Technical Report Summary

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Author(s): D.. J. Larsen - OH&ESD - 260-3B-08, T. V. Le - 260-3B-08			Employee Number(s): 287513, 317259	
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Project Objective & Report Abstract:
Accomplishments of the 1993 Diffusion Monitor Program include validation of the replacement carbon for Organic Vapor Monitors and Ethylene Oxide Monitors, revision of the Sampling and Analytical guides into a single document with new data for over 100 compounds, introduction of the new carbon, moving the manufacturing of OVMs and ETOs to Plastech, evaluation of a silica molecular sieve for alcohols and thermal desorption,validation of the OVM for HCFC124 and 134a, 6 month aging study of Vitek foil packaging as a replacement for the can.

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1993 MONITOR TECHNICAL REPORT

SUMMARY

1. Kuraray GA AW carbon was introduced in September. A new sampling and analysis guide containing new data on more than 110 compounds was published and distributed. Technical support and documentation was provided for the move to Plastech which occurred in September. A six month aging test on our primary candidate material (Vitek) showed that all monitors functioned properly after storage in foil. However, it was discovered that the OVM blank was unacceptable and the conversion to foil bags is on hold until a new material can be found. Evaluation of the new monitor molds showed that the elution cap mold was not acceptable and modification will be necessary.

2. Monitor research programs were prioritized to a) prepare and present paper at the AIHCE in May, 1994; b) research the thermal desorption/silica molecular sieve monitor; c) resolve NIOSH validation issues. Initial experiments in the lab and Med/Surg Pilot Plant have been run which show that extended sampling times with OVMs are possible. Teflon/silica molecular sieve wafers were prepared and tested using solvent desorption. An oven has been constructed to try thermal desorption. Validation issues will be addressed in 1994.

3. Sampling rates were determined for HCFCs 124 and 134a. Recoveries for acetic acid were determined showing that use of the OVM may be possible. We responded to many tech service requests for information and testing.

4. Initial experiments were run to validate the sampling rate for the mercury monitor and to investigate the response for short exposures. The mercury monitor computer calculation was improved to remove anomalies at short sampling times. We worked with 3M Singapore and 3M Ecuador to assist local labs attain proficiency in monitor analysis.

CARBON QUALIFICATION

Four lots of carbon/Teflon wafers were successfully produced using the new carbon on December 111, 1991 (Lot 236), December 10, 1992 (Lot 259), February 16, 1993 (Lot 265) and April 13, 1993 (Lot 272). All the lots passed the OVM contamination, MEK recovery, and CTA tests. ETO wafers were made from three of the lots and passed the ETO recovery test. OVMs made from Lot 259 were tested with a toluene exposure and found to have the same sampling rate as Witco wafers. Recoveries and capacities were determined for over 110 compounds on both the new carbon and the original Witco carbon (See Section 2). A new combined Sampling and Analysis Guide which includes all the new recovery and capacity data for both the Witco (original) and Kuraray (current) carbons was published and distributed.

Toluene Uptake Rate - Kuraray GA AW monitors were exposed to 99.4 ppm of toluene for 135 minutes at 50%RH and then analyzed. The amount expected was 1.588 mg. The average amount found for monitors aged in Vitek bags was 1.608 +/- .064 mg and for aged cans was 1.622 +/- .047 mg and for Witco Lot 2140 controls was 1.658 +/- .068 mg. The OSHA accuracy for all the aged monitors including controls was 9.14% which meets the OSHA accuracy requirement of 25%.

A smooth transition was made from the original carbon (Witco) to the current carbon (Kuraray GA Acid Washed) in September. All new OVMs and ETOs (3500, 3510, 3520, 3530, 3550, & 3551) carry the carbon lot designation "009" on the shipping box and have monitor codes with a "C" following the four digits. The labels for the new carbon have the B184 adhesive rather than the B82 used previously. (See Section 2 Subsection OVM Contamination) New Make-Orders were written for wafer making (MO #56) and assembly (MO #57) to reflect the use of the new carbon.

OVM

ACETIC ACID - An analytical method was developed for acetic acid. I found that using methanol as the solvent and chromatography on a 30 M X .25 mm ID X .25 um film DB-FFAP column would give good results. The recovery of acetic acid from the OVM was determined to be 87%. It was necessary to spike directly onto the wafer as some of the acetic acid was retained in the filter paper disc in our standard procedure. The calculated sampling rate for acetic acid is 42.1 cc/min.

ETOH - Validation of the OVM for EtOH was done using the double decker (see the attached figures) with desorption by acetonitrile which has much higher recovery than CS2. The sampling rate was 43.9 +/- 1.2 cc/min (+/-2.7%) using an exposure of 4 hours at 73 ppm and 30% RH and 43.5 +/- 3.3 cc/min (+/-7.6%) using 1-4 hours at 183 ppm and 80% RH. The calculated sampling rate in 44.7 cc/min and the sampling rate listed in the pink sheet is 51.2 cc/min. The recovery was 98% from Kuraray GAAW Lot 272 carbon wafers with acetonitrile compared to 37% with CS2.

