conoco

Interoffice Communication

To R. B. Martin

From D. S. Cox

Date August 27, 1979

Subject CHECKING THE CALIBRATION OF THE "REAL" MINIMONITOR AND REPRODUCIBILITY MEASUREMENT OF THE CARBON ANALYSIS

A program was developed to determine if the calibration of the "REAL" badge membrane would change; however, the work changed to more of a precision study for the carbon adsorption test.

SUMMARY

1. A series of badges were exposed to known concentrations of VCM in nitrogen for known times and the calibration values measured.

2. Carbon was exposed to VCM (without using the badge) and the precision measured. Ultrasonic treatment improved the precision by almost a factor of 10.

3. Carbon was exposed to VCM and analysis done by the OSHA approved carbon disulfide method. The precision was only marginally better.

CONCLUSIONS

1. The badge calibrations had changed indicating the membrane was partially blocked. Replicate measurements are needed to overcome the inherent variability of the carbon analysis.

2. The head space method gives equivalent results to the carbon disulfide method.

3. Under normal analysis methods, the precision (1 standard deviation) of the carbon analysis is 19% relative (1 ppm TWA-8 hr.). There is some indication that improvement is possible using an ultra sonic treatment.

EXPERIMENT I

The badges were exposed to known concentrations of flowing vinyl chloride gas. The exposures were made in a special chamber so each badge had its own atmosphere unaffected by any of the other units. The analysis was done by F-42 head space analysis using a mixture of dimethlacetimide (DMA) and water (see Appendix for analysis details). The "Standard" used was the average value of 10 knowns. Table I shows the results of the calibration checks.

Due to the poor relative standard deviation, a search was made for the source of the variability.

cc CLM
AHS
RAF
JVL

EXPERIMENT II

A systematic search for variability was made in the test. Six vials were filled with a 12 ppm VCM standard gas and run on the F-42 (Table 2). The errors due to the injection step were ± 2.7% relative.

A solution of VCM in DMA was prepared and an equal amount of this solution put into five F-42 vials. The extraction solvent was added and the vials tested on the F-42 (Table 3). The precision was still ± 2.7% relative and showed that the equilibrium of VCM in the level-space was constant.

EXPERIMENT III

The regular 90°C method of analysis of the carbon standards (Table 4) showed a relative error of 19.3%. A test was made at a lower bath temperature (70°C) to check for VCM degradation. None was evident. The relative error for standards in the 70°C bath was not significantly better.

EXPERIMENT IV

Carbon was put into a flask and exposed to VCM vapors then the carbon was put into vials (equal weights) and run. The precision was much better (Table 5) indicating standard preparation contributes to the errors.

EXPERIMENT V

A test was carried out with propane to confirm that the errros were not due to the reactivity of VCM. Table 6 shows the results of this test. Propane behaved the same as VCM on carbon.

EXPERIMENT VI

A set of standards were analyzed by the carbon disulfide method to confirm that the head space method was not the source of errors. Table 7 shows the results of that test. There was some improvement over the regular carbon analysis.

EXPERIMENT VII

A test was made using the ultrasonic bath to dislodge any gas bubbles from the carbon after extraction was complete.

The results (Table 8) were favorable with a relative error of only 3.5%. More tests will be needed to confirm that the ultrasonic treatment results were typical and not a fluke.

David S. Cox

David S. Cox
Mfg. Chemist

TABLE I

CALIBRATION VALUES

BADGE #	209	210	211	213	214	116
Run #1	1.01	1.05	1.17	1.29	1.09	1.71
2	1.00	1.01	1.15	0.93	1.03	1.00
3	1.03	1.04	0.90	1.00	1.02	1.02
4	0.89	0.90	0.94	0.90	0.98	1.04
5	0.93	0.92	0.88	0.80	0.89	0.75
6	1.47	1.48	0.87	1.47	1.66	-
7	1.25	1.30	1.23	1.58	1.60	-
8	1.41	1.28	1.09	-	1.18	1.48
9	1.96	1.79	1.86	-	2.44	2.52
10	1.43	1.10	-	-	1.36	1.38
11	1.17	0.81	1.34	-	1.21	1.42
12	1.23	1.42	1.78	-	1.30	0.91
Average	1.23	1.18	1.20	1.14	1.31	1.32
Rel. Std. Deviation	± 10%	24%	29%	27%	32%	39%

$K = \frac{CT}{m}$

K = Calibration #

T = Hours

M = Microliters of VC on Carbon

C = Concentration of the VC in microliters per liter (ppm).

