are gas-tight. The flow rate of the VCM-air stream was 4.6 lpm. The inner diameter of the chamber in the plane of the badge is 75 mm. The flow rate there converts to 0.039 miles per hour. The VCM-air stream flows around the badge and then out through the five ports of the supply manifold. We thus charged five MSA tubes during each badge charging period.

We charged Badges No. 1 and No. 2 separately for 6 hours each at three VCM concentrations. The VCM concentrations were 1, 5, and 10 ppm. We obtained the concentrations by mixing pure 50% R.H. air with 9.0, 45, and 90 ml of 508 ppm VCM to give a 4.6 lpm stream. We charged the five MSA tubes at the nominal flow rate of 10 ml per minute during each badge charging. One purpose for the MSA tubes was to monitor the VCM concentration in the air stream. A second purpose was to provide data for later comparisons at BFG plants.

VCM Analyses

All analyses involved desorbing the VCM from the charcoal with carbon disulfide. We transferred all of the charcoal from an MSA tube into a 1 cc glass vial (Supelco, Inc. catalog no. 3-123). We added 1.0 ml of carbon disulfide and closed the vial with a gas-tight septum seal. A 7-ml vial (Pierce catalog no. 13028) with a Mininert screw cap (Pierce catalog no. 10145) was used to contain all of the charcoal from a badge. We put 3.0 ml of carbon disulfide into the vial through the septum seal with a syringe. The MSA tube contains a nominal 150 mg of charcoal. We filled each badge with what we considered to be a full load of charcoal (Nuchar WV-H) each time. The weights of charcoal each time (Table 1) were obtained after analysis by drying it and weighing by difference.

TABLE I

Summary of Charcoal Weights of LSU Badges

Badge No.	Exposure (ppm)	Wt. of Vial Plus Charcoal (g)	Wt. of Vial (g)	Wt. of Charcoal (g)
1	1	14.0268	12.8550	1.1718
1	5	14.0201	12.8221	1.1980
1	10	13.8903	13.0980	0.7923
2	1	14.3257	12.9606	1.3651
2	5	14.3703	12.9533	1.4170
2	10	14.1377	12.8651	1.2726

The variations of charcoal weight in Table I resulted from several factors. First, the 8x30 mesh size range of charcoal granules was too wide. Not all particles would go through the filler hole of the badge. Second, one cannot see far enough into the badge to know how nearly full it is. Also, one cannot see how well-packed the granules are inside the badge. Sieving and trials indicated that an 18x30 mesh range would permit easier and faster filling and better packing.

Three 5-µl aliquots of each solution of VCM from a badge were analyzed with a gas chromatograph (Hewlett-Packard Model 5711A). We used a 1/8"x36" Porapak QS column and a flame ionization detector. The temperature program included 2 minutes at 80°C, a rise of 32°C per minute, and then 2 minutes at 160°C. The results of analysis appear in Table II and Figure 2.

TABLE II

Calibration of the VCM Monitor Badges

LSU Badge Number	VCM Weight (mg)	VCM Concentration in Air (ppm)	Calibration Factor (ppm/mg)
1	0.021_5	1.0	(47)*
1	0.057_9	5.0	86
1	0.12_7	10.	79
Average:			82 ± 4
2	0.023_7	1.0	(42)*
2	0.082_3	5.0	61
2	0.15_9	10.	63
Average:			62 ± 1

* This value was omitted in calculating the average for the reasons discussed below. Note that this omission results in a conservative value for VCM personnel exposures at about 1 ppm.

The best plot through the data points for Badge No. 1 in Figure 2 gives a calibration factor of 7.8 ppm per 0.10 mg of VCM analyzed. That value agrees well with the 8.2 ppm per 0.10 mg average value in Table II. The best plot through the data points for Badge No. 2 in Figure 2 gives a calibration factor of 6.0 ppm per 0.10 mg of VCM analyzed. Again, that value agrees well with the 6.2 ppm per 0.10 mg average value in Table II. The calibration factors for Badges 1 and 2 at 1 ppm are about 60% of the factors at 5 and 10 ppm. These lower calibration factors suggest that the diffusion rate is slower at 1 ppm than at 5 and 10 ppm. However, the following results of our standardization of the VCM-air mixtures show that all three calibration factors for each badge are the same within the limits of precision.

