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Collection and Analysis of NASA Clean Room Air Samples

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1.0 Introduction

Analysis for semivolatile compounds including dioctylphthalate (DOP) and polychlorinated biphenyls (PCBs) was performed on nine air samples collected at the HALOE assembly clean-room at NASA-Langley Research Center during January, 1985. Each sample was extracted, concentrated, and analyzed using fused silica capillary gas chromatography with electron capture detection (FSCGC/ECD). Total DOP and PCB concentration was determined for each sample.

Analysis for total airborne volatile organic compounds was performed on eight samples collected at the same time as the nine semivolatile samples. Each sample was analyzed by capillary column gas chromatography mass spectrometry (GC/MS/COMP). The amounts of 23 target compounds listed in Table 1 in each sample were calculated using relative response factors. Qualitative identification of all compounds found was performed on a single sample.

2.0 Volatile Organics

2.1 Experimental Methods

Eight samples of volatile organics were collected on Tenax GC solid sorbent. Two sets of triplicate samples and one set of duplicates were collected over the 72 hour sampling period. For all samples, 60 L of air were drawn passed through the sample cartridges. The samples were collected in three locations within the clean-room. Figure 1 shows the relative placement of the samplers within the room. Once collected the samples were sealed in uncoated paint cans and transported directly to Research Triangle Institute (RTI). They were immediately placed in a freezer at -20°C until their analysis.

TABLE 1. BACKGROUND LEVELS OF TENAX FIELD BLANKS

Compounds	Nanograms/Cartridge FB-01	FB-02	FB-03	Average	Std Dev
1,2-dichloroethane	.0	.0	.3	.1	.17
1,1,1-trichloroethane	6.0	.8	.7	2.5	3.03
benzene	8.0	11.4	40.4	19.9	17.81
carbon tetrachloride	.2	.0	.0	.1	.12
trichloroethylene	.4	.2	.3	.3	.10
n-butylacetate	.0	.0	.0	.0	.00
tetrachloroethylene	.0	.0	.0	.0	.00
chlorobenzene	.0	.1	.0	.0	.06
ethylbenzene	.0	.0	.0	.0	.00
m-xylene	.3	1.0	.0	.4	.51
styrene	1.3	.4	.2	.6	.59
o-xylene	.1	.0	.0	.0	.06
isopropylbenzene	.0	.0	.0	.0	.00
α-pinene	.0	.0	.0	.0	.00
n-propylbenzene	.0	.0	.0	.0	.00
m-ethyltoluene	.0	.1	.0	.0	.06
1,3,5-trimethylbenzene	.2	.0	.0	.1	.12
1,2,4-trimethylbenzene	.0	.2	.0	.1	.12
m-dichlorobenzene	.0	.0	.0	.0	.00
p-dichlorobenzene	.0	.0	.0	.0	.00
o-dichlorobenzene	.0	.0	.0	.0	.00
n-undecane	.0	.0	.0	.0	.00
n-dodecane	.0	.0	.0	.0	.00

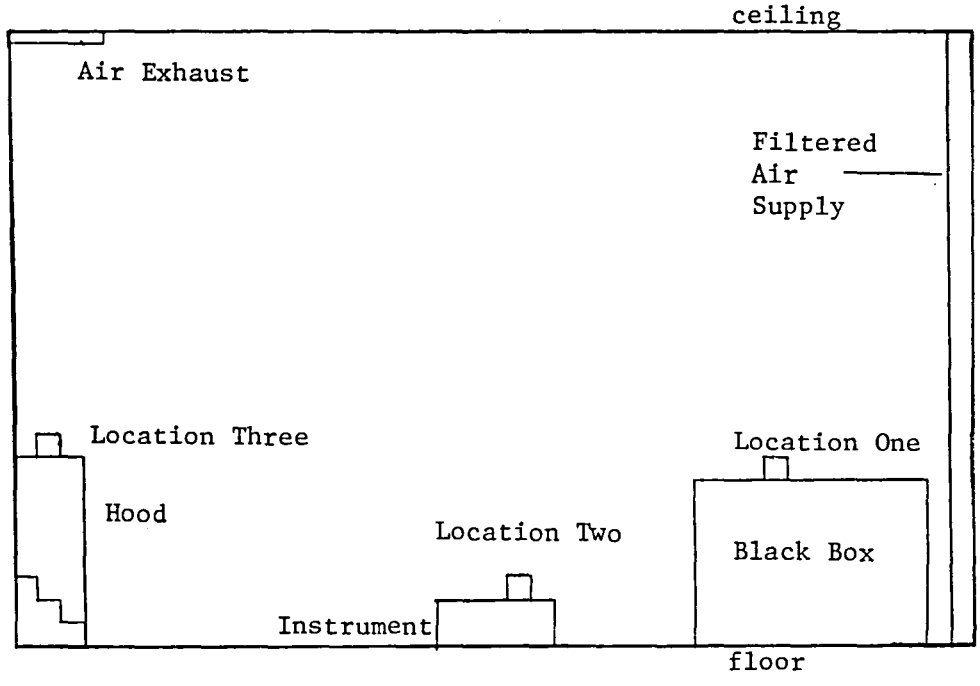


Figure 1. Location of multiple samplers in cleanroom.

The eight air samples collected on modified Tenax GC cartridges were analyzed for 23 target compounds (Table 1). Appendix A describes the preparation of Tenax cartridges by RTI. In order to reduce the possibility of particulate contamination of the cleanroom from the Tenax cartridges, the glass wool plugs normally used to hold the Tenax bed intact were replaced with 60 mesh stainless steel screens. A validation study of the modified Tenax cartridges was conducted prior to the sample collection. The results of this study are listed in Appendix B.

During analysis, the entire sample is introduced into the analytical system by thermal desorption into a cryogenic capillary trap and rapidly swept onto the chromatographic column by the carrier gas while heating the trap. In order to perform quantitative analysis of volatile organic compounds adsorbed on Tenax, the combined thermal desorption-liquid injection system shown in Figure 2 was employed. This unit allows calibration of the mass spectrometer by liquid injection and analysis of the field samples by thermal desorption. The configuration of the injection unit in the mass spectrometer is shown in Figure 3.

Each cartridge was loaded prior to analysis with a known amount of bromopentafluorobenzene (212 ng) for use as an external standard in quantitation. Quantitation of each target compound was achieved by integration of a characteristic mass for a compound over the chromatographic peak. The amount of compound in the sample was then calculated using a response factor and the integrated area for a standard. Response factor (RF) data generated for each of the target compounds by liquid injection of a standard solution was calculated relative to the external standard, bromopentafluorobenzene as:

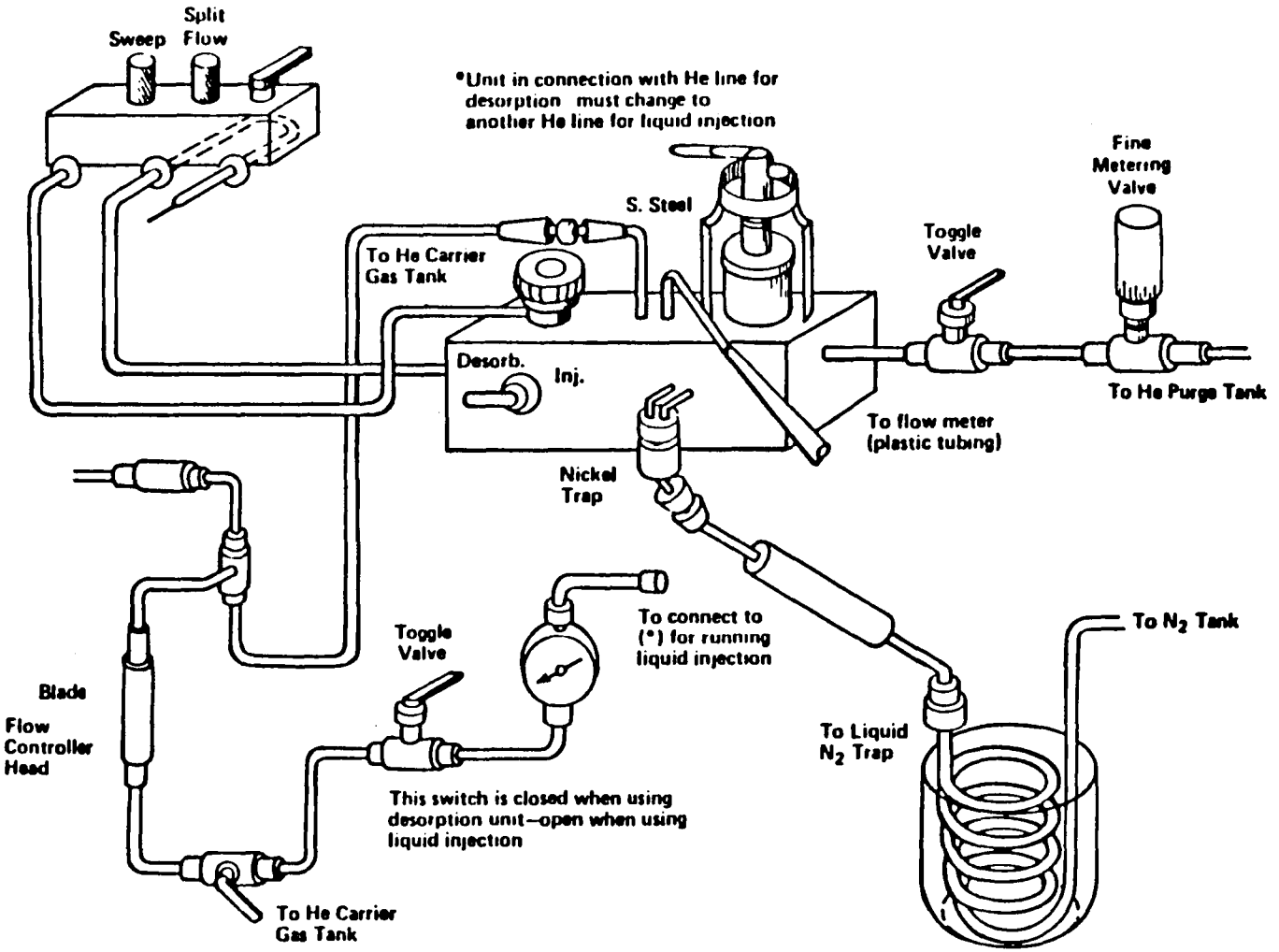


Figure 2. Configuration of the injection unit in mass spectrometer system.