Double-decker Kuraray 265 monitors were exposed to EtOH at 347 ppm and 31 % RH for 1 to 6 hours. The average sampling rate was 43.8 +/- 2.1 cc/min. The uptake rate was linear for 6 hours. The amount collected on the primary section deviated from linearity after 2 hours or 3.5 mg collected. We can conclude from this that the 3500 OVM capacity is at least 3.5 mg.

FREON SUBSTITUTES - Sampling rates were determined for two DuPont Freon substitutes, HCFC 124 and HFC 134a. Testing of the 134a at 178 ppm and <30% RH indicates that a Kuraray GAAW double-decker is good for 2 1/2 hours vs. only 1 hour for Witco. The capacity was 3.9 mg for Kuraray vs. 1.5 for the Witco. At 155 ppm and 50% RH the uptake rate was linear for 2 hours and at 80% RH linear for 1 1/2 hours with respective capacities of 2.4 mg and 1.9 mg for the Kuraray carbon. The recovery of 134a with isopropanol was 0.62 for Witco and 0.61 for Kuraray. The experimental sampling rate of 37.1 +/- 3.9 cc/min showed excellent agreement with the calculated rate of 37.5. Testing of the 124 at 133 ppm and <30% RH indicates that a Kuraray GAAW double-decker has a linear uptake rate for 4 hours with a capacity of 6.3 mg. At 133 ppm and 80% RH the monitor is linear up to 1 1/2 hours with a capacity of 2.7 mg. The recovery of 124 with isopropanol was 0.87 with Kuraray. A sampling rate of 35.8 +/-2.1 cc/min was found compared to the calculated rate of 33.7 cc/min.

ALCOHOLS - Alcohols generally have poor recovery from charcoal with CS2. NIOSH methods recommend using 1% isopropanol in CS2 to improve the recovery for n-butanol. This isn't possible when the sample also contains isopropanol. The use of 5% 2(2-butoxyethoxy)ethanol in CS2 has been reported in the literature and was tested on Witco wafers and reported in my 1990 Technical Report. Tests on the Kuraray 259 monitors are shown in the following table:

ALCOHOL	Spike (mg)	Rec MC	Rec 5% 2-(2-BEE)
IPA	.236	0.83	0.81
	.471	0.86	0.82
n-Butanol	.243	0.86	0.99
	.486	0.86	0.91

FIELD TEST - A field test was run December 6-8 to compare charcoal tubes to OVMs for mixtures of solvents at PPG Industries, Inc. in Pittsburgh.

OUS MONITOR ANALYSIS - We prepared and sent QA OVM spikes containing two levels of benzene, toluene and xylene to Soh Guat Hiong, Eduardo Suarez, and our monitor analysis lab.

RECOVERY AND CAPACITY FOR WITCO AND KURARAY GA AW

		RECOVERY	
COMPOUND	SPIKE(mg)	WITCO	K265
Acetone	3.16	0.91	0.91
Allyl Alcohol	0.043	0.78 MC	0.74 MC
Allyl Chloride	.047	0.86	0.86
n-Amyl Alcohol	2.43	1.01 MC	0.96 MC
n-Amyl Alcohol	3.24	0.72	0.70
#Benzene	0.05	0.97	0.97
Benzyl Chloride	.033	0.87	0.89
i-Butyl Acetate	5.21	1.01	1.02
n-Butyl Acetate	5.29	1.04	1.07
t-Butyl Acetate	6.90	0.99	0.98
Butyl Acrylate	0.36	1.07	1.06
n-Butyl Alcohol	2.43	0.95 MC	0.95 MC
i-Butyl Alcohol	1.61	0.96 MC	0.93 MC
s-Butyl Alcohol	2.42	0.89 MC	0.89 MC
t-Butyl Alcohol	2.36	0.77	0.75
t-Butyl Alcohol	2.36	0.74	0.73
Butyl Cellosolve	0.90	0.91 MC	0.91 MC

