1991 DIFFUSION MONITOR TECHNICAL REPORT

January 10, 1992

EXECUTIVE SUMMARY

Accomplishments of the Diffusion Monitor program in 1991 include selection of a replacement carbon for the Organic Vapor Monitors, resolving formaldehyde manufacturing problems, improving the quality control for the 3510 analysis, approval for a 3530 OVM (3520 with laboratory analysis), evaluation of a carbon monoxide monitor, and validation of the OVM for a number of compounds.

After many recovery, capacity and sampling rate studies, Kuraray GA Acid Washed carbon was chosen as the replacement for the Witco carbon. A three to five year supply was purchased. The carbon was ground and sieved locally (Particle Technology, Inc., Burnsville, MN). A trial batch of carbon wafers was prepared and tested. Recoveries are very similar to the Witco carbon. Capacities for small molecules like acetone and methylene chloride are somewhat better than the Witco carbon. A full scale batch was prepared successfully. This lot will be qualified during the first quarter of 1992. A decision will be made then on the timing of the introduction of the new carbon.

The Organic Vapor Monitor was revalidated for methylene chloride to provide additional documentation as the new OSHA standard is introduced. The OVM was validated for long exposure times and low concentrations of solvents. Many experiments were run to validate the use of our monitors in response to customer inquiries. This work will continue as an integral part of the Q90s effort.

Improvements to the Formaldehyde quality assurance procedure have eliminated the historical low bias in the recovery which has led to many fewer failing lots of wafers. The occurrence of high blanks continues to plague us. The blank values increase with ageing, especially at higher temperatures. This effect is worse for some lots than others. Initial experiments with a glass fiber wafer have shown promise and this effort will be increased in 1992. Examination of alternate chemistries such as the 2,4-DNPH and 2-HMP methods will also be pursued.

The Quantum Group, Inc. carbon monoxide monitor was evaluated. The qualitative SX-1 chip shows promise but the quantitative MD-3 chip demonstrates a different rate of response at different concentrations which precludes its use as a TWA monitor.

Approval was obtained to proceed with the introduction of a 3530 Organic Vapor Monitor which will be an OVM with backup and analysis. The laboratory has completed its input and we are awaiting the completion of the labels, packaging and sales literature by marketing.

CARBON QUALIFICATION

The Witco 964 petroleum-based carbon used in the Organic Vapor Monitors is no longer commercially available. Previous work described in Monitor Technical Report 12, had narrowed the choice of replacement carbon to Kuraray GC, GA, GA Acid Washed, and Kreha BAC. Results of testing shown in Table 1 have led us to choose the Kuraray GA AW carbon as the replacement carbon for our OVMs because of its similar recoveries to the Witco carbon and its somewhat improved capacity for several important compounds.

Table 1

RECOVERIES (AMOUNT FOUND/AMOUNT SPIKED)
January, 1991

CMPD	SPIKE (MG)	W	BAC	GA	GA AW	GC	KC-10
CH2CL2	2.65	0.98	1.01	0.99	0.97	0.99	0.98
MEK	1.61	0.92	0.96	0.78	0.96	0.95	0.94
MEK 2 WKS WET	1.61	0.52	0.52	0.32	0.60	0.41	0.75
IPA	3.93	0.66	0.70	0.58	0.67	0.68	0.64
CELL	0.28	0.33	0.65	0.02	0.53	0.56	0.51
ECH	0.35	0.89	0.83	0.78	0.76	0.84	0.84
ETOH	2.36	0.44	0.44	0.36	0.42	0.42	0.41

CAPACITIES (MG FOUND AFTER 1 DAY OPEN)
January, 1991

CMPD	SPIKE(MG)	W	BAC	GA	GA AW	GC	KC-10
CH2CL2	26.5	0.64	0.89	2.0	2.5	0.17	2.1
FREON 113	31.5	18	18	21	20	14	20
1,1,1 TCE	33.5	21	22	25	24	18	21
CCL4	39.9	25	25	31	30	20	27
MEK	20.1	9.3	10	13	14	7.5	11
TOLUENE	43.4	31	34	34	31	31	26

Kuraray GA Acid Washed carbon has good capacity for small volatile molecules (methylene chloride) as well as large molecules (dodecane). Dynamic tests show that the Kuraray GA AW and cloth yield the same sampling rate as the Witco carbon.