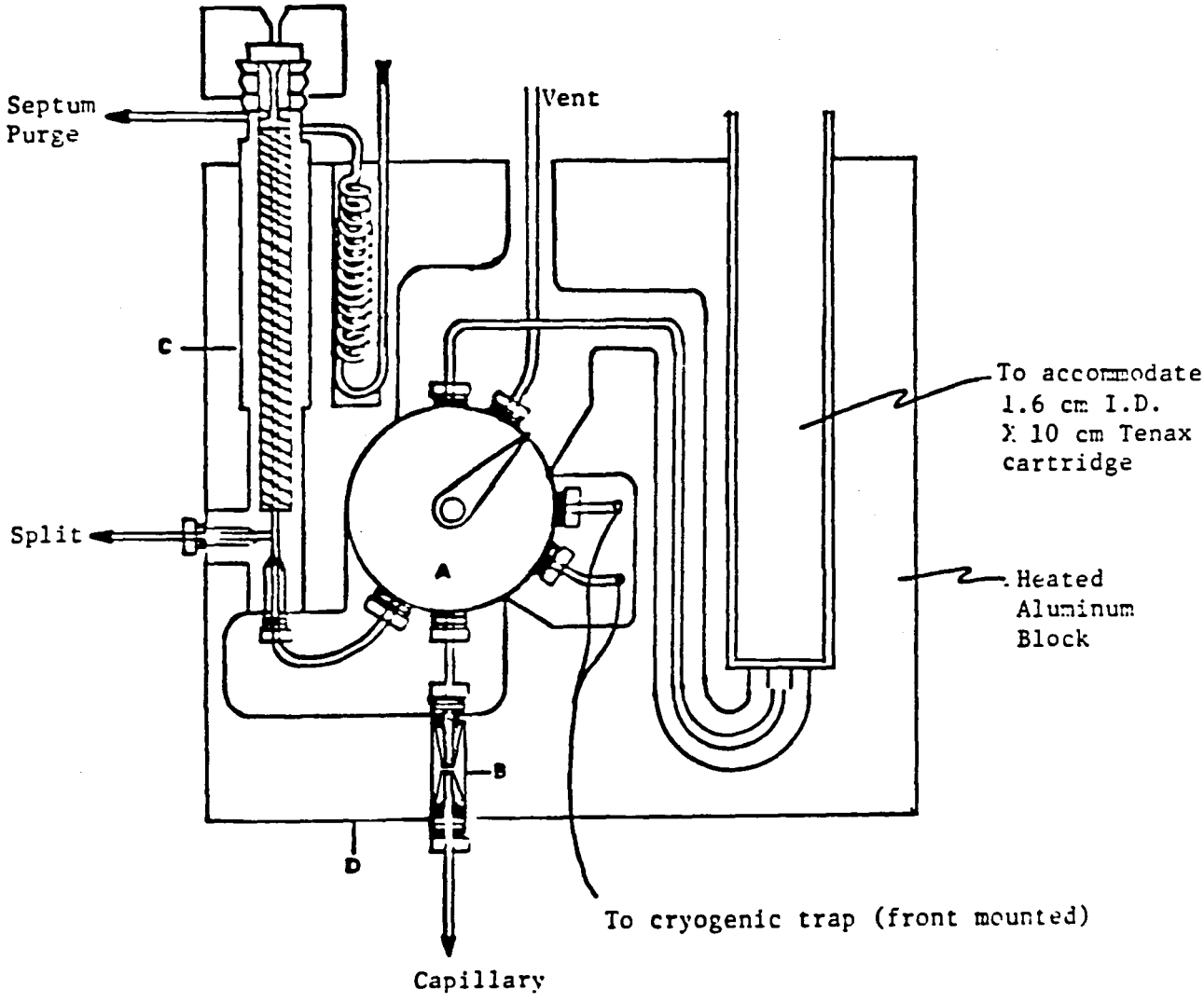


Figure 3. Combined thermal desorption - liquid injection system.

$$RF = A_T\ (ng)_{es}/A_{es}\ (ng)_T$$

where A_T and A_{es} are the peak areas of the target volatile and the external standard, respectively. The amounts of target compounds and external standard injected into the GC/MS system are represented by $(ng)_T$ and $(ng)_{es}$, respectively.

The linear range for quantitation using fused silica capillary columns on a GC/MS system is generally three orders of magnitude (e.g., 5-5000 ng). Based on air concentration, LODs for the proposed target compounds range from 1 to 50 ppt. Overall accuracy is generally $\pm$10-30% but depends on the chemical and physical nature of the compound.

The concentration in ambient air of the target compounds was then calculated using the volume sampled during the 72 hour period. For some of the very volatile compounds, the total volume of air will cause the elution of compounds from the sampling tube. These "breakthrough volumes" have been determined and verified by previously described techniques and are defined as that point at which 50% of a discrete sample introduced into the cartridge is lost. For cases where the breakthrough volume has been exceeded during sampling, the concentration reported based upon the volume sampled represents a semiquantitative amount of that compound only.

All samples were processed together as a set. The set contained, in addition to the study samples, a number of blanks and controls. The blanks were employed as a reference for background contamination. Table 1 contains the mass of the target compounds found on the blanks exposed during the study. The controls consisted of Tenax cartridges loaded with known amounts of the target compounds. Their purpose is to monitor

TABLE 2. RECOVERY DATA OF VOLATILE ORGANICS FROM TENAX CONTROLS

Compounds	FC-01	FC-02	Bkg. Avg.	Bkg. Avg.	Std. Dev.	Loaded	% Rec.
1,2-Dichloroethane	81	88	0	85	4.9	60	141
1,1,1-Trichloroethane	66	45	3	53	15	54	97
Benzene	78	30	20	34	44	42	81
Carbon tetrachloride	70	50	0	60	14	62	97
Trichloroethylene	91	50	0	71	28	58	122
n-Butylacetate	110	125	0	118	10	140	84
Tetrachloroethylene	110	128	0	119	12	124	96
Chlorobenzene	52	52	0	52	.00	58	90
Ethylbenzene	41	54	0	48	9	42	113
m-Xylene	31	34	0	33	2.1	34	96
Styrene	36	33	1	34	2.5	36	93
o-Xylene	69	68	0	69	.71	60	114
Isopropylbenzene	15	16	0	16	.71	20	78
α-Pinene	40	43	0	42	2.1	58	72
n-Propylbenzene	83	84	0	84	.71	80	104
m-Ethyltoluene	55	59	0	57	2.8	58	98
1,3,5-Trimethylbenzene	114	120	0	117	4.2	104	113
1,2,4-Trimethylbenzene	52	48	0	50	2.8	40	125
m-Dichlorobenzene	97	92	0	95	3.5	62	152
p-Dichlorobenzene	113	110	0	112	2.1	80	139
o-Dichlorobenzene	61	58	0	60	2.1	40	149
n-Undecane	72	87	0	80	10	60	133
n-Dodecane	134	111	0	123	16	60	204

the recovery of the target compounds from the Tenax cartridges. The results of the controls exposed during the study are shown in Table 2. Table 3 lists the GC/MS conditions for sample analysis.

This procedure for the collection and analysis of volatile organics was developed at RTI, and has been validated. It has also been used for the analysis of volatile organics (similar or identical to the proposed target list) from over 8000 samples, collected under many different programs during the past several years. The overall procedure has been published (1), and is currently used for indoor air volatile organics analysis (EPA Contract No. 68-02-3679) at RTI.

2.2 Analytical Results

Results of the sample analysis are given in Tables 4 to 6. Data in these tables include both the individual concentrations of the target compounds and the mean concentration of the replicate samples with their relative standard deviations. Concentrations are corrected for background contamination on the blank but not corrected for recovery of the controls. Table 7 lists the identification of volatile organics found in single sample collected at location one. Component identification was performed by searching the EPA/NIH data base using an interactive operator INCOS computer search alogrithm. These identifications are only tentative, based on the best fit of the deconvoluted spectra with the data base spectrum. Values for purity, fit, and retro-fit indicate how well the unknown spectrum matches the library spectrum for those compounds identified by a computer search. A value of 1000 would indicate a perfect fit. For each identified compound, an area count for the major ion has also been listed to suggest an approximate amount of compound

TABLE 3. GC/MS INJECTION CONDITIONS

Liquid Injection	
Carrier gas:	Helium
Carrier flow:	2 mL/min
Septum sweep:	1 mL/min
Injection conditions:	30 sec splitless, then 10:1 split
Injector temperature:	270°C
Column:	60 m wide-bore DB-1 fused silica, 1 μ film thickness
GC program:	Initial temperature 30°C, then 4°C/min to 230°C
Thermal Desorption	
Carrier gas:	Helium
Carrier flow:	2 mL/min
Desorption time:	8 min
Purge flow:	17-19 mL/min
Purge temperature:	270°C
Column:	60 m wide-bore DB-1 fused silica, 1 μ film thickness
GC program:	30°C (5 min) to 240°C at 4°C/min

TABLE 4. RESULTS OF VOLATILE SAMPLE ANALYSIS AT LOCATION ONE

Compounds	Concentration of Target Compounds (ng/L) Sample One	Sample Two	Sample Three	Mean	RSD
1,2-dichloroethane*	T	0.13	T	T	NC
1,1,1-trichloroethane*	1.39	2.34	0.88	1.54	0.48
benzene*	2.89	6.03	1.64	3.52	0.64
carbon tetrachloride*	0.56	0.94	0.48	0.66	0.37
trichloroethylene*	0.28	0.37	0.14	0.26	0.44
n-butylacetate	T	T	T	T	NC
tetrachloroethylene	0.56	0.94	0.76	0.76	0.25
chlorobenzene	ND	ND	ND	ND	NC
ethylbenzene	1.25	1.70	1.33	1.43	0.17
m-xylene	2.29	4.09	2.74	3.04	0.31
styrene	0.33	0.43	0.41	0.39	0.13
o-xylene	0.96	1.59	1.14	1.23	0.26
isopropylbenzene	0.15	0.16	0.14	0.15	0.06
α-pinene	1.01	1.33	1.46	1.27	0.19
n-propylbenzene	0.27	0.35	0.32	0.31	0.13
m-ethyltoluene	1.30	1.66	1.40	1.45	0.13
1,3,5-trimethylbenzene	0.39	0.49	0.46	0.45	0.12
o-ethyltoluene	0.38	0.44	0.36	0.39	0.10
1,2,4-trimethylbenzene	1.78	2.06	1.76	1.87	0.09
1,2,3-trimethylbenzene	0.40	0.47	0.47	0.44	0.08
m-dichlorobenzene	ND	ND	ND	ND	NC
p-dichlorobenzene	T	0.10	0.08	0.09	0.13
o-dichlorobenzene	T	T	ND	T	NC
n-undecane	0.88	1.00	0.93	0.94	0.06
n-dodecane	0.93	0.66	1.01	0.87	0.21

T = Trace (below quantifiable limit)
ND = Not detected
* = Breakthrough Volume Exceeded
NC = Not calculated

TABLE 5. RESULTS OF VOLATILE SAMPLE ANALYSIS FOR LOCATION TWO

Compounds	Concentration of Target Compounds (ng/L) Sample One	Sample Two	Average	RSD
1,2-dichloroethane*	T	T	0.10	0.02
1,1,1-Trichloroethane*	1.92	2.13	2.03	0.08
benzene*	4.63	5.77	5.20	0.16
carbon tetrachloride*	1.29	1.16	1.23	0.07
trichloroethylene*	0.35	T	0.19	1.19
n-butylacetate	ND	ND	0.00	0.00
tetrachloroethylene	0.39	0.58	0.49	0.27
chlorobenzene	ND	ND	0.00	0.00
ethylbenzene	0.85	0.71	0.78	0.13
m-xylene	1.50	1.53	1.51	0.01
styrene	0.26	0.47	0.36	0.40
o-xylene	0.62	0.89	0.75	0.25
isopropylbenzene	0.05	0.17	0.11	0.79
α-pinene	1.09	1.64	1.36	0.29
n-propylbenzene	0.23	0.38	0.30	0.34
m-ethyltoluene	1.28	1.83	1.56	0.25
o-ethyltoluene	0.38	0.53	0.46	0.24
1,2,4-trimethylbenzene	2.02	2.63	2.33	0.18
1,2,3-trimethylbenzene	0.55	0.55	0.55	0.00
m-dichlorobenzene	ND	ND	ND	NC
p-dichlorobenzene	0.09	0.13	0.11	0.22
o-dichlorobenzene	T	T	T	NC
n-undecane	1.10	1.81	1.45	0.35
n-dodecane	1.49	1.41	1.45	0.04

T = Trace (below quantifiable limit)
ND = Not detected
* = Breakthrough Volume Exceeded
NC = Not calculated