TABLE 2

ANALYSIS OF 12 PPM VC STANDARD GAS

	Area
	2724
	2771
	2830
	2774
	2875
	2662
% Rel. Std. Deviation	2.7%

TABLE 3

REPLICATE ANALYSIS OF VCM SOLUTION

	2276
	2368
	2296
	2208
	2230
% Rel. Std. Deviation	2.7%

TABLE 4

ANALYSIS OF VC INJECTED INTO A VIAL CONTAINING CARBON

(10 µl VC)

Water Bath 90° for 2 Hrs.			Bath 70° for 17 Hrs.	
#1	#2	#3		
10.7	8.1	12.5		10.4
13.2	14.4	9.6		13.2
7.4	10.8	11.9		10.6
8.3	8.2	10.6		10.0
11.9	9.3	11.9		10.6
9.4	9.9	7.0		8.8
10.1	7.9	8.8		10.6
8.9	10.7	12.1		8.0
	9.9	9.0		6.9
	10.8	6.5	% Rel. Std.	11.1
COMBINED % REL. STD. DEV. 19.3%			Deviation	17.5%

TABLE 5

ANALYSIS OF CARBON EXPOSED TO VC IN A GLASS FLASK

(Equal Weights of Carbon)

Area @ 90° for 1 Hr.	Area @ 70° for 2 Hr.
1006	909
995	1021
1028	925
1003	917
973	1095
962	947
1031	797
866	1006
894	1032
966	1023
% Rel. Std. Deviation 5.6%	8.8%

TABLE 6

ANALYSIS OF PROPANE ON CARBON

	2.18
	2.20
	3.30
	3.89
	4.14
	2.58
	4.34
	3.32
% Rel. Std. Deviation	26.3%

TABLE 7

ANALYSIS OF CARBON WITH 10 µl VC BY

CARBON DISULFIDE METHOD

9.1	17.9
9.6	10.5
8.8	7.9
13.8	9.2
9.2	16.1
7.7	8.8
8.0	8.8
8.4	8.2
8.8	9.0

10% Rel. Std. Deviation

TABLE 8

ANALYSIS OF CARBON BY F-42 AFTER ULTRASONIC TREATMENT

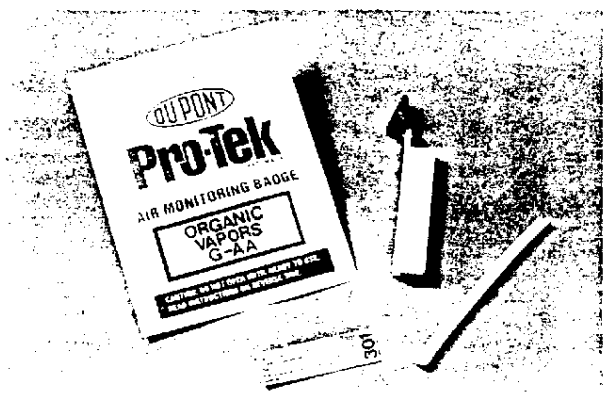
10 nl STD ON CARBON (DMA EXTRATANT)

	AREA
	3380
	3598
	3477
	3509
	3368
	3494
	3745
	3426
% Rel. Std. Deviation	3.5%

DU PONT "PRO-TEK"*

ORGANIC VAPOR G-AA AIR MONITORING BADGE

GENERAL INSTRUCTIONS



*Trademark

DUPONT

SAL 000048128

E-27804

NOTICE

The recommended procedures and product performance described herein have been developed and are the result of primary research completed by Du Pont, as well as the current state of the art knowledge.

The systems are designed to be used under the supervision of knowledgeable technicians and the Du Pont Company does not offer any warranty expressed or implied for the products or their performances. Further, Du Pont does not assume and will not be responsible for any injuries or damage to persons or property which result from the improper use of this system.

DU PONT "PRO-TEK"*
ORGANIC VAPOR G-AA AIR MONITORING BADGE

Du Pont "Pro-Tek" Organic Vapor G-AA Air Monitoring Badge is a new passive badge monitor used to determine the time-weighted average (TWA) concentration of organic vapor contaminants in air. It is designed to be worn near the breathing zone of personnel exposed to potentially hazardous environments. After exposure, the badges are analyzed with gas chromatographic procedures similar to those outlined in NIOSH Method Physical & Chemical Analytical Method 127 for charcoal tubes.

The "Pro-Tek" badge is small (2.8" x 0.3" x 0.5") and lightweight (less than 0.5 oz.). It can be used for sampling times ranging from 15 minutes to 16 hours.

PRINCIPLE OF THE METHOD

The "Pro-Tek" Air Monitoring Badge collects organic vapors through the mechanism of molecular diffusion and adsorption onto an activated charcoal collection strip. The amount of vapor pollutants collected is determined by the concentration in the environment and the sampling time.

*Trademark

After exposure, the activated charcoal strip is removed from the badge and desorbed with a measured volume of desorbing solvent.

