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FINAL REPORT

EVALUATION OF PORTABLE MULTISORBENT AIR SAMPLERS FOR USE WITH AN AUTOMATED MULTITUBE ANALYZER

by

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16. ABSTRACT The objective of this study was to evaluate the operational characteristics of the Perkin-Elmer Model STS 25 Sequential Tube Sampler and IITRI/IIT (IIT Research Institute/Illinois Institute of Technology) Total Isolated-by-Microenvironment Exposure (TIME) monitor. Both units use multisorbent carbon-based sampling tubes to collect volatile organic compounds (VOC'S) in ambient air and a analytical procedure that does not require cryogens for analysis. A Perkin Elmer Auto Thermal Desorption System (Model ATD 400) was used to process the collection tubes for analyses of the target species (VOC's listed in the EPA TO-14 method). The Model STS 25 is designed to sample air with up to 24 tubes, one at a time for a preset period of time. The TIME monitor is designed to measure total exposure to volatile organics and apportion the exposure into its micro-environmental components indoor (workplace/residential), outdoor or in-transit. The TIME unit uses ultrasound reflection to identify a subject's location. Very good precision for collection and analysis of these volatile organic compounds was achieved. Details of the study are presented along with recommendations for further evaluation and developmental efforts for these samplers and the sorbent/analytical methodology.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature of processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency, including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of ongoing significance to EPA. The development of new and improved methods for sampling these compounds such as the use of solid sorbents in conjunction with portable air sampling devices is being actively pursued by EPA in order to offer practical, cost-effective solutions to monitoring. The evaluation of two novel air samplers that employ multisorbent collection tubes is presented in this report. A discussion of the methodology involved in processing these sorbent tubes is also discussed. The techniques described herein should provide an important aid in the measurement of the extent of human exposure to toxic organic compounds.

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ABSTRACT

The objectives of the work described in this report were to evaluate two novel portable air sampling devices, using an improved carbon-based sorbent system for sample collection and an analytical procedure that does not require the use of cryogens for analysis of 42 selected toxic air pollutants.

The Perkin Elmer Model STS 25 Sequential Tube Sampler is designed to sample air with up to 24 sorbent tubes, one at a time, for a preset period of time. The device was tested under different operating conditions. When used to sample ambient air, the analytical results obtained were comparable with those from a stainless steel canister sample using the US-EPA Method TO-14. When tested under stringent laboratory conditions in a small chamber, the STS 25 produced a number of artifacts that were attributed to emissions from the materials used in the sampler housing. These interfered with the analysis of the compounds of interest. No mechanical problems were experienced with the operation of the STS-25 sampler.

The IITRI/IIT (IIT Research Institute/Illinois Institute of Technology) Total Isolated-by-Microenvironment Exposure (TIME) monitor is designed to measure total exposure to volatile organics and apportion the exposure into its microenvironmental components (indoor-residential, indoor-workplace, outdoor, or in-transit). The unit uses ultrasound reflection to identify and record a subject's presence in a specific microenvironment and directs the air being sampled to the sorbent tube associated with that microenvironment. The device was modified to reduce its size and weight, and the software to control the operation of the unit was refined. The unit was tested in several environments and the exposed sorbent tubes were analyzed under the same conditions and for the same compounds that were targeted in the STS 25 evaluation.

Both air samplers made use of three-stage tubes packed with Carbosieve S-III, Carbotrap, and Carbotrap C. With this sorbent combination, the target species were collected in both dry and humidified air samples of up to 3 L volume. In the analytical step, the compounds were desorbed and then refocused onto an electrically cooled secondary sorbent bed containing Carbosieve S-III and Carbotrap. After desorption, analysis was accomplished using a thick-film capillary column without the use of cryogen. Very good precision for collection and analysis of these volatile compounds was achieved, with only the most volatile species showing a tendency to break through the sorbent bed.

This report is being submitted in fulfillment of Contract No. 68-D0-0007 by Battelle Columbus Operations under sponsorship of the U.S. Environmental Protection Agency. It covers a period from March 15, 1992, to September 30, 1992, and work was completed as of September 30, 1992.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables viii
Acknowledgment ix

1. Introduction 1
2. Conclusions and Recommendations 4
3. Experimental 7
   Instrumentation 7
   Air sampling devices 12
   Gas standards 18
   Sampler tube and refocusing trap sorbents 18
   Environmental chamber 20
   Procedures 22
4. Results and Discussion 28
   Task 1: Selection and validation of multisorbent system 28
   Task 2: STS 25 sequential tube sampler evaluation 52
   Task 3: TIME monitor evaluation 66

References 71
Appendices

A. TIME monitor operating instructions 73
B. Summary of command structure to transfer mobility data from TIME monitor to PC 76

FIGURES

Number		Page
1-a	Model 1020X Data System analytical method	9
1-b	Model 1020X Data System analytical method	10
1-c	Model 1020X Data System analytical method	11
2	Perkin Elmer Sequential Tube Sampler (STS 25)	13
3	TIME monitor schematic	15
4	TIME monitor electronics diagram	16
5	IITRI/IIT TIME monitor	17
6	Small-scale environmental chamber	21
7	STS 25 (front), Tylan-controller pump/tube sampler (left rear), and stainless steel canister (right rear)	26
8	FID (upper) and ECD (lower) chromatograms for a dry 0.5-L volume TO-14 sample at 2 ppbv	31
9	FID chromatograms for primary (upper) and secondary (lower) Carbosieve S-III "Train" tubes showing TO-14 retained species	36
10	FID chromatograms for primary (upper) and secondary (lower) Carbotrap "Train" tubes showing TO-14 retained species	37
11	FID chromatograms for primary (upper) and secondary (lower) Carbotrap C "Train" tubes showing TO-14 retained species	38
12-a	Typical FID chromatogram for a humidified 3-L volume TO-14 calibration run at 2 ppbv	42

FIGURES (Continued)

Number		Page
12-b	Typical FID chromatogram for a humidified 3-L volume TO-14 calibration run at 2 ppbv	43
13	Typical ECD chromatogram for a humidified 3-L volume TO-14 calibration run at 2 ppbv	44
14	FID chromatograms for two tubes loaded with dry 3-L volume TO-14 calibration mixtures	46
15	FID chromatograms for a tube loaded with humidified 3-L volume Aadco air (upper) and a tube loaded with dry 3-L volume Aadco air (lower) samples	47
16	FID chromatogram for humidified 3-L volume polar mixture at 2 ppbv	48
17	FID chromatogram for environmental chamber blank sample collected by the STS 25 (60% RH, 37°C, 3-L)	55
18	FID chromatogram for environmental chamber TO-14 mixture collected by the STS 25 (60% RH, 37°C, 3-L volume, 10 ppbv)	60
19	FID chromatograms for indoor air sample collected on multisorbent tubes by the STS 25 (upper) and a Tylan-controlled pump sampler (lower)	63
20	FID chromatograms for outdoor air sample collected on multisorbent tubes by the STS 25 (upper) and a Tylan-controlled pump sampler (lower)	65
21	FID chromatogram of sample taken in a microenvironment using the TIME monitor	67
22	Data system listing of target compound concentrations from sample chromatogram shown in Figure 21	68

TABLES

Number		Page
1	Target Compounds: Nonpolar TO-14 and Polar VOCs	19
2	Results from Loading 0.5-L Dry Standards Onto Peltier Cooled Refocusing Trap	29
3	Relative Performance of a Three-Stage Sorbent Tube for Collecting Dry Multi-Liter TO-14 Samples at 2 ppbv Concentration	32
4	Recovery Efficiency of TO-14 Target Compounds in a Six-Tube "Train" of Sorbent Beds	34
5	Average FID Peak Areas and Precision Data for Humidified 3-L TO-14 Standards Collected...	41
6	Recovery Efficiencies of TO-14 Target Compounds at 2 ppbv via Canister Sampling and Cryogenic/MSD Analysis	50
7	Recovery Efficiencies of TO-14 Target Compounds at 10 ppbv via Canister Sampling and Cryogenic/MSD Analysis	51
8	Background Air Samples (3 L) Collected with the STS 25 and in Canisters	53
9	Comparison of Recovery Efficiencies of TO-14 Target Compounds at 2 ppbv Obtained with the STS 25 and in Canisters	56
10	Comparison of Recovery Efficiencies of TO-14 Target Compounds at 10 ppbv Obtained with the STS 25 and in Canisters	57
11	Indoor Air Sampling Results Obtained Using STS 25, Tylan/Sorbent Tube Sampler, and Canister Sampler (Values in ppbv)	61
12	Outdoor Air Sampling Results Obtained Using STS 25, Tylan/Sorbent Sampler, and Canister Sampler (Values in ppbv)	64
13	Concentrations (in ppbv) of Target Compounds Obtained for Two Field Tests of the TIME Monitor	70

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SECTION 1

INTRODUCTION

Recognition of the importance of trace-level volatile organic compounds (VOCs) in breathing-zone air and their potential impact on human health (1) has stimulated interest in methods for characterizing these compounds. Most of the techniques in use today for measuring VOC concentrations have their origin in industrial hygiene monitoring methods. They generally rely on solid sorbents (2-5) or containers (6) to collect whole-air samples. Because of the logistics of handling the samples in the field and their subsequent analysis in the laboratory, they are restricted to time-integrated samples or individual grab samples at fixed locations.

Long-term integrative sample collection is the preferred approach for measuring relatively constant emissions and for assessing average exposure, such as in studies of chronic health effects. (7) However, to obtain detailed information on temporal or spatial changes, as in the case of intermittent emissions or acute exposures, short and frequent sampling periods in the various locations in which exposure may occur are more appropriate. A whole-air sequential sampler for performing time-resolved measurements of specific VOCs has been described by Pleil et al. (8) The system is portable and can be programmed to consecutively fill 12 stainless steel syringes (150 cc each) in-situ at a rate of 2 to 90 min per sample. Field tests conducted with the instrument showed that it was capable of measuring wide variations in VOC concentrations that typically occur in indoor environments in short periods of time.

A recent development in efforts to measure temporal variability of VOCs is the Perkin Elmer Sequential Tube Sampler (STS 25), which is designed for use with their Automated Thermal Desorption system (ATD 400) and gas chromatograph (GC). The STS 25 is a portable, self-contained unit that can collect air samples consecutively onto a batch of up

to 24 sorbent tubes, one at a time, at a preselected collection time of 0.1 s to 10 h per sample. (9) The tubes are packed with the sorbent material that is used to collect the VOCs from the air. Air is drawn through each tube in turn using a personal monitoring pump. When not in position to collect a sample, the tubes are sealed with diffusion-limiting caps to minimize further sampling.

The ATD 400 consists of a carousel that can be loaded with up to 50 sorbent tubes. Once a method has been established for analyzing the tubes, the ATD 400 will process the tubes sequentially without manual assistance. The process includes positioning and sealing the tube in the gas stream of the GC analyzer, leak-checking the system, thermally desorbing the tube and refocusing the analytes onto an electrically cooled sorbent trap, and finally desorbing the refocused sample onto the GC for analysis.

Pollack and Holdren (10) have evaluated the operation of a prototype version of the ATD 400 and the GC along with appropriate carbon-based sorbents for collecting and desorbing VOCs from ambient and indoor air. Sampler tubes were packed with combinations of five different carbon-based sorbents in order to determine the optimal configuration for processing C_2 to C_9 hydrocarbons. They showed that carbon-based multisorbent beds, together with automated analysis of the samples, offer important advantages in ease of use and application to a broad range of VOCs.

The shadow sensor, which was the precursor to the IITRI/IIT (IIT Research Institute/Illinois Institute of Technology) TIME monitor, was developed by Moschandreas and Relwani (11) to provide detailed information on spatial changes associated with exposure to toxic air pollutants. It serves as an electronic activity pattern sensor by identifying various microenvironments, namely indoors, outdoor and in-transit, and the time spent by a subject in each microenvironment. Although this device provides information on mobility patterns with improved and documented accuracy over traditional indirect methods (i.e., logs or recall responses), it is still limited because it does not measure the actual exposure, given by the product of concentration and time, in each microenvironment. Instead, it provides a means of estimating the total exposure by time-weighting the measured concentration in each microenvironment with the time the subject spent in that environment. The TIME monitor, which incorporates the shadow sensor, was developed in an attempt to independently measure

the microenvironmental components of the total exposure. An early version of the monitor was designed and tested in 1991. (12) This version measured the total VOC concentrations of three microenvironmental components (indoors, outdoors, in-transit) of total exposure over a twelve-hour period. However, the unit was relatively heavy and therefore not entirely unobtrusive. Moreover, it was incapable of resolving the indoor microenvironment into residential and workplace components.

The present study was undertaken to evaluate the performance of the Perkin Elmer STS 25 Sequential Tube Sampler and the TIME monitor using the same carbon-based sorbent tubes with the Perkin Elmer Automated Thermal Desorption system (ATD 400) and gas chromatograph (GC). Before the evaluations were begun, the performance of a three-stage carbon-based multisorbent bed for sample collection, along with the electrically cooled two-stage carbon-based trap used for refocusing the desorbed sample, was refined and validated. The analytical method validation work (Task 1) and evaluation of the STS 25 sampler (Task 2) were conducted at Battelle Columbus Operations; work on the redesign, miniaturization, and testing of the TIME monitor (Task 3) was carried out at IIT. Battelle supplied IIT with clean carbon-based multisorbent sampler tubes for use in their evaluation of the TIME monitor and analyzed the collected samples using the ATD 400/GC system.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Two portable air samplers have been evaluated using a specially-developed sampling and analysis methodology for characterizing selected toxic air pollutants. The sample collection and analysis procedures were refined in the first phase of the study. The approach involves passing air samples through a three-stage multisorbent bed comprised of Carbosieve S-III, Carbotrap, and Carbotrap C to collect the VOCs. After sampling, the VOCs are desorbed from the sorbent tube and refocused onto an electrically cooled two-stage sorbent trap packed with Carbosieve S-III and Carbotrap. This operation is carried out automatically using a Perkin Elmer Auto Thermal Desorption system Model ATD 400. The refocused materials are then desorbed and transferred to a Perkin Elmer Auto Gas Chromatograph model for analytical separation using a thick-film capillary column.

Laboratory tests demonstrated quantitative collection and analytical separation of 42 selected VOCs from prepared samples of up to 3 L in volume and relative humidities of about 60 percent. Measurement precision for the target species was excellent for these multiliter samples, with relative standard deviations generally < 10 percent.

This sampling and analysis methodology was used in the second and third phases of the study to evaluate the Perkin Elmer Sequential Tube Sampler (Model STS 25) and the IITRI/IIT Total Isolated-by-Microenvironment Exposure (TIME) Monitor.

In the second phase, the mechanical reliability of the STS 25 was first confirmed before the collection capabilities of the device were investigated. The instrument was challenged with the 42 target compounds in standard mixtures under controlled laboratory conditions and was also used to collect indoor and outdoor air samples. The laboratory tests were carried out in a 75-L environmental chamber. The temperature, relative humidity, and concentration of the target compounds were adjusted to test the STS 25 under various

sampling conditions. Background measurements were also made. These tests indicated that the STS 25 can produce artifacts that may interfere with the identification and quantification of the target compounds. This laboratory evaluation was, however, considered to be a very stringent test, since it was not practicable to purge the chamber with challenge mixtures at a rate equal to that at which air is drawn through the STS 25 unit (30 L/min) during air sampling. This restricted flow rate resulted in a build up of artifacts emitted by the sampler in the chamber atmosphere. These artifacts had an adverse effect on the characterization of the target compounds, since identification by the data system is based solely on flame ionization detector (FID) results and co-elution of the artifacts with the target species resulted in exaggerated recovery efficiencies. Nevertheless, within the limitations imposed by the chamber sampling environment and the analytical system, the operation of the STS 25 for collection of the target compounds was satisfactory.

When used to collect indoor and outdoor air samples, the artifact effects observed during chamber tests with the STS 25 were no longer present. Concurrent with the STS 25 sampling, a duplicate sorbent tube sample was collected using a standard pump/mass flow controller assembly. A canister sample was also collected. The tubes were analyzed using the method developed during this study and the canister was processed using a conventional cryogenic analytical system equipped with a mass selective detector (MSD). Agreement between the analytical results for the two tubes was very good. A comparison of the canister results and the sorbent tube data again emphasized the limitations of the FID detector when dealing with complex mixtures. Non-target compounds, such as butanes and pentanes, interfered with the identification and quantitation of the target compounds. For those compounds that were not affected by co-eluting non-target compounds, good agreement between tube and canister results was observed.

The TIME monitor, which was evaluated in the third phase of the study, measures the VOC levels in four microenvironments: indoor-residential, indoor-workplace, in-transit, and outdoors. The monitor is compact and lightweight, and can be used unobtrusively to sample continuously for a minimum of eight hours and as much as twelve hours. The control mechanisms built into the monitor protect it during operation and inform the user of any potential problems.

A problem that was addressed in a series of field experiments relates to the time that the transducer in the shadow sensor takes to react to a change from one microenvironment to another. The problem may be resolved either by replacing the transducer with a more advanced version that reacts more rapidly, or by modifications to the software that may speed up the reaction time. Software changes made during the field phase of the evaluation in fact reduced the reaction time from an initial value of between 45 and 50 seconds to 30 seconds. This is a considerable improvement over the two minute reaction time that was obtainable with the original shadow sensor. Special attention was also paid to the question of potential leaks in the valve system of the monitor and contamination of the sampler tubes. Indications are that both of these aspects can be controlled.

Further work is needed before the TIME monitor as it is presently configured will be ready for general field work. This includes: (1) Reducing the size of the monitor by about one-third, (2) Introducing a better quality transducer to further reduce the reaction time in changing from one microenvironment to another, and (3) Field testing the device with subjects randomly selected from the public instead of using trained investigators, as was the case in the present study. In addition, to fully identify the capabilities of the multisorbent approach used in this study, the ATD 400 should be attached to an analytical system that incorporates a conventional MSD or an ion trap detector. This modification would ensure reliable compound characterization and permit a more complete evaluation of multisorbent collection systems for complex air mixtures. Based on the results obtained here, an effort should also be made to develop suitable sorbent combinations for specific compound classes, such as polar VOCs or very volatile organic compounds. Finally, more extensive field testing of both the STS 25 and the TIME samplers is warranted in order to determine their respective capabilities for providing detailed temporal and spatial information on complex indoor and outdoor atmospheres.

SECTION 3

EXPERIMENTAL

INSTRUMENTATION

The gas chromatographic/thermal desorption system that was employed to develop a non-cryogenic TO-14 analytical procedure, and was subsequently used to evaluate the STS 25 and TIME air samplers, consisted of the following hardware components:

- Perkin Elmer Auto Gas Chromatograph equipped with flame ionization (FID) and electron capture (ECD) detectors
- Perkin Elmer Auto Thermal Desorption System (ATD 400) with optional internal standard valving assembly
- PE Nelson Model 1020X Integrator.

Analytical

The gas chromatograph was fitted with a 50 m x 0.32 mm x 5.0 μm dimethyl polysiloxane fused silica capillary column. The outlet end of the column was equipped with a splitter that directed the column effluent to two detectors. A 4-in. section of 0.32 mm ID deactivated fused silica was run from the splitter to the FID and a 14-in. section of 0.10 mm ID fused silica was connected to the ECD. This configuration resulted in a 30:1 split of the effluent, with approximately 97 percent of the sample being directed to the FID and the remainder to the ECD.

Zero grade helium was used as the carrier gas. The flow rate through the analytical column was 4.5 cc/min, which was achieved by setting the column pressure on the ATD 400 at 24.0 psig. FID gases were ultra zero grade air (300 cc/min) and zero grade hydrogen (30 cc/min). Zero grade nitrogen ($\sim$30 cc/min) served as makeup gas for the ECD. Ultra

zero grade air was supplied to the ATD 400 to drive the systems' pneumatic components and purge the compartment of the Peltier-cooled trap.

Typical analytical conditions for the resolution of the TO-14-based target compounds included an initial oven temperature of 40°C, which was maintained for 15 minutes. The oven was then heated at 8°C/min to a final temperature of 200°C, and was held at this temperature for 12 min. This temperature program made it possible to process a sample on an hourly basis.

Battelle's standard TO-14 cryogenic analytical system (14) was also used during this study as a reference to compare results obtained using carbon adsorption traps.

Auto Thermal Desorption (ATD 400) System

The ATD 400 (10) was used both to collect air samples directly onto the Peltier-cooled refocusing trap and to thermally desorb samples collected on multisorbent tubes. Typical operating conditions for the thermal desorption of a tube, included thermal desorption of the sample at 325°C (oven temperature) for 10 min with a purge flow of 60 cc/min helium carrier. The refocusing trap, while receiving the organic components from the heated tube, was held at 4°C and then was thermally desorbed at 325°C for 3 min. No inlet split was used, but the outlet split was operated at a flow of 6.5 cc/min. This resulted in a total trap desorption flow rate of ~11 cc/min (carrier gas flow through column + outlet split flow) which was conducive to rapid transfer of the refocused sample material onto the GC. The trap was operated in the "fast" heating mode. The valve and transfer line were maintained at 225°C and 220°C, respectively. A 58-minute cycle time was used when processing a series of tubes. When conditioning a sample collection tube, the oven temperature was set at 340°C with a 30 minute desorb time.

Integrator

A single PE Nelson Model 1020X dual channel integrator was used to collect and process the output signals from the FID and ECD detectors. The method used to screen for TO-14 target compounds is provided in Figure 1.

```
METHOD      AL4_____.MTH

CREATED       : 15:43:14 Mon Apr 13 1992
AUTHOR        : A. J. POLLACK
LAST MODIFIED : 07:43:24 Thu Sep 10 1992


Instrument  :PERKIN ELMER AUTO GC/ATD-400
Column(s)   :THICK FILM CAPILLARY
Carrier Gas :HELIUM @22 PSIG
Detector(s) :FID/ECD
Operating Conditions :TEST CONDITIONS




               ***************  Chan A  ***************

Calculation Type :  External Standard     Peak Data : Area
Calibration Sequence Number :  4

DATA COLLECTION                          PEAK INTEGRATION

Start Time     :    0.000 min            Lockout Time       :    0.000
End Time       :   50.000 min            Baseline Treatment :  B to B
Narrowest Peak :  1.4 - 3.2 sec          Area Sensitivity   :      300
Peak Width     :  Fixed                  Base Sensitivity   :       20
               :                         Skim Sensitivity   :    10.00 %

QUANTITATION                             PEAK IDENTIFICATION

RF of Unknowns     :  1.00000e+0         Identification Type    :  Relative
Peak Area Reject   :  5.00000e+4         Unretained Peak Time   :    0.000 min
Calibration Type   :  Single-Point       Component % Tolerance  :     0.50
Concn Units        :  ppbv

REPORTING

Report Device  :  Diconix #1             Plot Device      :  Diconix #1
Report Format  :   0                     Application      :
Special Report :  ASCII                  Interface Ready  :  Immediate
```

Figure 1-a. Model 1020X Data System analytical method.

COMPONENT IDENTIFICATION

RT	Component Name	Calib Amt	Resp Fact	Tol	Ref	Grp
3.190	FREON-12	2.46000e+0	7.34966e-6	0.200		
3.550	METHYL CHLORIDE	2.11000e+0	5.07430e-6	0.200		
3.780	FREON-114	2.44000e+0	3.12280e-6	0.200		
4.060	VINYL CHLORIDE	6.33000e+0	2.34011e-6	0.200		
4.360	1,3-BUTADIENE	2.81000e+0	1.65059e-6	0.200		
4.950	METHYL BROMIDE	2.90000e+0	1.10392e-5	0.200		
5.340	ETHYL CHLORIDE	2.66000e+0	2.87807e-6	0.200		
7.100	TRICHLOROFFLUOROMETH	2.39000e+0	1.96027e-5	0.200		
8.690	1,1-DICHLOROETHENE	2.85000e+0	2.62912e-6	0.200		
8.960	DICHLOROMETHANE	3.76000e+0	4.98269e-6	0.200		
9.320	3-CHLOROPROPENE	3.00000e+0	3.68914e-6	0.200		
9.740	TRICHLOROTRIFLUOROET	2.39000e+0	3.55772e-6	0.200		
12.480	1,1-DICHLOROETHANE	2.87000e+0	3.11557e-6	0.200		
15.660	CIS-1,2-DICHLOROETHE	3.06000e+0	2.49728e-6	0.200		
16.650	TRICHLOROMETHANE	3.07000e+0	5.84395e-6	0.200		
18.740	1,2-DICHLOROETHANE	2.95000e+0	2.43144e-6	0.200		
19.380	1,1,1-TRICHLOROETHAN	1.31000e+0	2.51578e-6	0.200		
20.470	BENZENE	2.57000e+0	6.57860e-7	0.200	R	
20.780	CARBON TETRACHLORIDE	2.71000e+0	1.39713e-5	0.200		
22.220	1,2-DICHLOROPROPANE	2.47000e+0	1.64307e-6	0.200		
22.690	TRICHLOROETHENE	2.55000e+0	1.68275e-6	0.200		
24.300	CIS-1,3-DICHLPROPENE	2.75000e+0	5.10582e-6	0.200		
25.240	TRANS-1,3-DICHLPROPE	2.98000e+0	5.11109e-6	0.200		
25.570	1,1,2-TRICLETHANE	2.55000e+0	2.92810e-6	0.200		
26.090	TOLUENE	2.17000e+0	7.71180e-7	0.200	R	
27.280	1,2-DIBROMOETHANE	2.90000e+0	3.85048e-6	0.200		
28.050	TETRACHLOROETHENE	2.29000e+0	2.12052e-6	0.200		
29.220	CHLOROBENZENE	2.38000e+0	8.27379e-7	0.200		
29.810	ETHYLBENZENE	2.06000e+0	1.20336e-6	0.200		
30.120	M+P-XYLENE	1.93000e+0	1.17139e-6	0.200		
30.730	STYRENE	2.15000e+0	8.53102e-7	0.200		
30.920	O-XYLENE/TETCLETHANE	2.07000e+0	8.55992e-7	0.200		
33.090	4-ETHYLTOLUENE	2.07000e+0	2.27261e-6	0.200		
33.210	1,3,5-TRIMETHBENZENE	1.75000e+0	1.15667e-6	0.200		
34.030	1,2,4-TRIMETHBENZENE	1.74000e+0	1.50552e-6	0.200		
34.410	BENZCHLOR/m-DICHLRBN	2.30000e+0	9.43370e-7	0.200		
34.540	p-DICHLOROBENZENE	2.13000e+0	8.73804e-7	0.200		
35.260	o-DICHLOROBENZENE	2.00000e+0	9.28650e-7	0.200		
39.960	1,2,4-TRICHLOROBENZE	2.06000e+0	1.51937e-6	0.200		
41.640	HEXACHLOROBUTADIENE	1.48000e+0	1.57675e-6	0.200		

PLOTTER

Plot Mode	: Continous	RT / Components	: Both
Chart Speed	: 10 mm/min	Timed Events	: No
Baselines	: Yes	Second Plot	: None

MAIN PLOT

Plot Scale	: User
Start Time	: 0.000 min
End Time	: 50.000 min
Y-Minimum	: 0 mV
Y-Maximum	: 90 mV

Figure 1-b. Model 1020X Data System analytical method.