TABLE 6. RESULTS OF VOLATILE SAMPLE ANALYSIS FOR LOCATION THREE

Compounds	Concentration of Target Compounds (ng/L) Sample One	Sample Two	Sample Three	Mean	RSD
1,2-dichloroethane*	T	T	T	0.07	0.43
1,1,1-trichloroethane*	1.20	0.70	0.57	0.82	0.40
benzene*	1.41	1.23	0.74	1.12	0.31
carbon tetrachloride*	0.39	0.42	0.26	0.36	0.24
trichloroethylene*	0.07	T	T	T	NC
n-butylacetate	T	T	T	T	NC
tetrachloroethylene	0.50	0.53	0.47	0.50	0.06
chlorobenzene	ND	ND	ND	ND	NC
ethylbenzene	0.96	0.94	0.86	0.92	0.05
m-xylene	1.74	1.80	1.71	1.75	0.03
styrene	0.40	0.27	0.26	0.31	0.24
o-xylene	0.72	0.81	0.79	0.77	0.06
isopropylbenzene	0.11	0.12	0.11	0.11	0.08
α-pinene	0.84	1.10	0.96	0.97	0.13
n-propylbenzene	0.19	0.25	0.21	0.22	0.12
m-ethyltoluene	0.90	1.18	1.01	1.03	0.14
1,3,5-trimethylbenzene	0.27	0.35	0.30	0.31	0.14
o-ethyltoluene	0.26	0.33	0.28	0.29	0.13
1,2,4-trimethylbenzene	1.12	1.54	1.23	1.30	0.17
1,2,3-trimethylbenzene	0.32	0.47	0.46	0.42	0.20
m-dichlorobenzene	ND	ND	ND	ND	NC
p-dichlorobenzene	T	T	T	NC	NC
o-dichlorobenzene	ND	T	ND	ND	NC
n-undecane	0.60	0.83	0.66	0.69	0.17
n-dodecane	0.40	0.63	0.61	0.55	0.23

T = Trace (below quantifiable limit)
ND = Not detected
* = Breakthrough Volume Exceeded
NC = Not calculated

TABLE 7. IDENTIFICATION OF VOLATILE ORGANICS IN SAMPLE 1F-1

Compounds	Scan Number	Ion (m/z)	Purity	Fit	Retro Fit	Major Ion[a]
2-Methylpentane (C_6H_{14})	225	86	850	918	867	3320
2-Butanone	237	72	919	940	972	106366
Hexane	265	86	902	918	939	28097
1-Propanol, 2-Methyl	294	74	882	928	915	6057
PFT (loaded)	306	236	-	-	-	208538
1,1,1-Trichloroethane	315	97	-	-	-	198044
Benzene	339	78	-	-	-	811759
Carbon tetrachloride	346	117	-	-	-	47922
2,4-Dimethylpentane	366	100	805	825	896	4567
3-Methylhexane	379	100	909	926	936	6018
Trichloroethylene	397	132	-	-	-	327
2,2,3-Trimethylpentane (C_8H_{18})	400	57	879	916	924	101919
Ethylhexane (C_7H_{16})	417	100	916	937	954	19626
Methylcyclohexane	449	98	834	928	888	11529
n-Ethylethanamine	469	73	844	901	877	20029
C_7H_8	503	91	892	952	928	1525270
Butylacetate	569	73	-	-	-	8853
Tetrachloroethylene	574	166	-	-	-	56734
Nitrogen Compound (unidentified)	578	58	609	892	633	627291
Chlorobenzene	619	114	-	-	-	318
Bromopentafluorobenzene (std)	637	117	-	-	-	391098 (std)
Ethyl benzene	647	106	-	-	-	110424
m-Xylene	659	106	-	-	-	191198
Cyclohexanone	670	98	891	939	929	626049
Styrene	685	104	-	-	-	43444
o-Xylene	692	106	-	-	-	79179
2-Ethoxyethyl acetate	691	72	-	-	-	24627
Triethanolamine	723	86	778	867	861	695125
Isopropylbenzene	737	103	-	-	-	39683
n,n-Diethylformamide	745	58	777	909	814	102813
Benzaldehyde	764	105	915	947	932	938563

(continued)

TABLE 7. (CONTINUED)

Compounds	Scan Number	Ion	Purity	Fit	Retro Fit	Area Counts of Major Ions
α-Pinene	766	136	-	-	-	9687
n-Propylbenzene	778	91	-	-	-	136098
m-Ethyltoluene	787	105	-	-	-	506565
1,3,5-Trimethylbenzene	797	105	-	-	-	142983
Phenol	800	94	813	899	887	627565
$C_{10}H_{22}$	805	57	766	922	788	385188
o-Ethyltoluene	811	105	-	-	-	139291
C_9H_{18}	822	41	623	877	623	155779
1,2,4-Trimethylbenzene	831	105	-	-	-	547352
m-Dichlorobenzene	840	146	-	-	-	463
p-Dichlorobenzene	846	146	-	-	-	13092
n-Decane	850	142	-	-	-	4895
1,2,3-Trimethylbenzene	867	120	-	-	-	26927
o-Dichlorobenzene	875	146	-	-	-	1408
o-Cresol	889	107	-	-	-	5750
1-Phenylethanone	902	105	913	977	927	1364150
m-Cresol	916	107	-	-	-	71664
$C_{10}H_{14}$	939	119	538	912	568	123285
$C_{10}H_{14}$	946	119	835	930	882	109406
n-Undecane	974	156	-	-	-	4286
$C_{10}H_{14}$	990	119	758	907	782	66080
n-Decanal	996	43	586	911	586	32632
C_4-Alkyl benzene	1032	105	503	797	517	53166
Benzoic Acid	1038	105	400	725	503	1699250
1,4-Benzenedicarbonitrile	1060	128	852	950	970	400278
2-Chlorooctane	1073	41	424	851	461	27410
n-Dodecane	1087	170	-	-	-	2066
Nitrogen compound (unidentified)	1110	55	716	945	718	360684
Hexahydro-2H-azepine-2-one ($C_6H_{11}ON$)	1115	55	903	952	918	1132460
Nonanoic acid	1140	60	677	923	718	37458

(continued)

TABLE 7. (CONTINUED)

Compounds	Scan Number	Ion	Purity	Fit	Retro Fit	Major Ion
Hydrocarbon	1169	57	-	-	-	18633
$C_{11}H_{10}$	1184	141	754	889	780	150085
Hydrocarbon	1195	57	-	-	-	128468
Siloxane (from column)	1232	73	-	-	-	468546
Unidentified	1245	82	-	-	-	23919
$C_9H_{18}OS$	1260	71	411	792	489	96932
C_9H_{18}	1275	57	-	-	-	152644
Siloxanes (from column)	1325	73	-	-	-	218220
2-Ethoxy-1-methoxyethoxyethene	1357	59	-	-	-	278349
$C_{20}H_{42}$	1389	57	701	803	847	150028
$C_{15}H_{24}$	1391	205	561	837	651	44359
C_9H_{18}	1404	71	592	789	691	2064360
3-Bromopentane	1468	71	624	912	668	134517
$C_{13}H_{28}$	1478	57	741	858	820	111484
Unidentified	1495	43	-	-	-	236990
Siloxane (from column)	1520	73	-	-	-	431606
Unidentified	1534	43	-	-	-	131622
9-Hexadecenoic acid	1542	55	486	869	549	31488
Siloxane (from column)	1552	73	-	-	-	231402
Octadecane	1563	57	714	889	784	93944
Hydrocarbon	1572	57	-	-	-	61211

[a]GC/MS counts of the major ion in the spectra of each compound.

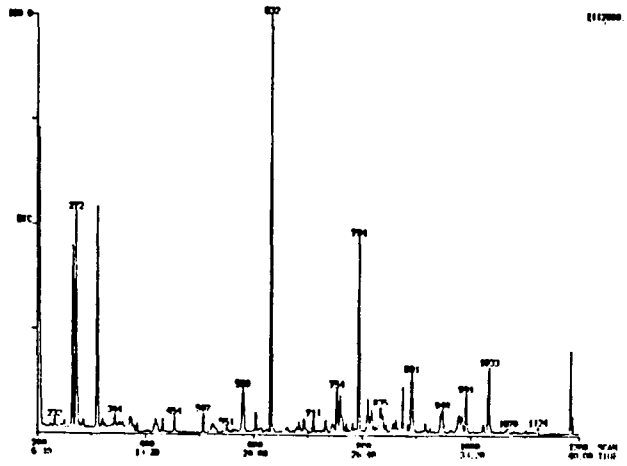
found on the cartridge. An area count of 373,000 was found for the major ion of the external standard bromopentafluorobenzene which had been loaded at a level of 212 ng/cartridge. A total sample volume of 60 L was collected. Figure 4 shows the reconstructed ion current chromatograms for the three field blanks exposed during the sample collection. The external standard, bromopentafluorobenzene, appears at scan number 633. Figures 5 to 7 show the reconstructed ion current chromatograms for the field samples analyzed. All chromatograms show scan number 200 through 1600 where the most intense ion of each plot is normalized to 100% full scale; therefore, each chromatogram is relative to a different absolute base scale.

3.0 Semivolatile Compounds

3.1 Experimental Methods

Nine polyurethane foam (PUF) samples were collected in the NASA cleanroom. Three sets of triplicate samples were simultaneously collected during the 72 hour sampling period. For all samples, 60 L were passed through the sample cartridges. The three sets were collected at the locations indicated in Figure 1. Once collected the samples were placed in uncoated paint cans and transported directly to Research Triangle Institute for storage at 4°C until analysis. The samples were extracted by Soxhlet extraction with 5% diethyl ether in hexane, concentrated, and analyzed by capillary gas chromatography employing electron capture detection.

The sampling and analysis performed on the nine samples was based upon the procedure developed by Lewis et al. (3-5). One modification to the method involved the collection of each sample on a set of two 22 mm



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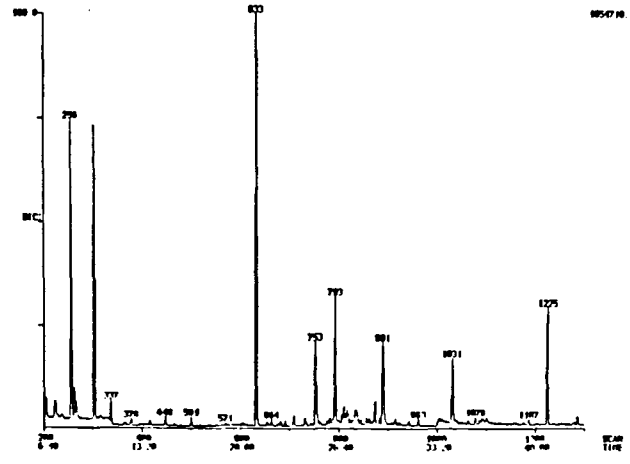