RECOVERY

COMPOUND	SPIKE(mg)	WITCO	K265
Butyl Glycidyl Ether	0.91	0.93	0.93
t-Butyl Methyl Ether	2.27	0.98	0.95
p-tert-Butyltoluene	0.34	1.08	1.07
Carbon tetrachloride	0.096	1.04	0.95
Cellosolve	0.23	0.93 MC	0.92 MC
Cellosolve Acetate	1.95	0.93	0.96
Chlorobromomethane	9.96	0.91	0.90
Chloroform	0.07	0.95	0.95
1-Chloro-1-nitropropane	0.06	0	0
1-Chloro-1-nitropropane	0.06	0 MC	0 MC
Cyclohexane	7.79	1.01	1.02
Cyclohexanol	1.93	1.03 MC	1.02 MC
Cyclopentane	15.0	1.02	1.02
Diacetone Alcohol	1.86	1.00 MC	0.94 MC
#1,2-Dibromoethane (Ethylene dibromide)	1.09	0.90	0.93
1,1-Dichloroethane	0.036	1.08	0.92
1,1-Dichloroethane	3.53	0.98	0.94
1,2-Dichloroethane (Ethylene Dichloride)	7.54	1.00	0.98
1,1-Dichloroethene (Vinylidene Chloride)	3.64	0.98	1.00
#1,2-Dichloroethylene	6.33	0.96	0.96
#Diethyl Ketone	5.12	0.98	0.98
#1,4-Dioxane	0.72	0.94	0.91
Divinyl Benzene	0.27	0.51	0.47
Epichlorohydrin	0.059	0.86	0.85
Epichlorohydrin	0.059	0.95 MC	0.91 MC
Ethrane	0.10	0.84	0.81
Ethyl Acetate	11.7	0.99	0.99
Ethyl Alcohol	7.85	0.89 A	0.89 A
Ethylbenzene	2.60	0.94	0.96
Forane	0.10	0.75	0.76
Halothane	0.11	0.93	0.91
n-Heptane	10.9	1.02	1.04
3-Heptanone	2.45	0.70	0.68
4-Heptanone	2.45	0.67	0.66
n-Hexane	1.32	1.00	1.03
2-Hexanone	0.16	1.00	1.00
Isoamyl Acetate	3.50	0.96	0.97
Isoamyl acetate	3.50	0.98	0.97
Isoamyl Alcohol	3.24	0.82	0.77
Isobutyl Alcohol	1.61	0.73	0.74

RECOVERY

COMPOUND	SPIKE(mg)	WITCO	K265
2-Isopropoxyethanol	0.48	0.95	0.92
Isopropyl Acetate	7.85	0.97	0.96
#Isopropyl Alcohol	4.71	0.59	0.57
#Isopropyl Alcohol	2.36	0.61	0.59
Isopropyl Ether	2.18	1.03	1.03
Isooctyl Alcohol	2.44	0.84	0.80
Methyl Acetate	5.59	1.02	0.92
Methyl Acrylate	0.287	0.91	0.87
#Methyl Amyl Ketone	3.28	1.03	0.98
Methyl Cellosolve Acetate	0.15	0.89	0.86
Methylcyclohexane	11.6	1.02	1.03
3-Methylcylcohexanol	1.83	0.88	0.83
Methylene Chloride	2.65	0.97	0.97
Methyl Ethyl Ketone	1.61		0.92
MEK	2.42	0.96	0.95
5-Methyl-3-heptanone	0.97	0.82	0.83
Methyl Isoamyl Ketone	1.78	1.01	1.01
Methyl Isobutyl Carbinol	0.80	0.83	0.81
Methyl Isobutyl Ketone	1.60	0.99	0.99
Methyl Isopropyl Ketone	5.64	0.95	0.91
Methyl Methacrylate	1.00	1.03	1.05
alpha-Methyl Styrene	1.82	1.07	1.02
Morpholine	1.00		0.25
#Naphtha	8.60	1.00	0.92
n-Nonane	5.74	1.05	1.09
n-Pentane	8.14	1.00	0.98
2-Pentanone	5.68	0.94	0.93
n-Propyl Alcohol	4.82	0.85 MC	0.85 MC
PGMEA	2.90	1.00	1.01
Propylene Oxide	0.42	0.99	0.84
Propyl nitrate	3.17	1.03	1.02
#Stoddard Solvent	3.02	1.09	0.98
#Styrene	1.82	0.94	0.90
Styrene (2 wks RT)	1.82	0.96	0.89
Styrene (2 wks Cold)	1.82	0.98	0.91
#Tetrahydrofuran	5.32	0.99	1.01
1,1,2-Trichloroethane	2.87	1.00	0.95
Trichloroethylene	2.93	1.02	1.01
1,2,3-Trichloropropane	0.69	1.03	0.99
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	0.36	0.96	0.92
Vinyl Acetate	0.28	0.87	0.82