	DODECANE		DECANE		OCTANE
	REC	CAP(MG)	REC	CAP(MG)	REC
Witco	1.04	25.2	1.13	23.7	1.13
Kur. GA AW	1.03	24.9	1.08	23.7	1.13
Kur. Cloth	1.01	23.5	1.12	23.5	1.04

SAMPLING RATE (CC/MIN)

	OCTANE	DECANE	DODECANE
Witco	24.9	21.3	21.5
Kuraray GA AW	24.5	22.5	21.5
Kuraray 700 CH-10		22.3	22.2

MEK RECOVERIES
May, 1991 (1.61 MG SPIKE HELD TWO WEEKS)

CARBON	RECOVERY DRY	RECOVERY WET
Witco	0.92	0.52
Ambersorb	0.91	0.88
Kur. GA AW	0.91	0.63
Kur 700CH10	0.86	0.77
Kur 700CH15	0.86	0.87
Std CT	0.79	0.41

An order for 1500 kg of the Kuraray GA AW carbon was placed. The carbon was ground and sieved by Particle Technology, Inc., Burnsville, MN. Trial batches of wafers from the new carbon were successful as shown by the data in Table 2. A full-scale lot of wafers was successfully milled and is now being evaluated. After a successful evaluation, a decision will be made about the timing of the introduction of the new carbon. A significant capacity advantage for small molecules exists for the new carbon which may encourage us to introduce it now, rather than wait until the Witco carbon is used up.

Kansai Coke & Chemical is supplying small quantities of a high CTA carbon called Maxsorb using the same process as the Anderson AX-21 carbon. A sample of <400 mesh powder was made into wafers and tests indicated very poor MEK recovery

and methylene chloride capacity. No further evaluation of this carbon is planned.

Table 2
October, 1991

RECOVERIES (AMOUNT FOUND/AMOUNT SPIKED)

Compound	Witco	GAAW#1	GAAW#2	Max	Max+10% Teflon
MEK(1 day dry)	(0.92)	0.91	0.90	0.71	0.67
MEK(2 wks wet)	(0.52)	0.57	0.57	0.49	0.39
Isopropanol	0.63	0.64	0.63	0.49	0.49
Cellosolve	0.54	0.57	0.55	0.05	0.05
Toluene	1.00	0.99	1.01	1.02	1.02
CH2CL2	0.87	0.86	0.86	0.89	0.84

CAPACITIES (MG FOUND AFTER 1 DAY OPEN)

COMPOUND	WITCO	GAAW	MAX
CH2CL2	2.9	7.1	0.3
Toluene	26.5	27.0	25.0
Acetone	4.6	10.3	
1,1,1-TCE	23.4	26.0	
Freon 113	18.8	23.0	

GAAW = Kuraray GA Acid Washed
MAX = Kansai Maxsorb
MAX = Kansai Maxsorb plus additional Teflon

ORGANIC VAPOR MONITOR

Recoveries, capacities and sampling rates were determined for a number of compounds shown in the following tables and charts.

Table 3

COMPOUND	RECOVERY	ELUENT	DATE
CS2	0.42	toluene	1-91
DMF	0.32	CS2	1-91
DMF	0.92	CH2CL2	1-91
MTBE	1.00	CS2	7-91
Decane	1.04	CS2	7-91
Dodecane	1.04	CS2	2-91
Octane	1.02	CS2	7-91

COMPOUND	CAPACITY	DATE
MTBE	10	1-91
Dodecane	25	2-91
Decane	24	3-91
Vinyl Acetate	17	10-91
Butyl Acrylate	22	10-91
HCFC-123	14	9-91

COMPOUND	SAMPLING RATE	DATE
Decane	23.0	7-91
Dodecane	21.5	3-91
Octane	27.4	7-91
MTBE	32.8	7-91
PO	40.2	8-91
ave	37.9+/-3.0	
HCFC-123	31.3+/-2.6	9-91

DMF = Dimethyl Formamide
MTBE = Methyl t-Butyl Ether
HCFC-123 = 1,1-Dichloro-2,2,2-trifluoroethane
PO = Propylene Oxide

MEK RECOVERY

Recovery of MEK did not show improvement using 5% 2-Butoxyethoxyethanol like the alcolhols have shown indicating that decomposition or reaction is occurring on the charcoal.