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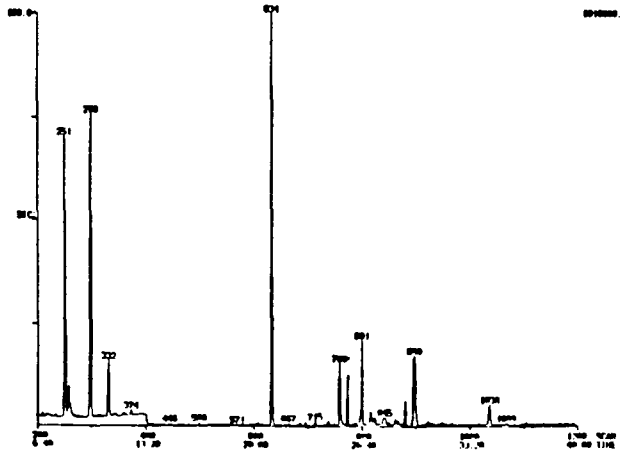
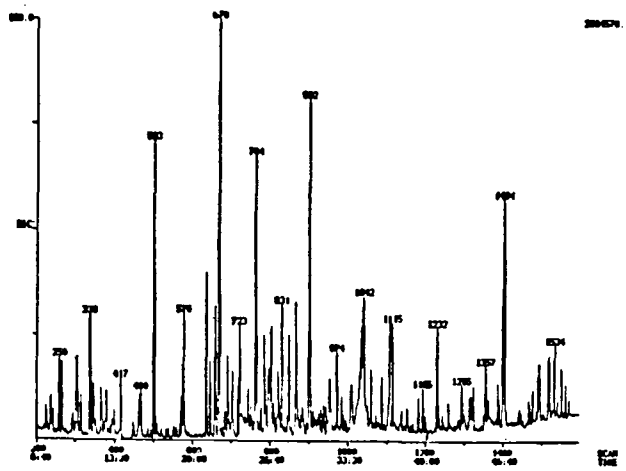
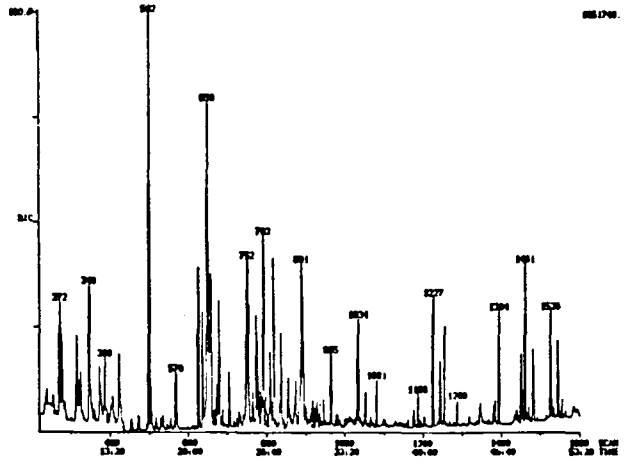


Blank 3

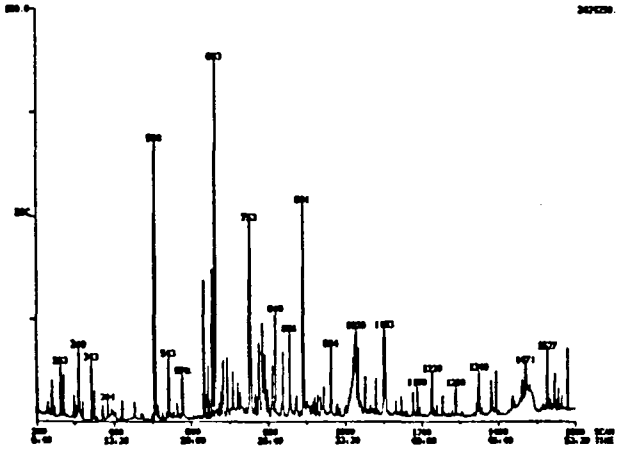
Figure 4. GC/MS total ion chromatograms of field blanks 1-3.



Sample 1

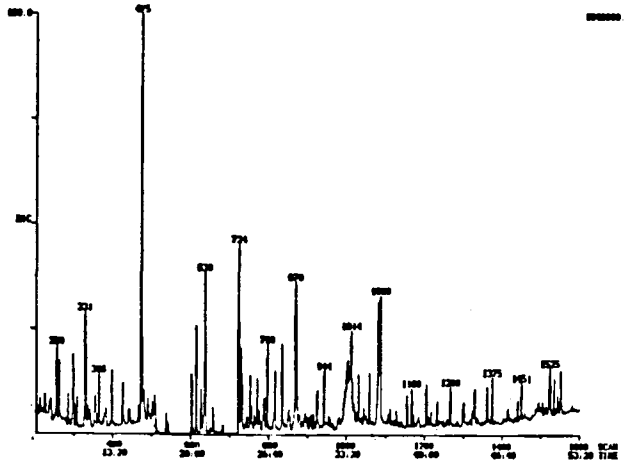


Sample 2

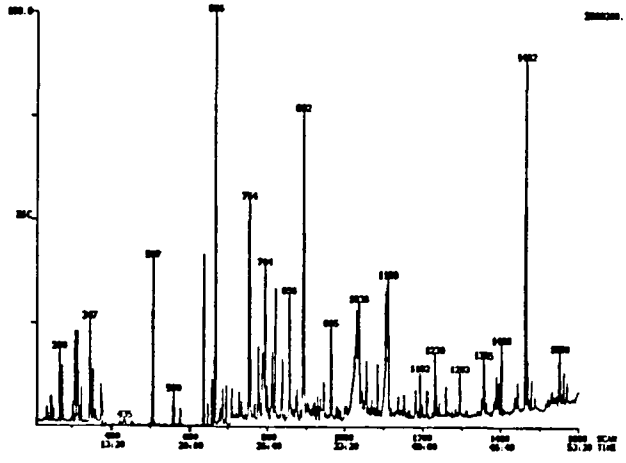


Sample 3

Figure 5. GC/MS total ion chromatograms of location one samples 1-3.



Sample 1



Sample 2

Figure 6. GC/MS total ion chromatograms of location two samples.

ID x 7.6 cm long PUF plugs placed end-to-end rather than a single PUF plug. The modification was employed in order to trap compounds which might otherwise exceed their breakthrough volumes on a single PUF plug. The breakthrough volume of DOP was experimentally determined to be greater than the volume collected on the field samples. Results of the breakthrough study are shown in Appendix C.

Exposed PUF plugs sets were extracted overnight in 250 mL Soxhlet extractors using 125 mL of .5% diethyl ether in hexane. The extracts were reduced to approximately 5 mL in a Kuderna-Danish (K-D) apparatus. A modified Snyder column was attached to the K-D receiver tube containing the 5 mL extract and the extract blown down to 1.0 mL using cryogenically cleaned nitrogen gas.

All sample extracts were analyzed by fused silica capillary gas chromatography using electron capture detection. A Varian 3700 gas chromatograph employing a ^{63}Ni electron capture detector and a Varian 8000 autosampler were used for the analysis of the PUF extracts. Table 8 shows the GC conditions under which the samples were analyzed.

Each sample was spiked with a known amount of dichloronaphthalene, tetrachloronaphthalene, and octachloronaphthalene for use in quantitation. Quantitation of DOP was achieved by integration over the chromatographic peak. The amount of DOP in the sample was then calculated using the integrated area of the target peak, a response factor, and the integrated area for a standard. The response factor for DOP was calculated relative to the external standard octachloronapthalene (OCN) as:

$$RF = \frac{A_{DOP}\ (ng)_{es}}{A_{es}\ (ng)_{DOP}}$$

TABLE 8. CHROMATOGRAPHIC CONDITIONS FOR PUF ANALYSIS

Parameter	Setting, Etc.
Column, analytical Inner diameter: Film thickness	30 M DB-5 fused silica capillary 0.32 mm 0.025 μ
N_2 carrier flow	1.4 mL/min
Split Ratio	18:1
Splitless	60 sec.
Temperature Program Final hold	100-260° @ 2°C/min 15 minutes
Injector temperature	270°C
Detector Temperature	300°C
Detector type	Variable pulse frequency ^{63}Ni ECD
Makeup gas	N_2 @ 25 mL/min
Injection Volume	1.0 μL

where A_{DOP} and A_{es} are the peak areas of the DOP and the external standard, respectively. The amount of DOP and external standard are represented by $(ng)_{DOP}$ and $(ng)_{es}$, respectively. Quantitation of the total PCBs present was achieved by integration of the characteristic peaks of Aroclor 1254. Aroclor 1254 represents a mixture of PCB isomers containing 54% chlorinated species by weight. The amount of PCBs present in the PUF extracts was then calculated using the sum of the integrateD peak areas corresponding to those seen in Aroclor 1254, a response factor, and the integrated area of the external standard. The response factor for the PCBs was calculated realtive to the external standard octachloronaphthalene as:

$$RF = \frac{A_{PCB}\ (ng)_{es}}{A_{es}\ (ng)_{PCB}}$$

where A_{PCB} and A_{es} represent the sum of the integrated areas for all the characteristic peaks of Aroclor 1254 and the external standard, respectively. The amount of Aroclor 1254 and external standard are represented by $(ng)_{PCB}$ and $(ng)_{es}$, respectively. Since the quantitation of PCBs in the samples were based upon an Aroclor mix rather than every possible PCB isomer, the concentrations calculated using the above equation represent semiquantitative values only. The concentration in ambient air of the compounds was then calculated using the volume sampled during the 72 hour period.

3.2 Analytical Results

Results of the sample analysis are given in Table 9. Figure 8 shows the chromatograms of three of the field blanks exposed during the sample collection. The external standards, dichloronaphthalene (DCN), tetrachloronaphthalene (TCN), and octachloronaphthalene (OCN) appears as

TABLE 9. RESULT OF SEMIVOLATILE ANALYSIS

Site	Concentration (ng/M^3)	
	PCBs	Dioctylphthalate
1 F1	325	0.722
1 F2	482	0.350
1 F3	223	1.98
Average	343 ± 130	1.02 ± 0.85
2 F1	333	1.09
2 F2	487	1.74
2 F3	330	2.76
Average	384 ± 89	1.86 ± 0.84
3 F1	278	0.003
3 F2	549	5.54
3 F3	511	2.06
Average	446 ± 147	2.53 ± 2.79

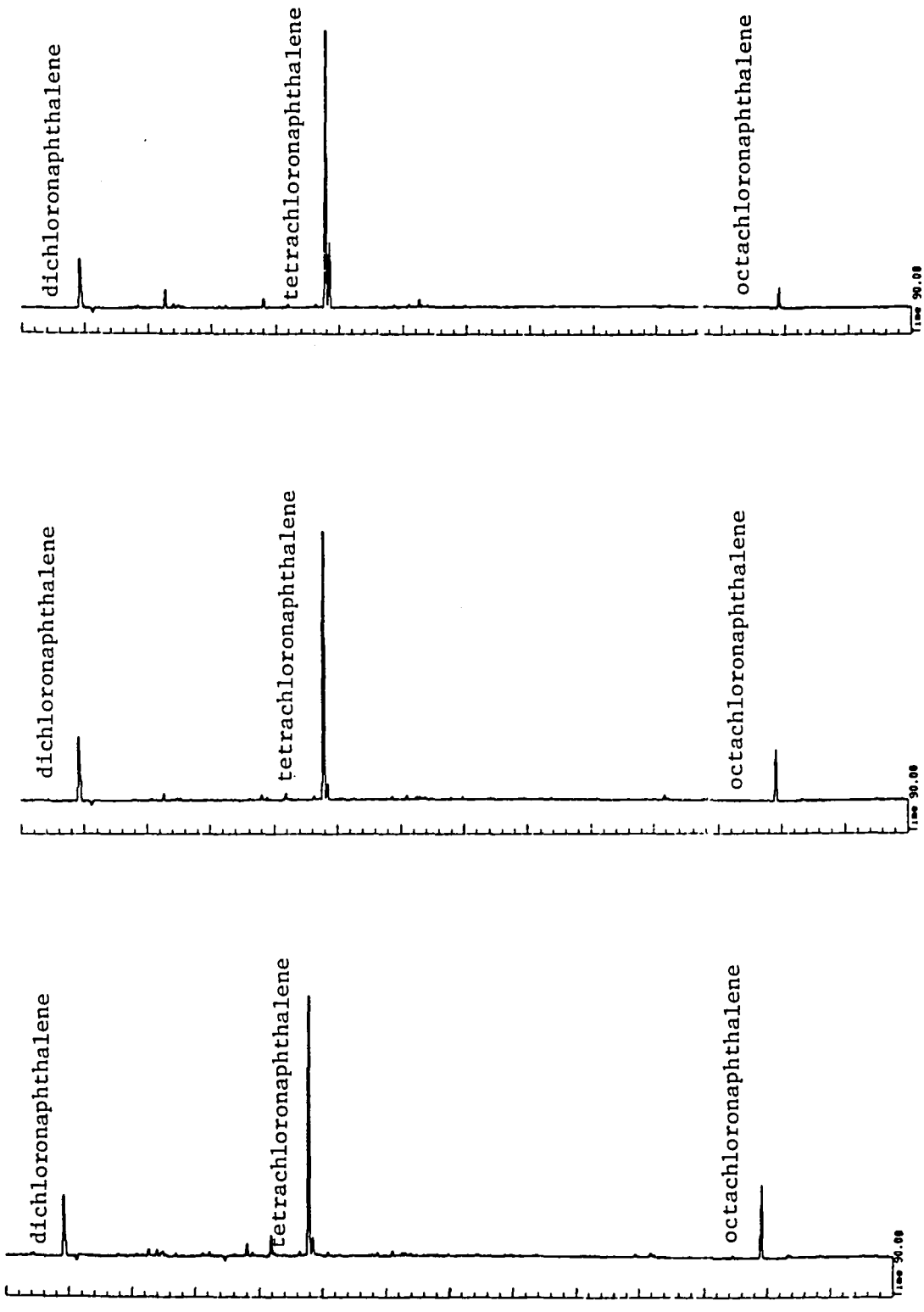


Figure 8. PUF plug field blanks.