********** Chan B **********

Calculation Type : External Standard.. Peak Data : Area
Calibration Sequence Number : 0

DATA COLLECTION

Start Time : 0.000 min
End Time : 50.000 min
Narrowest Peak : 1.4 - 3.2 sec
Peak Width : Fixed
:

PEAK INTEGRATION

Lockout Time : 0.000
Baseline Treatment : B to B
Area Sensitivity : 1000
Base Sensitivity : 70
Skim Sensitivity : 10.00 %

QUANTITATION

RF of Unknowns : 1.00000e+0
Peak Area Reject : 1.00000e+5
Calibration Type : Single-Point
Concn Units : Concn

PEAK IDENTIFICATION

Identification Type : Absolute
Unretained Peak Time : 0.000 min
Component % Tolerance : 0.50

REPORTING

Report Device : Diconix #1
Report Format : 0
Special Report : ASCII

Plot Device : Diconix #1
Application :
Interface Ready : Immediate

COMPONENT IDENTIFICATION

RT	Component Name	Calib Amt	Resp Fact	Tol	Ref	Grp
3.610	FREON-12	0.00000e+0	1.00000e+0	0.200		
4.210	FREON-114	0.00000e+0	1.00000e+0	0.200		
5.500	METHYL BROMIDE	0.00000e+0	1.00000e+0	0.200		
7.660	FREON-11	0.00000e+0	1.00000e+0	0.200		
9.540	1,1-DICHLOROETHENE	0.00000e+0	1.00000e+0	0.200		
10.380	TRICHLTRIFLUORETHANE	0.00000e+0	1.00000e+0	0.200		
17.280	CHLOROFORM	0.00000e+0	1.00000e+0	0.200		
19.940	1,1,1-TRICLOROETHANE	0.00000e+0	1.00000e+0	0.200		
21.320	CARBON TETRACHLORIDE	0.00000e+0	1.00000e+0	0.200		
22.500	1,2-DICHLOROPROPANE	0.00000e+0	1.00000e+0	0.200		
23.200	TRICHLOROETHENE	0.00000e+0	1.00000e+0	0.200		
27.790	1,2-DIBROMOETHANE	0.00000e+0	1.00000e+0	0.200		
28.570	TETRACHLOROETHENE	0.00000e+0	1.00000e+0	0.200		
31.410	TETRACHLOROETHANE	0.00000e+0	1.00000e+0	0.200		
40.670	1,2,4-TRICHLRBENZENE	0.00000e+0	1.00000e+0	0.200		
42.400	HEXACHLOROBUTADIENE	0.00000e+0	1.00000e+0	0.200		

PLOTTER

Plot Mode : Paged
Num Pages : 1
Baselines : Yes

RT / Components : RT
Timed Events : No
Second Plot : None

MAIN PLOT

Plot Scale : User
Start Time : 0.000 min
End Time : 50.000 min
Y-Minimum : 0 mV
Y-Maximum : 90 mV

Figure 1-c. Model 1020X Data System analytical method.

AIR SAMPLING DEVICES

Two portable air sampling devices were evaluated in this study. The first unit was a Sequential Tube Sampler (Model STS 25) manufactured by Perkin Elmer. The second device was the TIME monitor developed for U.S. EPA at IITRI and IIT. Both devices made use of sampler tubes packed with carbon sorbents to collect VOCs from ambient or indoor air.

Sequential Tube Sampler (STS 25)

The STS 25 air sampler is a prototype unit supplied by Perkin Elmer (Figure 2). The device consists of a plastic box that contains a sample tube carousel, an electronic timer, and a personal monitoring pump. A fan mounted in the rear of the unit draws ambient air through the box at a rate of ~30 L/min, which is sufficient to change the air above the sample tubes once every second. The air enters through an opening in the lid which is positioned above the collection tubes. The air stream is sampled by the one collection tube that is located in the single position that allows the air monitoring pump to draw the air through a tube. The other tubes are essentially sealed from the air stream through the use of diffusion-limiting caps. Up to 24 sample tubes can be loaded onto the carousel. The 25th position is the "home" position and is not normally used for sample collection.

The sample volume is regulated by time and flow rate. The timing device in the STS 25 will maintain a tube in the sampling position from 0.1 seconds to 10 hours. During this study, each tube was used for sampling for 75 minutes. At the end of the sampling period, the carousel rotates and the next tube is positioned to receive an air sample. An SKC Model 224-PCXR7 personal monitoring pump was used to draw air through the tube and was operated at a nominal flow rate of ~43 cc/min. This flow setting resulted in a 40 cc/min flow through each of the three the packed sampling tubes. All flow rates were confirmed using a Buck Model M-5 calibrator.

Power for the STS 25 can be obtained either from a rechargeable 12 v battery or from a DC power supply/battery charger. The DC power unit was used throughout this study. The STS 25 is also capable of maintaining a trickle charge to the battery of the personal

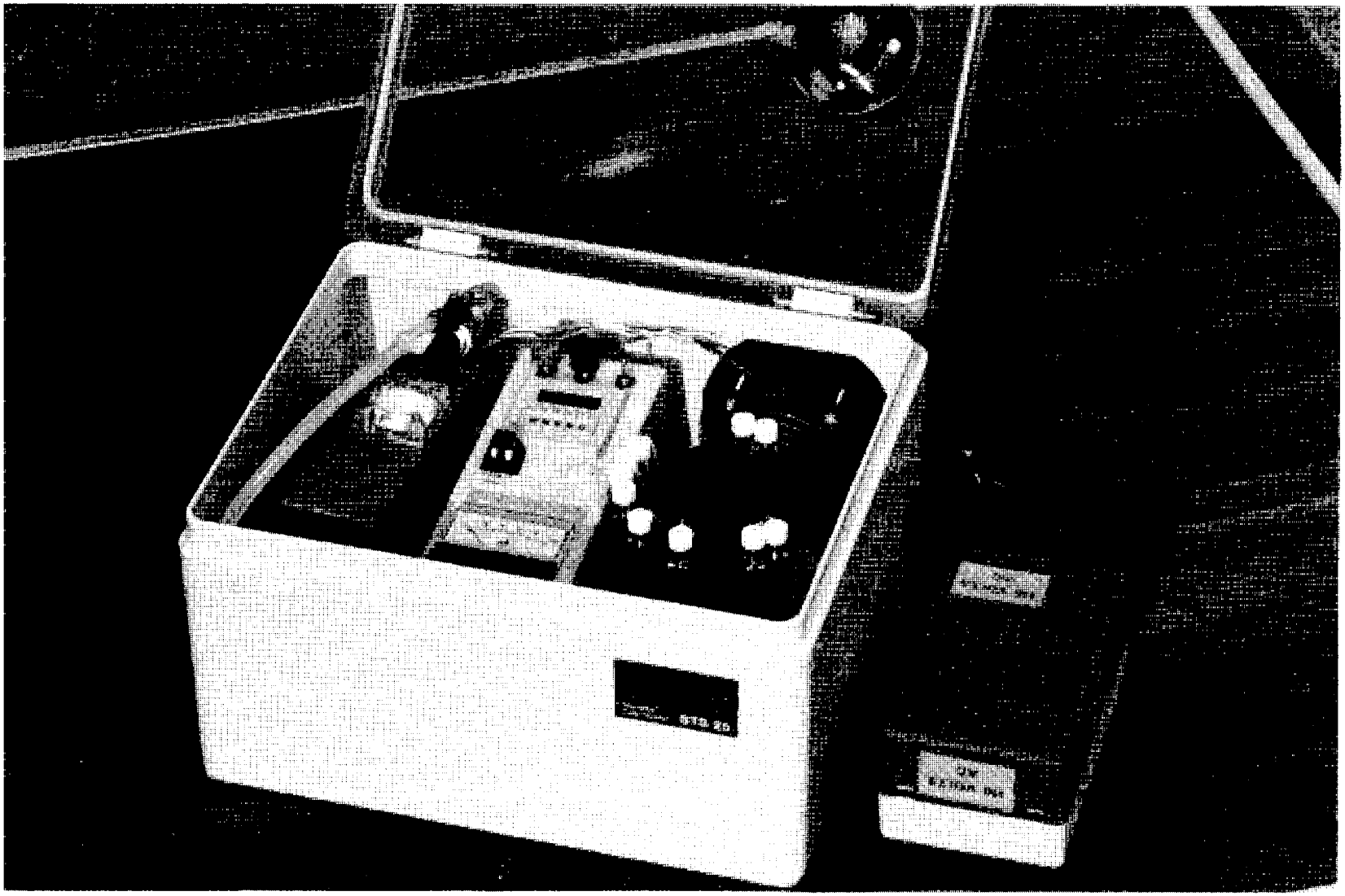


Figure 2. Perkin Elmer Sequential Tube Sampler (STS 25).

monitoring pump. This was used to ensure that the performance of the pump remained constant over long sampling periods. The charging current for the SKC pump was 100 mA.

TIME Monitor

The TIME monitor is based on the shadow sensor, which was developed by Moschandreas and Relwani (11) to provide human mobility patterns electronically. The TIME monitor is shown schematically in Figure 3 and the associated electronics are shown in Figure 4. Besides the transducer from the shadow sensor, which provides information on microenvironments by measuring vertical distances, the monitor includes a miniature air pump and miniature solenoid valves (Lee) to control the air flow through the sampler tubes. The device can operate for at least 8 hours at a time using a 12 V, 2.5 Ah rechargeable battery pack. Software has been incorporated into the system to control the direction and flow rate of the air sample, based on the microenvironment identified by the shadow sensor. The unit also includes an RS-232 interface for downloading data to an IBM-compatible personal computer. Flow rate adjustments are made with the aid of a personal computer and are checked with a 5-50 cc/min flowmeter. The monitor, which is contained in a 7-in. x 4-in. x 1.5-in. housing and weighs about 1.8 lb, can be easily carried by a subject during the day and is unobtrusive (Figure 5).

The need to distinguish between the indoor-residential and indoor-workplace micro-environments required the inclusion of an audible chime which sounds each time the subject changes indoor microenvironments. When the subject enters an indoor-workplace micro-environment, only then does he/she trigger the system manually, and the sampled air stream is directed by the valve system to the corresponding indoor-workplace microenvironment sampler tube.

Operation of the monitor involves three stages: (1) the pre-monitoring period; (2) the sampling period; and (3) data transfer. Appendix A lists the TIME monitor operating instructions from the sampler tube change and start-up, to the motor speed control, i.e., from setting the flow rates to the collection of the data. The sampling period does not require detailed instructions; the subject must check the indicator lights intermittently to insure that the monitor is sampling the correct microenvironment. If the monitor indicates an erroneous

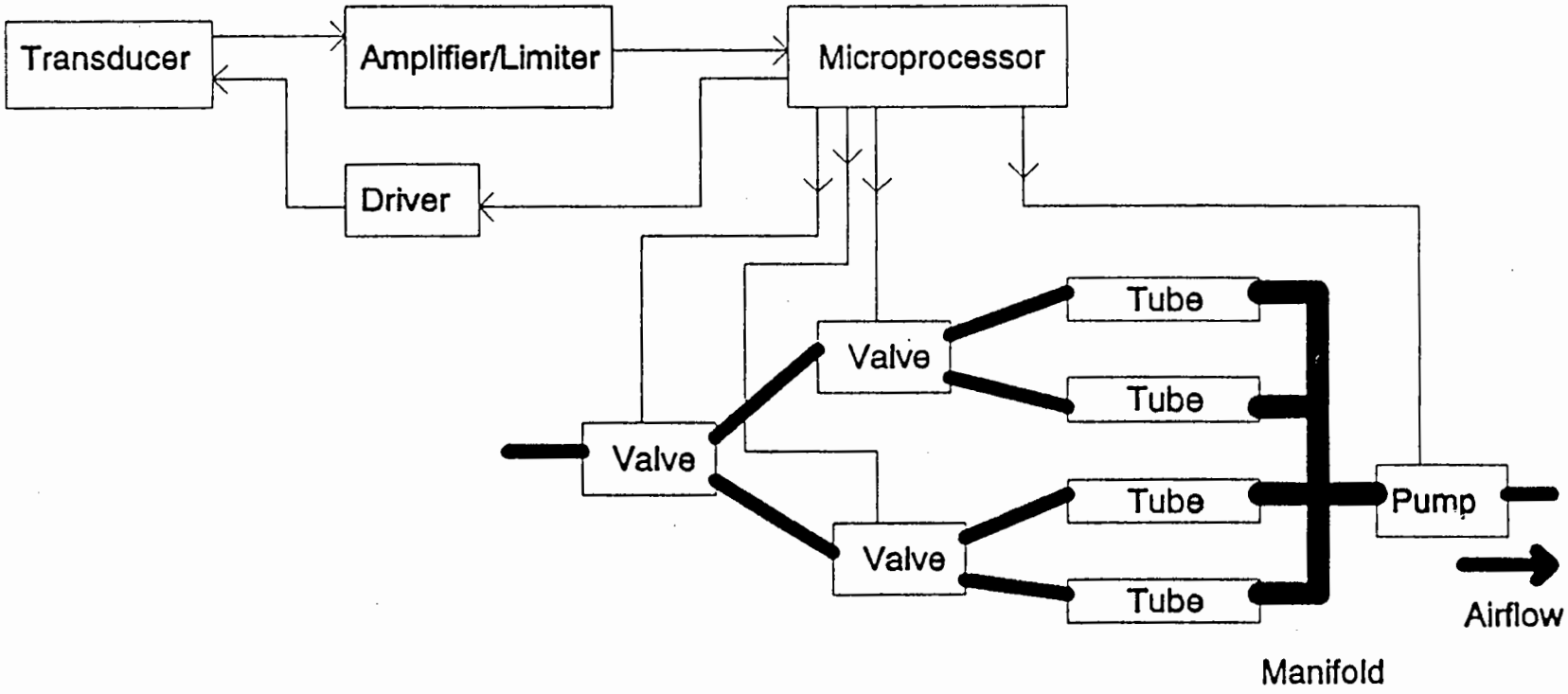


Figure 3. TIME monitor schematic.

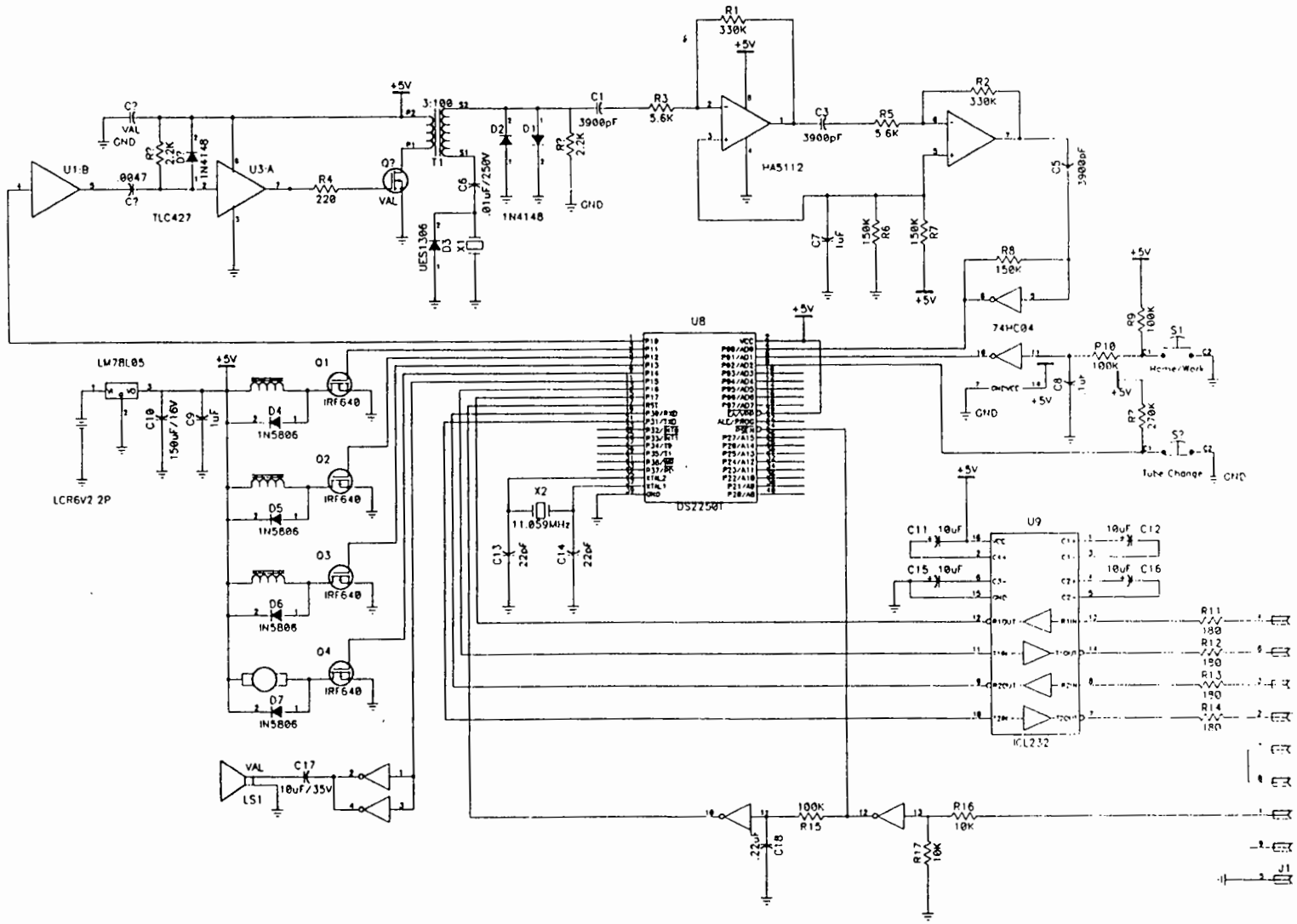


Figure 4. TIME monitor electronics diagram.

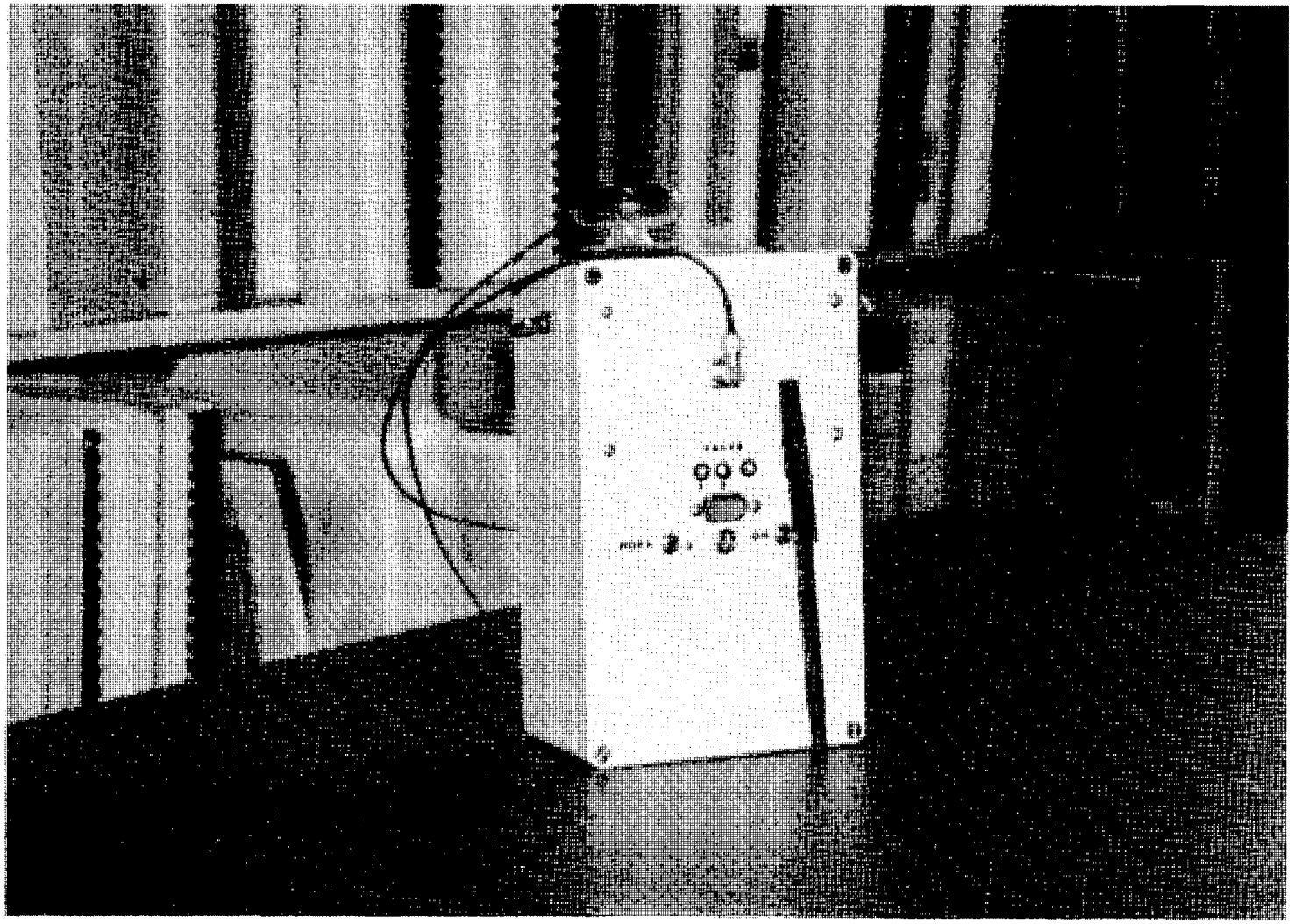


Figure 5. IITRI/IIT TIME monitor.

microenvironment, the subject must note this fact and determine what corrective action to take. If necessary, the experiment may be terminated at this point. At the end of the sampling period, the subject returns the monitor to the laboratory where the sampler tubes are removed from the device, capped, and stored appropriately until analysis. Appendix B illustrates how the mobility data generated is transmitted from the monitor to the personal computer for further analysis.

GAS STANDARDS

Two gas standards were used during this task. The primary challenge mixture was the TO-14 component mix with a limited amount of work also conducted with a polar calibration mix (Table 1). Both standards were prepared at Battelle (15) at nominal concentrations of ~200 ppbv per component in the parent cylinders. Working mixtures in the low ppbv range (2 ppbv to 10 ppbv) were generated via a dynamic mass flow dilution system with Aadco high purity air as the diluent.

SAMPLER TUBE AND REFOCUSING TRAP SORBENTS

During this study, carbon sorbents were evaluated as the medium for collecting both dry and humidified TO-14 calibration samples.

The three sorbents used were: Carbotrap C (20/40 mesh), Carbotrap (20/40 mesh), and Carbosieve S-III (60/80 mesh). All of these materials were obtained from Supelco, Inc. and were purchased in 10 gram bulk lots so that all tubes were loaded with similar material.

Sampler tubes were packed with two and three-stage sorbent loadings during the methods development phase of this task. The two-stage tubes contained Carbotrap (284 mg) and Carbosieve S-III (251 mg). The three-stage tubes contained Carbotrap C (300 mg), Carbotrap (200 mg), and Carbosieve S-III (125 mg). These were maximum mass loadings for the sampler tubes yet still allowed all of the sorbents to be held in the heated zone of the tube during desorption.

Throughout this study, the Peltier-cooled refocusing trap was operated with 38 mg of Carbotrap and 23 mg of Carbosieve S-III.

TABLE 1. TARGET COMPOUNDS: NONPOLAR TO-14 AND POLAR VOCs

TO−14 Nonpolar Compounds	Polar Compounds
1) dichlorodifluoromethane	1) methanol
2) methyl chloride	2) 1,3−butadiene
3) 1,2−dichloro−1,1,2,2−tetrafluoroethane	3) ethylene oxide
4) vinyl chloride	4) ethanol
5) 1,3−butadiene	5) acetonitrile
6) methyl bromide	6) acetone
7) ethyl chloride	7) propylene oxide
8) trichlorofluoromethane	8) 2−propanol
9) 1,1−dichloroethene	9) acrylonitrile
10) dichloromethane	10) methyl t−butyl ether
11) 3−chloropropene	11) vinyl acetate
12) 1,1,2−trichloro−1,2,2−trifluoroethane	12) methyl ethyl ketone
13) 1,1−dichloroethane	13) ethyl acetate
14) cis−1,2−dichloroethene	14) ethyl t−butyl ether
15) trichloromethane	15) benzene
16) 1,2−dichloroethane	16) n−butanol
17) 1,1,1−trichloroethane	17) ethyl acrylate
18) benzene	18) toluene
19) carbon tetrachloride	
20) 1,2−dichloropropane	
21) trichloroethene	
22) cis−1,3−dichloropropene	
23) trans−1,3−dichloropropene	
24) 1,1,2−trichloroethane	
25) toluene	
26) 1,2−dibromoethane	
27) tetrachloroethene	
28) chlorobenzene	
29) ethylbenzene	
30) m+p−xylene	
31) styrene	
32) 1,1,2,2−tetrachloroethane	
33) o−xylene	
34) 4−ethyltoluene	
35) 1,3,5−trimethylbenzene	
36) 1,2,4−trimethylbenzene	
37) benzyl chloride	
38) m−dichlorobenzene	
39) p−dichlorobenzene	
40) o−dichlorobenzene	
41) 1,2,4−trichlorobenzene	
42) hexachlorobutadiene	

ENVIRONMENTAL CHAMBER

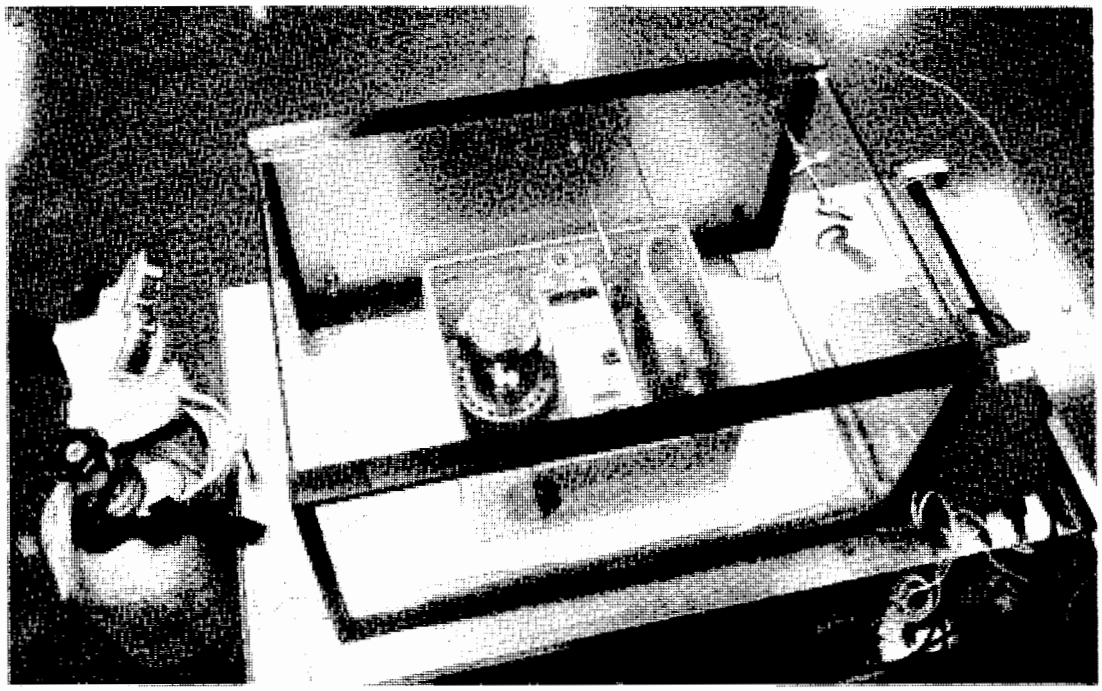
A 75-L glass/stainless steel test chamber was used to evaluate the collection efficiency of the STS 25 under controlled conditions. Both Aadco high purity air and TO-14 standard mixtures were directed through the chamber to serve as sampling environments.