CAPACITY

COMPOUND	SPIKE(mg)	WITCO	K265
Acetonitrile	3.9	.007	.02
Allyl Alcohol	17.1	3.1	5.6
Allyl Chloride	4.7	2.7	3.1
n-Amyl Alcohol	24.3	23.5	22.4
Benzyl Chloride	33	30.6	29.7
i-Butyl Acetate	26.0	22.6	25.1
n-Butyl Acetate	26.5	26.3	26.5
t-Butyl Acetate	25.9	22.1	22.1
Butyl Acrylate	26.8	26.5	26.9
n-Butyl Alcohol	24.3	19.2	21.2
i-Butyl Alcohol	24.1	17.8	19.2
s-Butyl Alcohol	24.2	15.5	19.6
t-Butyl Alcohol	23.6	11.8	15.3
Butyl Cellosolve	27.1	25.4	24.6
Butyl Glycidyl Ether	27.3	27.3	25.6
t-Butyl Methyl Ether	26.5	12.5	16.9
p-tert-Butyltoluene	25.6	31.4	25.9
Cellosolve (2-Ethoxyethanol)	27.9	17.7	25.5
Cellosolve Acetate	29.3	29.5	29.2
Chlorobromomethane	29.9	7.4	18.6
1-Chloro-1-nitropropane	24.2	13.9	13.4
Cyclohexane	23.4	7.4	13.1
Cyclohexanol	24.1	23.0	22.6
Cyclopentane	26	3.0	5.4
#1,2-Dibromoethane (Ethylene Dibromide)		21.0	21.0
1,2-Dichlorobenzene	26.1	26.8	26.8
1,1-Dichloroethane	23.5	7.6	13.3
1,2-Dichloroethane (Ethylene Dichloride)	25.1	9.5	16.2
1,1-Dichloroethene (Vinylidene Chloride)	24.3	3.8	4.7
#1,2-Dichloroethylene	25.3	2.0	3.3
#Diethyl Ketone	25.6	22.9	23.7
#1,4-Dioxane	25.9	14.0	21.0
Divinyl Benzene	27.4	21.9	20.0
Epichlorohydrin	29.6	13.4	20.3
Ethrane	15.2	6.0	8.6
Ethyl Alcohol	19.6	0.90	0.19
Ethylbenzene	26.0	23.0	24.5
Forane	14.5	6.0	7.4
Halothane	18.7	7.6	10.8

CAPACITY

COMPOUND	SPIKE(mg)	WITCO	K265
2-Hexanone	24.4	23.6	24.0
Isoamyl Acetate	26	25.7	26.4
2-Isopropoxyethanol	27	24	23
#Isopropyl Alcohol	15.7	4.2	9.6
Methyl Acetate	18.6	1.7	3.3
Methyl Acrylate	19.1	11.0	11.7
#Methyl Amyl Ketone	24.6	24.0	24.0
Methylcyclohexane	23.2	20.2	21.9
5-Methyl-3-heptanone	24.7	24.3	24.9
Methyl Isoamyl Ketone	26.6	26.2	27.1
Methyl Isobutyl Carbinol	24.1	21.5	21.0
Methyl Isobutyl Ketone	28	26	27
alpha-Methyl Styrene	27.3	25.2	25.0
#Naphtha	25.8	25.0	24.0
n-Pentane	18.8	9.3	12.0
2-Pentanone	28	24	24
n-Propyl Alcohol	24.1	5.1	8.5
Propylene Oxide	24.9	0.22	0.94
Propyl Nitrate	26.5	22.7	25.6
#Stoddard Solvent	22.7	22.0	21.0
1,1,2-Trichloroethane	28.7	27.3	27.9
1,2,3-Trichloropropane	27.7	29.4	29.4
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	28.7	5.1	11.4
#Vinyl Acetate	23.4	6.2	9.5

Recoveries and capacities not yet included in the sampling and analytical guide are marked with an #.

OVM CONTAMINATION - We have recently noticed several contamination peaks which appear to be coming from the plastic parts. The contamination peaks were identified by Joe Schroepfer and Rick Rossiter at CRL using GC/MS as C6 caprolactam, C11 caprolactam, and butyl benzyl sulfonamide. The contamination peaks are present in older resins and parts but appeared at lower levels in our QC tests which did not integrate on the GC. We have not determined a reason why we are now seeing larger contamination peaks but are keeping records of the levels and will try to correlate this with levels in incoming raw resin so as to be able to write a specification for the raw material. At this time we will not include the three raw resin peaks in our quality control contamination calculation but will report it to any client that expresses interest in documentation of blank levels (NATLSCO, EXXON). I rewrote the test method to include these calculations and wrote a variance to the test specifications for the resin related peaks.

Kuraray monitors were aged for 6 months at 130 C in cans and in Vitek foil bags. Both the Vitek bag and the can show similar results. Both show the presence of several contamination peaks which we have associated with problems with the raw resin. We recently have seen this problem in recently manufactured room temperature monitors, but it took 3 months at 130 C to show the contamination from monitor bodies that we were using around the first of the year.