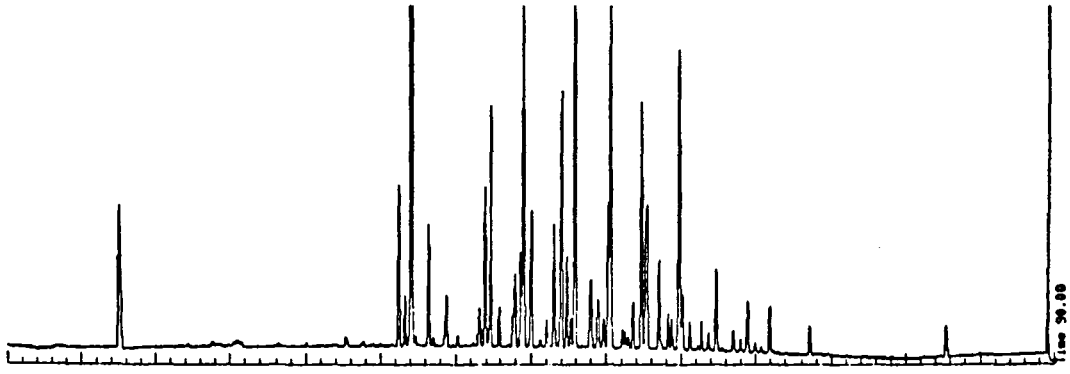
shown. Figure 9 shows a representative chromatogram of both the Aroclor 1254 standard and a DOP standard used for quantitation. Figures 10 to 12 show the chromatograms for the field samples analyzed. All chromatograms show traces from 20 to 90 minutes after sample injection. Each chromatogram is plotted at 150 mμ full scale rather than normalized to the most intense peak. Samples 2F-3 and 3F-3 show a loss of lighter compounds due to evaporation of the sample extract prior to analysis.

The instrumental limit of detection (LOD) for the PCBs was calculated as 9.9 pg/μL of a standard injected which is equal to 1.6 ng/m^3 for all samples collected. The limit of detection for dioctylphthalate was calculated from the DOP contamination on the nine field blanks where:

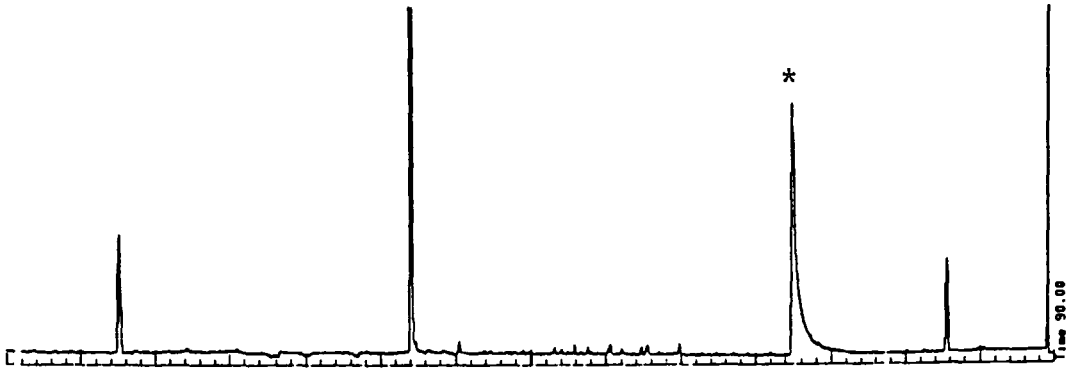
$$LOD = \bar{\chi}_{DOP} + 2\ S.D.$$

where $\bar{\chi}_{DOP}$ is the mean concentration of DOP detected in the field blanks and S.D. is the standard deviation of the individual measurements.

The limit of detection of dioctylphthalate is equal to 0.89 ng/m^3 in our samples.



Aroclor 1254



Dioctylphthalate (*)

Figure 9. Aroclor 1254 and dioctylphthalate standards.

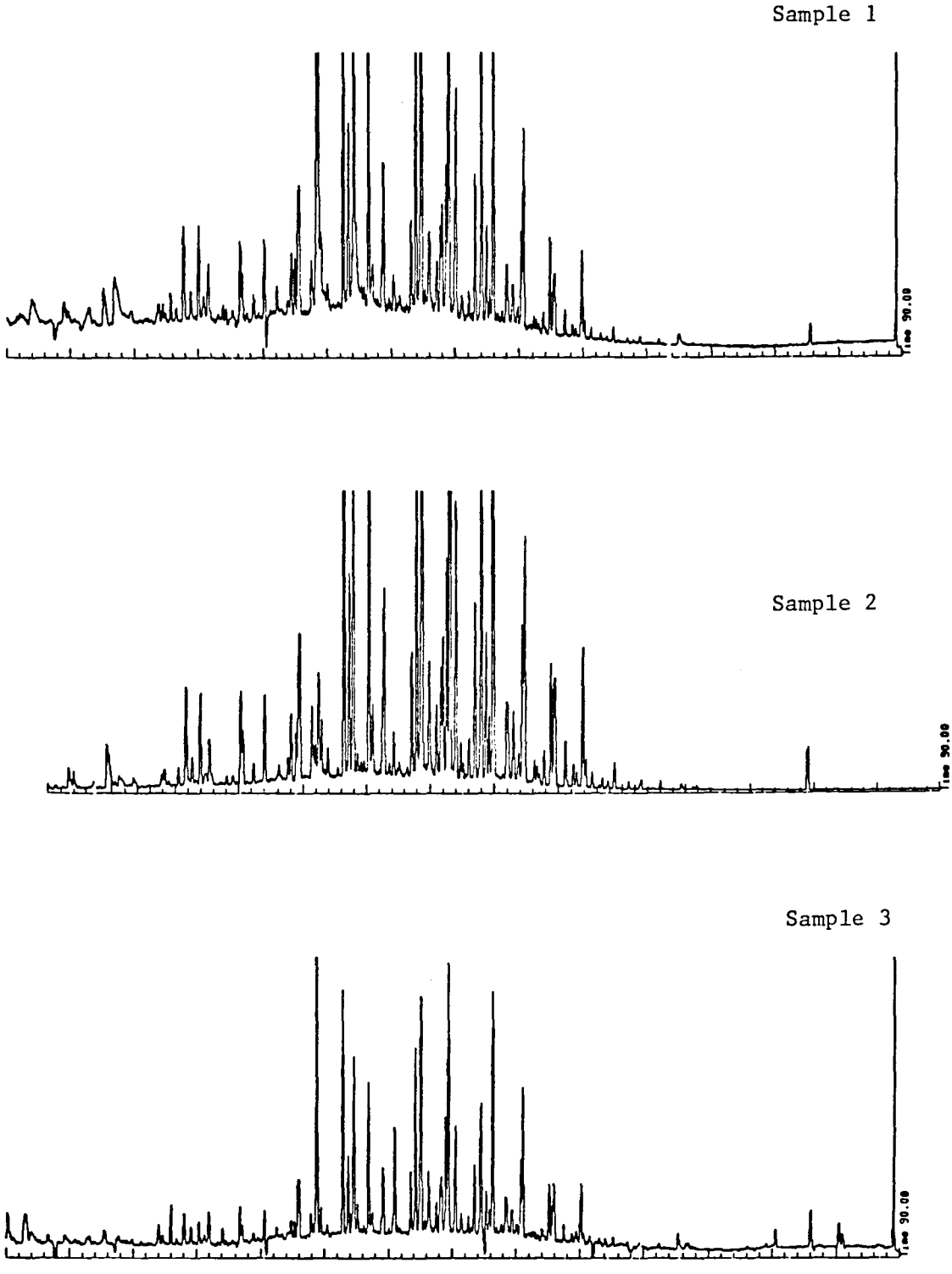


Figure 10. Semivolatile samples from Location One.

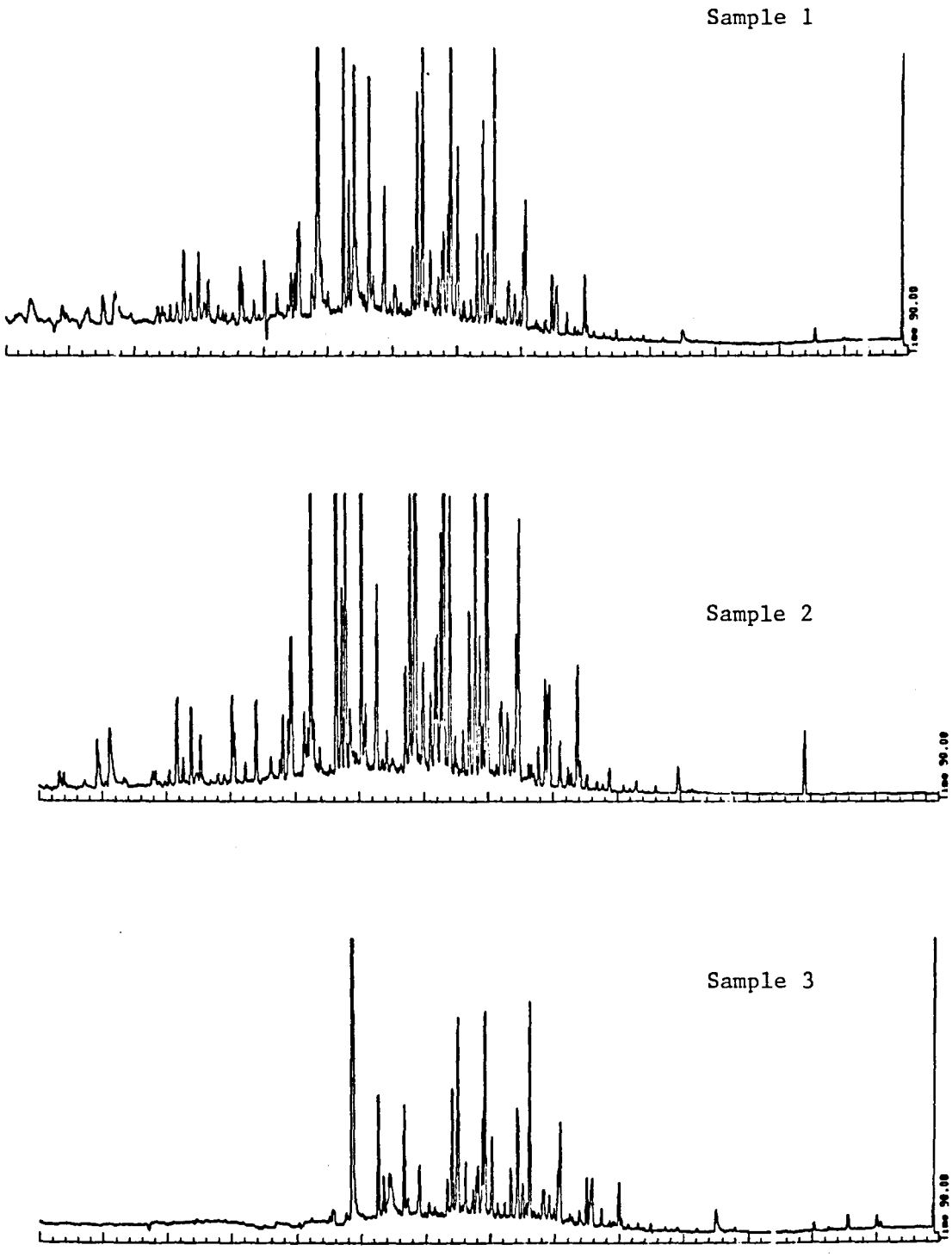


Figure 11. Semivolatile samples from Location Two.