The chamber (Figure 6) was designed to act as an inert container in which the challenge gases could be generated. A dynamic mass flow dilution system generated 2 and 10 ppbv mixtures of the TO-14 target compounds. In all cases, Aadco high purity air served as the diluent gas. The relative humidity (RH) in the chamber was controlled at ~10 and ~60 percent. The 10 percent level was generated by using the Aadco air, as obtained from the Model #737 Clean Air Generator, along with the calibration mixture. This represented a low humidity test environment. The high humidity environment (60 percent RH) was achieved by passing the Aadco air/TO-14 mixture through a Nafion membrane humidifying system (15) before introduction into the chamber. Dry and humid blank Aadco air atmospheres were also generated.

The temperature of the chamber during tests was held at 25°C (± 2°C) and 37°C (± 2°C). The 25°C level was room temperature and was not adjusted with external heating or cooling. The 37°C level was achieved by placing a heating element (pad type) under the chamber and was controlled with an OMEGA Model CN9000 Controller. The heater was set at 55°C on the Omega controller, which resulted in an internal chamber temperature of 37°C.

At all times, a constant 2-L/min gas flow was supplied to the chamber. This flow purged the system with a fresh supply of either Aadco air or the TO-14 mix. When a changeover from one sampling condition to another was desired, a period of 3.75 hours was allowed for this operation. This provided a 450-L flush of the chamber prior to any sampling, and corresponded to a 6-fold exchange of the atmosphere in the chamber.

Before any tests were run to determine the performance of the STS 25, the chamber itself was evaluated. It was challenged with 2 and 10 ppbv TO-14 mixtures at the various temperatures and humidity levels mentioned above. Canister "grab" samples were collected, via a valved port on the chamber, and these samples were analyzed using Battelle's standard



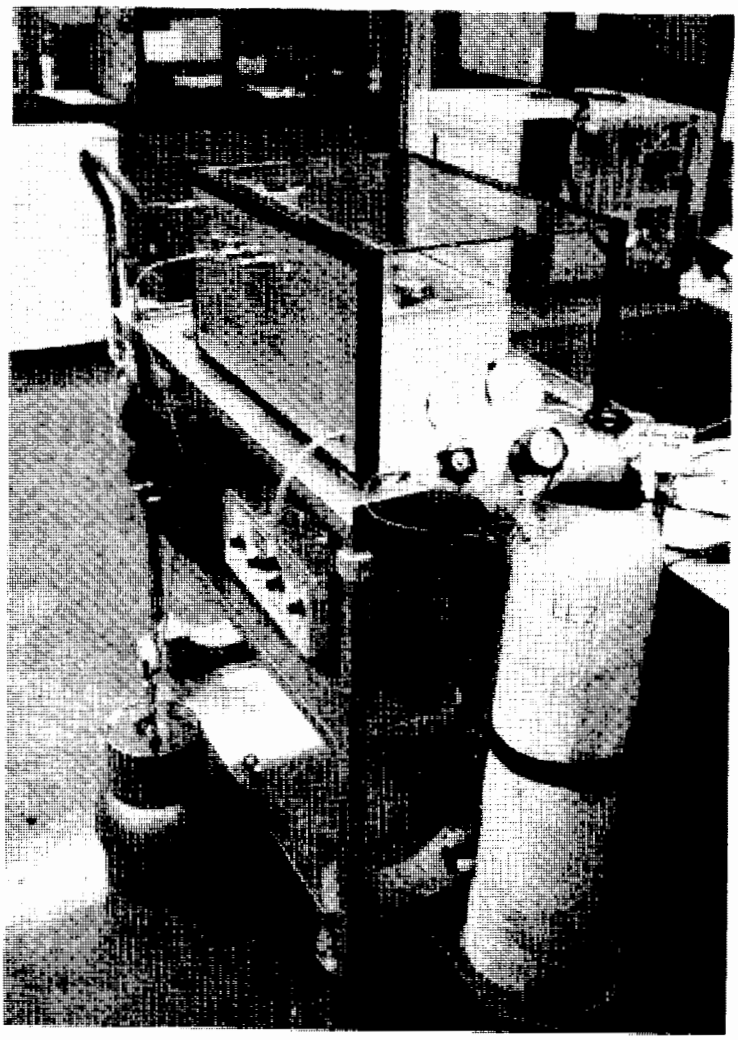


Figure 6. Small-scale environmental chamber.

TO-14 cryogenic analytical system. These analyses were used to confirm that the desired challenge atmospheres could be generated and maintained in the test chamber.

PROCEDURES

Loading Standards onto Sampler Tubes and the Peltier-Cooled Refocusing Trap

During the methods development portion of this study, calibration mixtures were loaded onto the sorbents by drawing the air sample through the packed sampler tube. This was done by using a pumping system comprised of a Thomas (Model #2107CA18) dual diaphragm pump, and a Tylan (Model R032) readout control unit with a 0-100 cc/min mass flow controller (Model FC-260). The tubes were loaded with calibration standards while in a vertical position. The flow rate was fixed at 40 cc/min with the total volume determined by the period of time over which a sample was collected. The temperature was held at 30°C (± 2°C). Sample volumes ranged from 0.5 L to 3.0 L. Both humidified (~ 60 percent RH) and dry (~ 10 percent RH) samples were collected on the tubes.

Besides the standards that were loaded onto tubes, the TO-14 mixture was also loaded directly onto the Peltier-cooled refocusing trap of the ATD 400. This was accomplished by using the auxiliary standard injection valve assembly. The six-port valve permitted the collection of samples on the trap through the standard plumbing of the ATD 400 when an empty tube was loaded into the system. The same pump/Tylan mass flow controller used to load tubes was used to load the trap. The flow rate used was 33 cc/min and the sampling time was set using the standard injection method input parameter on the ATD 400. A 15 minute collection time gave a 0.5-L sample loading on the trap. Samples were dried, using a Nafion dryer, prior to loading since during these tests the trap was cooled to -30°C. The results from these test loadings were used to evaluate the performance of the sampler tubes for the collection of multiliter samples that were processed in the standard two-stage desorption mode using the ATD 400.

Selection and Validation of a Suitable
Multisorbent Sampling Combination

The initial phase in the development of a non-cryogenic TO-14-based analytical procedure involved a review of existing data from previous studies. In selecting the most promising multisorbent combination for further evaluation, we were guided by the results of earlier work conducted at Battelle (10) and elsewhere. (4,5)

All of these studies used three-stage tubes packed with the carbon sorbents, Carbotrap C, Carbotrap, and Carbosieve S-III, in order of increasing retention capacity. Our decision to select the same carbon sorbent combination was guided by the findings that this combination provides high collection efficiencies for a wide range of C_2-C_{14} hydrocarbons, displays low artifact levels, and generally are hydrophobic in nature.

The first tests to evaluate the multisorbent tubes involved loading dry TO-14 mixtures directly onto the Peltier-cooled refocusing trap. These samples were analyzed, the TO-14 compounds were identified by elution order, and the associated peak areas were measured. During these initial tests, GC operating conditions were adjusted to maximize the resolution attainable within a one hour cycle time.

Once the precision of collection and analysis for this trap loading was established, based upon three consecutive runs, attention was turned to a consideration of the most suitable sorbents to use in the sampler tubes. Using Supelco's Carbotrap 300 configuration as a starting point, and based upon the previous work with multisorbent carbon samplers mentioned earlier, the three-stage sorbent tube (Carbotrap C, Carbotrap, Carbosieve S-III) was loaded with 1-, 2-, and 3-L dry samples of the TO-14 mixture at the 2 ppbv level. These results were not only compared to those obtained by loading the standard directly onto the refocusing trap, but were used to determine if any breakthrough was occurring. To confirm breakthrough occurrences, a "train" experiment was also performed in which each of the three sorbents was packed into separate sampler tubes. The mass of sorbent packed into each tube was the same as that used for the sorbent in the three-stage tube. Duplicate tubes were prepared and the six-tube "train" was assembled and loaded with 3 L of dry TO-14 mixture at 2 ppbv. Analysis of each tube first provided information on the partitioning of

the TO-14 compounds, and secondly gave information on breakthrough effects by examining the backup tube results.

Tests were also carried out using a two-stage tube to determine if a Carbotrap/ Carbosieve S-III combination, using larger amounts of the two strongest sorbents, was better suited to collect and retain the TO-14 compounds.

After data from these dry samples had been generated, moisture was introduced during the loading of the TO-14 mixture onto the tubes. Modifications to the existing ATD 400 processing method were made at this point to handle the moisture associated with the samples so that chromatographic analysis could be reliably performed. These tubes were then analyzed and the data processed in the same way as before.

The results of this evaluation process led to the analytical/collection methodology that was applied to the evaluation of both the STS 25 and TIME portable samplers.

Evaluation Using Polar Compounds

A limited study was conducted to evaluate the ability of the sorbent tubes to collect and desorb selected polar species. The 18-component polar mix (Table 1) was loaded onto three-stage sampler tubes at sample volumes of 1, 2, and 3 L and 2 ppbv concentration. These samples were processed, and the results were evaluated to determine if the ATD 400, as configured to analyze for TO-14 species, would also permit the detection and quantification of polar compounds.

STS 25 Evaluation Experiments

The STS 25 was subjected to three types of tests. First, it was mechanically tested to determine if it would reliably cycle as specified to collect ambient and indoor air samples using sorbent tubes. The timing mechanism, pump reliability, flow rates through tubes, and general operation were evaluated. The system was operated over several 24 hour periods to identify any deficiencies.

Secondly, the STS 25 was placed in the environmental chamber and programmed to collect background air samples and samples of TO-14 standard atmospheres at 2 and 10 ppbv concentrations. The unit was challenged at two temperature levels (25°C and 37°C) and two

relative humidity levels (10 percent and 60 percent) during these tests. In all cases, 3-L samples were collected. The tubes were analyzed and the results were compared to those from the chamber validation tests to determine whether the STS 25 unit was able to collect laboratory-controlled atmospheres without either contributing to, or removing, any of the TO-14 target compounds.

Finally, two field tests were performed to evaluate the STS 25 unit under "real world" conditions. The STS 25 was set up to collect 3-L air samples in both an indoor and outdoor location. Simultaneously, in each experiment, a second sorbent tube and a 6-L air sampling canister were used to sample the air at the same location (Figure 7). A Tylan-controlled pumping assembly drew air through this second tube at the same 40 cc/min flow rate as the STS 25 was using. The canister was pre-evacuated and was filled using a restrictive orifice that allowed air to enter the canister at ~60 cc/min. This flow decreased to ~40 cc/min as the pressure approached atmospheric pressure during the 75 min collection period. At the end of the sampling period, the canister was still at less than atmospheric pressure (~200 mm Hg).

The exposed sorbent tubes were processed using the ATD 400 using the TO-14 methodology developed earlier during this study. The canister was pressurized to 5 psig with humidified (~70 percent RH) Aadco high purity air and then was analyzed using Battelle's standard TO-14 cryogenic analytical system.

Data from all these collection systems were compared to evaluate the operation of the STS 25 system.

TIME Monitor Evaluation Experiments

Three different types of experimental checks were performed on the monitor. The first addressed the flow rates through the sampler tubes before, during, and on completion of a run. Here, the flow rates specified by the computer were checked with a flowmeter before initiating the field experiments. The flow rates were also measured during a field test and were measured again after a 10-hour test. The flow rates remained within the experimental error associated with the flowmeter, namely ± 8 percent. In the second series of checks, the reliability of the indicator lights in designating the correct microenvironment occupied by the

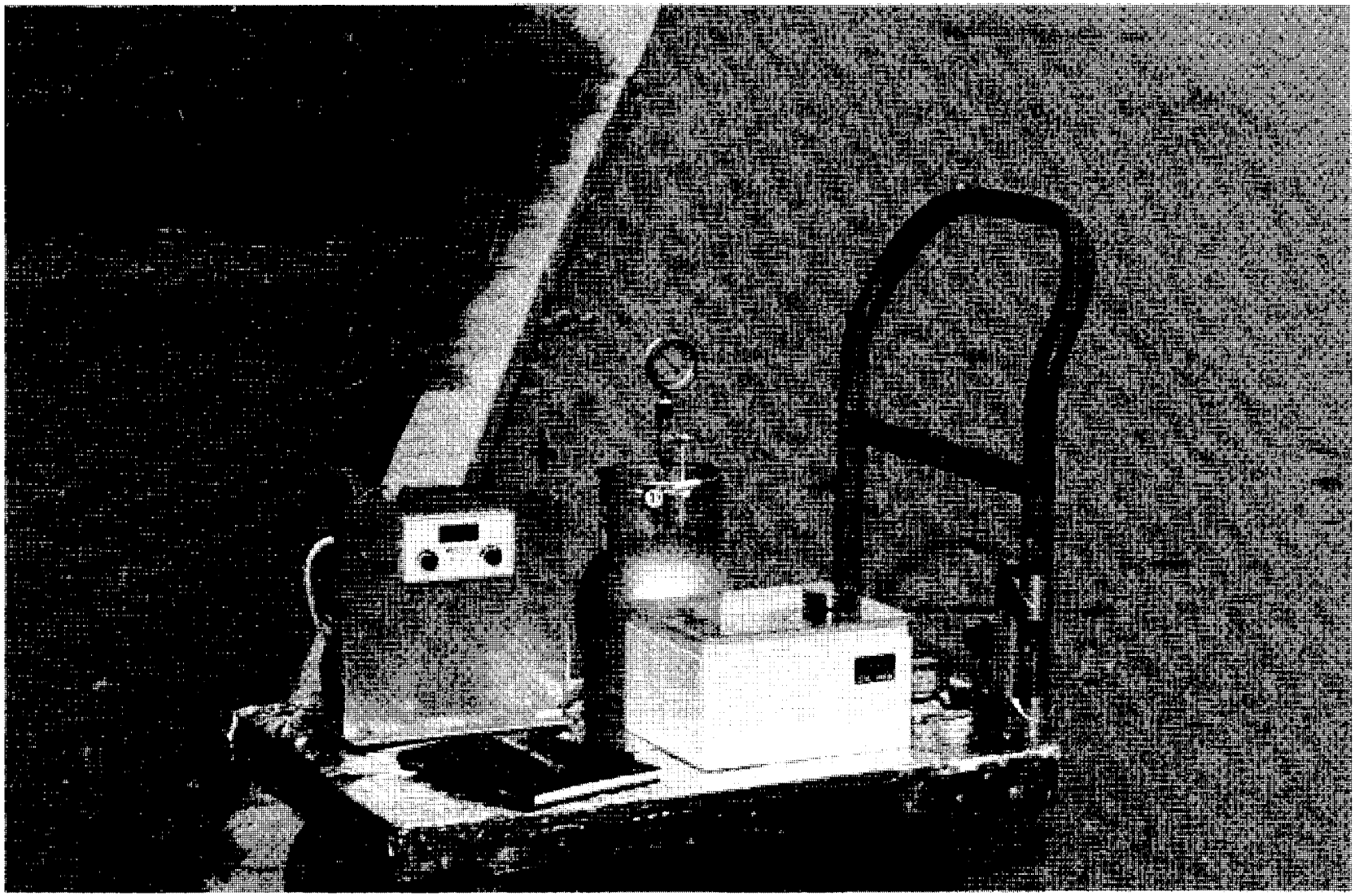


Figure 7. STS 25 (front), Tylan-controller pump/tube sampler (left rear), and stainless steel canister (right rear).

subject was tested. The lights were found to indicate the microenvironment correctly as long as the power to the unit was sufficient. Finally, the operation of the power supply itself was checked. It was verified that when the power drops below a certain value, the flow rates are affected and the sensor stops operating. Data are, however, not lost because there is a backup power supply which operates long enough to allow the replacement of the primary battery.

Two field experiments were performed with the device. The first lasted for 11.5 hours and the second for slightly more than 6 hours. After these tests, traces of black powder, presumably from the carbon-sorbents, were observed in the tubing that connects the sorbent tubes to the pump (see Figure 3). This effect is probably due to the normal physical movement to which the monitor is subjected when it is carried during the day by a subject.

SECTION 4

RESULTS AND DISCUSSION

This study consisted of three tasks. The first task was to develop a method for collecting and analyzing TO-14-based target compounds in air without the use of cryogen. This involved the evaluation of a sorbent-based procedure. Sorbent selection, methods development, and method validation for both dry and humidified samples was investigated and will be discussed here. The second task involved an evaluation of both the mechanical and sample collection behavior of the STS 25 sampler. This system was challenged under controlled laboratory conditions and with indoor and outdoor air samples. The results of these tests are reported in this section. Finally, the TIME monitor was modified and operated to determine its ability to differentiate between common microenvironments and collect the associated air samples. The outcome of these tests will also be presented and discussed.

TASK 1: SELECTION AND VALIDATION OF MULTISORBENT SYSTEM

Peltier Cooled Trap Sample Collection

The initial experiments involved in the selection and validation of a suitable multisorbent system focused on loading the TO-14 mixture directly onto the refocusing trap in the ATD 400. These tests were designed to establish a baseline set of data which could be used to determine if the sampler tubes had the necessary efficiency for the enrichment of multiliter air samples.

The results from loading 0.5-L samples of 2 and 10 ppbv standards onto the trap are presented in Table 2. It should be noted that all of the data reported here is based upon the FID response. Although the ECD generated a signal for these samples, the detector

TABLE 2. RESULTS FROM LOADING 0.5-L DRY TO-14 STANDARDS ONTO PELTIER COOLED REFOCUSING TRAP (THREE RUNS)

Compound	Average Area 2 ppbv	RSD, % 2 ppbv	Average Area 10 ppbv	RSD, % 10 ppbv
1) dichlorodifluoromethane	83658	4	323582	5
2) methyl chloride	94598	12	355572	2
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	132198	21	366133	5
4) vinyl chloride	362222	3	2010368	2
5) 1,3-butadiene	126121	17	659168	2
6) methyl bromide	n.d.	**	248214	1
7) ethyl chloride	151158	10	718149	2
8) trichlorofluoromethane	n.d.	**	83341	2
9) 1,1-dichloroethene	108862	22	542106	5
10) dichloromethane	n.d.	**	236788	4
11) 3-chloropropene	n.d.	**	304678	6
12) 1,1,2-trichloro-1,2,2-trifluoroethane	109585	6	441180	4
13) 1,1-dichloroethane	99295	12	552766	1
14) cis-1,2-dichloroethene	126877	11	702084	2
15) trichloromethane	n.d.	**	135676	2
16) 1,2-dichloroethane	98192	10	586016	4
17) 1,1,1-trichloroethane	65399	8	314888	2
18) benzene	543153	6	2483427	1
19) carbon tetrachloride	n.d.	**	n.d.	**
20) 1,2-dichloropropane	123689	5	706086	3
21) trichloroethene	137196	3	694575	5
22) cis-1,3-dichloropropene	n.d.	**	88536	13
23) trans-1,3-dichloropropene	n.d.	**	68906	6
24) 1,1,2-trichloroethane	n.d.	**	291733	2
25) toluene	215496	5	1124036	4
26) 1,2-dibromoethane	n.d.	**	155159	29
27) tetrachloroethene	79800	9	427776	4
28) chlorobenzene	378867	6	1885694	2
29) ethylbenzene	111124	11	546259	7
30) m+p-xylene	116685	2	469171	7
31) styrene	136420	23	799124	14
32) 1,1,2,2-tetrachloroethane and o-xylene	132556	6	662793	10
34) 4-ethyltoluene	n.d.	**	165439	7
35) 1,3,5-trimethylbenzene	130447	19	473700	8
36) 1,2,4-trimethylbenzene	154985	41	525939	8
37) benzyl chloride and m-dichlorobenzene	204179	11	1017750	12
39) p-dichlorobenzene	230119	20	1494159	4
40) o-dichlorobenzene	346693	19	1637856	1
41) 1,2,4-trichlorobenzene	173191	32	1167271	14
42) hexachlorobutadiene	223537	10	637194	2

n.d.= not detected

** = no data

appeared to be saturated at the levels loaded onto the trap, even with the 30:1 split. Carbon tetrachloride and the other highly electrophilic compounds in the standard indicated the same ECD area response for both 2 and 10 ppbv concentrations. The auto GC system does not offer the option to desensitize the detector, as there is only a single range available. Consequently, the ECD data were only used in a qualitative capacity in this study.

The relative standard deviation (RSD) obtained for the three analyses of the 2 ppbv standard show some scatter, and several values exceed 10 percent. This is undoubtedly due to the low concentration and small sample volume used in this test. The ATD 400, when operated with ~50 percent outlet split to enhance the transfer of sample from the trap to the GC column, is apparently not optimized for this low mass loading. However, a review of the results obtained from the 10 ppbv test indicates good precision, with RSD values generally < 10 percent. Also, a comparison of the average area counts obtained shows that, for most peaks, the expected 5-fold increase in response is observed between the 2 and 10 ppbv standards. No effort was made to enhance the 2 ppbv response since the thrust of this study was to quantify multiliter samples.

Figure 8 shows the FID and ECD chromatograms obtained for a 0.5-L, 10 ppbv sample. Total analytical run time was 50 minutes, and the GC operating conditions established during these initial analyses were employed in the remainder of the study.

The results of this test indicated that the TO-14-based target compounds could be collected and analyzed quantitatively using a non-cryogenic procedure. It also identified the limitations of the ECD detector in this instrument and the need for methods development to quantify small sample volumes (< 1 L) of low ppbv concentrations of the TO-14 mixture.

Dry Multiliter Samples Loaded Onto Multisorbent Tubes

The purpose of the next test was to establish the collection and recovery efficiencies for 1-, 2-, and 3-L TO-14 samples at the 2 ppbv level. The dry mixture was loaded onto the three-stage sorbent tubes. The analytical results from these experiments are presented in Table 3. The FID areas for the 2- and 3-L samples have been normalized with respect to the values obtained for the 1-L loading so that the relative recoveries over this range can be compared.

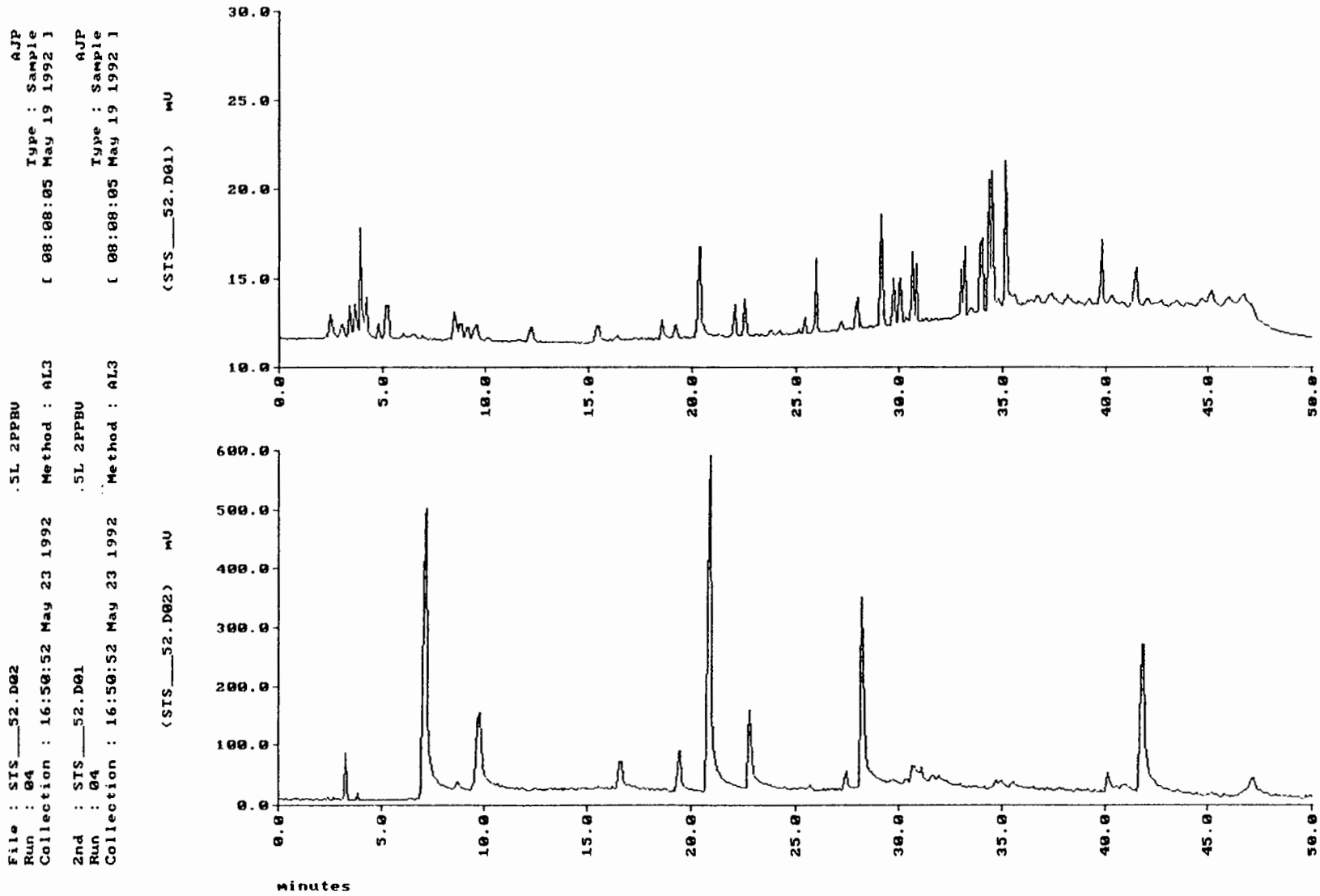


Figure 8. FID (upper) and ECD (lower) chromatograms for a dry 0.5-L volume TO-14 sample at 2 ppbv.

TABLE 3. RELATIVE PERFORMANCE OF A THREE-STAGE SORBENT TUBE FOR COLLECTING DRY MULTILITER TO-14 SAMPLES AT 2 PPBV CONCENTRATION.