The desorbing solution is then analyzed with gas chromatographic techniques. The weight of the adsorbed contaminant is determined by peak area comparison to known calibration standards.

By knowing the amount of material collected (mass uptake) and the sampling rate of the "Pro-Tek"* Organic Vapor G-AA Air Monitoring Badge (determined by diffusion coefficient data), the analyst can determine the TWA concentration.

RANGE

The sampling range of the "Pro-Tek" Badge is 0.2 to 2000 ppm-hours for most organic vapors being measured. This range is possible because of:

1. Variable sampling rates of approximately 50 to 100 cc/min., depending upon whether one or both covers are removed.
2. Charcoal capacity of approximately 300 mg.
3. Desorbing solvent volume of 1.0 ml.

ACCURACY

The Du Pont "Pro-Tek" Air Monitoring Badge method meets both OSHA and NIOSH requirements for sampling organic vapors.

*Trademark

INSTRUCTIONS FOR USE

MONITORING INSTRUCTIONS

1. Do not open pouch until ready to use badge. Open the foil-lined pouch by cutting along the designated line. (See Figure 1.)
2. Remove contents from pouch (badge with covers). Pouch closures and labels are supplied in each box of 10 badges.
3. Use the label (See Figure 2) provided to record:
   a. User I.D.
   b. Date.
   c. Start time.
   d. Test environment temperature.
   e. Test environment relative humidity.
   f. Complete chemical name of vapors to be analyzed.
   g. Any comments or unusual circumstances.
4. Place completed label on empty pouch.
5. Affix badge number (corresponds to number on label) to badge clip.
6. Remove badge cover(s). (See Figure 3.) Both badge covers should be removed if low contaminant concentrations are suspected. If high contaminant concentrations are suspected, one badge cover should be left on the badge to reduce the sampling rate by half. (For use of one badge cover only, it is necessary to cut the cover's connecting hinge.)

7. Attach badge near user's breathing zone. (See Figure 4.)
8. Replace cover(s) after exposure to deactivate the badge. (See Figure 5.)
9. Record end time and total exposure time on pouch label.
10. Place badge into labeled pouch; fold pouch, and seal with closure provided. (See Figure 6.)
11. Submit for analysis.
12. Provide one unexposed badge as a control or blank for the analyst.

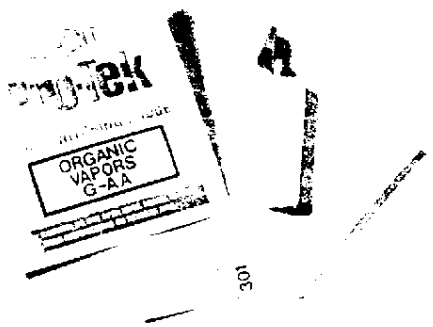


Figure 1
Pouch and Contents
(closure and label supplied
in box of 10 badges)