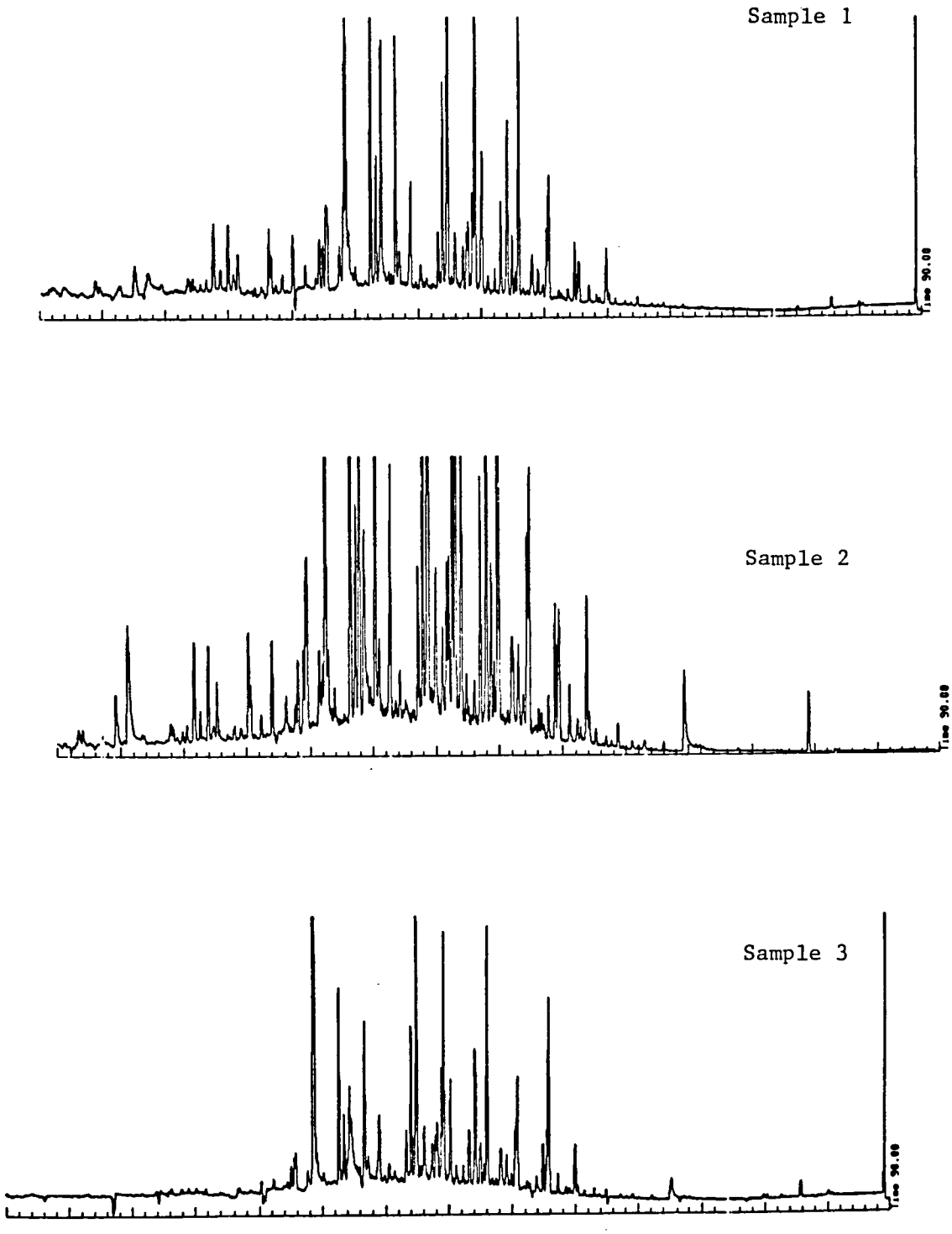


Figure 12. Semivolatile samples from Location Three.

4.0 References

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2. Pellizzari, E.D.: "Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors," EPA Report No. 600/2-75-075, November, 1975.

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APPENDIX A

Standard Operating Procedure for Tenax Cleanup and Preparation of Tenax Cartridges for Use in the Collection of Organic Compounds

RTI/ACS-SOP-320-001
December 1983
Revision 0

Standard Operating Procedure for Tenax Cleanup and Preparation of Tenax Cartridges for Use in the Collection of Organic Compounds

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Standard Operating Procedure for Tenax Cleanup and Preparation of Tenax Cartridges for Use in the Collection of Organic Compounds
RTI/ACS-SOP-320-001

1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure is two-fold: (1) it describes the methodology for cleaning Tenax and (2) it describes step-by-step the preparation and purification of the Tenax cartridges.

2.0 SUMMARY OF THE METHOD

All Tenax, whether new or recycled, must be purified before it is used for sample collection of organic compounds. The following routine shall be followed when Tenax is cleaned and packed into cartridges: (1) selection of the Tenax to be used; (2) solvent extraction; (3) drying the Tenax; (4) sieving the Tenax; (5) packing the Tenax into glass cartridges; (6) thermally desorbing the Tenax cartridges; (7) ensuring the integrity of the cleaning and desorbing procedure; and (8) packing and storing the cartridges.

3.0 CLEANING THE TENAX

3.1 If new Tenax is to be used follow Steps 3.1.1 to 3.1.3

3.1.1 Assign a unique number to the batch of Tenax to be cleaned.

NOTE: Tenax is subjected to the different steps of the cleaning procedure by batch.

3.1.2 In a bound RTI notebook assigned for Tenax only, begin a section every time a new batch is created.

3.1.3 Keep a record of the Tenax Lot number used.

NOTE: Before a new lot of Tenax is purchased, a small amount is subjected to the cleanup procedure and the background checked for acceptability.

3.2 If the Tenax to be cleaned is recycled Tenax follow Steps 3.2.1 to 3.2.4.

3.2.1 Select Tenax from the same matrix that was previously sampled (i.e., breath, personal air, fixed-site air).

3.2.2 Assign a unique batch number to the quantity to be used.

3.2.3 In the Tenax RTI notebook, begin a section for the new batch.

3.2.4 Enter the complete history of the Tenax (e.g., number of times used, including date(s) of preparation, number of cartridges in the last batch, etc...).

CAUTION

If a Tenax batch was previously known to be dirty, do not mix with another batch.

3.3 Solvent Extraction

3.3.1 Solvents

3.3.1.1 Methanol, B&J distilled in glass

3.3.1.2 n-Pentane, B&J distilled in glass

3.3.2 Apparatus and Materials

3.3.2.1 Extraction thimbles, cellulose (60 mm x 180 mm)

3.3.2.2 Glass wool, unsilanized

3.3.2.3 Soxhlet extractor, large 71/60 joint

3.3.2.4 Flask, round bottom 2000 mL

3.3.2.5 Condenser

3.3.2.6 Tweezers

3.3.2.7 Beaker, 100 mL

3.3.2.8 Variable transformer

3.3.2.9 Heating mantle for 2000 mL flask

NOTE: All glassware must be cleaned by soaking for at least one hour in Amway SA-8 Laundry compound, followed by several rinses with deionized water; and finally, baking for a minimum of four hours at 550-550°C.

3.3.3 Procedure

3.3.3.1 In a hood, set up a sufficient number of Soxhlet extraction units, each with a 2000 mL round bottom flask and a water cooled condenser.

3.3.3.2 Load approximately 50 g of Tenax into each thimble.

3.3.3.3 Cover the Tenax with approximately two centimeters of unsilanized glass wool.

3.3.3.4 Place the thimble in the Soxhlet.

3.3.3.5 Add 1200 mL of methanol to the 2000 mL flask.

3.3.3.6 Carefully pour an additional 600 mL of methanol onto the Tenax.

NOTE: The 600 mL of extra methanol are added directly onto the Tenax to ensure sufficient solvent for the extraction process after the initial adsorption of solvent.

3.3.3.7 Turn on the water to the condenser.

3.3.3.8 Turn on the Variac controlled heating mantle.

3.3.3.9 After the first extraction cycle, adjust the temperature with the variable transformer to obtain five cycles per hour.

3.3.3.10 Record in the Tenax notebook the date and time the extraction was started.

3.3.3.11 Begin a Tenax cleanup worksheet (see Example 1) and keep this worksheet in the laboratory next to the hood.

3.3.3.12 Continue the extraction for 24 hours.

3.3.3.13 Check the extraction units twice daily and enter the information on the worksheet.

CAUTION

To avoid solvent losses, ensure that sufficient water is flowing to cool the condensers.

3.3.3.14 After 24 hr cool the system and discard the methanol.

3.3.3.15 With a pair of tweezers carefully pull out the thimble and let it drain in a 100 mL beaker for 10 minutes.

3.3.3.16 Rinse the thimble with 50 mL of clean pentane. Repeat the rinse twice and then return the thimble to the Soxhlet. Discard the pentane.

CAUTION

To avoid contamination do not handle the thimble with your hands.

3.3.3.17 Transfer 1400mL of clean pentane to the flask. Reposition the Soxhlet and heat to reflux.

3.3.3.18 After the first cycle, adjust the temperature to obtain five cycles per hour.

3.3.3.19 Record in the notebook the date and time that the pentane extraction began.

3.3.3.20 Complete the information on the worksheet for this Tenax batch.

3.3.3.21 Continue the extraction for 24 hr.

3.3.3.22 Check the extraction units twice daily and enter the information on the worksheet.

3.3.3.23 After 24 hr of extraction, cool the system to room temperature.

3.3.3.24 Remove the thimble from the Soxhlet with a pair of tweezers.

3.3.3.25 Discard the pentane.

3.4 Drying the Tenax

3.4.1 Apparatus and Materials

3.4.1.1 Desiccator with gas connectors

3.4.1.2 Jar, wide mouth amber

3.4.1.3 Crystallizing dish, Kimax®

3.4.1.4 Vacuum oven equipped with a dry ice trap

3.4.1.5 Aluminum foil

3.4.1.6 Funnel

3.4.2 Procedure

3.4.2.1 Place the beakers containing the thimbles in the desiccator at room temperature under a slow "house" nitrogen flow (i.e., 25 mL/min).