	Witco	GA AW
3 weeks dry (CS2)	0.87	0.91
2 weeks dry (5% 2BEE)	0.90	0.91
2 weeks wet (5% 2BEE)	0.54	0.58

Tabl 4

GLYCOL ETHER RECOVERIES

	CS2	CH2CL2	5%2BEE/CS2	10%MEOH/CH2CL2
BC	0.73	1.03	0.95	1.36
BCA	0.98	1.09	0.96	1.35
C	0.57	0.95	0.83	
CA	(1.03)**			
MC	0.44	0.93	0.70	
MCA	(1.00)**			
PGME	0.68	0.97	0.90	
PGMEA	(0.99)*	(1.12)*		

2BEE = 2-Butoxyethoxyethanol

GYCOL ETHER SAMPLING RATES (CC/MIN)

	CALCULATED	PINK SHEET	GREEN SHEET	EXPERIMENT
BC	27.2	28.2+/-0.6	27.3	27.5+/-1.5
BCA	24.2	24.5+/-1.5	24.4	24.3+/-1.0
C	31.9	32.4+/-0.9	32.4	
CA	27.3	26.6+/-0.4	26.6	
MC	35.3	36.3+/-0.4	36.3	
MCA	29.4	29.0+/-0.5	29.0	
PGME	32.2	32.4	32.4	
PGMEA	27.6	----	----	(25.1)*

*Data from 1-90 **Data from pink sheet

BC = BUTYL CELLOSOLVE
BCA = BUTYL CELLOSOLVE ACETATE
C = CELLOSOLVE
CA = CELLOSOLVE ACETATE
MC = METHYL CELLOSOLVE
MCA = METHYL CELLOSOLVE ACETATE
PGME = PROPYLENE GLYCOL METHYL ETHER
PGMEA = PROPYLENE GLYCOL METHYL ETHER ACETATE

METHYLENE CHLORIDE

Two and four hour dynamic exposures to 50 ppm methylene chloride were made with Witco, Kuraray GA AW and 700 CH-10 wafers in 3520 OVM monitors. No difference was observed within experimental error between the amounts collected using the 3 sorbents. A seventeen minute dynamic exposure to 120 ppm methylene chloride at 77% RH was made with Witco, Kuraray GA AW and 700 CH-10 wafers in 3520 OVM monitors. This was then followed by 2 hour and 4 hour exposures to 0 ppm methylene chloride at 77% RH. All provided acceptable results for the initial exposure and the 2 hour high

humidity exposure. The Kuraray cloth and Witco wafers allowed more than our recommended 50% to migrate to the back-up wafer with 4 hours of high humidity exposure. The Kuraray GA AW wafers worked acceptably for all the exposures. The charcoal tubes showed sufficient migration to the back-up section after 2 hours that they would not meet NIOSH's criteria and after 4 hours showed losses of over 2/3 of the methylene chloride.

Several experiments were performed to revalidate the sampling rate for methylene chloride for our existing Witco wafers in the 3520 monitor in preparation for the proposed OSHA standard which came out in November.

METHYLENE CHLORIDE SAMPLING RATE VALIDATION

DATE	RH	PPM	EXPOSURE TIME	EXP.SAMP.RATE	NO.MON'S
2-14-91	77	103	17 min	39.0 +/- 3.8	6
6-6-91	80	41	1-5 hrs	39.3 +/- 1.7	10
7-10-91	dry	20	4 hrs	36.8 +/- 1.2	8
7-11-91	dry	63	4 hrs	37.1 +/- 2.2	6

The average recovery for 24 monitors was 0.910 +/-0.056. The average recovery for 16 charcoal tubes was 0.875 +/- 0.038. The average experimental sampling rate was 38.1 +/- 2.2 cc/min compared to the theoretical sampling rate calculated from the Hirschfelder equation of 37.9 cc/min. The laboratory validated sampling rate listed in our Sampling and Analytical Guides is 37.9 +/- 0.3 cc/min.

The relative capacity of several sorbents was determined for methylene chloride. The Supelco experimental carbon molecular sieves had the highest capacity. Ambersorb XEN-564 was next, followed by the Kuraray GA carbons which were still significantly better than the Witco carbons and Kuraray cloths.