Compound	Sample*		
	1 L	2 L*	3 L*
1) dichlorodifluoromethane	1.00	0.63	0.59
2) methyl chloride	1.00	0.90	0.79
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	1.00	0.78	0.49
4) vinyl chloride	1.00	1.12	1.25
5) 1,3-butadiene	1.00	0.95	0.90
6) methyl bromide	1.00	1.49	1.49
7) ethyl chloride	1.00	1.19	1.18
8) trichlorofluoromethane	1.00	0.82	0.49
9) 1,1-dichloroethene	1.00	1.11	1.68
10) dichloromethane	1.00	1.17	1.10
11) 3-chloropropene	1.00	1.02	0.71
12) 1,1,2-trichloro-1,2,2-trifluoroethane	1.00	0.95	0.94
13) 1,1-dichloroethane	1.00	1.06	1.00
14) cis-1,2-dichloroethene	1.00	1.04	1.13
15) trichloromethane	1.00	1.13	1.10
16) 1,2-dichloroethane	1.00	1.08	1.13
17) 1,1,1-trichloroethane	1.00	0.97	0.86
18) benzene	1.00	0.95	0.95
19) carbon tetrachloride	1.00	0.84	0.50
20) 1,2-dichloropropane	1.00	1.04	1.05
21) trichloroethene	1.00	0.98	1.00
22) cis-1,3-dichloropropene	1.00	1.04	1.13
23) trans-1,3-dichloropropene	1.00	0.95	0.82
24) 1,1,2-trichloroethane	1.00	1.15	1.17
25) toluene	1.00	1.02	1.04
26) 1,2-dibromoethane	1.00	1.20	1.15
27) tetrachloroethene	1.00	1.09	1.11
28) chlorobenzene	1.00	1.02	1.02
29) ethylbenzene	1.00	1.06	1.04
30) m+p-xylene	1.00	1.05	1.04
31) styrene	1.00	1.32	1.44
32) 1,1,2,2-tetrachloroethane and o-xylene	1.00	1.15	1.30
34) 4-ethyltoluene	1.00	0.95	0.97
35) 1,3,5-trimethylbenzene	1.00	1.03	0.97
36) 1,2,4-trimethylbenzene	1.00	1.06	1.00
37) benzyl chloride and m-dichlorobenzene	1.00	1.27	1.32
39) p-dichlorobenzene	1.00	1.20	1.39
40) o-dichlorobenzene	1.00	1.18	1.10
41) 1,2,4-trichlorobenzene	1.00	1.50	1.51
42) hexachlorobutadiene	1.00	0.95	0.78

* normalized to 1 L sample

The data indicate that, in general, the TO-14-based target compounds are collected and recovered linearly up to a sample volume of 3-L. There are indications that some of the earlier eluting species in the 2- and 3-L samples exhibited breakthrough based upon the low recovery values obtained. Carbon tetrachloride is also not recovered as well as expected. This is most likely due to poor analytical resolution from benzene resulting in poor integration results. Recovery for hexachlorobutadiene was also poor. This was thought to be due to incomplete desorption from the sampler tube, although a repeat desorption of a processed tube did not result in more of this compound being recovered. (Another possible explanation for this low recovery will be discussed later in this report.)

When the total peak areas from these experiments were compared to the results for the 0.5-L samples loaded directly onto the trap, it was noted that the increased area response scaled linearly with sample volume. This shows that the process of loading the dry sample onto the sampler tube does not adversely affect the recovery of most of the target compounds in 1-, 2-, and 3-L samples.

"Train" Experiment

A "train" experiment was performed to determine the distribution of the target compounds between the sorbents in the tube and to further identify breakthrough problems.

The data in Table 4 show the percent recovery of the compounds of interest from each of the tubes in the train, in their order of elution from the GC column. These values were determined by taking the total area counts for a compound from the six tubes, and relating that total to the portion collected in any one tube. It should be noted that the total areas for the six tubes were generally within $\pm$ 20 percent of those obtained earlier for a 3-L sample collected on a single tube packed with the three sorbents.

The data show that, generally, the first 11 components of the TO-14 mix are retained by the Carbosieve S-III, although they are also present to some extent in the other sorbents. We believe that these extraneous recoveries were actually artifacts associated with Carbotrap and Carbotrap C, and this was subsequently confirmed by the analysis of the tubes as blanks. However, the first three compounds were present in both the primary and

TABLE 4. RECOVERY EFFICIENCY OF TO-14 TARGET COMPOUNDS IN A SIX-TUBE "TRAIN" OF SORBENT BEDS.

	Percent Recovery					
Compound	Carbosieve S-III Primary	Carbosieve S-III Secondary	Carbotrap Primary	Carbotrap Secondary	Carbotrap C Primary	Carbotrap C Secondary
1) dichlorodifluoromethane	46.1	11.3	42.6	0.0	0.0	0.0
2) methyl chloride	84.7	15.3	0.0	0.0	0.0	0.0
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	35.5	23.9	13.4	10.8	9.3	7.1
4) vinyl chloride	88.9	0.0	2.6	0.0	8.5	0.0
5) 1,3-butadiene	10.1	0.0	36.5	53.4	0.0	0.0
6) methyl bromide	100.0	0.0	0.0	0.0	0.0	0.0
7) ethyl chloride	100.0	0.0	0.0	0.0	0.0	0.0
8) trichlorofluoromethane	100.0	0.0	0.0	0.0	0.0	0.0
9) 1,1-dichloroethene	0.0	0.0	55.9	44.1	0.0	0.0
10) dichloromethane	100.0	0.0	0.0	0.0	0.0	0.0
11) 3-chloropropene	0.0	0.0	64.2	35.8	0.0	0.0
12) 1,1,2-trichloro-1,2,2-trifluoroethane	0.0	0.0	100.0	0.0	0.0	0.0
13) 1,1-dichloroethane	15.9	0.0	84.1	0.0	0.0	0.0
14) cis-1,2-dichloroethene	0.0	0.0	100.0	0.0	0.0	0.0
15) trichloromethane	0.0	0.0	100.0	0.0	0.0	0.0
16) 1,2-dichloroethane	0.0	0.0	89.1	0.0	10.9	0.0
17) 1,1,1-trichloroethane	0.0	0.0	100.0	0.0	0.0	0.0
18) benzene	3.0	1.5	59.9	4.7	16.3	14.6
19) carbon tetrachloride	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
20) 1,2-dichloropropane	0.0	0.0	44.6	0.0	41.0	14.3
21) trichloroethene	0.0	0.0	46.6	0.0	43.6	9.8
22) cis-1,3-dichloropropene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
23) trans-1,3-dichloropropene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
24) 1,1,2-trichloroethane	0.0	0.0	23.5	0.0	59.3	17.2
25) toluene	0.0	0.0	3.3	0.0	93.2	3.5
26) 1,2-dibromoethane	0.0	0.0	0.0	0.0	100.0	0.0
27) tetrachloroethene	0.0	0.0	0.0	0.0	100.0	0.0
28) chlorobenzene	0.0	0.0	0.0	0.0	97.3	2.7
29) ethylbenzene	0.0	0.0	0.0	0.0	100.0	0.0
30) m+p-xylene	0.0	0.0	0.0	0.0	88.4	11.6
31) styrene	0.0	0.0	0.0	0.0	100.0	0.0
32) 1,1,2,2-tetrachloroethane and o-xylene	0.0	0.0	0.0	0.0	100.0	0.0
34) 4-ethyltoluene	0.0	0.0	0.0	0.0	100.0	0.0
35) 1,3,5-trimethylbenzene	0.0	0.0	0.0	0.0	100.0	0.0
36) 1,2,4-trimethylbenzene	0.0	0.0	8.4	0.0	72.2	19.4
37) benzyl chloride and m-dichlorobenzene	0.0	0.0	0.0	0.0	89.7	10.3
39) p-dichlorobenzene	0.0	0.0	2.9	3.3	84.2	9.5
40) o-dichlorobenzene	0.0	0.0	6.6	0.0	79.5	13.9
41) 1,2,4-trichlorobenzene	0.0	0.0	8.7	4.5	73.7	13.1
42) hexachlorobutadiene	0.0	0.0	0.0	0.0	92.6	7.4

secondary Carbosieve S-III tubes, indicating that these species were indeed breaking through with a 3-L sample volume.

The Carbotrap sorbent plays a dominant role in retaining the compounds from 3-chloropropene through benzene. Two compounds that indicated the effects of breakthrough are 1,1-dichloroethene and 3-chloropropene. Although the total area counts for these two compounds compared well with that observed in a single tube collection, there may be concern for incomplete recovery if these compounds migrate to the Carbosieve S-III where desorption was not indicated.

From benzene onwards, Carbotrap C becomes the sorbent that collects most of the TO-14 species. Generally, the primary tube retains most of the compounds, and whatever breaks through is retained and subsequently desorbed by the primary Carbotrap tube. From these data, indications are that from benzene to hexachlorobutadiene in the chromatogram, the Carbotrap/Carbotrap C sorbent combination collects the compounds with high efficiency.

Several compounds were not identified by the data system during this test. Carbon tetrachloride, as stated earlier, is incompletely resolved from benzene using the thick film nonpolar dimethyl polysiloxane column. The isomers cis-1,3-dichloropropene and trans-1,3-dichloropropene were not detected at all. This may be due to an affinity of these compounds for the metallic surfaces in the partially packed tubes or for the coupling hardware between the tubes. The "train" experiment indicates that the mass of Carbosieve S-III being used in the three-stage sampler tubes is not enough to completely retain some of the early eluting TO-14 species. The test also shows that all three sorbents play an important role in collecting various portions of the calibration mixture. Figures 9 to 11 show the FID chromatograms obtained from the six tubes.

Two-Stage Sorbent Sampler Tube

To improve the retention of the lighter compounds that broke through the three-stage sorbent tube, a two-stage tube packed with larger amounts of Carbosieve S-III and Carbotrap was evaluated. The use of this tube configuration with a 3-L sample resulted in only a slight improvement in collection efficiency for the low molecular weight components and some loss of efficiency for the heavier species. Increasing the mass of Carbosieve S-III from 125 mg

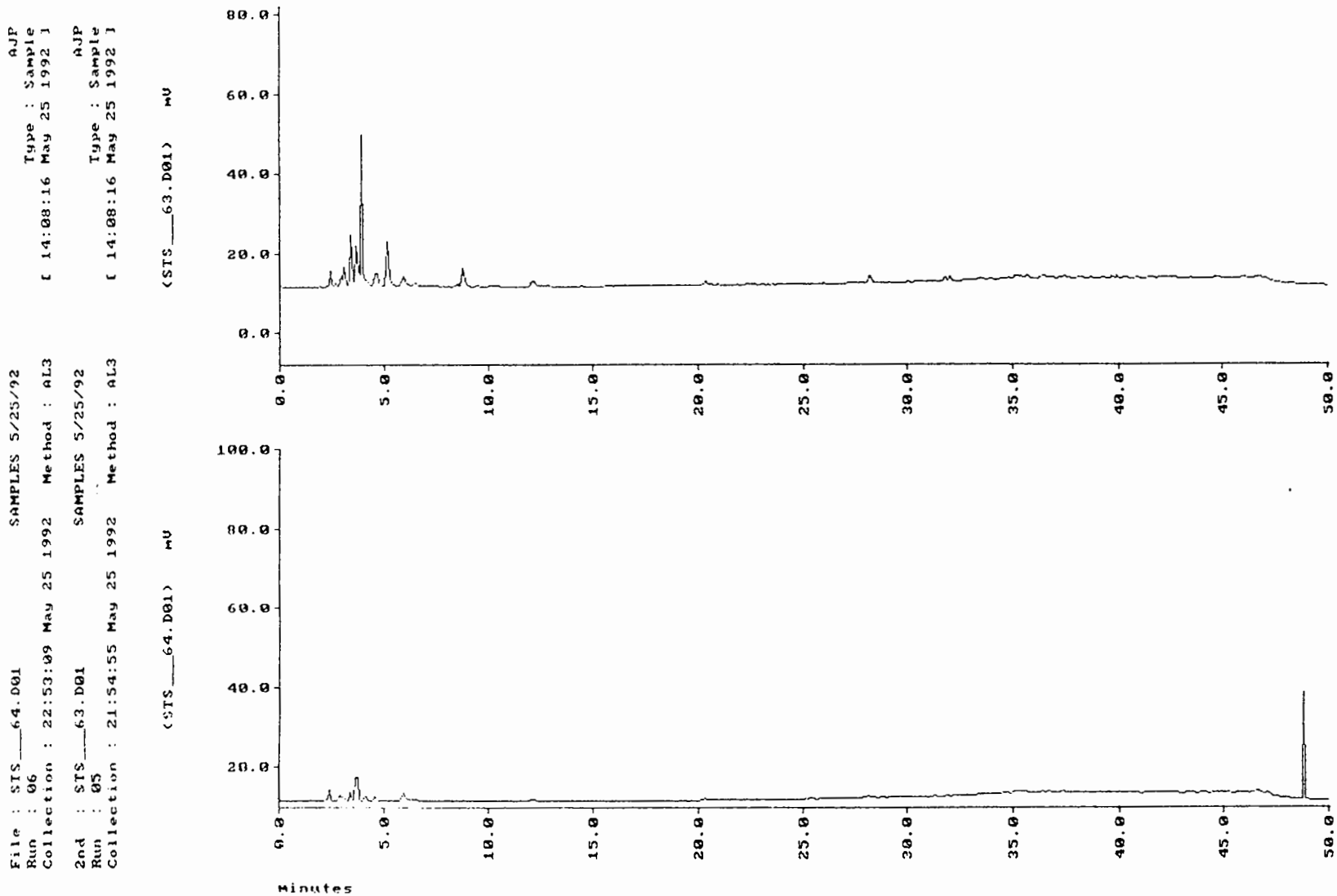


Figure 9. FID chromatograms for primary (upper) and secondary (lower) Carbosieve S-III "Train" tubes showing TO-14 retained species.

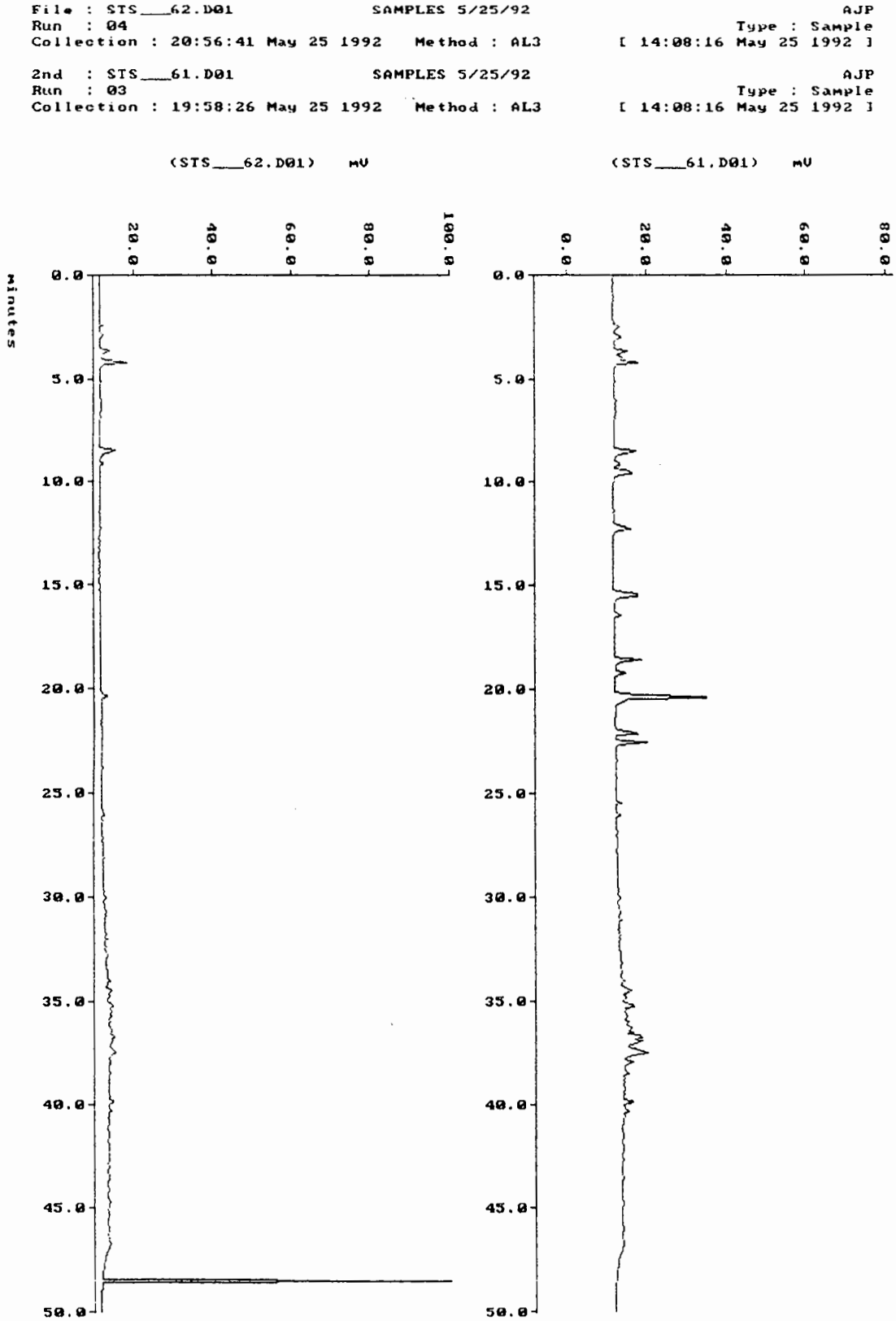


Figure 10. FID chromatograms for primary (upper) and secondary (lower) Carbotrap "Train" tubes showing TO-14 retained species.

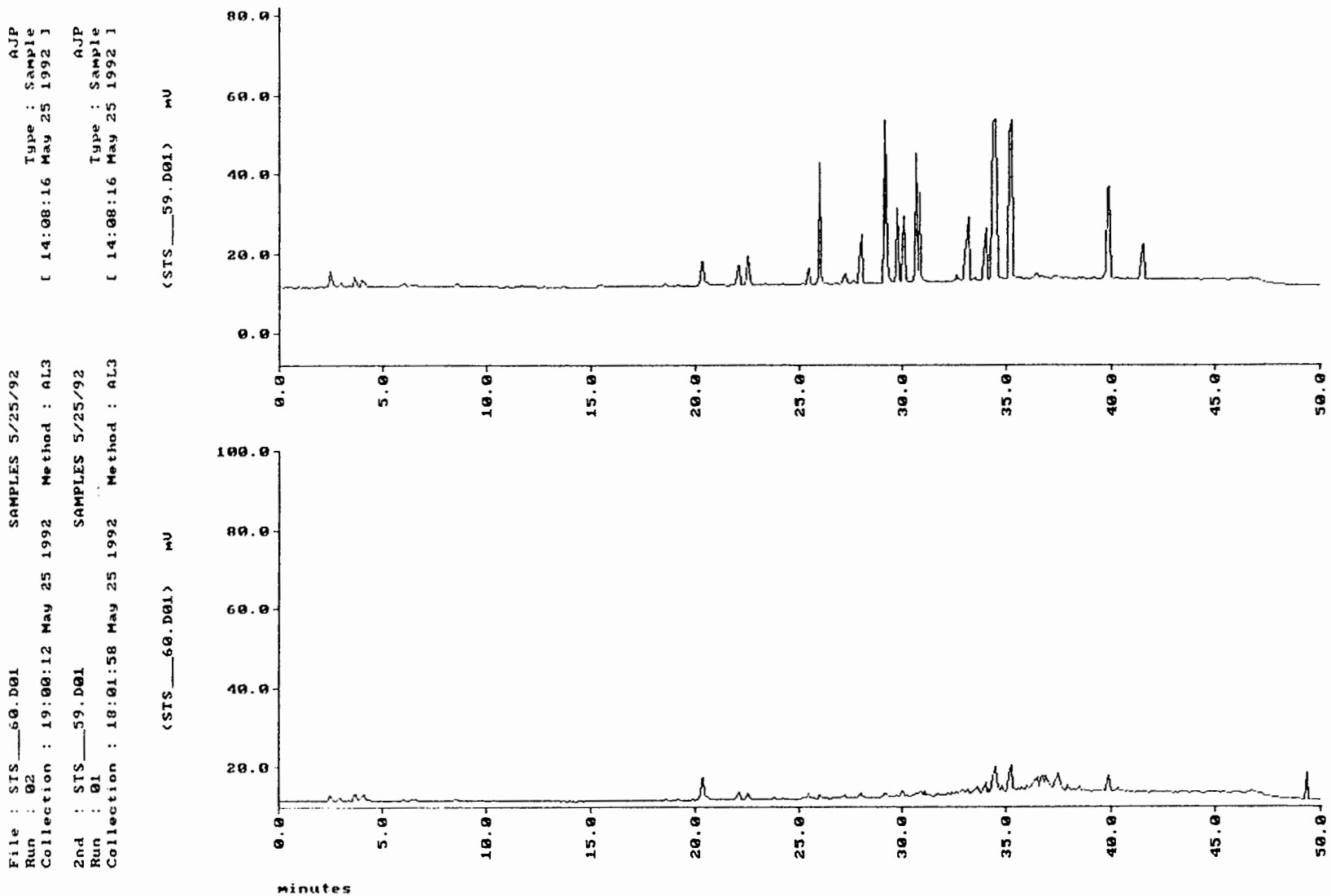


Figure 11. FID chromatograms for primary (upper) and secondary (lower) Carbotrap C "Train" tubes showing TO-14 retained species.

to 251 mg was apparently still not sufficient to prevent breakthrough. At the same time, the heavier species migrated deeper into the stronger sorbent bed so that it was difficult to desorb them. No further effort was made to modify the sampler tube configuration and all the remaining work was done with the three-stage sorbent tube.

Humidified Multiliter Samples Loaded Onto Multisorbent Tubes

In order to simulate atmospheric conditions that are normally encountered in field sampling studies, humidified 3-L samples were loaded onto the three-stage sorbent tubes.

The first sample was analyzed under the same conditions that were used for dry samples, including a 3 minute desorption of the tube at 325°C with the trap at -30°C. This resulted in the FID flame being extinguished by the moisture transferred from the tube to the trap and with the ECD exhibiting no response for the first ~22 minutes of the run.

To allow the moisture in the tube to be swept from the trap, the trap temperature was raised to 4°C for the next sample. Personnel at Perkin Elmer suggested that this would allow a large portion of the moisture in the desorbed sample to pass through the trap while at the same time still retaining the volatile organics. (17) Once again, however, the detector flame was extinguished.

In an attempt to remove more moisture from the sample, the tube desorption time was extended from 5 min to 10 min. This additional time was designed to provide a longer period for the moisture to be purged from the trap, which was still operated at 4°C. The flame remained lit under these conditions, but a retention time delay of 0.2 to 0.3 min was observed for the compounds on the chromatogram. It was also noted that the area counts, particularly for the later-eluting components of the TO-14 mix, were greater than they had been for a dry sample of the same concentration and sample volume. Under these conditions, the ECD still gave a flat baseline for the first ~22 minutes of the run.

To see if an even longer drying period would regain the ECD response, the tube was desorbed for 15 minutes. The early-eluting peaks showed lower area counts, indicating that breakthrough of these components was occurring in the trap. For example, 1,1-dichloroethane showed a 50 percent decrease in FID response compared to that for the

10-min desorption time. Later-eluting peaks also displayed a drop in area counts, although the decrease was not as great (~25 percent). There was no improvement in ECD response.

The final test involved increasing the trap collection temperature from 4°C to 10°C with a 10-min tube desorption time. Recovery efficiencies for the later-eluting compounds (ethyl benzene and later) were satisfactory and, although the area counts for the earlier peaks were greater than when the tube was desorbed for 15 minutes, they were still less than those obtained with a 10-min tube desorption with the trap at 4°C. The ECD still gave limited signal response.

These tests led to the decision to operate the ATD 400 with a 10-minute tube desorption time at 325°C and the trap at 4°C. Three consecutive sample loadings and analyses were carried out, and the results are presented in Table 5. The RSDs for the early-eluting peaks still indicate some breakthrough problems in this region. The remaining compounds show acceptable levels of precision. The results obtained here indicated that the desorption/analytical system could be used under these conditions for the evaluation of the samplers when collecting humidified air. A calibration table was generated using the area counts from the data in Table 5. An expanded FID chromatogram of a humidified 3-L sample at 2 ppbv is shown in Figure 12, along with a condensed presentation of an ECD trace for the same run in Figure 13.

A second effort was made to resolve the problem associated with the loss of ECD response since the qualitative information from this detector was desired. By monitoring the millivolt signal from the ECD during the processing of a humidified sample it was determined that the detector was not being affected by the water vapor in the sample but rather that the 0.1 mm I.D. splitter line was being physically plugged with moisture, which prevented any sample material from reaching the detector. When the oven temperature reached ~95°C, approximately 22 minutes into the run, the moisture plug vaporized and sample once again began to flow to the ECD. This problem may be solved by attaching an independent heater to the splitter to maintain any moisture in the vapor phase when the oven temperature is <100°C. This modification was not made during this study, so FID data alone was used.