CAUTION

Ensure that the activated charcoal in the carbon trap set up on line is replaced every three months.

3.4.2.2 The following day transfer the contents of two thimbles to a large crystallizing dish.

3.4.2.3 Transfer the rest of the Tenax to a wide mouth jar and label it indicating that has not been dried.

3.4.2.4 Cover the dish loosely with aluminum foil.

3.4.2.5 Set the dish in the vacuum oven.

3.4.2.6 Place dry ice/isopropanol in the vacuum trap.

3.4.2.7 Dry the Tenax overnight at 100°C and 28 inches of water.

3.4.2.8 The following day turn off the heater and allow the oven to reach room temperature before opening the oven.

NOTE: The oven needs approximately 3 hours to cool to room temperature.

3.4.2.9 To open the vacuum oven, first close off the valve leading to the pump.

3.4.2.10 Connect the "house" nitrogen line to the other valve connector on the vacuum oven.

3.4.2.11 Slowly turn on the nitrogen flow with one hand while opening the valve with the other hand.

NOTE: This procedure allows the oven to reach normal pressure under a nitrogen atmosphere.

CAUTION

Ensure that the nitrogen is vented out the oven through an activated charcoal tube.

3.4.2.12 Record every operation on the "Tenax Cleanup Worksheet" and in the notebook.

3.4.2.13 Remove the Tenax from the vacuum oven.

3.4.2.14 Open the valve leading to the pump and then immediately turn the vacuum pump off.

3.4.2.15 Carry the Tenax to the "clean room" and store it protected from the light, in a clean wide mouth jar with Teflon-lined cap.

3.4.2.16 Dry the rest of the Tenax batch following the steps 3.4.2.2 to 3.4.2.15.

4.0 PREPARATION OF TENAX CARTRIDGES

4.1 Sieving

4.1.1 Apparatus and Materials

4.1.1.1 Cotton gloves

4.1.1.2 Sieves, 40 and 60 mesh

4.1.1.3 Glass funnel

4.1.2 Procedure

4.1.2.1 Combine the contents of the jars containing Tenax from the same batch.

4.1.2.2 Sieve the material and collect the contents in the 40/60 mesh range.

4.1.2.3 Return the contents to the jar. Label the jar "sieved" and indicate the date.

4.1.2.4 Record this operation in the notebook.

4.2 Packing

4.2.1 Materials

4.2.1.1 Cotton gloves

4.2.1.2 Glass wool, unsilanized

4.2.1.3 Kimax culture tubes, 15 cm x 2.5 cm O.D.

4.2.1.4 Teflon cap liners, 24 mm new

4.2.1.5 Stainless steel tweezers

4.2.1.6 Screw caps, 24 mm

4.2.1.7 Silicone septa, Teflon-backed

4.2.1.8 One gallon metal paint cans

4.2.1.9 Glass tubes, 10 cm x 1.6 cm O.D.

4.2.2 Preparation of the Culture Tubes

4.2.2.1 Place the Teflon liners in a beaker and sonicate them in methanol for 10 minutes.

4.2.2.2 Rinse the liners with fresh methanol.

4.2.2.3 Repeat Steps 4.2.2.1 and 4.2.2.2 with pentane instead of methanol.

4.2.2.4 Dry the Teflon liners in the vacuum oven for five hours at 100°C and 28 inches of water.

4.2.2.5 Store the liners in a wide mouth jar in the "clean room".

CAUTION

To avoid contamination of the Tenax, always use a pair of tweezers to handle the liners.

4.2.2.6 Follow steps 4.2.2.1 to 4.2.2.5 to clean the silicone septa.

4.2.2.7 Soak the 24 mm screw caps in methanol for 30 minutes.

4.2.2.8 Remove the paper-lined foil from the caps with a spatula.

4.2.2.9 Rinse the caps in clean methanol and dry them in the vacuum oven overnight at 100°C.

4.2.2.10 Wrap the Kimax culture tube with aluminum foil and secure it with clear tape.

4.2.2.11 Place a 2-cm glass wool plug at the bottom of the culture tube.

4.2.2.12 Place a silicone septum in the screw cap. Cover the septum with a cleaned Teflon-liner.

4.2.2.13 Loosely close the culture tube with the screw cap.

4.2.3 Cartridge Packing

4.2.3.1 Carefully inspect the glass tubes before packing. Discard any tube with rough ends or cracks.

4.2.3.2 Set the glass tubes in a test tube rack.

4.2.3.3 Insert a 1-cm glass wool plug into one end of the glass tube and press with a dowel.

4.2.3.4 Transfer 6 cm of Tenax to the glass tube, using a glass funnel.

4.2.3.5 Insert another 1 cm glass wool plug into the other end of the tube (see Figure 1). Lightly compress it with a dowel.

NOTE: A 10 cm glass tube packed with Tenax is referred to as a Tenax cartridge.

4.2.3.6 Store the Tenax cartridges in the prepared culture tubes until desorption.

4.3 Desorption

4.3.1 Equipment and Materials

4.3.1.1 Desorption chambers

4.3.1.2 Helium, (certified 99.995%), with regulator

4.3.1.3 Tweezers

4.3.1.4 Clean paint cans, 1 gallon

4.3.2 Procedure

4.3.2.1 Turn on the desorption units to 270°C.

4.3.2.2 Turn on the helium tank.

4.3.2.3 Place liquid nitrogen in the cryogenic trap.

4.3.2.4 Open the helium line to the desorption chambers.

4.3.2.5 Adjust the helium flow under each chamber to approximately 15 mL/min.

4.3.2.6 Place the cartridges in the desorption chambers with the bottom end down (see Figure 1).

4.3.2.7 After all the cartridges are in place recheck the flows from each chamber.

CAUTION

To avoid contamination of the Tenax, ensure that helium is flowing through every cartridge.

4.3.2.8 Desorb the Tenax cartridges for five hours.

4.3.2.9 Refill the cryogenic trap with liquid nitrogen every hour, or when the level of liquid nitrogen is less than one-third full.

CAUTION

If liquid nitrogen in the trap is depleted all the impurities trapped in the line will be transported to the Tenax.

4.3.2.10 Record all pertinent information on the Tenax Cleanup Worksheet (see Figure 2) for the specific Tenax batch.

4.3.2.11 Recheck the helium flow every two hours and before removing the cartridges.

4.3.2.12 Remove each cartridge with a pair of tweezers and immediately place the hot cartridge in a Kimax culture tube.

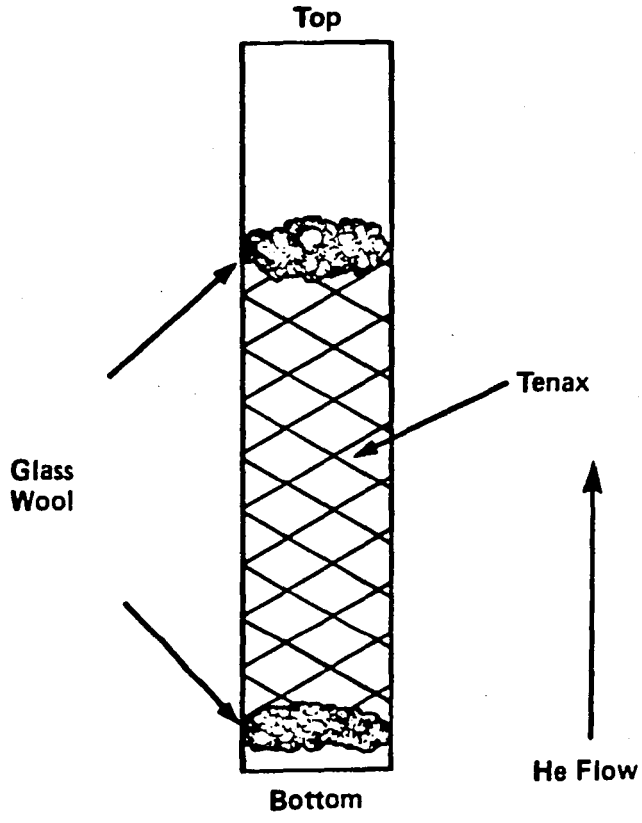

Figure 1. Tenax cartridge.

TENAX CLEANUP WORKSHEET

Tenax Batch No. _____ Projected Use_____

Virgin/Recycled. Recycled Source _____ No. of Cartridges _____

Extraction

Number of Soxhlet Units (circle one): 1 2 3 4 5

Methanol Extraction: Date (Hours)

Siphon Rate

Pentane Extraction: Date (Hours)

Siphon Rate

Drying

Nitrogen Chamber: Date (Hours)

Approx. Flowrate

Vacuum Oven: Date (Hours)

Pump Trap

Cooldown (Hours)

N_2 Vent Thru Act. C

Sieving/Packing

Sieve (40/60) Date:

Packing Date(s):

Cleanup

Teflon Septum; Date:

Teflon Liner; Date:

Figure 2. Tenax cleanup worksheet - Form A

TENAX CLEANUP WORKSHEET

Desorption

Lot:	A	B	C	D	E	F	G	H
Date:								
Hours:								
Temp.:								
Liq. N_2:								
He Flow:								

GC Check

Date:

GC Identifier No.

No. of Cart.

Peaks >30% fs:

Peaks <30% fs:

OK/NG:

Redesorption

Lot:

Date:

Reason:

GC Check:

Figure 2. Tenax cleanup worksheet - Form B.

4.3.2.13 Seal the tube.

4.3.2.14 Label the screw cap with the Tenax batch number and the culture tube with the desorption date.

4.3.2.15 Store the culture tubes in the "clean" room in one gallon paint cans.

4.4 Background Check

Ten percent of the cartridges from each batch are analyzed for background contamination using GC/FID. The ten percent selected must include cartridges from each desorption unit and from every desorption period of that batch.

4.4.1 Analyze the Tenax cartridges using a Varian 3700 GC equipped with a thermal desorption injection unit and a flame ionization detector, and interfaced to a Varian CDS III integrator.

4.4.2 Select one cartridge from each desorption period and from every unit.

4.4.3 Analyze each cartridge at least 24 hours after desorption.

NOTE: Studies have shown evidence for the migration of contaminants from the interior of Tenax beads as a function of time.

4.4.4 Analyze the cartridges using the following instrumental conditions.

4.4.4.1 Colum: fused silica capillary column (30 m X 0.25 μm) Liq. phase DB1; or equivalent.

4.4.4.2 Detector temperature: 300°C

4.4.4.3 Injector temperature: 280°C

4.4.4.4 Desorption unit temperature: 260°C

4.4.4.5 Temperature program: 30°C (5 min), 4°C/min to 220° (10 min)

4.4.4.6 Attenuation: 128 X 10^{-12} (or as required for adequate recorder response)

4.4.4.7 Desorption time: 8 min

4.4.4.8 Helium carrier flow: 1.2 mL/min

4.4.4.9 H_2 flow to FID ~35 mL/min

4.4.4.10 Air flow to FID: ∿300 mL/min

4.4.4.11 Make-up gas: ∿30 mL/min

4.4.4.12 Recorder chart speed: 1 cm/min

4.4.5 Examine the chromatographic retention window for each target. The window is defined as the mean retention time (5 replicates) $\pm$ 1σ.

NOTE: The chromatographic retention window for each target compound is determined prior to the cartridge evaluation from the analysis of cartridges loaded with known amounts of the compounds of interest (see SOP-630-001 and SOP-630-002).

4.4.6 In your notebook, record the total area counts for each window.

4.4.7 Compare the area counts to the historical area count data corresponding to the limits of detection (LOD) for each compound as determined by GC/MS analysis (see Table 1).

