conoco

Interoffice Communication

To R. B. Martin

From D. S. Cox

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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.

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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%