TABLE 5. AVERAGE FID PEAK AREAS AND PRECISION DATA FOR HUMIDIFIED 3-L TO-14 STANDARDS COLLECTED ON CARBOTRAP C, CARBOTRAP, AND CARBOSIEVE S-III TUBES (THREE RUNS)

Compound	Conc. (ppbv)	Average Area Counts	RSD, %
1) dichlorodifluoromethane	2.46	367344	20
2) methyl chloride	2.11	463807	23
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	2.44	810726	10
4) vinyl chloride	6.33	2731003	5
5) 1,3-butadiene	2.81	1710764	11
6) methyl bromide	2.90	265805	14
7) ethyl chloride	2.66	930053	14
8) trichlorofluoromethane	2.39	139841	33
9) 1,1-dichloroethene	2.85	1089031	7
10) dichloromethane	3.76	755082	3
11) 3-chloropropene	3.00	808306	9
12) 1,1,2-trichloro-1,2,2-trifluoroethane	2.39	679123	8
13) 1,1-dichloroethane	2.87	924949	9
14) cis-1,2-dichloroethene	3.06	1244552	5
15) trichloromethane	3.07	527305	6
16) 1,2-dichloroethane	2.95	1221626	7
17) 1,1,1-trichloroethane	1.31	521067	7
18) benzene	2.57	3964751	9
19) carbon tetrachloride	2.71	194902	11
20) 1,2-dichloropropane	2.47	1506310	5
21) trichloroethene	2.55	1516751	4
22) cis-1,3-dichloropropene	2.75	534324	8
23) trans-1,3-dichloropropene	2.98	575697	9
24) 1,1,2-trichloroethane	2.55	870787	8
25) toluene	2.17	2812267	4
26) 1,2-dibromoethane	2.90	748685	7
27) tetrachloroethene	2.29	1081445	3
28) chlorobenzene	2.38	2891783	3
29) ethylbenzene	2.06	1718436	8
30) m+p-xylene	1.93	1652205	8
31) styrene	2.15	2520014	1
32) 1,1,2,2-tetrachloroethane	2.14	2414730	6
and o-xylene	2.07		
34) 4-ethyltoluene	1.75	910544	6
35) 1,3,5-trimethylbenzene	1.74	1517935	4
36) 1,2,4-trimethylbenzene	1.80	1155921	2
37) benzyl chloride	2.30	2433001	5
and m-dichlorobenzene	2.13		
39) p-dichlorobenzene	2.00	2435966	7
40) o-dichlorobenzene	2.06	2170459	9
41) 1,2,4-trichlorobenzene	1.48	1357213	11
42) hexachlorobutadiene	1.31	943121	5

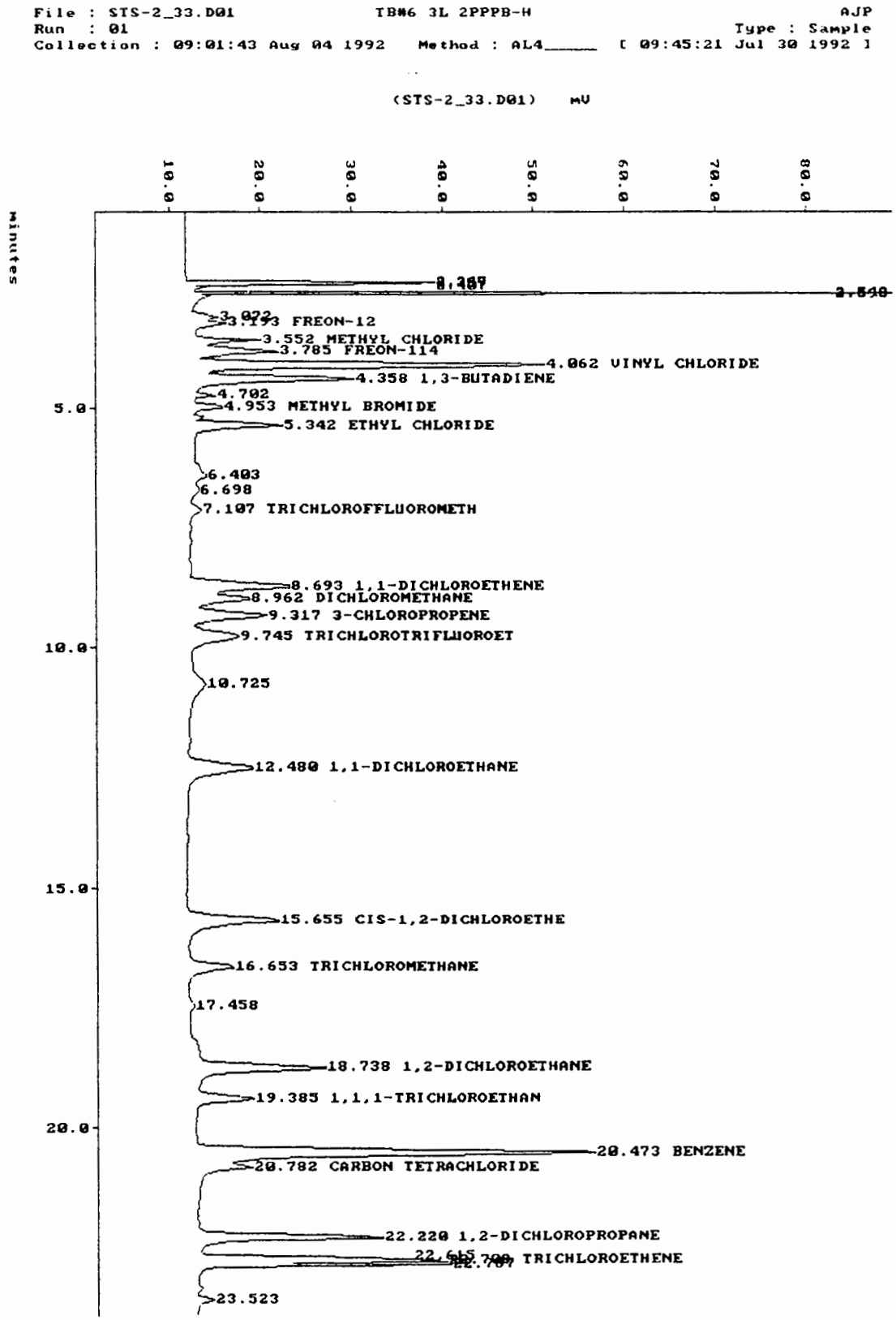


Figure 12-a. Typical FID chromatogram for a humidified 3-L volume TO-14 calibration run at 2 ppbv.

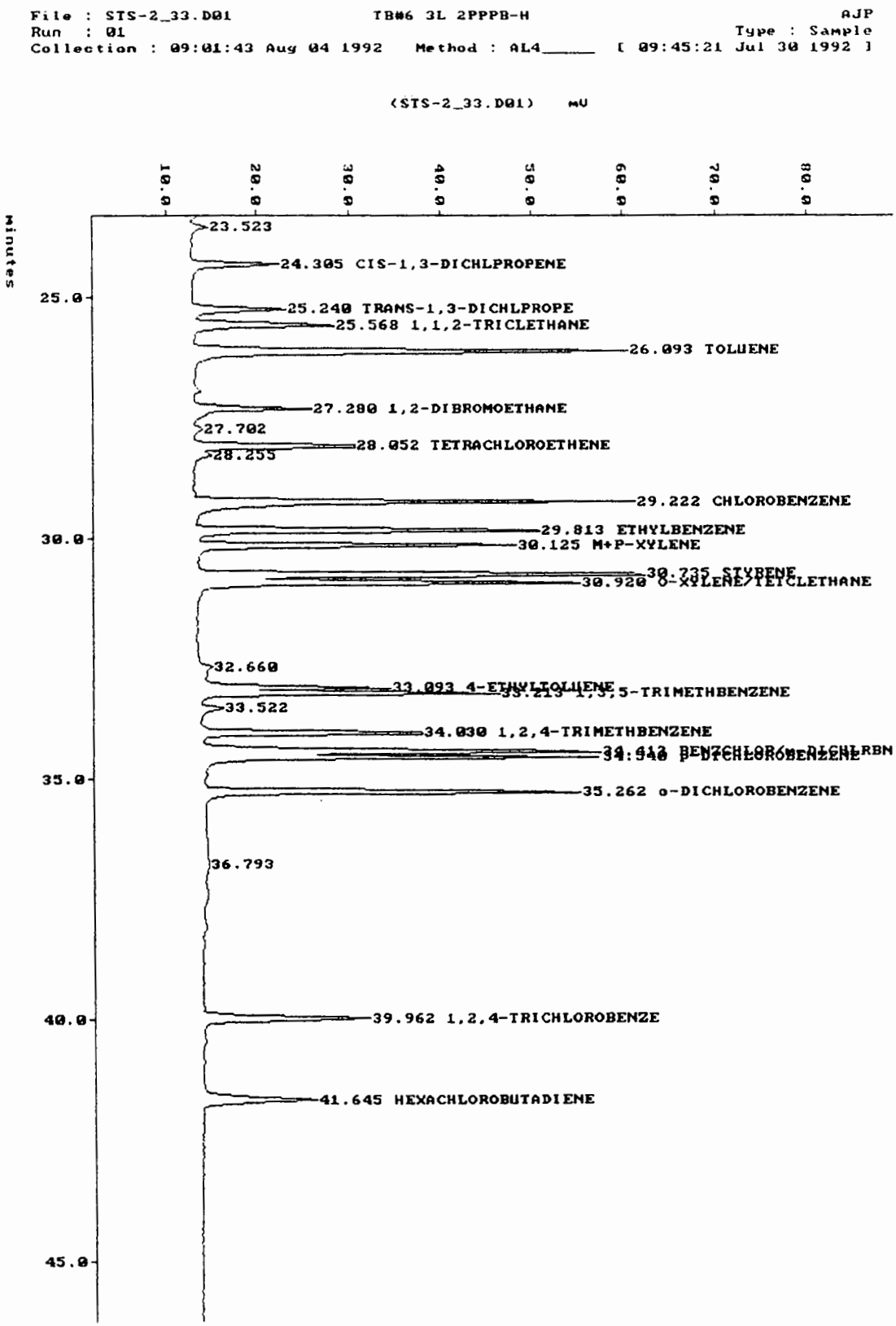


Figure 12-b. Typical FID chromatogram for a humidified 3-L volume TO-14 calibration run at 2 ppbv.

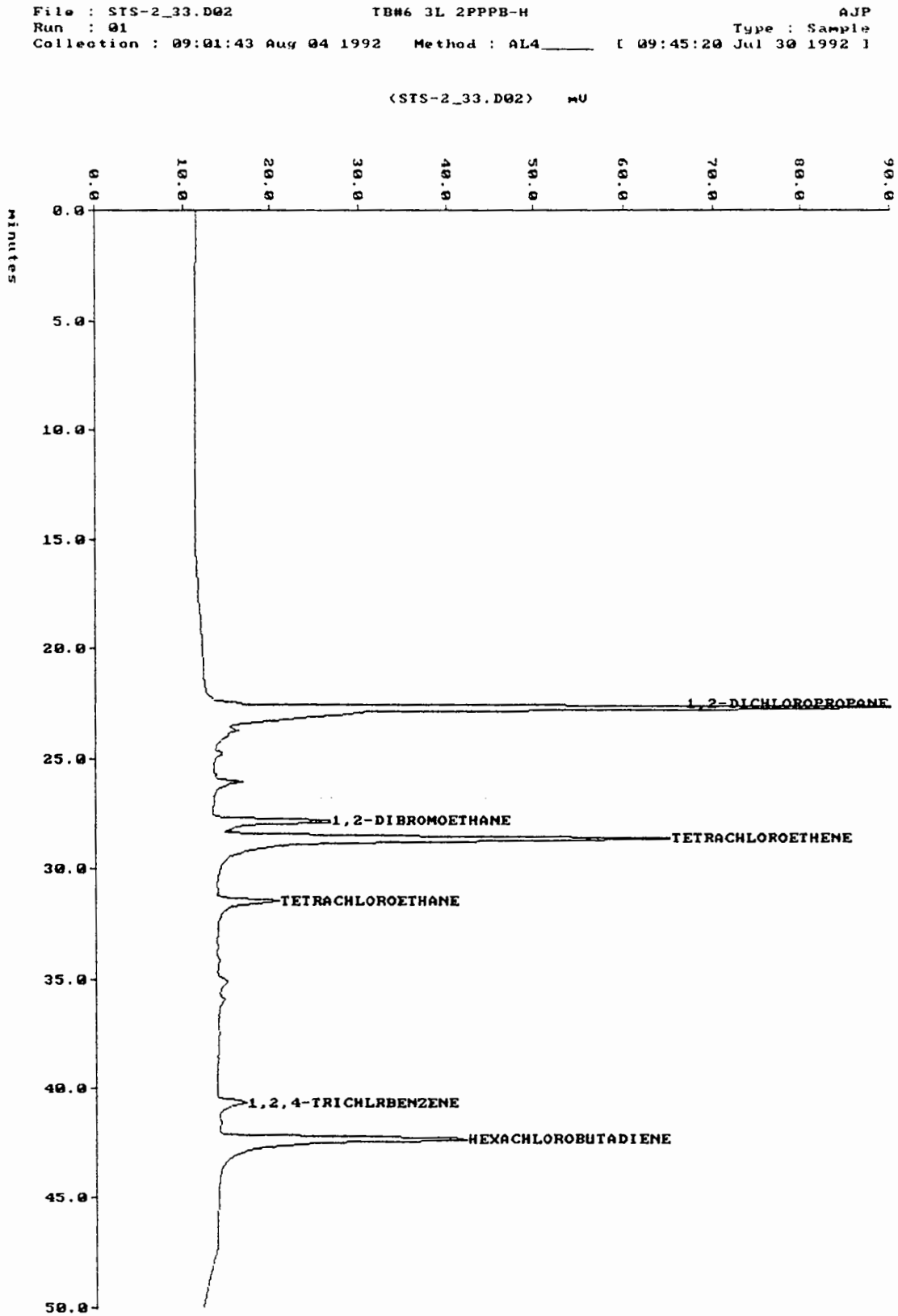


Figure 13. Typical ECD chromatogram for a humidified 3-L volume TO-14 calibration run at 2 ppbv.

The increased FID response observed when a humidified sample was processed deserves comment. This effect appears to be due to the moisture in the sample that tends to enhance the desorption of the collected organics because of the interaction of the water vapor with the carbon sorbents. According to Coutant, (18) the combination of the relatively high concentration of water vapor and its polarizability causes the water to selectively occupy the most active sorption sites in the sorbent bed. As a result, the release of the trapped organics during thermal desorption is improved.

To investigate this effect further, two sorbent tubes were loaded with a dry 3-L sample of the TO-14 mix at 2 ppbv concentration. These tubes were desorbed and analyzed, giving FID area counts that were typical of those observed for dry samples during this study. The same two tubes were then loaded with 3-L samples of Aadco high purity air. One of the tubes was loaded with dry air and the other loaded with humidified air. The two tubes were analyzed again. Some of the later eluting compounds were obtained from the dry tube, however, the humidified sample yielded these same late-eluting species at twice the level observed for the dry sample (see Figures 14 and 15). This suggests that moisture may indeed enhance the recovery of heavier VOCs from carbon sorbents. Further investigation of this effect seems to be warranted.

Analysis of Polar Compounds

The polar calibration mixture was loaded onto the three-stage sorbent tubes as a humidified sample at 2 ppbv concentration. Sample volumes were 1, 2, and 3-L.

Analysis of these tubes showed that several of the target compounds were detected, and their peak areas increased with sample volume. However, the peaks, other than 1,3-butadiene, benzene, and toluene, were broad and compound identification by elution order was difficult. It appeared from this test that the analytical conditions used for TO-14 analysis are inappropriate for the polar species, and no further effort was made to establish a method specifically for these compounds. A FID chromatogram for the 3-L sample is presented in Figure 16.

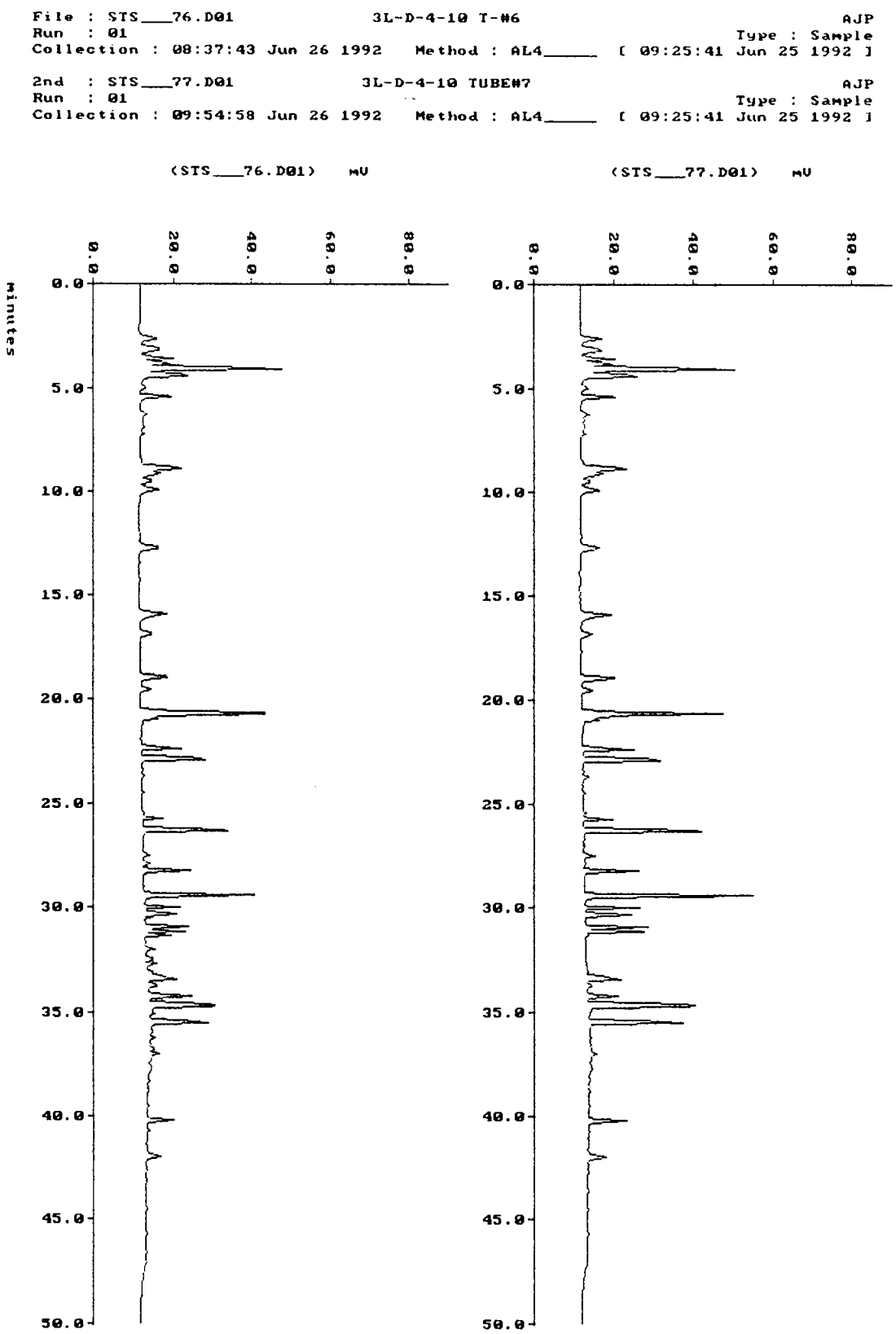


Figure 14. FID chromatograms for two tubes loaded with dry 3-L volume TO-14 calibration mixtures.

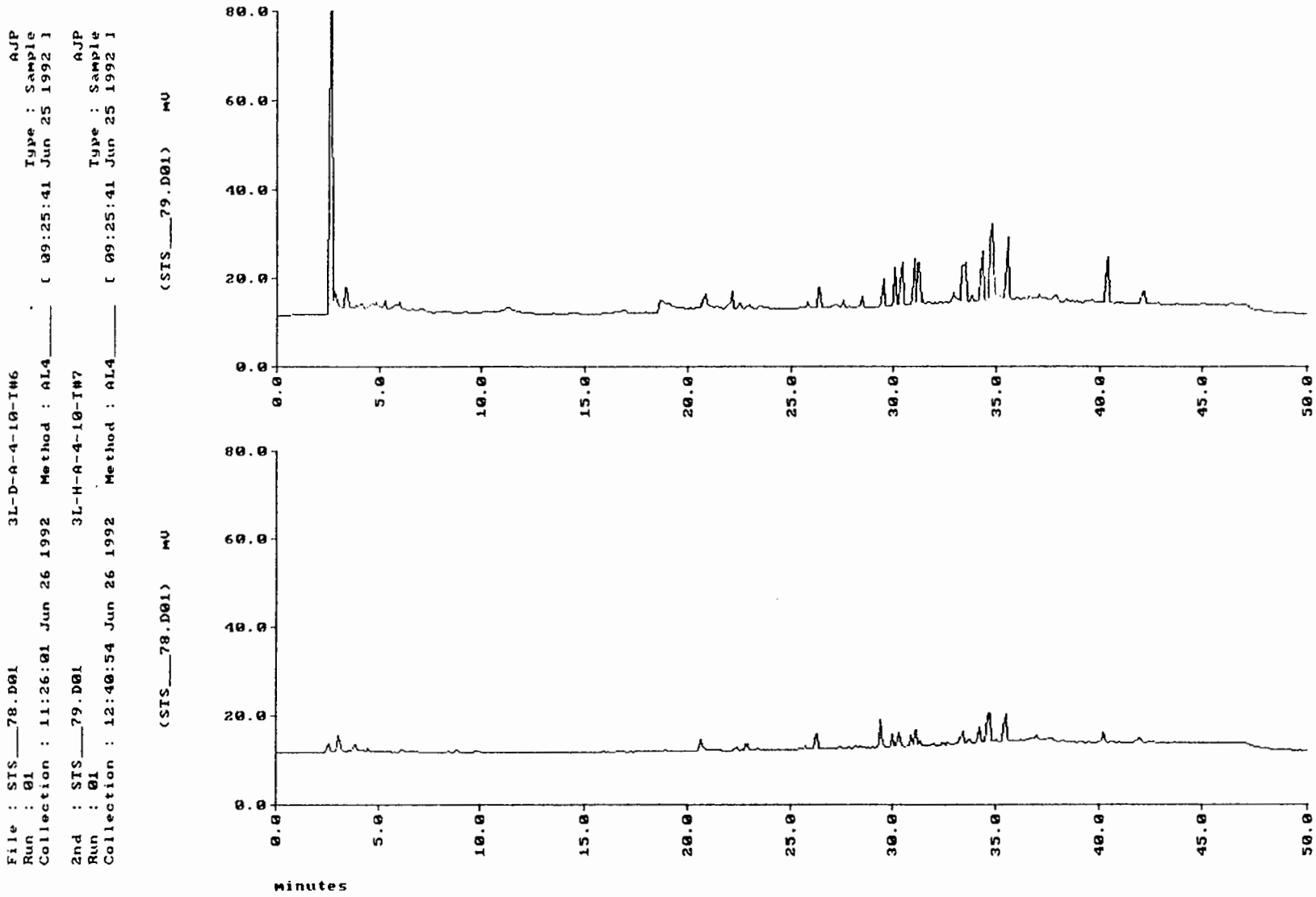


Figure 15. FID chromatograms for a tube loaded with humidified 3-L volume Aadco air (upper) and a tube loaded with dry 3-L volume Aadco air (lower) samples.

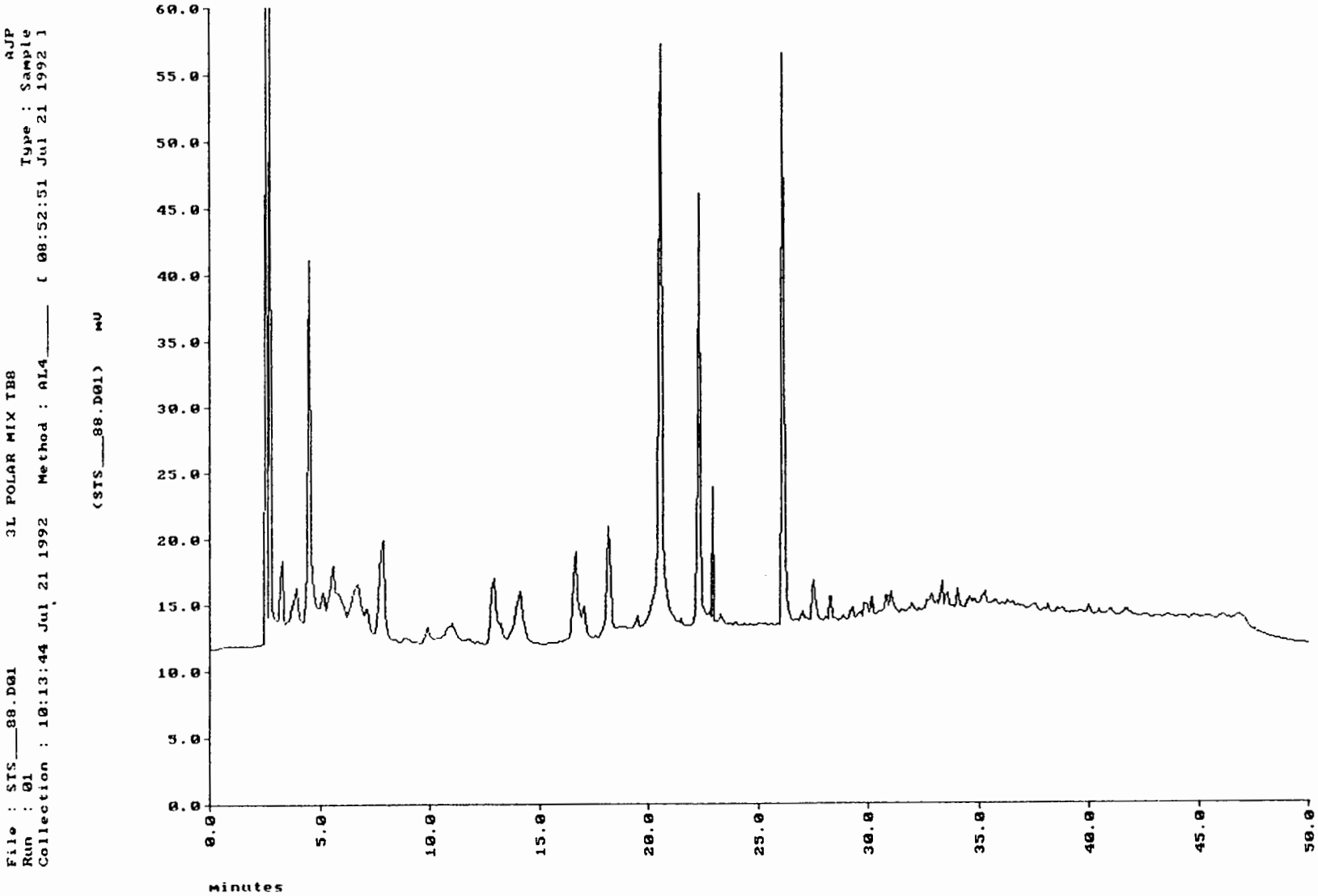


Figure 16. FID chromatogram for humidified 3-L volume polar mixture at 2 ppbv.

Environmental Chamber Evaluation

Prior to evaluating the STS 25 under controlled conditions in the environmental chamber, the empty chamber was challenged with pure air and TO-14 loadings. Canister grab samples were collected and the results obtained from the analysis of these samples, using Battelle's cryogenic analytical system, are presented. For Aadco pure air (background) runs, the only target compound observed above the detection limit was benzene, which occurred at sub-ppbv levels. Table 6 lists the recoveries obtained for the TO-14 compounds at the 2 ppbv level. The recovery efficiencies for most compounds exceed 80 percent at this concentration. It appears that cis-1,3-dichloropropene may be coming from some source in the chamber, particularly at the higher temperature, and that trans-1,3-dichloropropene may be adsorbed on a chamber surface. The results also indicate that the higher boiling species probably condense to some extent on the walls of the chamber, since these recovery efficiencies are less than 80 percent. The results are presented in Table 7 for the 10 ppbv standard. The pattern of recovery is similar to that obtained for the 2 ppbv sample. In addition, the recovery efficiency for benzyl chloride at 25°C was low (~35 percent), but when the temperature was raised to 37°C, the levels were elevated (~140 percent). It may be that the compound was first deposited on the walls of the chamber, then was desorbed at the higher temperature.

In general, the environmental chamber displayed very low blank levels and acceptable recoveries for the 2 and 10 ppbv concentrations. Temperature effects seemed to account for variability in the concentrations of compounds to a greater extent than did the humidity levels.

TABLE 6. RECOVERY EFFICIENCIES OF TO-14 TARGET COMPOUNDS AT 2 PPBV VIA CANISTER SAMPLING AND CRYOGENIC/MSD ANALYSIS.