In 1991 CRL identified by GC/MS several contamination peaks coming from the label adhesive as oxidized Santovar A and trimethoxydibenzofuran. Testing in the pilot plant indicated that the B184 adhesive showed less contamination peaks than the B82 adhesive previously used, so labels ordered from Label Products, Inc. since September, 1993 have the B184 adhesive.

RECOVERY AGING STUDIES - The recoveries of methylene chloride, toluene, styrene, MEK and vinyl acetate were determined after one day and after 2 weeks.

The recovery of methylene chloride from the Organic Vapor Monitor was determined after 1 day at room temperature, 2 weeks at room temperature and 2 weeks refrigerated at 8 C. No significant differences were observed.

Fifteen original carbon monitors and 15 current carbon monitors were spiked with 1.590 mg methylene chloride and 40 mg water (maximum amount picked up at 80% RH) using our published recovery procedure and allowed to stand overnight at room temperature. The filter paper was removed and one set of monitors was analyzed, one set was allowed to stand 2 weeks at room temperature of 22 C before analysis and one set was allowed to stand 2 weeks refrigerated at 8 C. The monitors were desorbed with 1 1/2 mL CS2 for 30 minutes and analyzed by gas chromatography using a 30 m DB5 capillary column. Results are shown in the following table.

TIME	RECOVERY ORIGINAL CARBON	RECOVERY CURRENT CARBON
1 DAY	0.945 +/- .007	0.930 +/- .018
2 WEEKS RT	0.909 +/- .025	0.918 +/- .019
2 WEEKS COLD	0.934 +/- .007	0.926 +/- .014

No significant change in recovery occurred during two weeks of storage.

The recovery of styrene from the Organic Vapor Monitor was determined after 1 day at room temperature, 2 weeks at room temperature and 2 weeks refrigerated at 8 C. No significant difference was observed.

Twelve original carbon monitors and 12 current carbon monitors were spiked with 1.818 mg styrene using our published recovery procedure and allowed to stand overnight at room temperature. The filter paper was removed and one set of monitors was analyzed, one set was allowed to stand 2 weeks at room temperature of 22 C before analysis and one set was allowed to stand 2 weeks refrigerated at 8 C. The monitors were desorbed with 1 1/2 mL CS2 for 30 minutes and analyzed by gas chromatography using a 30 m DBWAX capillary column. Results are shown in the following table.

TIME	RECOVERY ORIGINAL CARBON	RECOVERY CURRENT CARBON
1 DAY	0.94 +/- .02	0.90 +/- .01
2 WEEKS RT	0.96 +/- .01	0.89 +/- .02
2 WEEKS COLD	0.98 +/- .01	0.91 +/- .04

No significant change in recovery occurred during two weeks of storage.

RECOVERY

COMPOUND	SPIKE(mg)	WITCO	K265
MEK(1dayRT)	4.03 (wet)	0.76	0.85
MEK(2wksRT)	4.03 (wet)	0.64	0.72
MEK(2wksCold)	4.03 (wet)	0.75	0.82
VA (5daysRT)	.28 (dry)	0.99	0.96
VA (1dayRT)	.28 (dry)	—	0.99
VA (1dayRT)	.28 (wet)	—	0.91
VA (2wksRT)	.28 (dry)	—	0.92
VA (2wksRT)	.28 (wet)	—	0.81
VA (2wksCold)	.28 (wet)	—	1.01
VA (5daysRT+1wkCold	.28 (wet)	—	0.82

At high humidities, both MEK and vinyl acetate showed significant decreases in recovery at room temperature and should therefore be refrigerated if analysis is delayed.

Toluene at high humidity did not show any significant decrease in recovery in storage. See data in the subsection on NIOSH/CEN validation.

CUSTOMER COMPLAINT INVESTIGATIONS - A complaint was received from Traveler's Insurance that monitor recoveries for alcohols had decreased significantly lately. The lots in question were 3194 and 3239. I also tested a much older lot and the Witco and Kuraray wafers I use for validation. I spiked the monitors with 2.36 mg of isopropanol.

LOT	RECOVERY (3M Method)	RECOVERY (Equil. Meth.)
2161	0.60+/-.03	0.39
3194	0.57+/-.02	0.44
3239	0.50+/-.02	0.34
WITCO	0.61+/-.01	0.48
K265	0.59+/-.01	0.53

A complaint was received from HIH Labs that their recovery for Methyl Methacrylate recoveries had recently decreased significantly (Lot 3200). Historically we have gotten about 100%. They are now seeing 30%. Our tests on retains from Lot 3200, Witco wafers and Kuraray 265 wafers showed an average recovery of 1.02 +/- .03.

A complaint was received from Miles that their OVMs are showing a large number of contaminant peaks (Lot 3084). We did not see evidence of this on our retains but did see it on one of three returned monitors. We are trying to resolve whether this is due to old labels, resin peaks or some other problem which is below our present detection limit for the QC test.