METHYLENE CHLORIDE CAPACITIES
May, 1991 (33.13 MG SPIKE OPEN 1 DAY)

CARBON	CAPACITY (MG)
Witco	0.46
Ambersorb	2.25
Kuraray GA	0.56
Kuraray GA AW	0.63
Kuraray A1	1.22
Kur. 700CH-10	0.46
Kur. 700CH-15	0.26
Supelco 80-1	6.12
Supelco 80-2	4.18
Supelco 82-1	7.67
Supelco 82-2	5.59

HFC 123

The use of the OVM for the new Freon 12 substitute, HCFC-123, was documented. The calculated sampling rate is 31.4 cc/min. The laboratory validated rate at 2.9 ppm for 210 min was 31.3 +/- 2.6 cc/min. The uptake rate was shown to be linear at 2.9 ppm for 210 min and at 39 ppm for 170 min. No migration to the backup section occurred. The capacity determined in a static experiment to be 13.7 mg and in an exposure to 3418 ppm for 23 min to be 15 mg. In this latter experiment less than 1% migration to the backup was observed.

STYRENE

An industrial hygiene survey using OVMs was made at Larson Boats in Little Falls to evaluate the expected styrene concentrations in preparation for a workplace protection factor study. One monitor and charcoal tube were taken side-by-side and showed almost identical concentrations for three compounds (styrene, acetone and 1,1,1-trichloroethane). During the workplace protection factor study, 15 pairs of side by side monitors and charcoal tubes were taken. A very good correlation was obtained with the monitor showing an approximate 10% high bias when compared to charcoal tubes (see attached graph).

$$PPM(MONITORS) = 1.12*PPM(CTs) - 2.42$$

LONG TERM - LOW LEVEL EXPOSURES

Validation of the OVM for use as a long-term low level monitor has begun with a 65 3/4 hr 1.6 ppm toluene exposure followed by a 0 ppm exposure for additonal days. No toluene was found on any secondary section of the 3520 monitor. The amount predicted by our published 31.4 cc/min sampling rate was 1.088 mg. The amount found was 1.074 mg for the Witco monitors and 1.108 mg for the GA AW monitors. Our conclusion is that OVMs will work with acceptable accuracy for toluene at low concentrations for extended sampling times (5 3/4 days) at low RH.

The ACGIH has proposed to lower the TLV for benzene from 10 ppm to 0.1 ppm. The present OSHA standard is 1 ppm. We have been asked by customers for validation data at the 0.1 ppm level. Monitors and charcoal tubes were exposed to a low concentration of benzene for 8 hours at 80%RH. The concentration determined with the charcoal tubes was 0.119 ppm and with the monitors was 0.118 ppm. The OSHA accuracy was 11.6% which is well within the 25% requirement.

Long term low exposure tests with 1,1,1-trichloroethan were performed to validate the OVM use for ambient air and indoor air quality exposures. Tests were run at 93.75 Lpm, 30 % RH and 23 °C.

Exposure Time (days)	Exposure Conc. (ppm)	Amount Found (mg)	Amount Expected (mg)	OSHA Accuracy (%)
1	2.6	0.61	0.65	15.8
8	0.45	0.85	0.83	13.4

Nothing was found on the backup section after 1 day at 2.9 ppm or after 4 days at 0.45 ppm. Less than 1 % was found on the backup after 8 days at 0.45 ppm. These tests combined with the toluene test reported earlier show that the 3M OVM is suitable for ambient air and indoor air quality monitoring.

CONTAMINATION

Blank contamination tests on canned OVM retains have indicated that the adhesive in the monitor label is the source of the contamination. GC/MS tests at CRL have identified the major contaminants as oxidized Santovar A and trimethoxydibenzofuran. The oxidized Santovar A is a plasticizer/stabilizer used in adhesives and is known to impart a yellow color which we see in many desorbed samples. We are looking for a different adhesive for the label stock to resolve this problem. This would allow us to increase the shelf life.

CELGARD COMPARISON TESTS

The 3M RM specification for Celgard 2400 quotes the Hoechst-Celanese specification of a 25-60 sec Gurley. The Hoechst-Celanese test parameters are for a 10cc through 1 sq. in. test. All our Gurley tests are for 50 cc through 0.95 sq. in. Tests were run to determine the Gurley for the Celgard used in the past for monitor validations and the Celgard we are using now. Significant differences were seen. Significant differences were also seen in the readings between the Gurley meters in the lab and the pilot plant. I ran Gurleys in the pilot plant on the just received material, material we just finished using in production, old Celgard from the lab, and some 1984 monitors. The Gurley readings varied from 322 to 549 sec. All readings were outside the Celanese specification range even if our tests results are divided by 5 to make them comparable.

We ran an exposure test to see if the differences in the older and newer Celgard used in lab validations affected the

sampling rate. Monitors exposed to 59 ppm of methylene chloride for 261 min collected 1.69 +/- 0.10 mg with ld Celgard and 1.76 +/- 0.10 mg with newer Celgard which are not significantly different.