		Percent Recovery			
	Conc.	25 C		37 C	
Compound	(ppbv)	10% RH	60% RH	10% RH	60% RH
1) dichlorodifluoromethane	2.42	88.3	85.7	87.5	91.2
2) methyl chloride	2.12	109.7	94.4	85.1	112.4
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	2.35	86.2	88.1	92.9	89.9
4) vinyl chloride	5.95	69.8	75.6	78.0	79.7
5) 1,3-butadiene	2.47	93.6	115.9	118.2	134.5
6) methyl bromide	2.67	84.8	86.8	84.3	90.7
7) ethyl chloride	2.40	91.8	87.3	96.6	97.5
8) trichlorofluoromethane	2.66	76.5	79.4	79.1	76.8
9) 1,1-dichloroethene	2.70	90.0	89.6	88.4	90.5
10) dichloromethane	3.59	86.4	89.8	90.7	85.0
11) 3-chloropropene	2.74	76.8	70.8	81.3	91.2
12) 1,1,2-trichloro-1,2,2-trifluoroethane	2.24	80.2	86.3	88.8	84.6
13) 1,1-dichloroethane	2.69	85.6	79.4	85.9	91.0
14) cis-1,2-dichloroethene	3.02	70.4	63.5	76.6	72.6
15) trichloromethane	2.97	80.2	81.0	83.4	86.7
16) 1,2-dichloroethane	2.90	74.7	80.4	74.6	77.4
17) 1,1,1-trichloroethane	1.29	84.9	83.7	80.2	90.6
18) benzene	2.52	77.6	78.0	81.2	88.3
19) carbon tetrachloride	2.68	84.3	83.7	82.8	87.1
20) 1,2-dichloropropane	2.39	75.6	75.2	70.5	73.9
21) trichloroethene	2.44	74.3	74.8	82.3	78.5
22) cis-1,3-dichloropropene	2.70	98.5	116.9	134.4	160.0
23) trans-1,3-dichloropropene	2.91	46.6	49.6	58.1	60.1
24) 1,1,2-trichloroethane	2.53	91.5	81.9	75.0	94.6
25) toluene	2.19	84.7	77.3	76.7	86.1
26) 1,2-dibromoethane	2.83	80.8	74.9	66.8	78.0
27) tetrachloroethene	2.26	79.7	81.1	75.4	70.7
28) chlorobenzene	2.30	79.6	82.5	67.6	75.8
29) ethylbenzene	2.00	98.9	88.5	79.9	87.3
30) m+p-xylene	1.96	93.5	83.3	71.9	80.7
31) styrene	2.01	83.8	78.9	67.0	86.6
32) 1,1,2,2-tetrachloroethane	2.12	85.8	93.4	72.6	87.3
33) o-xylene	2.05	92.7	97.0	73.4	85.2
34) 4-ethyltoluene	1.71	86.3	82.3	56.2	72.2
35) 1,3,5-trimethylbenzene	1.68	84.1	81.6	60.3	69.9
36) 1,2,4-trimethylbenzene	1.76	88.2	97.4	61.8	76.1
37) benzyl chloride	2.29	35.4	54.2	66.6	68.6
38) m-dichlorobenzene	2.04	70.9	77.0	52.9	62.4
39) p-dichlorobenzene	2.05	60.3	61.1	38.6	50.2
40) o-dichlorobenzene	2.02	71.1	76.1	51.8	65.7
41) 1,2,4-trichlorobenzene	1.49	30.2	75.3	16.8	58.2
42) hexachlorobutadiene	1.31	60.3	70.4	44.9	50.1

TABLE 7. RECOVERY EFFICIENCIES OF TO-14 TARGET COMPOUNDS AT 10 PPBV VIA CANISTER SAMPLING AND CRYOGENIC/MSD ANALYSIS.

		Percent Recovery			
	Conc.	25 C		37 C	
Compound	(ppbv)	10% RH	60% RH	10% RH	60% RH
1) dichlorodifluoromethane	12.10	90.7	90.3	93.2	92.6
2) methyl chloride	10.60	97.4	88.0	95.6	99.4
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	11.75	91.7	92.0	96.2	95.2
4) vinyl chloride	29.75	82.6	78.4	85.7	85.7
5) 1,3-butadiene	12.35	115.0	132.7	111.0	126.5
6) methyl bromide	13.35	92.8	92.0	87.9	90.1
7) ethyl chloride	12.00	89.3	89.8	94.8	91.9
8) trichlorofluoromethane	13.30	81.7	80.2	85.5	81.4
9) 1,1-dichloroethene	13.50	94.4	96.1	97.0	97.0
10) dichloromethane	17.95	110.6	107.0	117.0	114.8
11) 3-chloropropene	13.70	106.3	109.6	118.0	112.1
12) 1,1,2-trichloro-1,2,2-trifluoroethane	11.20	100.6	101.0	104.6	104.2
13) 1,1-dichloroethane	13.45	96.1	95.4	102.8	99.4
14) cis-1,2-dichloroethene	15.10	98.5	94.6	101.9	106.8
15) trichloromethane	14.85	94.3	92.1	95.8	95.3
16) 1,2-dichloroethane	14.50	94.4	92.8	100.3	101.0
17) 1,1,1-trichloroethane	6.45	96.1	95.8	100.0	101.4
18) benzene	12.60	90.2	87.4	95.3	94.7
19) carbon tetrachloride	13.40	96.5	97.2	97.3	100.4
20) 1,2-dichloropropane	11.95	98.2	99.3	105.3	103.1
21) trichloroethene	12.20	87.1	85.0	96.7	91.1
22) cis-1,3-dichloropropene	13.50	187.9	199.3	219.6	217.3
23) trans-1,3-dichloropropene	14.55	90.8	92.9	91.3	98.3
24) 1,1,2-trichloroethane	12.65	103.7	106.1	119.1	119.3
25) toluene	10.95	93.0	94.3	101.9	100.2
26) 1,2-dibromoethane	14.15	98.2	103.8	101.4	113.4
27) tetrachloroethene	11.30	77.8	80.9	89.3	83.0
28) chlorobenzene	11.50	88.0	89.3	97.9	95.0
29) ethylbenzene	10.00	95.5	96.6	112.4	102.3
30) m+p-xylene	9.80	98.6	99.0	119.0	113.5
31) styrene	10.05	98.5	99.2	109.9	112.4
32) 1,1,2,2-tetrachloroethane	10.60	88.1	88.2	96.4	93.8
33) o-xylene	10.25	93.9	94.9	107.7	100.9
34) 4-ethyltoluene	8.55	81.5	87.9	94.3	91.9
35) 1,3,5-trimethylbenzene	8.40	78.9	92.1	92.5	92.7
36) 1,2,4-trimethylbenzene	8.80	87.3	91.1	92.7	93.9
37) benzyl chloride	11.45	35.1	32.6	137.5	143.4
38) m-dichlorobenzene	10.20	73.3	74.9	82.4	78.0
39) p-dichlorobenzene	10.25	68.3	66.4	69.0	73.5
40) o-dichlorobenzene	10.10	77.4	78.8	86.7	86.1
41) 1,2,4-trichlorobenzene	7.45	67.1	70.6	77.2	75.5
42) hexachlorobutadiene	6.55	55.2	56.6	54.5	50.5

TASK 2: STS 25 SEQUENTIAL TUBE SAMPLER EVALUATION

Mechanical

The STS 25 was operated over two 24-hour periods to evaluate the operational characteristics of the unit. The device was programmed to collect 75-min and 10-min samples. In both cases, the system performed with no mechanical problems. The charging system on the STS 25 also performed well. The SKC personal monitoring pump maintained a constant flow rate (~43 cc/min) over a 24-hour period based upon flow measurements at the beginnilng and end of the test. No mechanical problems were encountered with the operational aspects of the STS 25.

Environmental Chamber Tests

The STS 25 was placed in the environmental chamber and used to collect background air samples and TO-14 standard mixes at various concentrations, temperatures, and relative humidity levels. In all cases reported here, the percent recoveries for the samples collected by the STS 25 are based upon the levels that were generated in the empty chamber which were validated through canister sampling and TO-14 analysis using Battelle's standard cryogenic analytical system.

Blank Test--

The results for the background samples collected by the STS 25 are shown in Table 8. As discussed earlier, the empty chamber contained only low levels of benzene. With the STS 25 present in the chamber, however, several of the TO-14 target compounds were observed. The 25°C runs indicate that the concentrations of these compounds do not change greatly with RH. The 37°C run does show higher concentrations, which are probably due to compounds being liberated from the STS 25 itself. It is important to note that the conditions under which all the chamber tests were run reflect a very stringent test of the artifact characteristics of the STS 25. Since the device is in a relatively small volume that is being purged at 2 L/min, while the STS 25 is cycling air through itself at 30 L/min, it is evident that any volatile compounds that may be associated with the materials used in the construction of this sampler are being concentrated in the chamber atmosphere.

TABLE 8. BACKGROUND AIR SAMPLES (3 L) COLLECTED WITH THE STS 25 (USING MULTISORBENT TUBES) AND IN CANISTERS (values in ppbv).

Compound	25C @ 10%RH		25C @ 60%RH		37C @ 60%RH	
	Tube	Canister	Tube	Canister	Tube	Canister
1) dichlorodifluoromethane	n.d.	n.d.	3.4	n.d.	n.d.	n.d.
2) methyl chloride	0.4	0.1	n.d.	0.1	n.d.	0.1
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	16.7	n.d.	2.6	n.d.	279.6	n.d.
4) vinyl chloride	0.4	n.d.	n.d.	0.1	2.7	n.d.
5) 1,3-butadiene	0.1	n.d.	0.4	n.d.	0.9	n.d.
6) methyl bromide	n.d.	n.d.	0.8	n.d.	n.d.	n.d.
7) ethyl chloride	0.5	n.d.	n.d.	n.d.	3.8	0.1
8) trichlorofluoromethane	2.1	n.d.	n.d.	0.1	1339.6	0.2
9) 1,1-dichloroethene	0.3	n.d.	n.d.	n.d.	0.3	n.d.
10) dichloromethane	n.d.	0.7	0.4	0.4	n.d.	1.0
11) 3-chloropropene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
12) 1,1,2-trichloro-1,2,2-trifluoroethane	n.d.	n.d.	0.2	n.d.	0.2	0.4
13) 1,1-dichloroethane	0.3	n.d.	n.d.	n.d.	n.d.	n.d.
14) cis-1,2-dichloroethene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15) trichloromethane	n.d.	n.d.	n.d.	0.1	2.2	0.6
16) 1,2-dichloroethane	n.d.	n.d.	n.d.	n.d.	0.5	n.d.
17) 1,1,1-trichloroethane	0.2	0.1	0.2	0.1	0.6	0.2
18) benzene	0.4	0.1	1.3	0.1	2.8	0.2
19) carbon tetrachloride	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
20) 1,2-dichloropropane	n.d.	n.d.	1.2	n.d.	0.5	n.d.
21) trichloroethene	0.3	n.d.	0.4	n.d.	1.2	0.1
22) cis-1,3-dichloropropene	n.d.	n.d.	0.5	n.d.	0.8	n.d.
23) trans-1,3-dichloropropene	n.d.	n.d.	n.d.	n.d.	0.4	n.d.
24) 1,1,2-trichloroethane	n.d.	n.d.	n.d.	n.d.	0.4	n.d.
25) toluene	0.5	0.2	0.6	0.1	2.1	0.7
26) 1,2-dibromoethane	0.6	n.d.	0.5	n.d.	0.7	n.d.
27) tetrachloroethene	0.6	n.d.	1.0	n.d.	0.1	0.1
28) chlorobenzene	0.3	0.1	0.4	0.1	0.4	0.2
29) ethylbenzene	0.3	0.1	0.3	0.2	0.7	0.4
30) m+p-xylene	0.7	0.4	1.0	0.5	1.9	1.5
31) styrene	0.6	0.1	0.6	0.2	1.1	0.6
32) 1,1,2,2-tetrachloroethane	0.6	n.d.	0.7	n.d.	1.3	0.1
and o-xylene	0.6	0.4	0.7	0.5	1.3	1.5
34) 4-ethyltoluene	1.7	0.6	2.1	0.6	2.8	0.1
35) 1,3,5-trimethylbenzene	1.4	0.2	1.8	n.d.	2.5	2.7
36) 1,2,4-trimethylbenzene	6.0	2.5	8.3	3.1	10.0	18.1
37) benzyl chloride	n.d.	n.d.	0.3	n.d.	0.4	n.d.
and m-dichlorobenzene	n.d.	n.d.	0.3	n.d.	0.4	0.1
39) p-dichlorobenzene	0.4	n.d.	0.3	n.d.	0.4	0.2
40) o-dichlorobenzene	0.2	n.d.	0.2	0.1	0.4	0.2
41) 1,2,4-trichlorobenzene	0.8	n.d.	0.1	0.1	0.8	0.3
42) hexachlorobutadiene	1.0	0.1	0.8	0.1	6.0	0.2

n.d. = compound not detected.

Nonetheless, the blank test does indicate that there is the potential for artifact contribution from the STS 25 during ambient air sampling.

Canister samples were also collected from the chamber while the STS 25 was in the last 15 minutes of drawing the sample onto the collection tube. Major differences are identified between the tube concentrations and the canister analysis(e.g., Freon species). We believe that these discrepancies are the first indications of the limitations associated with quantifying complex mixtures with only an FID detector. The differences observed are generally such that the STS 25 tube identifies compounds being present at higher levels than the MSD canister analysis. This is easily justified inasmuch as compounds other than the TO-14 species could be eluting at the same time as one of the target compounds and since retention times are the only qualifier on the ATD 400/GC analytical system, they are mistakenly being identified. A FID chromatogram from the blank run collected by the STS 25 at 37°C with 60 percent RH is shown in Figure 17.

TO-14 Chamber Tests--

The results from challenging the STS 25 with the TO-14 calibration mixture under controlled conditions are presented in Tables 9 and 10. The compounds will be discussed in three sets. First, the light species from analytical start time through 1,1,2-trichloro-1,2,2-trifluoroethane; secondly, intermediates from 1,1-dichloroethane through ethyl benzene; and finally the heavier species from m&p-xylene to hexachlorobutadiene.

For the light compounds, trends are evident in data from both the 2 and 10 ppbv tests. The STS 25 results tend to exaggerate the concentrations present for several of the earliest eluting species (e.g., Freon compounds). We believe that this is a further example of artifact compounds coeluting with compounds of interest. This exaggeration is particularly evident during the 2 ppbv test where a slight contribution from an artifact results in a pronounced variance in percent recovery. Relative humidity does not seem to play as much of a role in liberating light artifacts as does the increased temperature. The >100 percent recovery values from the STS 25 were confirmed to be due to artifact coelution since the canister results generally did not reflect increased TO-14 species presence with changes in relative humidity and temperature.

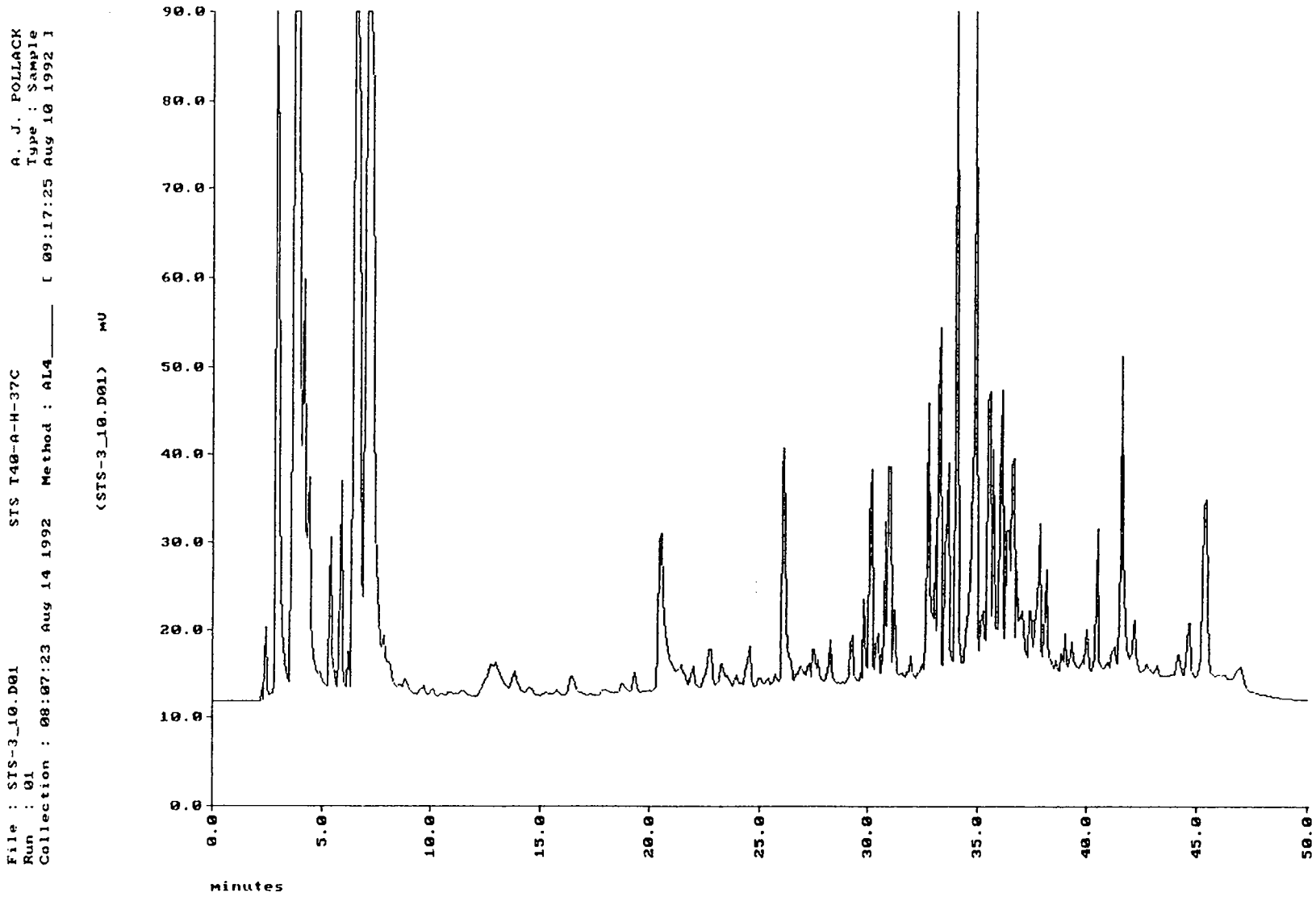


Figure 17. FID chromatogram for environmental chamber blank sample collected by the STS 25 (60% RH, 37°C, 3-L).

TABLE 9. COMPARISON OF RECOVERY EFFICIENCIES OF TO-14 TARGET COMPOUNDS AT 2 PPBV OBTAINED WITH THE STS 25 (USING MULTISORBENT TUBES) AND IN CANISTERS.

	25C @ 10% RH			25C @ 60% RH			37C @ 60% RH		
Compound	Chamber Conc. (ppbv)	Tube Recovery (%)	Canister Recovery (%)	Chamber Conc. (ppbv)	Tube Recovery (%)	Canister Recovery (%)	Chamber Conc. (ppbv)	Tube Recovery (%)	Canister Recovery (%)
1) dichlorodifluoromethane	2.14	146.4	81.4	2.07	187.0	90.6	2.21	305.7	103.1
2) methyl chloride	2.33	107.1	45.6	2.00	334.5	51.5	2.38	301.5	50.7
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	2.03	428.1	112.2	2.07	312.1	123.0	2.11	494.7	114.3
4) vinyl chloride	4.15	131.3	142.1	4.50	160.7	131.0	4.74	108.2	149.8
5) 1,3-butadiene	2.31	100.5	57.9	2.86	116.8	64.3	3.32	142.1	61.3
6) methyl bromide	2.27	61.0	82.7	2.32	319.8	80.9	2.42	22.9	94.1
7) ethyl chloride	2.20	85.5	91.4	2.10	141.7	95.7	2.34	81.4	113.0
8) trichlorofluoromethane	2.04	198.6	78.8	2.11	95.1	82.6	2.04	1170.3	44.0
9) 1,1-dichloroethene	2.43	96.9	110.3	2.42	99.7	116.3	2.44	84.2	104.4
10) dichloromethane	3.10	93.9	138.3	3.22	112.6	120.7	3.05	103.4	154.2
11) 3-chloropropene	2.11	62.0	139.7	1.94	138.8	145.1	2.50	21.2	91.1
12) 1,1,2-trichloro-1,2,2-trifluoroethane	1.80	98.1	115.6	1.93	102.0	109.9	1.90	90.5	107.2
13) 1,1-dichloroethane	2.30	89.1	116.5	2.14	150.0	131.5	2.45	80.3	114.9
14) cis-1,2-dichloroethene	2.13	112.4	125.8	1.92	134.3	147.9	2.19	116.5	127.2
15) trichloromethane	2.38	81.1	123.9	2.41	112.1	116.8	2.57	47.5	114.7
16) 1,2-dichloroethane	2.17	85.6	117.3	2.33	110.2	103.5	2.25	71.8	113.2
17) 1,1,1-trichloroethane	1.10	84.7	121.8	1.08	127.4	111.7	1.17	92.0	114.5
18) benzene	1.96	98.9	109.4	1.97	180.3	102.0	2.23	153.7	112.5
19) carbon tetrachloride	2.26	78.2	112.7	2.24	109.2	107.7	2.33	103.4	103.5
20) 1,2-dichloropropane	1.81	83.5	139.9	1.80	115.1	129.0	1.77	76.6	137.8
21) trichloroethene	1.81	105.7	123.4	1.83	104.2	120.4	1.92	98.9	119.0
22) cis-1,3-dichloropropene	2.66	31.4	92.5	3.16	79.8	80.6	4.32	38.1	55.8
23) trans-1,3-dichloropropene	1.36	47.4	181.0	1.44	157.5	176.9	1.75	70.7	183.8
24) 1,1,2-trichloroethane	2.31	57.8	87.0	2.07	98.4	88.2	2.39	56.4	84.1
25) toluene	1.86	87.2	86.5	1.69	134.1	111.4	1.89	131.3	99.3
26) 1,2-dibromoethane	2.29	94.1	99.5	2.12	108.3	114.7	2.21	108.7	109.2
27) tetrachloroethene	1.80	69.0	106.3	1.83	78.1	104.0	1.60	90.9	129.3
28) chlorobenzene	1.83	95.2	124.5	1.90	86.2	112.9	1.74	127.9	161.7
29) ethylbenzene	1.98	64.9	81.2	1.77	98.7	98.4	1.75	118.3	122.5
30) m+p-xylene	1.83	81.8	87.9	1.63	129.4	90.4	1.58	196.5	195.1
31) styrene	1.68	97.0	87.7	1.59	137.2	104.9	1.74	152.6	160.5
32) 1,1,2,2-tetrachloroethane	1.82	111.7	80.9	1.98	111.4	73.1	1.85	189.5	93.4
and o-xylene	1.90	107.0	105.8	1.99	110.8	107.7	1.75	200.4	298.7
34) 4-ethyltoluene	1.48	83.7	86.7	1.41	103.7	146.9	1.23	128.8	228.8
35) 1,3,5-trimethylbenzene	1.41	143.6	161.2	1.37	152.8	199.0	1.18	516.8	227.1
36) 1,2,4-trimethylbenzene	1.55	425.4	608.1	1.71	380.2	506.8	1.34	1906.8	2790.3
37) benzyl chloride	0.81	131.2	60.2	1.24	90.5	29.2	1.57	88.4	42.1
and m-dichlorobenzene	1.45	73.3	64.7	1.57	71.5	128.9	1.27	109.3	105.5
39) p-dichlorobenzene	1.24	81.9	64.8	1.25	82.9	117.0	1.03	126.7	184.5
40) o-dichlorobenzene	1.44	87.3	93.1	1.54	94.8	109.7	1.33	117.9	141.1
41) 1,2,4-trichlorobenzene	0.45	465.3	148.9	1.12	95.6	132.3	0.87	226.0	184.8
42) hexachlorobutadiene	0.79	220.8	62.5	0.92	112.3	80.2	0.66	1468.8	121.8

TABLE 10. COMPARISON OF RECOVERY EFFICIENCIES OF TO-14 TARGET COMPOUNDS AT 10 PPBV OBTAINED WITH THE STS 25 (USING MULTISORBENT TUBES) AND IN CANISTERS.

	25C @ 60%RH			37C @ 60%RH		
Compound	Chamber Conc. (ppbv)	Tube Recovery (%)	Canister Recovery (%)	Chamber Conc. (ppbv)	Tube Recovery (%)	Canister Recovery (%)
1) dichlorodifluoromethane	10.9	181.5	141.0	11.2	121.0	125.6
2) methyl chloride	9.3	118.1	78.9	10.5	96.3	101.7
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	10.8	108.7	114.1	11.2	138.3	112.6
4) vinyl chloride	23.3	131.0	120.8	25.5	121.2	143.5
5) 1,3-butadiene	16.4	68.4	77.7	15.6	56.9	76.9
6) methyl bromide	12.3	137.4	123.3	12.0	89.8	121.4
7) ethyl chloride	10.8	140.6	124.3	11.0	100.3	109.3
8) trichlorofluoromethane	10.7	667.7	108.1	10.8	210.7	85.5
9) 1,1-dichloroethene	13.0	96.2	106.4	13.1	78.6	103.3
10) dichloromethane	19.2	89.7	100.5	20.6	88.7	96.3
11) 3-chloropropene	15.0	46.5	107.1	15.4	4.4	108.2
12) 1,1,2-trichloro-1,2,2-trifluoroethane	11.3	96.5	80.6	11.7	79.2	68.8
13) 1,1-dichloroethane	12.8	73.8	117.0	13.4	21.4	102.2
14) cis-1,2-dichloroethene	14.3	94.6	102.2	16.1	75.5	89.3
15) trichloromethane	13.7	74.3	110.7	14.2	88.6	104.2
16) 1,2-dichloroethane	13.5	77.9	108.5	14.7	62.5	97.0
17) 1,1,1-trichloroethane	6.2	75.1	106.3	6.5	73.3	102.5
18) benzene	11.0	100.9	105.9	11.9	88.2	102.2
19) carbon tetrachloride	13.0	68.3	104.0	13.5	70.3	100.6
20) 1,2-dichloropropane	11.9	80.8	100.5	12.3	68.1	101.1
21) trichloroethene	10.4	79.8	106.0	11.1	84.0	102.0
22) cis-1,3-dichloropropene	26.9	39.3	48.8	29.3	32.3	45.2
23) trans-1,3-dichloropropene	13.5	73.1	134.8	14.3	62.5	134.0
24) 1,1,2-trichloroethane	13.4	70.1	81.9	15.1	57.6	92.3
25) toluene	10.3	105.5	129.7	11.0	88.9	123.4
26) 1,2-dibromoethane	14.7	83.4	78.5	16.1	41.8	69.3
27) tetrachloroethene	9.2	101.1	102.3	9.4	87.2	105.8
28) chlorobenzene	10.3	83.9	110.9	10.9	68.0	116.6
29) ethylbenzene	9.7	81.5	95.7	10.2	60.7	96.9
30) m+p-xylene	9.7	92.8	98.0	11.1	72.0	132.4
31) styrene	10.0	82.4	88.7	11.3	64.5	102.2
32) 1,1,2,2-tetrachloroethane	9.4	104.8	80.2	10.0	92.1	85.9
and o-xylene	9.7	100.7	108.8	10.3	88.6	125.7
34) 4-ethyltoluene	7.5	81.6	94.5	7.9	61.6	109.9
35) 1,3,5-trimethylbenzene	7.7	113.9	97.0	7.8	127.8	80.9
36) 1,2,4-trimethylbenzene	8.0	273.7	240.6	8.3	321.9	507.2
37) benzyl chloride	15.6	39.9	37.8	16.4	28.7	35.1
and m-dichlorobenzene	7.6	81.8	105.2	8.0	59.1	97.6
39) p-dichlorobenzene	6.8	76.3	89.2	7.5	56.0	105.0
40) o-dichlorobenzene	8.0	66.7	89.2	8.7	53.5	95.5
41) 1,2,4-trichlorobenzene	5.3	99.0	94.3	5.6	52.4	123.8
42) hexachlorobutadiene	3.7	146.8	83.1	3.3	268.3	109.3

The 37°C test gave indications of breakthrough for 3-chloropropene in both the 2 and 10 ppbv tests while methyl bromide displayed this trend for only the 2 ppbv tests.