LOD IMPROVEMENT - Rich Bernier and I met with John Freeburg, Hewlett-Packard, to discuss ways to improve the limits of detection for our GCs. His suggestions included: 1)optimizing the H2/air ratio; 2)switching to N2 for make-up air instead of He; 3)using a narrower bore column; 4)put in a new jet; 5)switch to electronic pressure control and increase the amount injected. John told us that going to splitless or on-column injections would give us about 10X improvement but that these two techniques have the serious limitations that you lose any pre-CS2 eluting peaks and usually also lose any peaks which come shortly after the CS2.

LONG TERM LOW CONCENTRATION (AIHCE PAPER) - Bob Weber's and my paper on the use of diffusion monitors for long term ambient exposures has been accepted for the AIHCE.

Bob Weber exposed double-decker monitors to low concentrations of IPA and n-Butanol for 3 days in a Bldg. 270 pilot plant. Charcoal tubes were taken on day 1 and day 3. Results shown in the following table indicate that monitors can be used successfully for extended time periods.

COMPOUND	MONITOR PPM	CHARCOAL TUBE PPM
Isopropanol	0.55 +/-0.07	0.48 +/- 0.11
n-Butyl Alcohol	0.18 +/-0.008	0.17 +/- 0.03

I exposed 6 monitors to 2.86 ppm acetone at 30% RH for 5 days in our exposure chamber. After 5 days of exposure the monitors indicated 2.57 +/- 0.09 ppm. The bias was 10.3% with a CV of 3.55% for an OSHA accuracy of 17.4% which meets the 25% requirement.

NIOSH/CEN VALIDATION - Recoveries for toluene on the Kuraray GAAW carbon (Lot 265) were determined at the required four levels for NIOSH and the required four levels for CEN. The lowest spike level is different for NIOSH and CEN. The recovery for NIOSH must be >=75% for the upper 3 levels and have a pooled coefficient of variation <=0.1. The average recovery was 1.02 with a pooled CV of 0.017. The recovery was >=75% with a CV <=0.1 at the four CEN levels as well. The recovery must also be determined after 2 weeks of storage dry and at high humidity. These tests are included in the following table. Determination of recovery and storage effects requires 48 or 58 samples for each compound validated.

NIOSH VALIDATION - TOLUENE RECOVERY

SPIKE(MG)	NO.MON'S	AVE REC	CV	
11.27	4	1.0269+/-.013	0.0127	
5.636	6	1.0196+/-.011	0.0108	(Dry 1 Day)
	6	0.9959+/-.009	0.0090	(Dry 2 Wks)
	10	0.9888+/-.31	0.0310	(Wet 1 Day)
	10	0.9694+/-.026	0.0268	(Wet 2 Wks)
3.0345	4	1.0197+/-.026	0.0255	
0.434	4	0.9597+/-.021	0.0220	
0.035	4	1.0855+/-.020	0.0184	

NIOSH POOLED CV1 = 0.0166

I reviewed the NIOSH and CEN requirements for validation of diffusion monitors. A comparison of the requirements is attached. Comments on the CEN standard were prepared and sent to Toni San Justo, 3M Espana for input to the CEN committee.

NIOSH VS. CEN STANDARDS FOR VALIDATION OF DIFFUSIVE MONITORS

	NIOSH	CEN
1. Recovery	Spike 4 ea =.1,.5,1, 2XPEL for 8 hrs Rec @.5,1,2 X must be >=75% and CV<=0.1	3 ea @4 loadings from .1 LV 30 min to 2 LV 8 hrs DE≥75% w CV≤0.1 @ ea loading
2. Sampling Rate & Capacity	80%RH, >40fpm,2XPEL for 1/8,1/4,1/2,1,2, 4,6,8,10,12 hrs 4@ea time Cap=5% deviation from linearity MRST=.67X Cap	50%RH,100fpm,1LV 8 hrs (at least 6 hrs) SRexp within +/-25% SRcalc