Monitors were assembled with Celgard 2400 and three 3M experimental films with different Gurleys and exposed to 55 ppm toluene for 120 min. The amount collected is shown in the following table.

WINDSCREEN	GURLEY (SEC)	THICKNESS (MILS)	AMOUNT COLLECTED (MG)
CELGARD 2400	340	1.0	0.760 +/-.049
770-1	275	1.2	0.763 +/-.014
817-8	55	1.5	0.786 +/-.036
FS 4-20-89 BF	7.5	3.6	0.803 +/-.059

While a trend to increased sampling rate with lower Gurley is observed a much larger sample size would be needed to determine if the differences are significant. A 5% improvement in sampling rate wouldn't justify revalidation of our rates. On the other hand, if the Celgard 2400 were no longer available, we could probably use the 770-1 without having to do a lot of validation of sampling rates. The 3M films are made with mineral oil which is washed out with 1,1,1-trichloroethane. I would be concerned about residual oil and wash solvent contaminating the charcoal wafer and whether compounds that are being sampled with the monitors dissolving in the residual oil rather than diffusing to th charcoal.

ETHYLENE OXIDE

An experiment was run to compare standards prepared from 2-bromoethanol with standards from monitors spiked with ETO gas dissolved in water indicating a recovery of 0.85 compared to 0.78 for 2-bromoethanol spiked monitors.

The ETO analytical method was revised to reflect present practice and will be printed up for distribution for customer service and hotline requests.

PROPYLENE OXIDE

The sampling rates for the 3520 and 3550 monitors were determined for propylene oxide. The 3520 collected 0.545 +/- 0.022 mg which gives a sampling rate of 40.2 +/- 1.62 cc/min. The 3550 monitors which were exposed to the same concentration for the same time were analyzed by the pilot plant and showed 0.548 +/- 0.027 mg. Monitors spiked with 0.498 mg by us were also analyzed by the pilot plant and

showed 0.500 +/- 0.003 mg. This shows that the sampling rates for the two monitors are equal. The average sampling rate for 5 exposure experiments over the past 18 months was 37.9 +/- 3.0 cc/min using an average experimental recovery of 1.00 for the 3500/3520 monitors.

FORMALDEHYDE

LOW BIAS

Historically the average ug formaldehyde found on the exposed monitors in the manufacturing quality assurance testing has been close to the LCL (lower control limit). The daily variability in the standard deviation of the tests caused a lot to be rejected when it was somewhat higher than average and allowed a lot to pass when it was somewhat lower than average.

A series of experiments was run to resolve this historically observed low bias in the QC exposure results. The reason has been identified and corrected.

a. Titration of the pilot plant Fisher and lab Aldrich 37% formaldehyde showed identical and accurate 37% concentrations.

b. Lab and pilot plant working standards were compared and while some differences occurred, I believe they represent day-to- day variability in the method rather than any significant inter- lab bias.

c. Flat vs. upright orientation of the exposed monitors was investigated. Some differences occurred, but I believe them to be random day-to-day variations rather than a significant bias. We have however begun to use the upright orientation as it is easier to expose larger numbers of monitors at the same time.

d. A heated aluminum block rather than a heated flask is now being used to evaporate the formaldehyde. This keeps the exposure temperature closer to room temperature and avoids having to consider a temperature correction for the sampling rate.

e. A lower exposure concentration of 1.1 ppm rather than 2 ppm resulted in a lower amount of formaldehyde being collected on the monitors and in the impingers. This lower amount fell in the middle of the standard curve rather than at or above the highest standard. The range of standards is such that a curve rather than a straight line calibration exists on the Technicon analyzer and the amount of curvature appears to vary from day to day. I believe that the Technicon analyzer was not accurately determining the

absorbance of the monitor samples at the high end of the curve and that the lower concentration will correct the problem. We also found that the Technicon analyzer was drawing a straight line through the standards on some days rather than a curve so I have recommended that the curve be printed out with every run. I don't know if this was a software bug or operator error.

HIGH BLANK

Monitors containing experimental glass fiber wafers were packaged in cans. Samples were sent to NATLSCO and Parker Services for evaluation. Our analysis showed significantly lower blanks compared to paper wafers prepared at the same time.