The canister analysis for TO-14 species in this initial region were generally consistent with expected levels. The noticeable deviations were that methyl chloride and 1,3-butadiene were consistently reported with low recoveries. This could be indicative of compound affinity for the STS 25 sampler. It was not possible to validate this since the STS 25 values reported were high, once again being affected by artifact coelution.

The second set of compounds in the TO-14 mixture exhibited predictable recoveries. The 10 percent relative humidity STS 25 recovery data were generally lower than the 60 percent relative humidity test at the same 25°C. This is in agreement with the results reported earlier where the presence of humidity seems to enhance the desorption of these TO-14 species from the multisorbent collection bed. Also, agreement with the canister results was generally more reproducible. It appears that this region of the chromatogram was impacted less by artifact contribution from the STS 25. Therefore, FID quantitation was more reliable and this was reflected in the reported percent recovery values for the 25°C and 37°C tests. Cis-1,3-dichloropropene did exhibit breakthrough for two of the 2 ppbv tests with recoveries in the 30 percent range. The 10 ppbv test results for this compound were questionable because of the higher than expected chamber concentration reported at ~27 ppbv. The MSD data was validated for this concentration but this high level was not readily explainable. An upward drift in reported levels for this compound was observed during the chamber and STS 25 testing period and may be indicative of some external contamination. The canister and STS 25 results for cis-1,3-dichloropropene gave consistently low results.

The final set of compounds in the TO-14 mixture were the latest eluting species. From the STS 25 blank test run it was observed that there was a region of artifacts eluting where these heavy TO-14 species are detected. Because of this, artifact coelution, with contribution to the STS 25 values reported, was expected and observed. For the 2 ppbv test, higher percent recovery values were regularly reported when compared to the canister results. This was particularly true for the 37°C test. However, canister recoveries were also >120 percent in this region indicating that the STS 25 at 37°C was liberating TO-14 species

along with non-target compounds. One particular compound, 1,2,4-trimethylbenzene, was identified by both the tube and canister results as being a major TO-14 artifact associated with the sampler.

The artifact contribution during the 10 ppbv test was not as severe. Since these tests were the last performed using the STS 25 it is conjectured that artifact liberation may have been subsiding with the continued purging of the STS 25 system.

At 25°C, with the relative humidity at 10 percent, the canister data indicated some affinity of the target compounds to the chamber/STS 25 test system. This was overcome with the addition of moisture during the 60 percent relative humidity test.

There was no definitive indication of breakthrough occurring for these compounds. This was expected since the limited breakthrough data for compounds in this group indicated very large volumes for the adsorbents used. (10) Benzyl chloride did exhibit consistently low recoveries but this was thought to be due to an adsorptive affinity for the testing apparatus.

The general statement that can be made from evaluating the STS 25 under laboratory conditions is that the sampler will collect TO-14 compounds onto sorbent tubes. However, these tests resulted in as much of an evaluation of the sorbents as it was for the STS 25. The Perkin Elmer sampler apparently does contribute artifacts to the sampling process when operated in a confined environment that does not afford an air changeover rate that is as great as that of the STS 25 itself. Also, the analytical system employed was limited by the use of only the FID detector which was affected by coeluting artifacts. Nonetheless, the STS 25 operated acceptably within the confines of the testing environment, sorbents, and analytical system used. Figure 18 shows the tube analysis of the 10 ppbv, TO-14 atmosphere collected by the STS 25 at 60 percent RH and 37°C.

Indoor Sampling--

The indoor air sampling results from the analysis of the two sorbent tubes using the ATD400/GC and the canister using the GC/MSD system are presented in Table 11.

Agreement between the two tube samples was quite good with the same compounds being identified and comparable concentrations reported. From this information it was evident that when used in a non-confined environment the STS 25 collects a representative

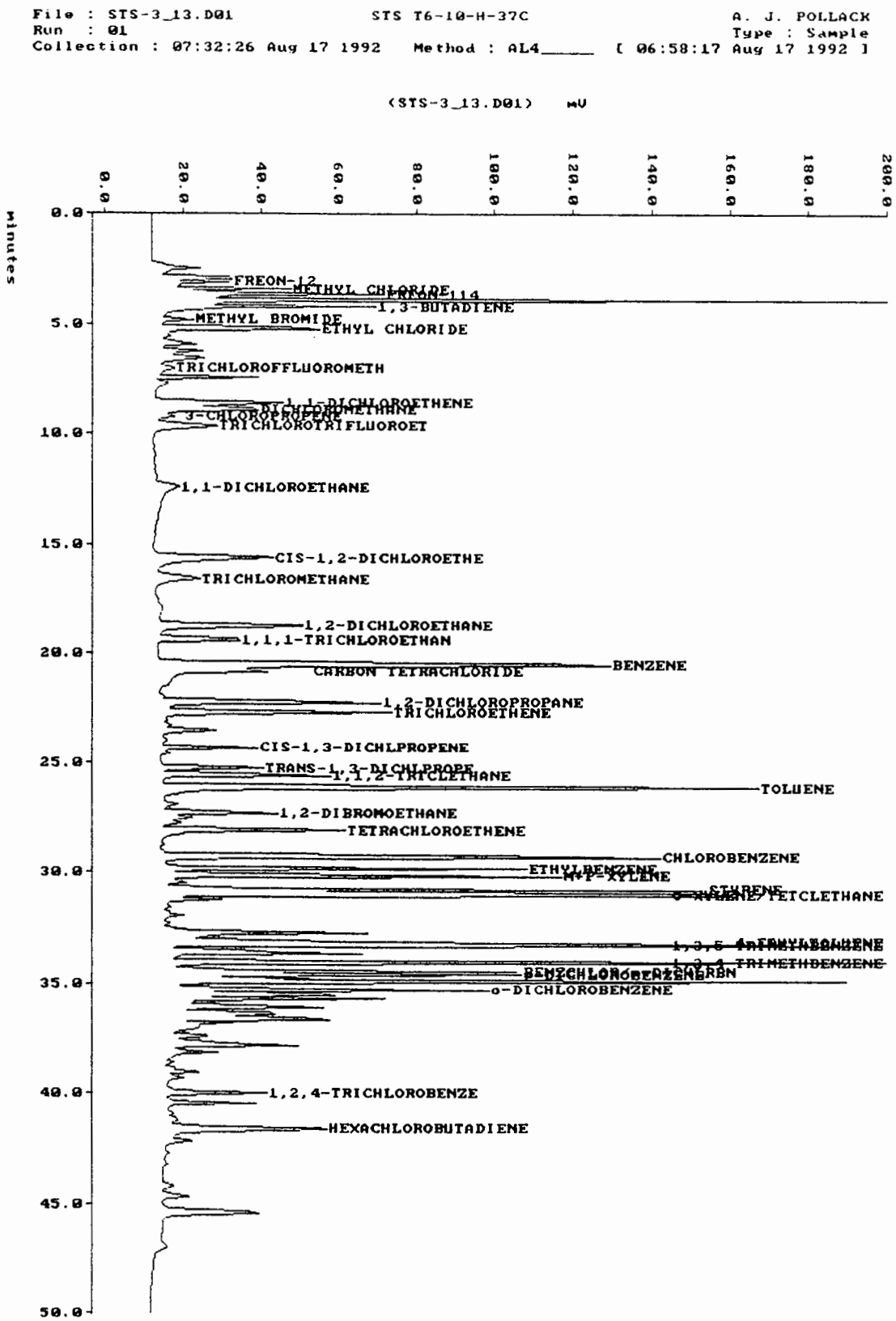


Figure 18. FID chromatogram for environmental chamber TO-14 mixture collected by the STS 25 (60% RH, 37°C, 3-L volume, 10 ppbv).

TABLE 11. INDOOR AIR SAMPLING RESULTS OBTAINED USING STS 25, TYLAN/SORBENT TUBE SAMPLER, AND CANISTER SAMPLER (values in ppbv).

Compound	STS 25 Tube 3L	Tylan Tube 3L	Canister Sample
1) dichlorodifluoromethane	n.d.	n.d.	4.2
2) methyl chloride	n.d.	n.d.	n.d.
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	12.4	12.3	n.d.
4) vinyl chloride	n.d.	0.5	n.d.
5) 1,3-butadiene	15.1	7.4	n.d.
6) methyl bromide	0.8	n.d.	n.d.
7) ethyl chloride	15.6	33.1	n.d.
8) trichlorofluoromethane	53.8	48.6	4.9
9) 1,1-dichloroethene	n.d.	n.d.	5.4
10) dichloromethane	160.7	138.2	28.2
11) 3-chloropropene	n.d.	n.d.	n.d.
12) 1,1,2-trichloro-1,2,2-trifluoroethane	1.0	1.6	2.6
13) 1,1-dichloroethane	0.8	n.d.	n.d.
14) cis-1,2-dichloroethene	n.d.	n.d.	n.d.
15) trichloromethane	4.6	5.6	0.2
16) 1,2-dichloroethane	0.8	1.0	n.d.
17) 1,1,1-trichloroethane	374.8	367.8	873.7
18) benzene	1.6	1.4	1.2
19) carbon tetrachloride	n.d.	n.d.	0.2
20) 1,2-dichloropropane	1.2	1.1	n.d.
21) trichloroethene	19.2	24.1	0.3
22) cis-1,3-dichloropropene	0.9	1.2	n.d.
23) trans-1,3-dichloropropene	0.3	0.3	n.d.
24) 1,1,2-trichloroethane	0.3	0.4	n.d.
25) toluene	3.6	4.4	4.2
26) 1,2-dibromoethane	1.0	0.7	n.d.
27) tetrachloroethene	1.1	1.1	1.0
28) chlorobenzene	0.5	0.6	n.d.
29) ethylbenzene	0.6	0.8	0.9
30) m+p-xylene	2.6	3.5	2.7
31) styrene	0.7	0.8	0.3
32) 1,1,2,2-tetrachloroethane	0.9	1.2	n.d.
and o-xylene	0.9	1.2	1.0
34) 4-ethyltoluene	5.5	7.1	0.9
35) 1,3,5-trimethylbenzene	1.3	1.5	0.5
36) 1,2,4-trimethylbenzene	10.8	13.8	2.2
37) benzyl chloride	0.1	0.1	n.d.
and m-dichlorobenzene	0.1	0.1	n.d.
39) p-dichlorobenzene	1.4	1.6	n.d.
40) o-dichlorobenzene	0.9	1.0	n.d.
41) 1,2,4-trichlorobenzene	1.6	1.7	n.d.
42) hexachlorobutadiene	1.1	0.9	n.d.

n.d. = compound not detected.

air sample. This was further confirmed by comparing the FID traces for the analysis of the two tubes (Figure 19). The qualitative duplication was very good, except for slight variances in peak height.

The canister samples quantitative results however did not reflect exact duplication of the tube data. This was particularly true for the early eluting peaks. Apparently non-target compounds were eluting at times designated for the TO-14 species and the FID was mistakenly identifying them. As the analytical run time continues, the tube/canister data tended to agree more acceptably. The multiple peaks eluting at the end of the chromatogram would account for the FID analysis identifying the later eluting TO-14 species while the MSD indicated that these compounds were not present.

An obvious contradiction in reported concentrations between the tubes and canister was the value for 1,1,1-trichloroethane. Data for this compound was rechecked for each analysis and no explanation for this discrepancy was found.

Outdoor Sampling--

The same collection/analytical scenario used for the indoor sampling was applied to an outdoor environment. The resulting data are presented in Table 12.

Similar trends for this sampling and the indoor test were observed. There was again good agreement between the two tube analyses. Also, the canister analysis did not quantify several of the early eluting species; agreed well for the middle TO-14 target compounds; and did not identify as being present the later compounds. Variability is again judged to be associated with the qualitative/quantitative differences of the FID and MSD detectors and not necessarily indicative of deficiencies with the STS 25 as a sampling unit or the sorbents used. In general, analytical agreement for this sampling was quite good and may be attributed to the less complex nature of the sample allowing better FID identification and quantification.

A copy of the FID traces from the two collection tubes is provided in Figure 20. It should be noted, that the relative humidity during the collection of these samples was at ~90 percent. It can be seen on both of the FID traces that there was a negative deflection in the baseline prior to the elution of the VOCs. Although the flame did remain lit, the conditions may have been close to the tolerable moisture limit for the FID.

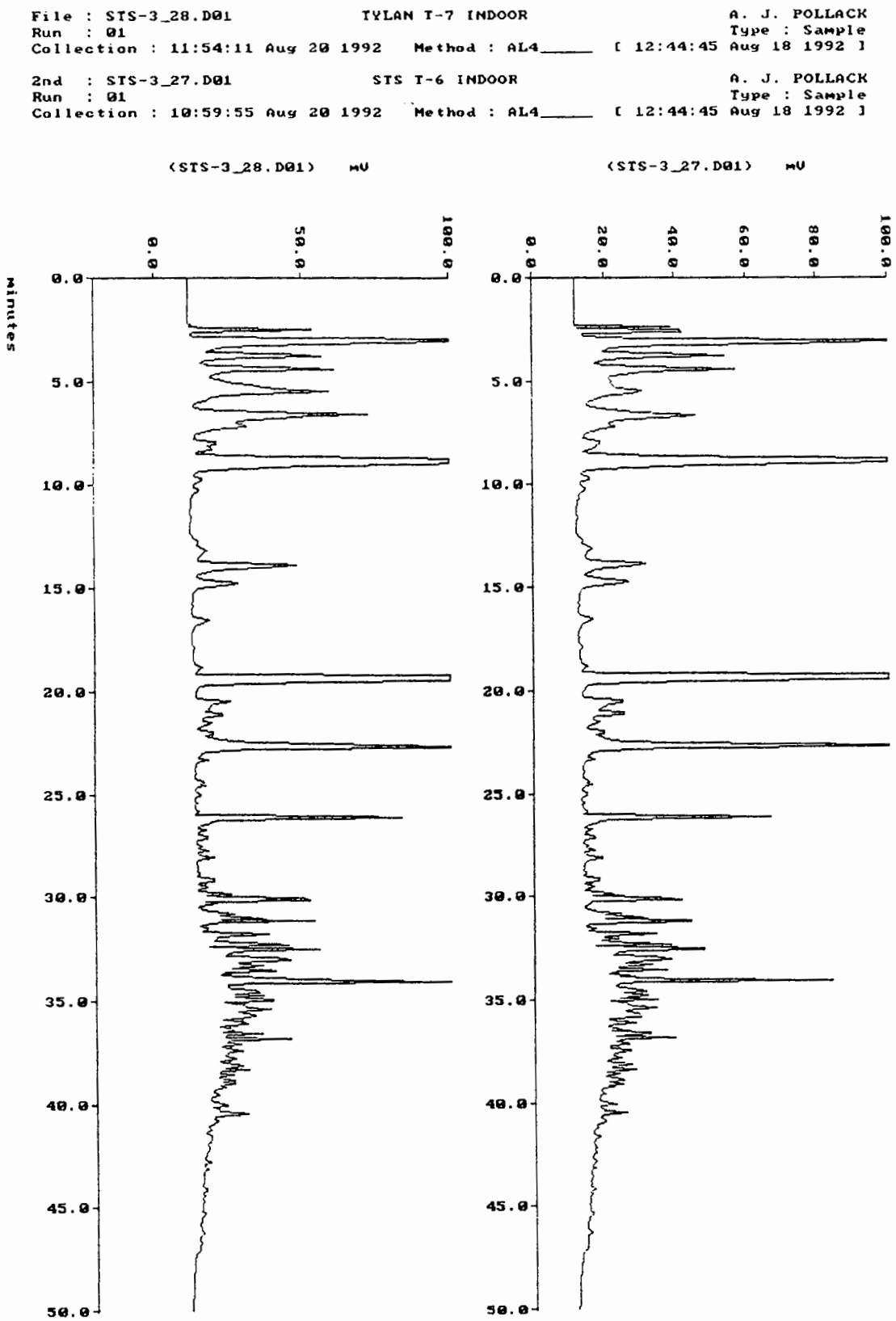


Figure 19. FID chromatograms for indoor air sample collected on multisorbent tubes by the STS 25 (upper) and a Tylan-controlled pump sampler (lower).

TABLE 12. OUTDOOR AIR SAMPLING RESULTS OBTAINED USING STS 25, TYLAN/SORBENT TUBE SAMPLER, AND CANISTER SAMPLER (values in ppbv).

Compound	STS 25 Tube 3L	Tylan Tube 3L	Canister Sample
1) dichlorodifluoromethane	3.1	0.8	0.5
2) methyl chloride	4.3	17.2	n.d.
3) 1,2-dichloro-1,1,2,2-tetrafluoroethane	0.2	0.2	n.d.
4) vinyl chloride	0.7	0.6	n.d.
5) 1,3-butadiene	3.2	2.7	n.d.
6) methyl bromide	37.4	34.3	n.d.
7) ethyl chloride	1.3	0.8	0.2
8) trichlorofluoromethane	128.9	109.4	0.5
9) 1,1-dichloroethene	3.1	2.5	n.d.
10) dichloromethane	22.5	19.8	24.6
11) 3-chloropropene	n.d.	n.d.	0.2
12) 1,1,2-trichloro-1,2,2-trifluoroethane	n.d.	n.d.	1.7
13) 1,1-dichloroethane	n.d.	n.d.	n.d.
14) cis-1,2-dichloroethene	0.1	0.2	n.d.
15) trichloromethane	12.8	8.7	0.5
16) 1,2-dichloroethane	1.9	2.9	n.d.
17) 1,1,1-trichloroethane	3.3	4.4	4.2
18) benzene	1.4	1.8	1.5
19) carbon tetrachloride	n.d.	n.d.	0.2
20) 1,2-dichloropropane	0.1	1.0	n.d.
21) trichloroethene	0.3	0.6	n.d.
22) cis-1,3-dichloropropene	0.5	1.4	n.d.
23) trans-1,3-dichloropropene	0.7	0.9	n.d.
24) 1,1,2-trichloroethane	0.5	0.7	n.d.
25) toluene	3.0	3.5	3.4
26) 1,2-dibromoethane	0.5	0.6	n.d.
27) tetrachloroethene	0.3	0.4	0.2
28) chlorobenzene	0.1	0.0	n.d.
29) ethylbenzene	0.6	0.6	0.7
30) m+p-xylene	2.2	2.2	2.4
31) styrene	0.3	0.2	0.2
32) 1,1,2,2-tetrachloroethane	0.6	0.6	n.d.
and o-xylene	0.6	0.6	0.7
34) 4-ethyltoluene	1.2	1.1	0.3
35) 1,3,5-trimethylbenzene	0.5	0.5	0.3
36) 1,2,4-trimethylbenzene	1.3	1.2	0.7
37) benzyl chloride	n.d.	n.d.	n.d.
and m-dichlorobenzene	n.d.	n.d.	n.d.
39) p-dichlorobenzene	0.3	0.2	n.d.
40) o-dichlorobenzene	0.3	0.2	n.d.
41) 1,2,4-trichlorobenzene	0.3	0.3	n.d.
42) hexachlorobutadiene	n.d.	0.2	n.d.

n.d. = compound not detected.

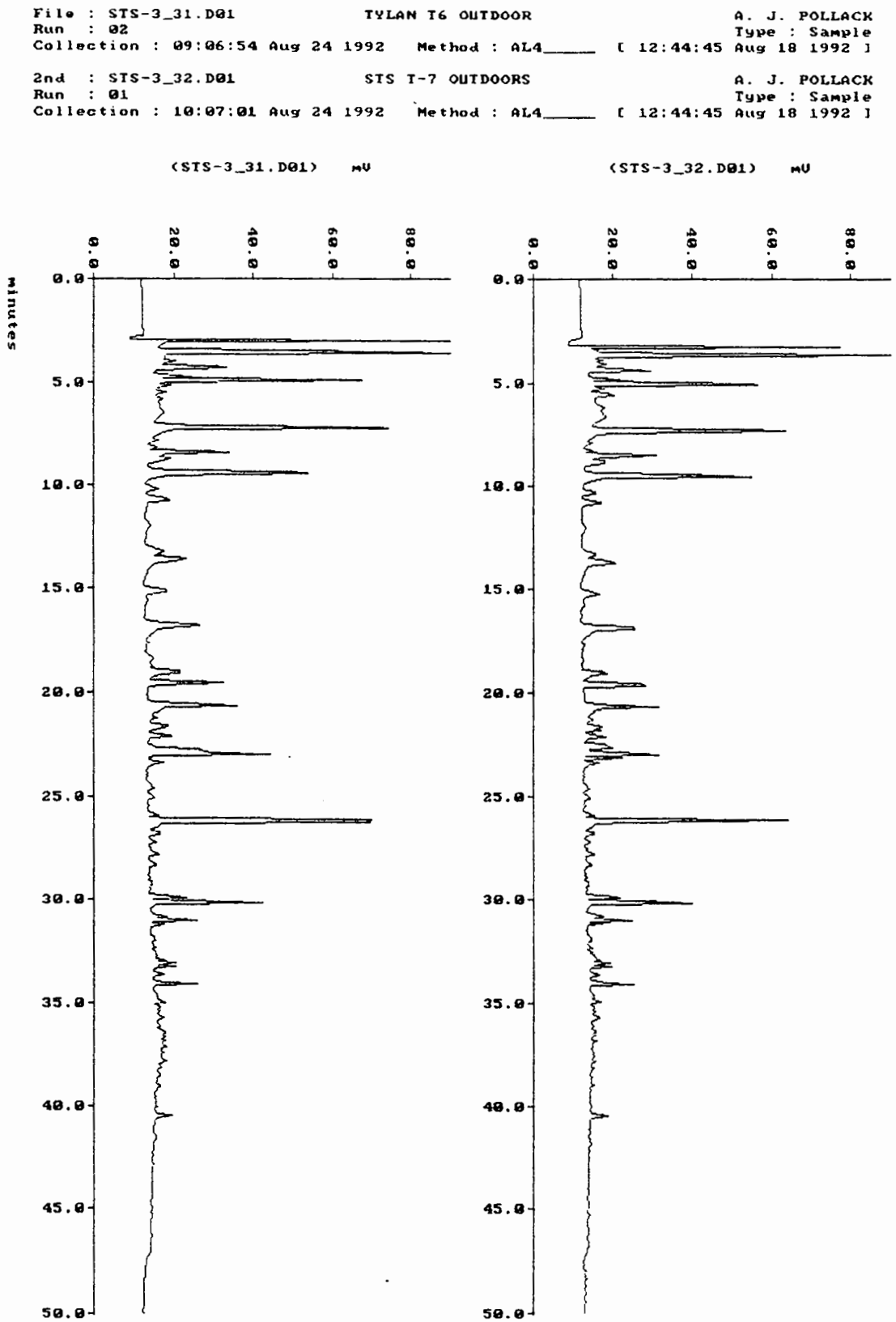


Figure 20. FID chromatograms for outdoor air sample collected on multisorbent tubes by the STS 25 (upper) and a Tylan-controlled pump sampler (lower).

Also noted, was that with the ambient air sampling, neither the independently collected tube or the STS 25 tube displayed an elevated baseline at the end of the analytical run. This feature had been seen in both the chamber tests and the indoor air sampling. The outdoor test confirmed that the STS 25 does not contribute compounds to this region.

TASK 3: TIME MONITOR EVALUATION

The sampler tubes were analyzed at Battelle using the Perkin Elmer ATD 400/GC system. FID and ECD chromatograms were obtained for each sample. Problems were, however, experienced with the response of the ECD due to moisture in the samples, and the ECD results are ignored in this review of the data. Besides the eight exposed tubes that were analyzed, one blank tube was analyzed to assess the effects of any inadvertent contamination. One 3-L TO-14 standard at 2 ppbv concentration was also analyzed under the same operating conditions for comparison purposes and to assist in the interpretation of the field data. The concentrations determined from the analyses were based on response factors generated at Battelle for three samples. Because the microenvironments sampled with the TIME monitor generally did not correspond to a sample volume of 3 L, the concentrations provided by the ATD 400/GC data system were corrected for the actual volume sampled in liters. An example of a FID chromatogram obtained from the analysis of a sampler tube exposed during field tests of the TIME monitor is shown in Figure 21. The output showing the corresponding concentrations of the target compounds identified in this experiment are shown in Figure 22.

The TIME monitor provides seven pieces of exposure information simultaneously: (1) mobility patterns; (2) exposure indoors in the residence; (3) exposure indoors in the workplace; (4) exposure outdoors; (5) exposure in-transit; (6) total exposure; and (7) VOC concentrations for the TO-14 target compounds in each of the microenvironments.