We standardized the three VCM-air mixtures as follows. We first charged a series of eight standard MSA tubes directly from a 508 ppm VCM-air cylinder. Second, we calibrated the gas chromatograph with these MSA tubes. The results appear in Table III. The calibration factors for standard MSA tubes 1 through 4 averaged 1.51 ± 0.18 ng of VCM per area unit (under the VCM peak on the GC recorder chart). The corresponding calibration factors for standard MSA tubes 5 through 8 averaged 1.88 ± 0.03 ng of VCM per area unit. Then we standardized the VCM-air mixtures by charging MSA tubes with the same VCM-air stream used to charge the badges. Table IV gives the results. The empirical result of 0.97 ppm (tubes 26 through 30) agrees with the nominal VCM concentration of 1.0 ppm. However, the results of 3.4 ppm (tubes 16 through 20) and 8.3 ppm (tubes 21 through 25) differ from the nominal values of 5.0 and 10. ppm. If we should use the empirical ppm values, the results in Table II would become 46, 58, and 66 ppm per mg of VCM analyzed for Badge No. 1 and 41, 41, and 52 ppm per mg for Badge No. 2. Then the average calibration factors would be 57 ± 7 ppm per mg for Badge No. 1 and 45 ± 5 ppm per mg for Badge No. 2. See Figure 3.

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Figure 2. Calibration of LSU VCM Monitor Badges

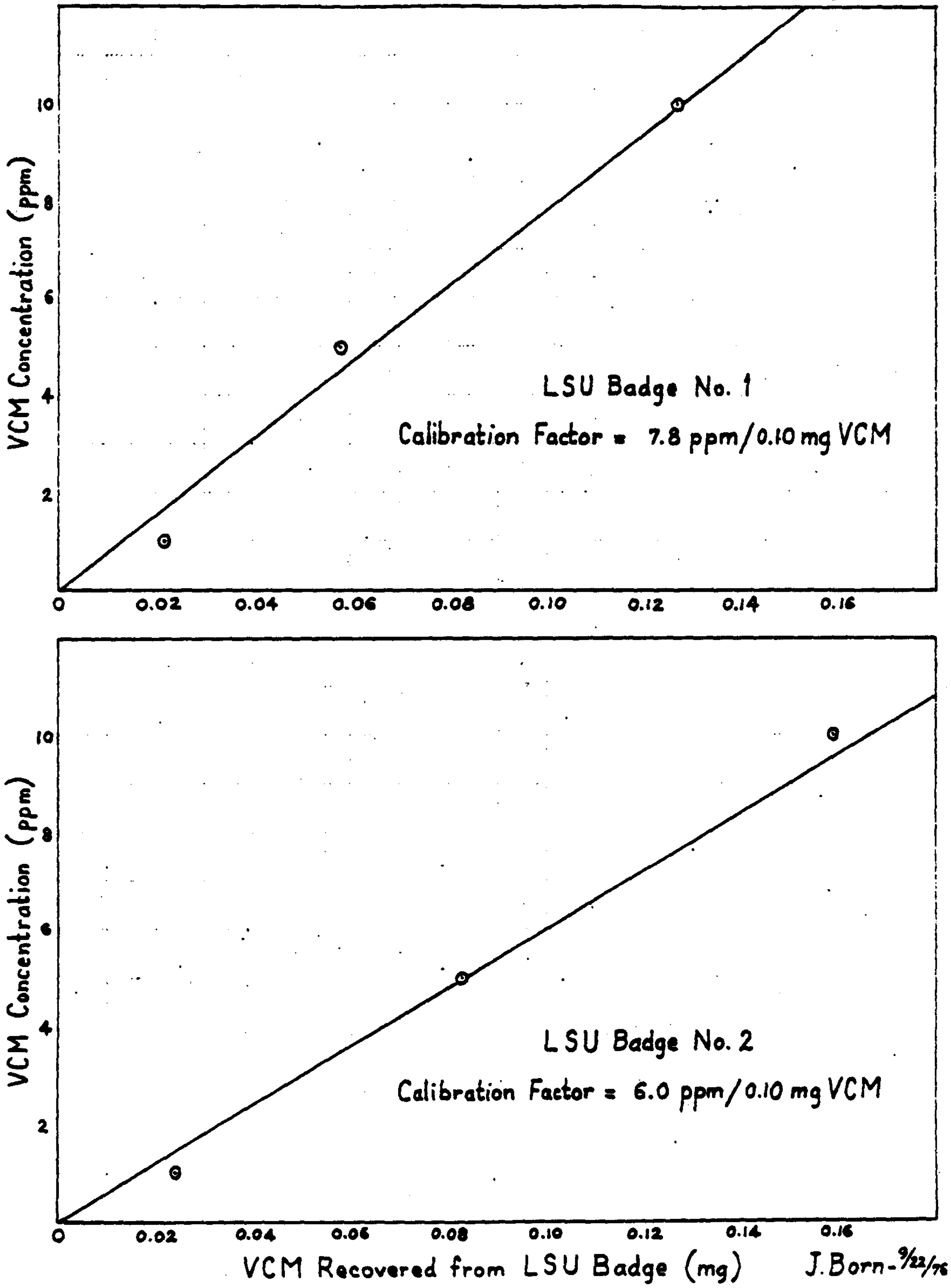

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Figure 3. Recalibration of LSU VCM Monitor Badges