FORMALDEHYDE BLANK LEVELS (UG)

Filter	Date Analyzed	Formaldehyde (ug)	
Paper 1056A	3-21	2.81	
	4-5	1.20	NATLSCO
	4-10	2.60	
	5-10	3.02	
	5-15	1.45	PARKER
	6-19	3.36	
	7-19	3.53	
Whatman	3-21	0.61	
	4-5	0.57	NATLSCO
	4-10	0.57	
	5-10	1.00	
	5-15	1.04	PARKER
Gelman	3-21	0.69	
	4-5	0.23	NATLSCO
	4-10	0.70	
	5-10	1.23	
	5-15	0.56	PARKER
	6-19	1.06	
	8-5	1.86	

FORMALDEHYDE BLANK LEVELS (UG)

Lot	Date Analyzed	Formaldehyde (ug)
9275	3-21	5.00
0229	4-10	3.99
0240	7-19	5.29
1169	7-19	1.55
8-17-90	8-5	5.03
8-22-90	8-5	5.34
9-10-90	8-5	4.42
12-13-90	8-5	2.38
3-15-91	8-5	2.53
1206	8-7	1.84
1168	9-27	2.55
1169	9-27	2.50
0240	11-15	6.15
0304	11-15	3.67
1059	11-15	2.59
1303	11-15	1.57
8097	11-15	2.90
8112	11-15	3.62
1206	11-15	2.48
1206	8-13	1.84

The lot 0240 has a much higher blank than monitors made over 3 years ago.

Periodic analysis of blanks from the first Gelman glass fiber lot shows increasing values with time, but still much lower than the paper wafer controls.

Packaged monitors containing glass fiber wafers which had undergone the ASTM 4919 vibration and NST drop tests were examined and no visible signs of deterioration were observed. Five of each were analyzed manually for blank contamination and no significant difference between those that had undergone the shipping tests and those that had not could be seen. Five of each were exposed in the pilot plant QC exposure chamber and analyzed on the Technicon. The Whatman filters had a large negative bias and large standard deviation which caused them to fail. The Gelman filters had a higher standard deviation than the paper wafers and just failed the QC test. I don't know if the failures are due to having ship tested them or if it is due to problems with the Technicon analysis of the fragile glass fiber filters generally.

Preparation of a second lot of wafers using Gelman and Whatman glass fiber filter material resulted in wafers with erratic levels of bisulfite (Gelman) and almost no bisulfite (Whatman). It is very possible that paper wafers would have failed also. We have since been able to make small batches

that pass QC and a full-scale test with elevated temperature ageing is in progress.

MERCURY

We exposed 3 used customer monitors to a known concentration of mercury equivalent to 8 hours at 0.024 mg/m^3 and found that our monitors performed as predicted in response to a complaint that our mercury monitors did not pick up any mercury when they should have.

Concentration = 0.096 mg/m^3 for 2 hours

Monitor No.	R_f	R_i	R_{diff}	Conc.	Equiv. 8 hr TWA
NF2453	2641	2584	57	0.098	0.025
NF2451	2692	2633	59	0.097	0.024
NF2434	2685	2623	62	0.102	0.026

ANALYSIS LABORATORY

A mixture of toluene, isopropanol and methyl chloroform is now being run with every set of samples to provide documentation of the GC response.

A second GC was obtained and installed for OVM analysis to handle overflow and provide backup for the HP5880. Calibration of the new instrument is in progress.

The computer program was updated to perform the calculations for 3520/3530 OVMs with backup. The report will fit on the existing report form.

The analytical method was rewritten to include analysis of 3520/3530 monitors, analysis of standards with every set of samples, and to reflect the present capillary column parameters. The method is being reproduced for use by technical service to answer customer requests.

Several compounds were added to the analysis list and the Monitor Record Form was revised to include the new compounds as well as the 3530 Monitor Analysis.

NEW MONITORS

The Quantum Group carbon monoxide qualitative monitor was exposed to approximately 1/2 the IDLH (739 ppm)and to the OSHA ceiling (200 ppm) for 15-20 min. At 739 ppm the monitors required 10 min to get to a dark green (Pantone

119U) and 15 min to get to a blue/gray color. At 200 ppm it took 15 min to get to a light green (117U) and 20 min to get to a medium green (from 117U-119U).

The Quantum Group, Inc. (QGI) MD-3 sensor chips were evaluated at 30, 50, and 100 ppm at 50%RH and at 30 ppm at 80%RH. The rate of response of the monitor varied with concentration. The amount collected in a classical diffusion monitor is directly proportional to the concentration times the time. The sampling rate depends on the geometry of the monitor and is independent of the concentration. No mathematical model has been established for the Quantum Group, Inc. (QGI) carbon monoxide monitor.