NIOSH VS. CEN STANDARDS FOR VALIDATION OF DIFFUSIVE MONITORS

	NIOSH	CEN
3. Reverse Diffusion	80%RH,2XPEL 10 ea Exp 50%MRST Cap 1/2 Exp rest to 0 for 50%MRST x2=0.90x1	80%RH,2LV 6 ea Exp 30 min Cap 1/2 Exp rest to 0 for 7 1/2 hrs Bias=(m2-m3)(m2-m3)/(m2+m3)
4. Storage	80%RH,100fpm 1XPEL, 1XMRST anal after 1 day & 2 wks RT & refrig 10 ea	2LV, 4hr, 50%RH, 100fpm or spike @ equiv level anal after 1 day & 2 wks RT 6 ea
5. Factor Effects (Fractional Factorial)	4 ea 16 run conc:.1&2XPEL time:SRST&MRST face vel:20-300fpm RH:10-80% inter:0&1PEL orient:=&!	6ea 4 combinations, high & low conc:.1,x,2LV time:1/2,x,8hrs face vel:.05-.5m/s RH=50% inter:@2LV orient:=&!
6. Temperature	10,25,40 C const RH .5PEL,.5MRST 10 ea temp	0,40 C & 20,80%RH @2LV, 8hr 6 ea
7. Precision Accuracy	80%RH,>=.5MRST .1,.5,1,2XPEL CVtot acceptable 10 ea conc CVtot for .5,1,2XPEL <=.105 for non-biased or Fig 1 for biased	Bias + 2xPrecision <=30% for .5-2LV per prEN482 Bias from #3 Precision from #5 conc/time & #6
8. Shelf Life	note shelf life	Sampler integrity 4hr @2LV
9. Field Tests	Mon vs indep. Area = 13 pairs Pers = 25 pairs	Area = 3 sets of 6 pairs Pers = >=20 pairs

ETO

Experiments were run to compare ETO monitors aged at room temperature for 9 months. Monitors were spiked with ETO dissolved in water per our usual analysis method standard preparation procedure. Results are shown in the tables below:

ETO Standards Vitek vs. Can

ug Spike Pk Ht

EXP #1 9-13-93

Witco Wafer	3.59	2870
Witco Wafer	14.4	11384
Vitek aged	3.59	2268
	2221	ave = 2175 +/- 123
	2035	
Can aged	3.59	1386
	1546	ave = 1547 +/- 162
	1709	
Vitek	14.4	8524
	10501	ave = 9866 +/- 1163
	10573	
Can	14.4	7920
	10505	ave = 9318 +/- 1305
	9530	

EXP #2 9-23-93

Witco Control	3.59	2404
	4121	ave = 2894 +/- 1069
	2158	
Kuraray Lot	272 3.59	2090
	1773	ave = 1740 +/- 367
	1358	
Vitek aged	3.59	1252
	2039	ave = 1811 +/- 487
	2142	
Can aged	3.59	1880
	1845	ave = 1884 +/- 42
	1928	

Witco Control	14.4 8154
	8307 ave = 8188 +/- 106
	8103
Kuraray Lot	272 14.4 7906
	8454 ave = 8827 +/- 1153
	10120
Vitek aged	14.4 7851
	7042 ave = 7688 +/- 582
	8171
Can aged	14.4 8395
	7851 ave = 8282 +/- 387
	8601

No significant difference was seen between the monitors aged in Vitek or cans, but the variability of these results is high.

ETO Interferences - ETO monitors were spiked with ETO, propylene oxide, acetone or isopropanol and allowed to stand overnight. Monitors were desorbed with 10% methylene chloride in methanol and analyszed on a 15m X .25mm X .25 um DB225 capillary column with an ECD.PO, acetone and IPA showed no interference peaks at the ETO retention time. The large peak at a retention time of 4.03 minutes did not interfere with the ETO peak. The response for acetone was about 10X the response for isopropanol. The isopropanol response was similar to an equivalent amount of ETO. Typical retention times for our GCs are shown in the following table.

	RT(min) GC#1	RT(min)GC#2
ETO	5.17	4.64
PO	4.64,5.90	4.20,5.30
Acetone	4.03,~7.2	3.64,~7
IPA	4.03,?	3.65,~7

FORMALDEHYDE

Complaints about high blanks have virtually ceased since the new packaging (nylon bag inside the can) was introduced. We continue to get requests for a STEL monitor and our existing monitor continues to be used for 15 minute samples even though we recommend against such use. Lots of monitors occasionally are rejected by the QC finished product test showing that the process still needs further definition.

Monitors were exposed to 0.75 +/- 0.014 ppm for 330 min. The amount expected was 18.7 ug. The monitors were analyzed after 3 months storage at room temperature and found 18.8 +/- 1.6 ug after correction for a 0.85 ug blank. The OSHA accuracy was 17.5%.

MERCURY

We have completed the revision of the mercury monitor concentration calculation to eliminate the inconsistent results for short sample times at low concentrations and the computer program has been modified.

Customers continue to request a Limit of Detection (LOD) in ug for our monitor which we are not able to provide. A theoretical calculated sampling rate for the 3600 is 52.3 cc/min. A calculated rate for the 3500 monitor geometry is 64.1 cc/min.