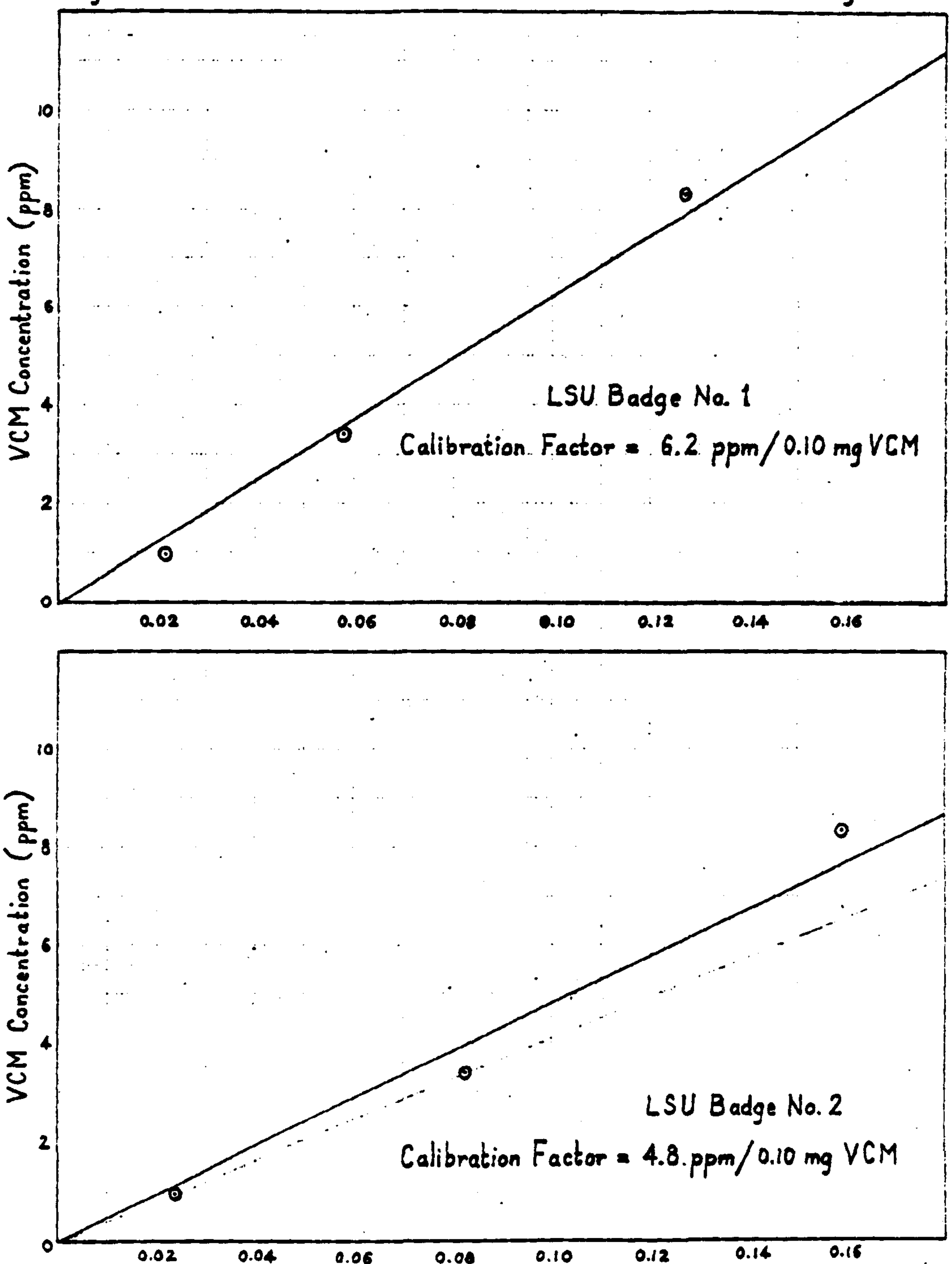

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TABLE III

Calibration of the Gas Chromatograph

VCM Badge No.	VCM Concn. (ppm)	MSA Tube No.	VCM Wt. (ng)	G.C. Peak Area (units)	G.C. Calibration Factor (F_{cal}) (ng per area unit)
1	1.0	Std. 7	441	230	1.92
1	1.0	Std. 8	499	266	1.88
Average:					1.90 ± 0.02
1	5.0	Std. 5	205	111	1.85
1	5.0	Std. 6	272	147	1.85
Average:					1.85 ± 0.00
1	10.	Std. 1	316	171	1.85
1	10.	Std. 2	453	312	1.45
1	10.	Std. 3	930	602	1.54
1	10.	Std. 4	455	378	1.20
Average:					1.51 ± 0.18
2	1.0	Std. 7	441	230	1.92
2	1.0	Std. 8	499	266	1.88
Average:					1.90 ± 0.02
2	5.0	Std. 7	441	230	1.92
2	5.0	Std. 8	499	266	1.88
Average:					1.90 ± 0.02
2	10.	Std. 7	441	230	1.92
2	10.	Std. 8	499	266	1.88
Average:					1.90 ± 0.02

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TABLE IV

Standardization of the VCM-Air Mixture

MSA Tube Number	VCM Weight (mg)	Air Volume Sampled (l)	VCM Concentration (ppm)[d]
26[a]	0.0050	1.90	1.02
27	0.013	4.57	1.09
28	0.0092	3.47	1.03
29	0.0075	3.46	0.84
30	0.0072	3.19	0.89
Average:			0.97 ± 0.088
16[b]	0.0396	3.64	4.26
17	0.0239	2.78	3.36
18	0.0345	4.39	3.07
19	0.0274	3.59	2.99
20	0.0268	3.42	3.07
Average:			3.38 ± 0.38
21[c]	0.0836	3.38	9.68
22	0.0918	4.32	8.31
23	0.0579	2.92	7.76
24	0.0645	3.14	8.04
25	0.0549	2.74	7.84
Average:			8.33 ± 0.54

[a] Tubes 26-30 were exposed to a 1.0 ppm VCM-air mixture.

[b] Tubes 16-20 were exposed to a 5.0 ppm VCM-air mixture.

[c] Tubes 21-25 were exposed to a 10. ppm VCM-air mixture.

[d] The calibration of the gas chromatograph was carried out only when the VCM-air mixture in the dynamic vapor generator was 1.0 ppm. The resulting calibration factor evidently does not apply as well when the VCM concentration is 5.0 or 10. ppm.

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DISCUSSION OF RESULTS