The log of the initial reading divided by the reading after exposure (log I_o/I_f) was plotted vs. the concentration times the exposure time (ppm-hrs). Each experiment yielded a straight line as shown in the attached graph.

$\log (I_o/I_f) = (0.0138)(\text{ppm-hrs}) + 0.296$ @100 ppm/50%RH

$\log (I_o/I_f) = (0.0104)(\text{ppm-hrs}) + 0.303$ @ 50 ppm/50%RH

$\log (I_o/I_f) = (0.0095)(\text{ppm-hrs}) + 0.137$ @ 30 ppm/50%RH

$\log (I_o/I_f) = (0.0090)(\text{ppm-hrs}) + 0.191$ @ 30 ppm/80%RH

No significant difference was seen between the response at 30 ppm with 50%RH and 80%RH. The effect of humidity when the monitor has sufficient silica gel capacity remaining appears to be insignificant.

The slope of the response curve varies with the concentration to which the monitor is exposed. It is not possible to determine the correct ppm-hrs of exposure unless you know which curve (i.e. slope) to use in programming the reader. If one chose to calibrate the reader using the slope for 50 ppm, the bias from the true TWA concentration would be +32% for a 1 hour exposure at 100 ppm and -26% for a 3 hour exposure at 30 ppm. Ambient concentrations above 100 ppm or below 30 ppm would be expected to show even greater biases.

The precision (coefficient of variation) for the 100 ppm experiment was 8.5%, 6.2% for 50 ppm and 8.1% for 30 ppm.

The OSHA accuracy ($1.98(CV)+|bias| \leq 25\%$) for the present monitor is well in excess of the acceptable +/-25%.

The capacity of the monitor is limited to 150-200 ppm-hrs for the present configuration. For a monitor to measure 8 hours at 2 times the PEL of 35 ppm we need 560 ppm-hrs.

Tighter specifications on manufactured monitors vs. prototypes would probably improve the precision to 5%. Changes in the monitor configuration, such as a longer distance from the opening to the chip or reduced opening size, might improve the capacity to the needed level. We are told that a reader with more range is also possible. The difference in response rate with concentration is a serious impediment to the use of the MD-3 chip in a TWA monitor. Changes in chemistry of the chip appear necessary to make a TWA monitor possible.

MISCELLANEOUS

Static saturated carbon tetrachloride activity tests were run on 35 X 35 mm sections of Polyethylene Loaded Carbon films made with Anderson AX-21 carbon (stretched and unstretched) and Calgon carbon. Typical OVM wafers which contain about 150 mg of Witco carbon will pick up 100 mg of carbon tetrachloride in one hour. The stretched Calgon carbon picked up <1 mg, stretched Anderson 6 mg and unstretched Anderson 33 mg. After 18 hours the stretched Calgon picked up 25 mg, stretched Anderson 39 and unstretched Anderson 186. After standing open overnight a typical Witco wafer will retain 25 mg of CCl_4. After 2 hours the carbon loaded films retained only 1-2 mg. Steamed Polyethylene Loaded Carbon was challenged at 813 ppm CCl_4 in the ASTM permeation test cell. Breakthrough was almost instantaneous. No improvement was observed over the unsteamed film. No further work is anticipated with the carbon loaded films.