NOTE: The historical area count data is obtained prior to the cartridge evaluation by loading each compound at the GC/MS limit of detection, and determining its respective area by GC/FID analysis.

4.4.8 If no peaks or only one peak falls within a window of study, the set of cartridges is accepted provided that the area of the peak does not exceed three times the LOD.

4.4.9 If more than one peak falls within the windows of study, but the areas are lower than those corresponding to the limits of detection, then the set of cartridges is acceptable.

4.4.10 If the areas of more than one peak exceed the area corresponding to the LOD for that window, the set of cartridges is rejected and must be redesorbed.

4.4.11 Cartridges may be deemed acceptable if analysis by GC/MS indicates clean windows, regardless of GC/FID results. Task Leader approval is required for acceptance of such cartridges (i.e., those deemed unacceptable by GC/FID, but acceptable by GC/MS).

Table 1. LIMITS OF DETECTION FOR TEAM TARGET COMPOUNDS

Compound	LOD (ng/cartridge)
Bromodichloromethane	10
Chlorodibromomethane	10
Chloroform	6
1,1,1-Trichloroethane	7
Benzene	3
Carbon tetrachloride	10
Tetrachloroethylene	10
Styrene	4
m- or p-Dichlorobenzene	4
Ethylbenzene	3
Xylene, o, m, or p	3
Trichloroethylene	14
Chlorobenzene	4
Tetrachloroethane (isom)	5
1,2-Dichloroethane	7
n-Decane	5
n-Undecane	5
n-Dodecane	5

Source: Historical LOD data from Finnigan 3300.

4.4.12 After a sample has been analyzed, label the desorption unit lot from which it was drawn according to the following criteria.

4.4.12.1 If the set of cartridges is acceptable label it "Ready to be packed".

4.4.12.2 If the cartridges are rejected, label the can "To be redesorbed" "Date".

4.4.13 Quality Assurance for the Background Check.

4.4.13.1 Every three days, run a control cartridge loaded with the GC/MS LOD amounts.

4.4.13.2 Determine the chromatographic retention windows for each target compound and the corresponding area counts.

4.4.13.3 Compare the retention window and the corresponding area with the historical data.

4.4.13.4 If an historical data base does not exist, create one after loading three cartridges with the appropriate amounts of target compounds.

4.4.13.5 If any major alterations are made to the GC (i.e., replacement of the thermal desorption/injection unit, cleaning of the detector; replacement of the column), create a new data base.

4.4.13.6 If the analysis of the control cartridge indicates that two or less compounds are out-of-control, begin the background check.

NOTE: A compound is considered out-of-control when its retention window deviates from the mean value by more than two standard deviations, and its mean area counts by more than three standard deviations.

4.4.13.7 If more than two compounds are out-of-control, load a second cartridge and analyze it.

4.4.13.8 If the second cartridge is in control, proceed with the background check.

4.4.13.9 If it is out-of-control, troubleshoot the instrument before proceeding with the background check.

APPENDIX B

Validation of Modified Tenax Cartridges

Purpose

Specially designed Tenax cartridges were prepared for use during the collection of volatile organic samples in the NASA clean-room during January, 1985. These cartridges employed the use of a stainless steel wire screen and a stainless steel retaining ring to hold the Tenax bed intact within the sampling cartridge. Standard Tenax cartridges used by RTI employs glass wool plugs within the cartridge for this purpose. However, due to the work being conducted in the clean-room it was necessary to eliminate any possible source of airborne particulates produced by the sample cartridges. Therefore, the glass wool plugs were replaced with the wire screens eliminating any fragmentation of the glass wool resulting in the generation of airborne particulates within the clean-room.

Validation

A mixture of target compounds was loaded onto both a standard Tenax cartridge and a modified Tenax cartridge. A comparison of the recovery of those compounds from the two types of cartridges was made in order to determine if the two cartridges performed in smiliar and acceptable manners.

Tenax from a single batch was prepared as described in Appendix A. Both standard and modified Tenax cartridges were prepared from the same batch of Tenax. The cartridges were thermally desorbed for 17 hours. Background levels were checked 25 hours after removal from the desorption units. Background checks were made on a capillary gas chromatograph showed no contamination resulting from the wire screens.

A clean standard Tenax cartridge with glass wool was loaded with 1 microliter of the standard solution shown in Table 1. This was considered

the standard reference which provided good recoveries of the target compounds. A second cartridge containing the wire screen was loaded in the same manner. Each cartridge was analyzed on a capillary gas chromatograph within a flame ionization detector. Recoveries of the target compounds were very similar for the two cartridges.

TABLE 1. STANDARD SOLUTION OF VOLATILE ORGANIC COMPOUNDS

Compound	Concentration (ng/uL)
benzene	42
epichlorohydrin	104
ethylbenzene	42
1,2-dichloroethane	60
1,1,1-trichloroethane	54
trichloroethylene	58
tetrachloroethylene	124
1,1,2,2-tetrachloroethane	62
carbon tetrachloride	62
chlorobenzene	58
m-dichlorobenzene	62
α-pinene	58
n-butylacetate	140
2-ethoxyethylacetate	156
o-Cresol	62
m-Cresol	124
o-xylene	60
m-xylene	34
n-propylbenzene	80
isopropylbenzene	20
m-ethyltoluene	58
1,2,4-trimethylbenzene	40
1,3,5-trimethylbenzene	104
styrene	36
n-decane	58
n-undecane	60
n-dodecane	60
bromodichloromethane	60
o-dichlorobenzene	40
p-dichbrobenzene	80

APPENDIX C

Breakthrough Determination for Two-Stage PUF Filters

Purpose

The purpose of the following experiment was to determine whether dioctylpthalate (DOP) would break through a two-stage PUF filter. The break through volume is defined as that point at which 50% of a discrete sample introduced into the filter is lost. For the study conducted at NASA, sample volumes were not to exceed 7000 liters per two-stage filter.

Validation

Two-stage PUF (each 22 mm ID x 7.6 cm long) filters spiked with DOP had air drawn through them at 2.0 L/min for 24, 48, and 72 hours, respectively. At the completion of the sampling, the backup or second filter in the series was analyzed for the presence of DOP. The amount of DOP found on the backup filter would then determine what percent break through had occurred for the specific volume of air drawn through the filters.

Three sets containing four replicate filters were prepared. Each set was comprised of three sample filters and one blank filter. Each filter contained two clean PUF plugs within a glass cartridge as shown in Figure 1. The filters were attached to vacuum pumps. Twenty micro-liters of a standard solution containing 9.8 micrograms DOP was added to the front of three filters from each set of four. The spiked samples equilibrated for five minutes in order for the solvent from the standard to evaporate. After this the sampling pumps were turned on and the flows adjusted to 2.0 L/min for all filters.

As stated previously, each set contained three replicate samples and a blank. The blank two consisted of two unspiked PUF plugs within a glass cartridge. Its purpose was to determine if any interferences or

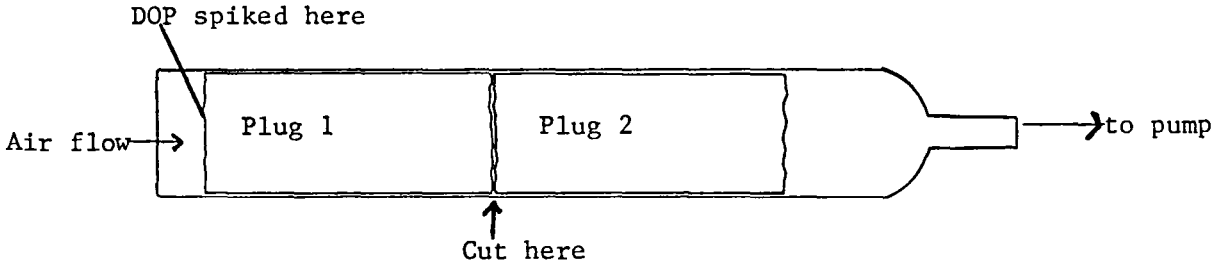

Figure 1. Two-stage PUF plug filter.

contamination from the laboratory air had occurred while the spiked samples were being exposed.

After 24 hours the first set of four filters were removed from the vacuum pumps. The front, spiked, PUF plugs were removed from the glass cartridges with clean forceps and placed in clean, foil-lined vials for storage. The glass cartridges were then cut in half just at the front of the backup plugs as shown in Figure 1. The backup PUF plugs were then removed using a second set of clean forceps, and placed into a foil-lined vial for storage. The glass cartridges were cut in half in order to prevent any DOP contamination of the backup plug by pulling it through the part of the cartridge which held the spiked PUF plug.

After 48 and 72 hours, respectively, the two other sets of triplicate plugs and blanks were removed and stored. Table 1 shows the volumes drawn through the three sets of PUF filters during their 24, 48 and 72 hours exposure periods.

The backup plugs were Soxhlet exracted in a 250 mL extractor with 150 mL HPLC grade hexane for approximately 18 hours. After the extraction was complete, the extracts were concentrated to approximately 5 mL in a Kuderna-Danish concentrators. A micro Snyder columns were added to the K-D receiver tubes and the extracts were reduced to 1.0 mL by cryogenically cleaned N_2 evaporation. The samples were removed and stored in septum cap vials.

The PUF plug extracts were analyzed by packed column gas chromatography using electron capture detection (GC/ECD). Table 2 lists the GC conditions used during the analysis.

TABLE 1. PERCENT BREAKTHROUGH OF DOP ONTO BACKUP PUF PLUG

Sample	Liters Air Sampled (L)	% Breakthrough	Mean ± CV
24-hour - 1	2880	11.0	
2	2880	1.0	4.7 ± 5.5
3	2880	2.0	
48-hour - 1	5768	0.0	
2	5768	37.0	12.3 ± 21.4
3	5768	0.0	
72-hour - 1	8678	58.0	
2	8678	4.0	20.7 ± 32.3
3	8678	0.0	

TABLE 2. INSTRUMENTAL CONDITIONS FOR ANALYSIS OF PUF EXTRACTS

Column:	1.7 mm x 2 mm 1% SE-30
Detector:	^{63}Ni ECD
Detector Temp.:	290°C
Injector Temp.:	220°C
Column Temp.:	220°C isothermal
Carrier gas:	N_2 @ 35 mL/min
Injection size:	1.0 µL

Table 1 lists the results of the backup PUF plug analysis. As shown, the percent recovery of DOP from the backup filters was relatively low yet increasing as the volume of air drawn through the filters increased. In all three sets, the major contribution of DOP found comes from a single plug, hence the large coefficients of variation. The reason for this occurrence is unknown at this time.

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15. Supplementary Notes

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16. Abstract

The environment of the HALOE assembly clean room at NASA Langley Research Center was analyzed to determine the background levels of airborne organic compounds. Sampling was accomplished by pumping the clean room air through absorbing cartridges. For volatile organics, cartridges were thermally desorbed and then analyzed by gas chromatography and mass spectrometry, compounds were identified by searching the EPA/NIH data base using an interactive operator INCOS computer search algorithm. For semivolatile organics, cartridges were solvent entracted and concentrated extracts were analyzed by gas chromatography-electron capture detection, compound identification was made by matching gas chromatogram retention times with known standards. The detection limits for the semivolatile organics were; 0.89 ng/M^3 for dioctylphlhalate (DOP) and 1.6 ng/M^3 for polychlorinated biphenyls (PCB). The detection limit for volatile organics ranged from 1 to 50 parts per trillion. Only trace quantities of organics were detected, the DOP levels did not exceed 2.5 ng/M^3 and the PCB levels did not exceed 454 ng/M^3.

17. Key Words (Suggested by Authors(s))	18. Distribution Statement
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