The mobility patterns for the two field experiments were within 6 minutes of the values for the time intervals spent in each microenvironment, as logged by a field experimentalist. The mobility pattern component of the TIME monitor has been improved to identify the subject's location once every 30 s, which represents an improvement of 90 s

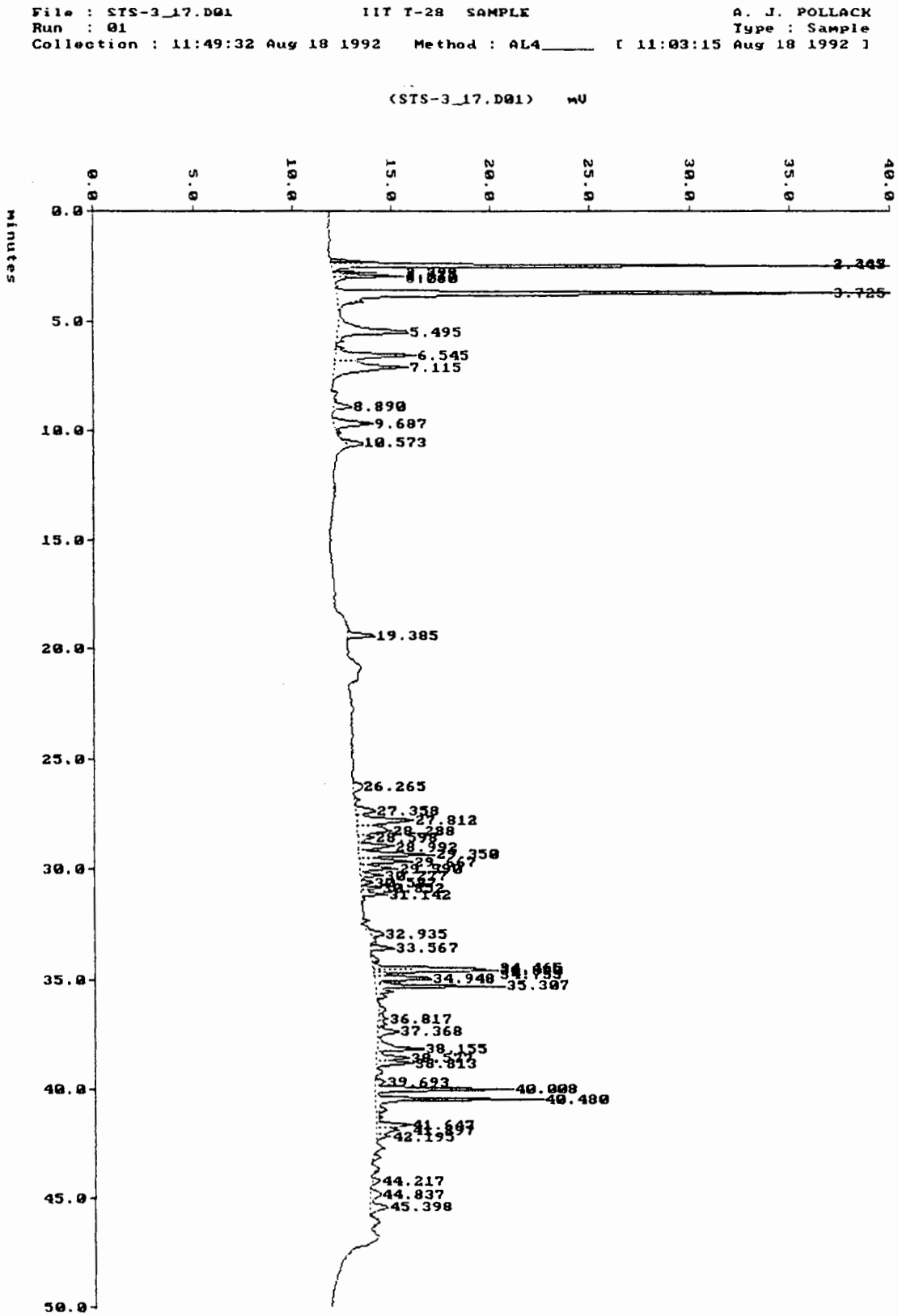


Figure 21. FID chromatogram of sample taken in a microenvironment using the TIME monitor.

File : STS-3_17.D01 IIT T-26 SAMPLE A. J. POLLACK
Run : [illegible] Type : Sample
Path : C:\CHR006
Collection : 11:49:32 Aug 18 1992 Meth(A): AL4_____ [11:03:15 Aug 18 1992]
Integration: 11:49:32 Aug 18 1992 Meth(A): AL4_____ [11:03:15 Aug 18 1992]
Report : 08:39:15 Sep 14 1992 Meth(A): AL4_____ [08:38:36 Sep 14 1992]

Sample Amt : 1.00000e+0 Dilution: 1.00000e+0

EXTERNAL STANDARD (AREA)

RT	Area	BC	ExpRT	RF	ppbv	Name
2.366	95174	T		1.00000e+0	95174.0000	Unknown
2.445	879091	T		1.00000e+0	879091.8125	Unknown
2.793	62867	T		1.00000e+0	62867.8750	Unknown
2.937	159034	T		1.00000e+0	159034.1250	Unknown
3.060	69233		3.211	7.34966e-6	0.5088	FREON-12
			3.574	5.07430e-6		METHYL CHLORIDE
3.725	3016333	T	3.805	3.12280e-6	9.4194	FREON-114
			4.087	2.34011e-6		VINYL CHLORIDE
			4.389	1.65059e-6		1,3-BUTADIENE
			4.983	1.10392e-5		METHYL BROMIDE
5.495	661544		5.376	2.87807e-6	1.9040	ETHYL CHLORIDE
6.545	520081	T		1.00000e+0	520081.7500	Unknown
7.115	749908		7.147	1.96027e-5	14.7003	TRICHLOROFFLUOROMETH
			8.748	2.62912e-6		1,1-DICHLOROETHENE
8.890	84186		9.020	4.98269e-6	0.4195	DICHLOROMETHANE
			9.382	3.68914e-6		3-CHLOROPROPENE
9.687	275584	T	9.805	3.55772e-6	0.9805	TRICHLOROTRIFLUOROET
10.573	111918			1.00000e+0	111918.5000	Unknown
			12.563	3.11557e-6		1,1-DICHLOROETHANE
			15.765	2.49728e-6		CIS-1,2-DICHLOROETHE
			16.761	5.84395e-6		TRICHLOROMETHANE
			18.865	2.43144e-6		1,2-DICHLOROETHANE
19.385	140245	V	19.510	2.51578e-6	0.3528	1,1,1-TRICHLOROETHAN
			20.607	6.57860e-7		BENZENE
			20.919	1.39713e-5		CARBON TETRACHLORIDE
			22.369	1.64307e-6		1,2-DICHLOROPROPANE
			22.842	1.68275e-6		TRICHLOROETHENE
			24.463	5.10582e-6		CIS-1,3-DICHLPROPENE
			25.409	5.11109e-6		TRANS-1,3-DICHLPROPE
			25.741	2.92810e-6		1,1,2-TRICLETHANE
26.265	95864	V	26.265	7.71180e-7	0.0739	R TOLUENE
27.358	133757	T	27.463	3.85048e-6	0.5150	1,2-DIBROMOETHANE
27.811	427854	T		1.00000e+0	427854.0000	Unknown
28.288	338698	T	28.238	2.12052e-6	0.7182	TETRACHLOROETHENE
28.598	91557	T		1.00000e+0	91557.5000	Unknown
28.992	213670	T		1.00000e+0	213670.7500	Unknown
29.350	416673	T	29.416	8.27379e-7	0.3447	CHLOROBENZENE
29.666	295857	T		1.00000e+0	295857.0000	Unknown
29.990	184387	T	30.010	1.20336e-6	0.2219	ETHYLBENZENE
30.276	113712	T	30.322	1.17139e-6	0.1332	M+P-XYLENE
30.587	56245	T		1.00000e+0	56245.5000	Unknown
30.852	92460	T	30.936	8.53102e-7	0.0789	STYRENE
31.142	147378		31.127	8.55992e-7	0.1262	O-XYLENE/TETCLETHANE
32.935	98709			1.00000e+0	98709.0000	Unknown
			33.312	2.27261e-6		4-ETHYLTOLUENE
33.566	96323	V	33.432	1.15667e-6	0.1114	1,3,5-TRIMETHBENZENE
			34.258	1.50552e-6		1,2,4-TRIMETHBENZENE
34.465	286420	T		1.00000e+0	286420.2500	Unknown
34.590	368227	T	34.640	9.43370e-7	0.3474	BENZCHLOR/m-DICHLRBN
34.755	100067	T	34.771	8.73804e-7	0.0874	p-DICHLOROBENZENE
34.948	192063	T		1.00000e+0	192063.1875	Unknown
35.307	419971	T	35.496	9.28650e-7	0.3900	o-DICHLOROBENZENE
36.816	51479	T		1.00000e+0	51479.2500	Unknown
37.368	117526	T		1.00000e+0	117526.5000	Unknown
38.155	283977	T		1.00000e+0	283977.0000	Unknown
38.577	171434	T		1.00000e+0	171434.0000	Unknown
38.813	159613	V		1.00000e+0	159613.1875	Unknown
39.693	58015	T		1.00000e+0	58015.0000	Unknown
40.008	496403	T	40.228	1.51937e-6	0.7542	1,2,4-TRICHLOROBENZE
40.480	680651	T		1.00000e+0	680651.1250	Unknown
41.647	184884	T		1.00000e+0	184884.2500	Unknown
41.897	133300	T	41.919	1.57675e-6	0.2102	HEXACHLOROBUTADIENE
42.195	85231	V		1.00000e+0	85231.6250	Unknown
44.217	53381			1.00000e+0	53381.0000	Unknown
44.837	111295	T		1.00000e+0	111295.5000	Unknown
45.398	151595	V		1.00000e+0	151595.5000	Unknown

Figure 22. Data system listing of target compound concentrations from sample chromatogram shown in Figure 21.

over the shadow sensor developed earlier to measure mobility patterns. (11) Although the field experiments were designed to evaluate the performance of the TIME monitor, not to determine mobility patterns, the following point should be noted. If it is assumed that a person changes microenvironments 40 times a day, and if it is further assumed that a full 30 s is required before each change is registered by the monitor, the total discrepancy would be 20 m over 24 h, or less than 1 percent. It follows therefore that the rest of the difference is due to false reading from misleading surfaces, such as trees, high indoor ceilings, or other surfaces that may not reflect the ultrasound waves.

The decomposition of the total exposure is illustrated for the two field samples in Table 13. The TIME monitor provides the required decomposition directly. The following observation bears further investigation. Vinyl chloride, one of the target compounds, was selected for this analysis. The investigator spent 33 percent of his time indoors in his residence, 11 percent in his workplace, 38 percent outdoors, and 17 percent in-transit. The measured concentrations of the test compound were 16.5, 0.98, 5.0, and 0.0 ppbv, respectively. The total exposure estimated by summing the component concentrations is 22.5 ppbv. If we were to decompose the total exposure into its microenvironmental components in the conventional way, by time-weighting the total exposure, i.e., by multiplying the total exposure with the portion of time spent in each microenvironment, the microenvironmental exposures would be substantially different from the measured values. This finding is of some interest, and although it was reinforced with an evaluation of other components and with data from other days, measurements by typical subjects and typical time patterns are needed before the importance of this preliminary finding can be properly assessed.

It is important to remember that the magnitude of the exposures in these field tests is not particularly meaningful because the investigators spent predetermined periods in each microenvironment. These tests were not performed to measure typical human exposures, but were carried out to demonstrate that the TIME monitor was functioning as expected.

TABLE 13. CONCENTRATIONS (IN PPBV) OF TARGET COMPOUNDS OBTAINED FOR TWO FIELD TESTS OF THE TIME MONITOR

COMPOUND	T27	T28	T29	T30	Total	T32	T33	T34	T35	Total
FREON-12	0.284	0.509	0.000	0.000	0.793	0.000	0.000	103.100	107.860	210.960
METHYL CHLORIDE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	91.816	0.000	91.816
FREON-114	0.221	9.419	90.782	66.680	167.100	199.340	25.833	64.530	191.710	681.420
VINYL CHLORIDE	5.020	0.000	0.980	16.463	22.463	10.325	0.710	5.410	3.667	20.112
1,3-BUTADIENE	0.000	0.000	0.442	0.305	0.747	32.945	0.000	2.096	2.047	37.089
METHYL BROMIDE	0.000	0.000	0.000	0.000	0.000	6.394	0.000	0.000	1.618	8.011
ETHYL CHLORIDE	0.000	1.904	30.332	27.646	59.882	105.700	4.164	165.360	144.310	419.530
TRICHLOROFFLUOROMETH	107.800	14.700	363.440	96.960	582.890	0.000	6680.300	0.000	5.782	6686.100
1,1-DICHLOROETHENE	0.830	0.000	2.870	1.589	5.288	2.072	0.350	1.568	1.091	5.082
DICHLOROMETHANE	16.848	0.420	10.868	15.483	43.620	5.168	0.496	17.830	10.497	33.991
3-CHLOROPROPENE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
TRICHLOROTRIFLUOROET	98.845	0.981	69.177	119.54	288.550	40.489	2.913	68.497	42.290	154.190
1,1-DICHLOROETHANE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	29.327	29.327
CIS-1,2-DICHLOROETHE	0.535	0.000	4.804	1.940	7.278	1.609	1.089	4.274	1.999	8.972
TRICHLOROMETHANE	0.690	0.000	0.000	0.625	1.315	9.291	0.000	0.000	5.723	15.014
1,2-DICHLOROETHANE	0.278	0.000	0.000	0.000	0.278	1.897	0.000	5.858	0.521	8.277
1,1,1-TRICHLOROETHAN	2.321	0.353	3.280	3.314	9.268	10.269	1.788	7.273	16.666	35.997
R BENZENE	0.979	0.000	1.882	1.474	4.335	9.482	1.182	2.547	4.632	17.844
CARBON TETRACHLORIDE	9.087	0.000	62.122	31.577	102.790	4.305	16.019	61.555	28.295	110.170
1,2-DICHLOROPROPANE	0.336	0.000	0.000	0.297	0.633	2.553	0.116	0.000	0.972	3.641
TRICHLOROETHENE	3.145	0.000	5.013	3.668	11.825	12.944	1.441	9.303	8.156	31.845
CIS-1,3-DICHLPROPENE	0.355	0.000	1.273	0.683	2.311	1.249	0.792	2.751	0.758	5.551
TRANS-1,3-DICHLPROPE	0.160	0.000	0.000	1.100	1.261	0.770	1.078	4.743	9.859	16.452
1,1,2-TRICLETHANE	0.332	0.000	0.000	0.368	0.700	4.027	0.000	0.000	2.439	6.466
R TOLUENE	2.608	0.074	3.500	3.426	9.607	17.938	1.555	6.443	10.615	36.552
1,2-DIBROMOETHANE	0.243	0.515	3.215	1.781	5.754	3.183	1.118	1.343	1.412	7.057
TETRACHLOROETHENE	0.257	0.718	13.763	4.315	19.053	1.854	3.273	16.843	1.251	23.222
CHLOROBENZENE	0.023	0.345	0.000	0.158	0.526	1.620	0.537	0.554	0.871	3.583
ETHYLBENZENE	0.098	0.222	1.859	1.012	3.190	2.903	0.969	1.668	1.496	7.037
M+P-XYLENE	0.160	0.133	1.283	0.790	2.367	5.616	0.415	2.811	4.038	12.882
STYRENE	0.128	0.079	0.798	0.469	1.473	3.226	0.000	2.636	2.696	8.558
O-XYLENE/TETCLETHANE	0.123	0.126	2.130	0.647	3.027	3.916	1.715	2.861	2.342	10.836
4-ETHYLTOLUENE	0.000	0.000	0.000	0.000	0.000	1.756	4.170	0.000	0.000	5.926
1,3,5-TRIMETHBENZENE	0.365	0.111	4.984	1.532	6.992	2.151	1.011	0.611	0.681	4.454
1,2,4-TRIMETHBENZENE	0.200	0.000	1.127	0.772	2.099	15.677	0.828	3.214	4.538	24.260
BENZCHLOR/m-DICHLRBN	0.187	0.347	0.625	0.114	1.273	7.319	0.130	0.569	0.709	8.728
p-DICHLOROBENZENE	0.235	0.087	0.864	0.211	1.398	0.303	0.168	0.621	0.150	1.243
o-DICHLOROBENZENE	0.368	0.390	0.801	0.221	1.781	0.131	0.388	0.572	0.475	1.567
1,2,4-TRICHLOROBENZE	0.807	0.754	5.471	1.738	8.770	10.867	1.466	7.312	2.253	21.899
HEXACHLOROBUTADIENE	0.276	0.210	4.982	1.426	6.895	7.074	4.651	18.961	10.766	41.452

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APPENDIX A

TIME MONITOR OPERATING INSTRUCTIONS

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TIME MONITOR OPERATING INSTRUCTIONS

I Sample Tube Change and start-up

II Motor Speed Control

III Data Collection

I. SAMPLE TUBE INSTALLATION AND CHANGE

A Remove the cover with four screws on front panel.
B Loosen but do not remove two screws on intake manifold.
C Slide manifold toward the flow valves far enough to slip the four sample tubes (GROOVES TOWARDS THE VALVE MANIFOLD) in place between the two manifolds.
D Using finger pressure, squeeze the two manifolds forcing a seal on the rubber seal rings inside the manifolds.
E Tighten the two screws on the intake manifold while holding pressure on the rubber seals.
F Reset the Microprocessor by depressing the switch located inside the box adjacent to the flow valves.
G Being careful not to pinch the wiring, close the front panel cover and tighten the four screws.
H The TIME SENSOR is now operational and sampling air depending on the location of the ultrasonic sensor.

II. MOTOR SPEED SETTING

A Using GW Basic load the MONITOR program.
B Select the comminution port and hit enter until the "OK" prompt is observed then using the CAPS LOCK input the letter M
C This will display the four motor speeds as described below.
D Type the letter M and follow it with the new motor speeds required for:

I	HOME
II	WORK
III	TRANSIT
IV	OUTSIDE

Note: The Hex values 0 to 100 percent flow are 0 to FF

Example: M0025FF45

I	00= motor off
II	25= low flow (value to be monitored by flow meter)
III	FF= full flow (motor speed)
IV	45= higher speed and flow

E Open the front cover with four screws.

F Remove the long hose (about 6 inches) which is connected to the center valve, from the box wall and attach the flow meter at the top fitting and repeat step D.

G After all four speeds have been set remove the hose from the flow meter and replace the hose in the intake hole in the box corner.

H If required reset the microprocessor database using the reset button.

I Replace the cover and tighten the four screws.

III. DATA REMOVAL/EXAMINATION

A Load GW Basic and run the EPALD program

B Using the prompts from this program a data file will be written to the disk for future manipulation.

APPENDIX B

SUMMARY OF COMMAND STRUCTURE TO TRANSFER MOBILITY DATA FROM TIME MONITOR TO PC

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SUMMARY OF COMMAND STRUCTURE TO TRANSFER MOBILITY DATA FROM TIME MONITOR TO PC

RS232 Command Summary for EPA1.ASM

This is a summary of the commands to which the reader (portable air quality monitor) will respond via the RS-232 Serial Port. The port is configured at 9600 baud with 8 data bits, 1 stop bit, and no parity. All data is transmitted in ASCII hexadecimal form (i.e. "00" through "FF") unless otherwise noted. <cr>=Carriage Return. The reader follows Xon/Xoff protocol, where data transmission will be suspended after receipt of Xoff (^S) , and resume after reception of Xon (^Q). Conversely, if the host receives Xoff, it should suspend data transmission until after receipt of Xon. After receipt of Xoff, the reader will timeout and sleep after two minutes to avoid battery drain in the event of cable disconnection.

```
Command:    <cr>        The null command. Host software should issue this command
                        until the OK response is received to insure proper
                        intialization of the reader's serial port.

Response:   <nul>OK<cr> <nul>=00H
```

```
Command:    xx<cr>      If an invalid character or unrecognized command is sent,
                        the reader will respond with a NO response. xx is any
                        invalid command. This response may also be sent the
                        first time communication is attempted.

Response:   <nul>NO<cr> <nul>=00H
```

```
Command:    D<cr>       Dump all 2048 records in the reader's circular data
                        buffer.
            Dnn<cr>     Dump the most recent nn records (nn= 01 to FF).

            D00<cr>     Dump all records since the last tube reset.

Response:   nnyyoottgghhmmssuu00000000000000<cr>
            ...             {more records}
            nnyyoottgghhmmssuu00000000000000<cr>
            DOK<cr>

            or
            DNO<cr>     Illegal character in nn.

Where:      nn =tube number
            yy =Year in decimal (i.e. "90")
            oo =Month in decimal ("01" - "12")
            tt =Date in decimal ("01" - "31")
            gg =Day in decimal ("01" - "07", "01"=Monday)
            hh =Hours in decimal ("00" -"23")
            mm =Minutes in decimal ("00" - "59")
            ss =Seconds in decimal ("00" - "59")
            00000000000000
```

Each record is 16 bytes long, and the unused bytes in each record are set to 00. nn indicates that the reader has switched to tube number nn at the date and time indicated in that record. In this case nn will be 01, 02, 03, or 04. nn=FF indicates that the power was switched on at the date and time in that record. nn=FE indicates that the power was switched off on the date and time indicated in that record. nn=80 indicates that the tube change button mounted inside the reader was pressed on the date and time indicated in that record.

During a dump command, if DSR is removed from the RS-232 port, the data dump will be aborted.

```
Command:    E<cr>       Single pulse the transducer, and return the location of
                        the first echo. This is done at two different freq's.

Response:   nn<cr>      Result from first frequency.
            nn<cr>      Result from second frequency.
            EOK<cr>     nn=00 to FF.  4.8 counts/mS, so FF=> 255/4.8 = 53mS
```

```
Command:    H<cr>       The H command is a diagnostic command.  The reader will
dump the memory buffer containing 2048 bytes of phase change information used to
detect the presence of an echo.  To save load time, each entry in the table os
represented by a single hex digit equal to 0 or 1.  0 indicates the presence of a
synchronous received signal, and the position of these 0's in the buffer indicate
the position in time the echo was received.  The close echos are sent first.

Response:   0100001...011010111000000111 0HOK<cr>
            2048 hex digits are sent.
```

```
Command:    M<cr>       Read the 4 motor speed settings.

Response:   aabbccddMOK<cr>   aa = Motor speed for tube 1
                              bb = Motor speed for tube 2
                              cc = Motor speed for tube 3
                              dd = Motor speed for tube 4
            00=> speed=0,  FF=> speed=maximum
```

```
Command:    Maabbccdd<cr>     Set the 4 motor speed settings.
                              The format is as described above.
Response:   MOK<cr>     If settings were changed.
            or
            MNO<cr>     Illegal character in nn.
```

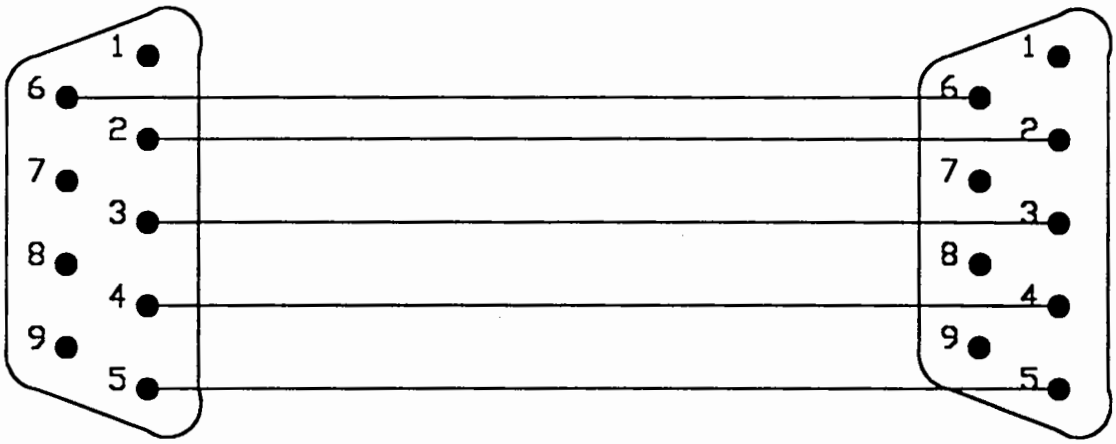
```
Command:    N<cr>       This is a diagnostic routine.  This returns the values of
three registers, along with the current environment.  There are three integrating
registers, one each for Transit, Inside, and Outside.  Each time a pulse is
emitted and analyzed, the respective register is incremented depending on the
echo position.  If any register fills to 33 (21H) readings, all three registers
are decremented.  Whenever the difference between the fullest register (always
containing 32 pulses), and the second fullest register exceeds 20 (14H), the
reader decides that the environment has changed.

Response:   aa<cr>      Number of readings in the "Transit" register.
            bb<cr>      Number of readings in the "Inside" register.
            cc<cr>      Number of readings in the "Outside" register.
            dd<cr>      The current Environment, 01=Transit, 02=Inside, and
                        03=Outside.
```

```
Command:    R<cr>       Read the state of processor port 1.  A diagnostic.

Response:   aaROK<cr>   In aa, 1=on, 0=off
            MSB=>DTR,DSR,Speaker,Motor,Sol1,Sol2,Sol3,Xducer Drive<=LSB
```

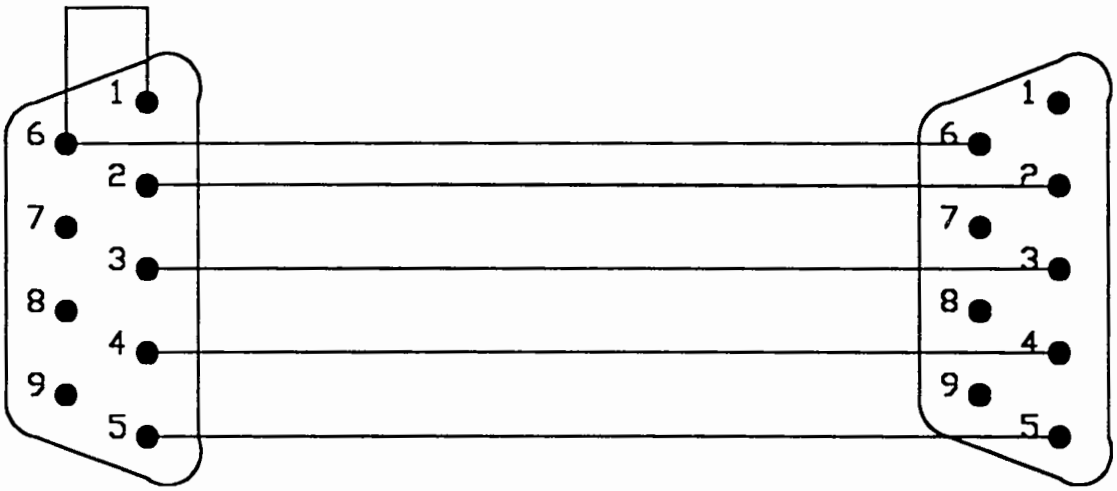
```
Command:    Rnn<cr>     Write the state of processor port 1.
                        Format is as described above.
```

```
Response:   ROK<cr>
            or
            RNO<cr>     Illegal character in aaaa.
-----------------------------------------------------------------------------
Command:    T<cr>       Read the current date and time.

Response:   Tyyoottgghhmmssuu<cr>

Where:      yy =Year in decimal (i.e. "90")
            oo =Month in decimal ("01" - "12")
            tt =Date in decimal ("01" - "31")
            gg =Day in decimal ("01" - "07", "01"=Monday)
            hh =Hours in decimal ("00" -"23")
            mm =Minutes in decimal ("00" - "59")
            ss =Seconds in decimal ("00" - "59")
            uu =Hundredths of seconds in decimal ("00" - "99")
-----------------------------------------------------------------------------
Command:    Tyyoottgghhmmssuu<cr>   Set the current date and time.
                        The data fields are as defined above.

Response:   TOK<cr>     Date/Time successfully saved, however no checking is done
                        to insure a valid date/time has been set.
            or
            TNO<cr>     Illegal character in data.
-----------------------------------------------------------------------------
Command:    U<cr>       Read the 8 bit checksum of the reader software.

Response:   hhUOK<cr>   hh is the checksum in ASCII hexadecimal.
-----------------------------------------------------------------------------
Command:    V<cr>       Read the reader software version number.

Response:   v.vttttttttttttttVOK<cr> v.v is the version number, and t..tt is an
                                ASCII message, usually containing the date of the
                                revision and the reader serial number.  The entire
                                field is 16 characters long.
-----------------------------------------------------------------------------
```

1	LOAD		
2	TXD	2	RXD
3	RXD	3	TXD
4	DTR	4	DSR
5	GROUND	5	GROUND
6	DSR	6	DTR
7	RTS	7	CTS
8	CTS	8	RTS
9	NO CONNECT		



READER NORMAL OPERATION COMPUTER



READER FOR LOADING NEW PROGRAM COMPUTER