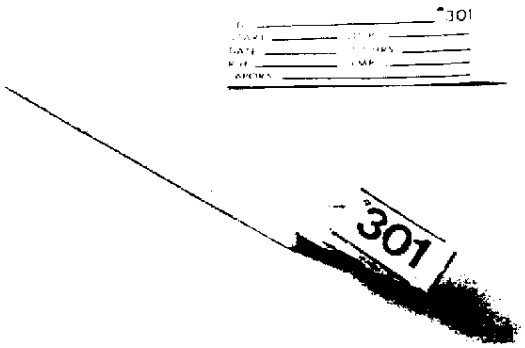


Figure 2
Badge and Label

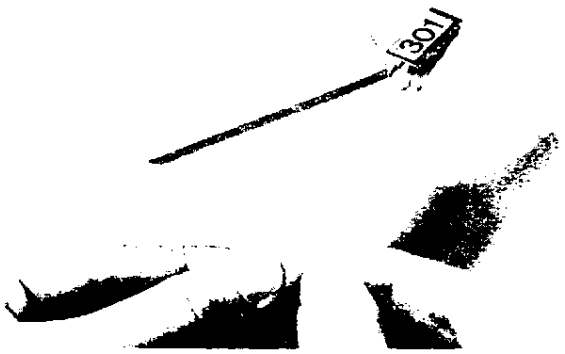


Figure 3
Removing Badge Covers

Figure 4
Attaching Badge Near User's
Breathing Zone

Figure 5
Deactivating Badge After Use

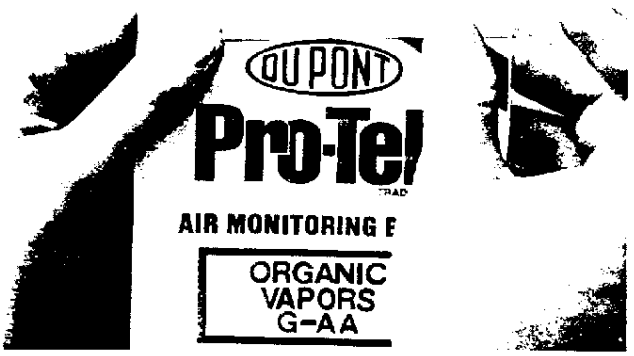


Figure 6
Sealing Exposed Badge in Pouch

TREATMENT OF EXPOSED SAMPLES

1. Open the badge in an area free of organic vapors. The badge is hinged at the bottom and can be opened from the clip end. (See Figure 7.)
2. Use tweezers to remove the activated charcoal strip. (See Figure 8.)
3. Place the strip immediately into the desorption vial. To do this, fold the insert lengthwise and tamp it into the bottom of the vial. (See Figure 9.) Placing the charcoal strip into the vial as illustrated requires practice. It is recommended that the analyst refine the technique using a charcoal strip from an unexposed badge before using valuable samples.
4. Seal the vial.
5. Identify the vial.
6. Treat the control sample in the same manner.

ANALYSIS

The analyst should verify that the desorption vial is sealed and properly labeled.

1. Inject 1.0 ml. of desorbing solvent into the vial. (See Figure 10.) The 1.0 ml. desorbing solvent volume is appropriate for most compounds. Different solvent volume may be used if desired, but corresponding desorption efficiency values must be verified.

2. Shake the vial gently over a period of 30 minutes.

3. Use a measured volume of the desorbing solution for gas chromatographic (GC) analysis. Follow the procedures outlined in NIOSH Method P&CAM 127. (See Figure 11.)

4. Calculate the corrected weight of each contaminant on the charcoal strip subtracting the contribution of the blank sample and divide the result by the desorption efficiency determined for the contaminants being analyzed.

5. Calculate the TWA user exposure, using the following equations:

$$\frac{mg}{m^3} = \frac{\text{corrected weight on badge (nanograms)}}{\text{sampling rate (} cm^3/\text{min.)} \times \text{sampling time (min.)}} = \frac{ng}{cm^3}$$

$$ppm = \frac{mg}{m^3} \times \frac{22.4 \text{ l/mole}}{\text{MW g/mole}} \times \frac{T^{\circ}K}{273^{\circ}K} \times \frac{760 \text{ mm Hg}}{P \text{ mm Hg}}$$

The sampling rate for each contaminant is obtained from diffusion coefficient data supplied by Du Pont. If one badge cover is left on the badge, the sampling rate will be reduced by 50 percent.

Figure 7
Opening Badge for Analysis

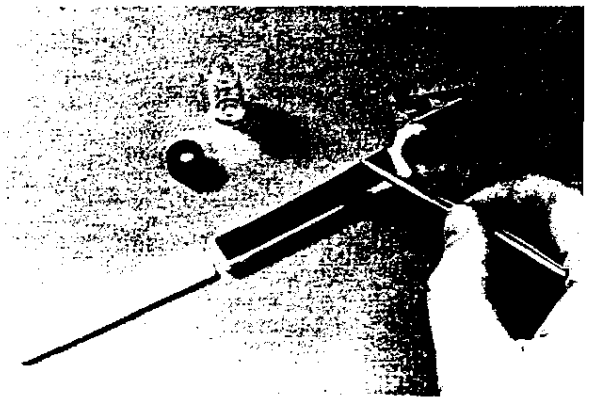


Figure 8
Removing Charcoal Strip

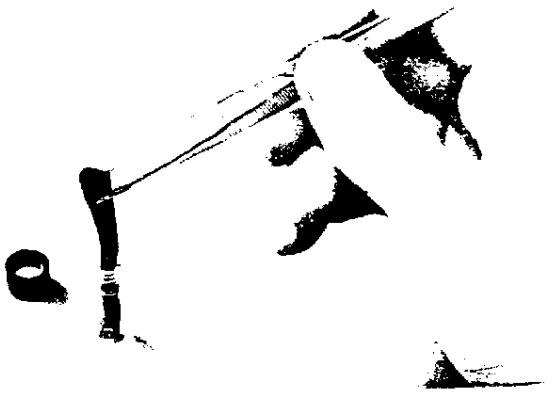


Figure 9
Placing Strip into
Desorption Vial

Figure 10
Injecting Desorbing Solvent
into Vial

Figure 11
Using Gas Chromatograph for Analysis

CONTENTS

10 PRO-TEK® BADGES	☒
1 PACKAGE CLOSURES	☒
10 IDENTIFICATION LABELS	☒
OPERATING MANUAL	☒
BADGE CALCULATION GUIDE	☒
PRODUCT SHEET	☒