An independent method has been found to analyze the mercury monitors. Wanda Bahmet, CRL, has found a way to dissolve the mercury and gold off the substrate and analyze it by ICP without having the gold plate out and readsorb the mercury. Monitors (Lot WB6476-6607) were exposed to the standard QC mercury concentration of 0.0966 mg/m3 for 15 min to 8 hours (Make-Order 3600-008). The resistance changes were determined and then the samples were analyzed by ICP. The plot of resistance change vs. time showed a linear uptake rate although high variability was observed for resistance changes at sampling times less than one hour (see attached graph). The average resistance change for a set of 10 blank monitors was found to be 22.3 +/- 18.9. The expected change is -20 for a blank monitor and the calculation of the concentration is based on this historical value. Results of the ICP analysis have not been evaluated yet. Additional experiments will be necessary to determine whether the ICP method has application to quality control of the mercury concentration and whether it might eventually replace the resistance measurements as the analysis method.

NEW MONITORS

Monitor web was successfully prepared from the UOP Abscents Silica Molecular Sieve on the Empore lab mill. Further experimentation with the milling parameters will be required, but the physical and visual quality of the web was much improved over my first attempt at the pilot plant. Testing of wafers prepared from the UOP Abscents Silica Molecular Sieve on the Empore lab mill began with the determination of the recovery of Ethanol using CS2 compared to acetonitrile.

WAFER	CS2 REC	ACETO REC
Kuraray GAAW	0.40	0.92
Abscents	0.02	0.84
Silica Gel	0.02	0.84

The hydrophobic silica wafers (Abscents) were also used in the double decker configuration and exposed to EtOH for 1-4 hours at 183 ppm and 80% RH. A sampling rate of 51.7 +/- 4.2 (+/-8.1%) and a recovery of 90% with acetonitrile was found.

An oven was designed by Jim Nelson and built in the shop to allow thermal desorption tests on 25 mm dia. disks cut from standard size OVM wafers. The oven is ready to be tested but will require modifying the HP5840 GC which is now set up to run methyl iodide breakthrough tests. A new GC is needed to handle these projects.

Y. T. and I met with Don Hagen to discuss the status of his work on UOP silicalite. He has found that a 50/50 mixture of Kevlar fibers with the silicalite gives an excellent sorbent material. Samples for our use are scheduled for preparation in January, 1994.

PACKAGING

The two most promising foil laminates identified in 1992 were the Vitek bag from Graphic Packaging and the biaxially oriented nylon foil from Printpack. Vitek is a 92 ga. PET/7.2# Surlyn 1652/0.001 foil/14.4# Surlyn 1652 extrusion laminate.

A six month aging test at room temperature, 100 F/70%RH and 130 F was completed. The OVM toluene uptake rate was determined by exposing monitors to 99.4 ppm of toluene for 135 minutes at 50%RH and then analyzed. The amount expected was 1.588 mg. The average amount found for aged Vitek was 1.608 +/- .064 mg and for aged cans was 1.622 +/- .047 mg and for Witco Lot 2140 controls was 1.658 +/- .068 mg. The OSHA accuracy for all the aged monitors including controls was 9.14% which meets the OSHA accuracy requirement of 25%. Analysis of the monitors for formaldehyde blanks, titration and recovery, OVM blanks and recovery, ETO blanks and standards, and toluene uptake rate has been completed. Results so far indicate no significant difference in the Vitek bags from the cans except for OVM blanks run on my GC. Tests run on my HP5880 GC showed a detectable difference in blanks between the OVMs in Vitek pouches compared to the cans which were not detectable on the pilot plant HP5890 GC. Bob Weber sent samples to Shell in Houston to confirm my observations. Their chromatograms showed even more dramatically that the foil pouches led to a higher blank than the cans. It can be noted that the contamination level appears to be the same in the Room Temperature aged and the 100F/70%RH aged monitors. This indicates to me the possibility that the contamination is due to the heat sealing process rather than outgassing of the material. Although the tests on the other monitors have shown satisfactory performance of the Vitek pouches, it is not practical or desirable to change the formaldehyde and ETO to foil without changing the OVMs. The conversion to foil pouches has been put on hold until such time as a better material or sealing process can be identified.

NEW MOLDS

New molds for the main body, elution cap and primary cup have been built. The primary cup was satisfactory. The mold for the main body was modified to make the base thicker to reduce warping. Tests still indicate an occasional leak. It does not appear that a specific cavity is the culprit. The elution cap does not seal properly. I have tested parts by epoxying the seal to the body to eliminate this as a source of leakage to see whether the new plug design is acceptable. The plug seal appeared to be acceptable. I ran 2 NSTA shipping tests on the new parts. None of the plugs popped open. In one test the controls were old style E-caps and 1 plug popped open. In the second test the controls were the current stress-relieved E-caps and all 5 had a plug pop open. Additional reworking of the mold will be necessary to achieve a proper seal.

MERCURY TEST 11-15-93

RESISTANCE CHANGE AT 0.097 MG/M3

+ WB6476-6607