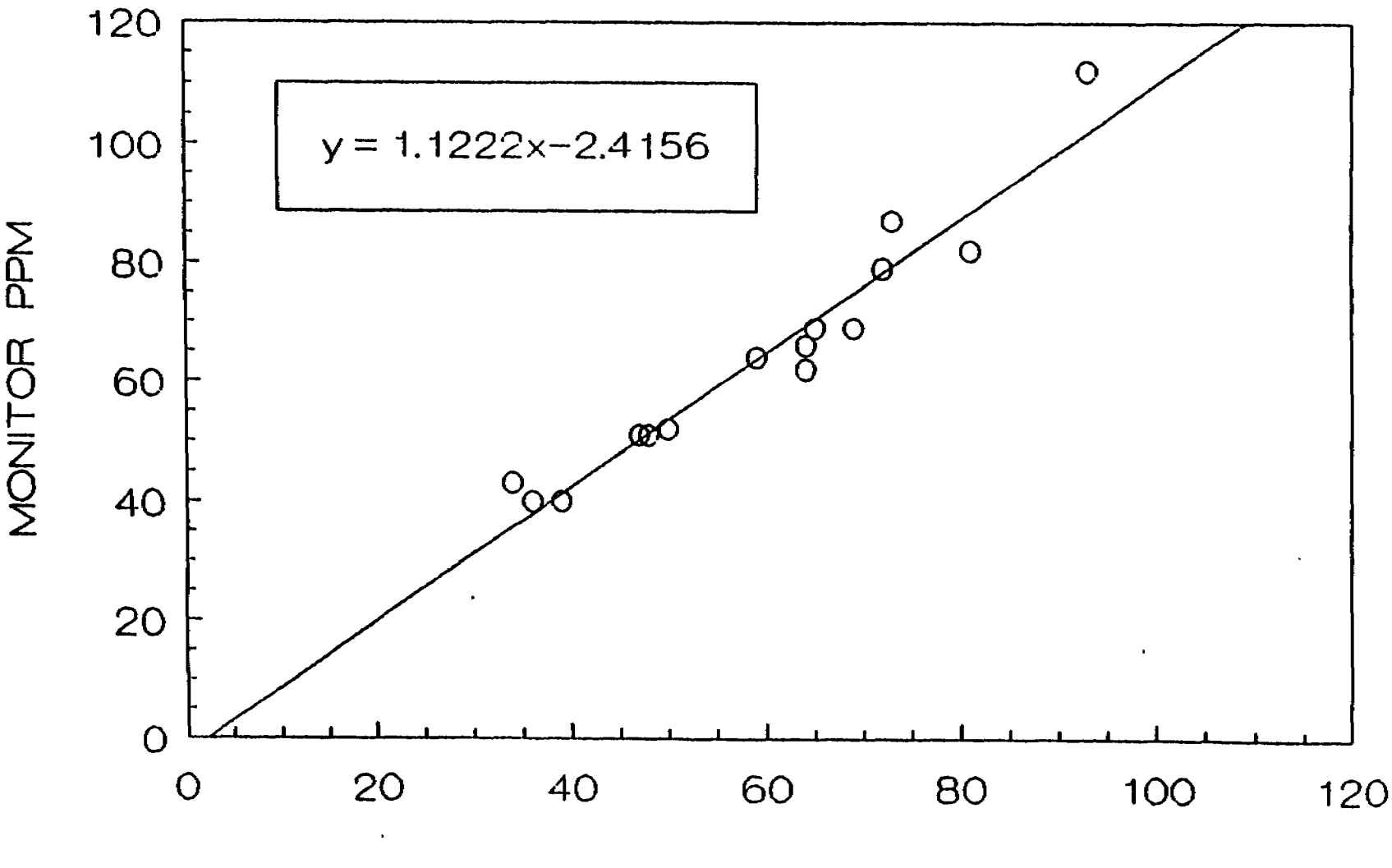
A gas chromatographic method was developed for methyl iodide using a gas sampling valve, 30 m X .53 mm ID X 3 um film J&W DB624 megabore capillary column and electron capture detector.

I participated in the evaluation of a proposal from Plastech, Corp., Rush City, MN to manufacture the monitors except for mercury. The proposal includes making the wafers, assembly and packaging the monitors and performing the quality control tests.

"Dishing" of the primary cups became a significant problem. I worked with Jim Burns, Mark Chouanard, Paul Flannigan and Plastech to resolve this problem by coating the mold as a temporary fix and proposing some design changes which will be tried in 1992 as a permanent solution.

Thermal Desorpti n - Two brainstorming sessions were held with members of the OH&ESD Lab to discuss ways to improve the sensitivity of our OVMs. Our concensus was that at least a 10X improvement was necessary to make any changes worthwhile. We concluded that geometric changes could at most improve the sensitivity by 4 times. Thermal desorption has the potential for up to 1000X improvement. Thermal desorption experiments on our Witco carbon wafer at CRL, EE&PC and Tekmar (thermal desorber/headspace analyzer manufacturer) have not been successful. The desorption efficiency was very low. Future work will include investigation of other sorbents such as carbon molecular sieves and Tenax. Future work will also depend on obtaining a thermal desorber for our own use as does not appear cost effective to perform the studies of the various parameters affecting the desorption with spiked samples submitted to CRL, EE&PC or an outside lab.

STYRENE FIELD TEST
CT VS MONITOR 4-91



CO MONITOR EVALUATION