The response of both LSU badges to six-hour exposures to VCM concentrations of 1.0, 5.0, and 10 ppm in air is linear. The VCM concentrations in air as measured via MSA tubes were 1.0, 3.4, and 8.3 ppm. The values obtained by MSA tube thus agreed exactly with the nominal value at 1.0 ppm but differed by 47% and 20% at 5.0 and 10 ppm, respectively. Thus, use of the nominal values gives 47% and 20% higher ppm values for the corresponding VCM weights. The nominal ppm values were calculated from the certified 508 ppm VCM value and the calibrated flow rates. Since the nominal and empirical values agreed exactly at 1.0 ppm, the nominal values at 5.0 and 10 ppm are probably correct. They represent fivefold and tenfold higher VCM concentrations (namely 45 and 90 ml per minute) in the 4.6 lpm VCM-air stream (as measured by calibrated flowmeters). In any event, using the nominal ppm values gives the more conservative calibration factors.

The precision of better than ±12% of the average within each set of standardization values (Table IV) was good. Note that this precision is about the same as that for the G.C. calibrations (Table III).

The similarity of weights of activated charcoal in the badges was good in five of the six cases (Table I). The one really low value (0.7923 g) came from the first badge that we filled. In effect we developed the technique during that first filling. The amount of charcoal in Badge No. 1 (excluding the 0.7923 g value) averaged 88% as much as was in Badge No. 2.

The calibration factors for both badges were much lower (47 and 42 ppm/mg VCM) at 1.0 ppm than at 5.0 and 10 ppm (82 and 62 average ppm/mg VCM, respectively). See Table II. This marked difference in calibration factor results from a proportionately larger weight of VCM recovered at the 1.0 ppm level than at the 5.0 and 10 ppm levels. The VCM weights at 10 ppm are about twice the weights at 5.0 ppm for both badges. But the VCM weights at 5.0 ppm are only about three times the weights recovered at the 1.0 ppm level. This reduced recovery efficiency at the 5.0 and 10 ppm exposure levels merits further investigation.

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REFERENCES

1. J. W. Born, P. M. Zakriski, and R. D. Hardesty, Evaluation of Bendix Flasher Tubes and MSA Tubes as VCM Monitors, Corporate Environmental Services, Project 8504-76, August 24, 1976.