QUANTIFICATION OF TOXIC MATERIALS IN AMBIENT AIR AT "OLD LOVE" CANAL, NIAGARA FALLS, NY

EPA Contract No. 68-01-4141
RTI/1371/17-01F

FINAL REPORT

by

Edo D. Pellizzari, Ph.D.
Research Triangle Institute
Post Office Box 12194
Research Triangle Park, NC 27709

Task Manager
Mr. William Librizzi, Director
Office of Toxic Substances
U.S. EPA, Region II
Edison, New Jersey 08817

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT
6th and Walnut Streets
Philadelphia, PA 19106

CONTENTS

1.0 Introduction

Old Love Canal is a 16 acre land field site owned by the city of Niagara Falls and a private individual. The land fill is bordered by single family residences and a playground and school are also located on this land fill. The canal was designed to provide a waterway around Niagara Falls. However, it was used as a disposal area for the Hooker Chemical and Plastics Company (a variety of drummed chemical wastes, including chemical residues, process sludges, fly ash, etc.) and the city of Niagara Falls (municipal solid waste). Records of the contents, locations and quantities of materials dumped were not available at the time this program was executed.

Beginning in about November of 1976, New York state and the city began taking samples in the area in response to citizens complaints. The program identified the presence of PCBs and hexachlorocyclopentadiene in the sumps of several homes. In early 1978 monitoring was increased and a multimedia sampling program was initiated. A survey of the atmosphere in several of the basements of homes indicated the presence of several organic compounds including benzene.

This contract was undertaken with the intention to sample ambient air at the site to determine if a health hazard might exist.

2.0 Experimental Methods

2.1 Ambient Air Sampling

The sampling strategy which was adopted included sampling at 1 upwind and several downwind sampling locations, concurrently. This was to be repeated during a second time period at a new set of locations. The sampling method employed is described in Appendix A. The collection method involved using battery operated personnel sampling systems which

were portable and independent of any power supply allowing the selection of optimum sampling sites near homes on the Old Love Canal. Table 1 presents the sampling protocol for this area. Table 2 presents the meteorology for the two day period of sampling. Figure 1 depicts the sampling locations throughout the Old Love Canal at the upwind and downwind locations respectively for the entire sampling period.

2.2 Analysis Methods

The samples collected on Tenax GC cartridges were analyzed using thermal desorption and glass capillary, gas chromatography/mass spectrometry/computer techniques. These procedures are described also in Appendix A. Prior to the analysis of samples, perfluorotoluene and perfluorobenzene were added as standards to each sampling cartridge in order that quantification could be achieved of the individual organics.

Quantitative analyses of the samples for the following compounds were conducted.

a. Benzene

b. Chloroform

c. Carbon tetrachloride

d. Trichlorethylene

e. 1,3-Hexachlorbutadiene

f. Other halogenated hydrocarbons which were identified in household basements in February of 1978.

2.3 Quality Control and Assurance

For quality control purposes, several cartridges which were transported and stored in a similar manner to the samples which were taken in the field. These blanks were employed to determine the background contribution and possible contamination from the preperation, transportation, and storage of the Tenax GC.

Table 1. AMBIENT AIR MONITORING PROTOCOL FOR "OLD LOVE" CANAL AREA OF NIAGARA FALLS, NY

	Location(Address)	Date	Time Period of Monitoring	Volume Air Collected (ℓ)
1.	(703 97th St.)	7/6/78	1028-1747[a]	22
2.	(703 97th St.)	7/6,7/78	1759-0810[a]	42
3.	(783 97th St.)[b,c]	7/6,7/78	2113-0838	34
4.	(791 97th St.)	7/6/78	0927-1515	17
5.	(915 97th St.)	7/6,7/78	1550-0857	51
6.	(746 99th St.)	7/6/78	0857-1720	25
7.	(502 99th St.)	7/6/78	1102-1737	17
8.	(476 99th St.)[b]	7/6/78	1045-1637	18
9.	(474 99th St.)[b]	7/6,7/78	1700-0927	49
10.	(99th St. Elementary School)	7/11/78	0910-1510	22
11.	(93rd St. Elementary School)	7/12,13/78	0840-1310	19.5

[a]Sampler was placed in nearby yard, a corner lot and upwind of the "canal".

[b]Houses which were previously included in the February 1978 basement air monitoring.

[c]Location of RMI weather station.

Table 2. METEOROLOGY FOR JULY 6 AND 7, 1978 IN THE OLD LOVE CANAL AREA, NIAGARA FALLS, NY

Date	Time	Temp (C°)	Wind Speed/Direction[a] (KM/Hr)		Wind Speed/Direction[b] (KM/Hr)	
7/6/78	1000	25	3	/ S	13	SW
	1200	28	3	/ S	17	SW
	1400	29	3	/ S	20	SSW
	1600	29	2	/ SSW	24	SW
	1800	29	<2	/ SSW	24	SW
	2000	27	<2	/ SSW	18	SW
	2200	23	calm		15	SW
	2400	22	calm		13	SW
7/7/78	0200	20	calm		13	SSW
	0400	20	calm		9	SSW
	0600	19	calm		13	SSW
	0800	23	calm		14	SSW
	1000	27	2	/ S	20	SSW

[a] MRI weather station, 6' above ground level.

[b] Niagara Falls, NY Weather Station.

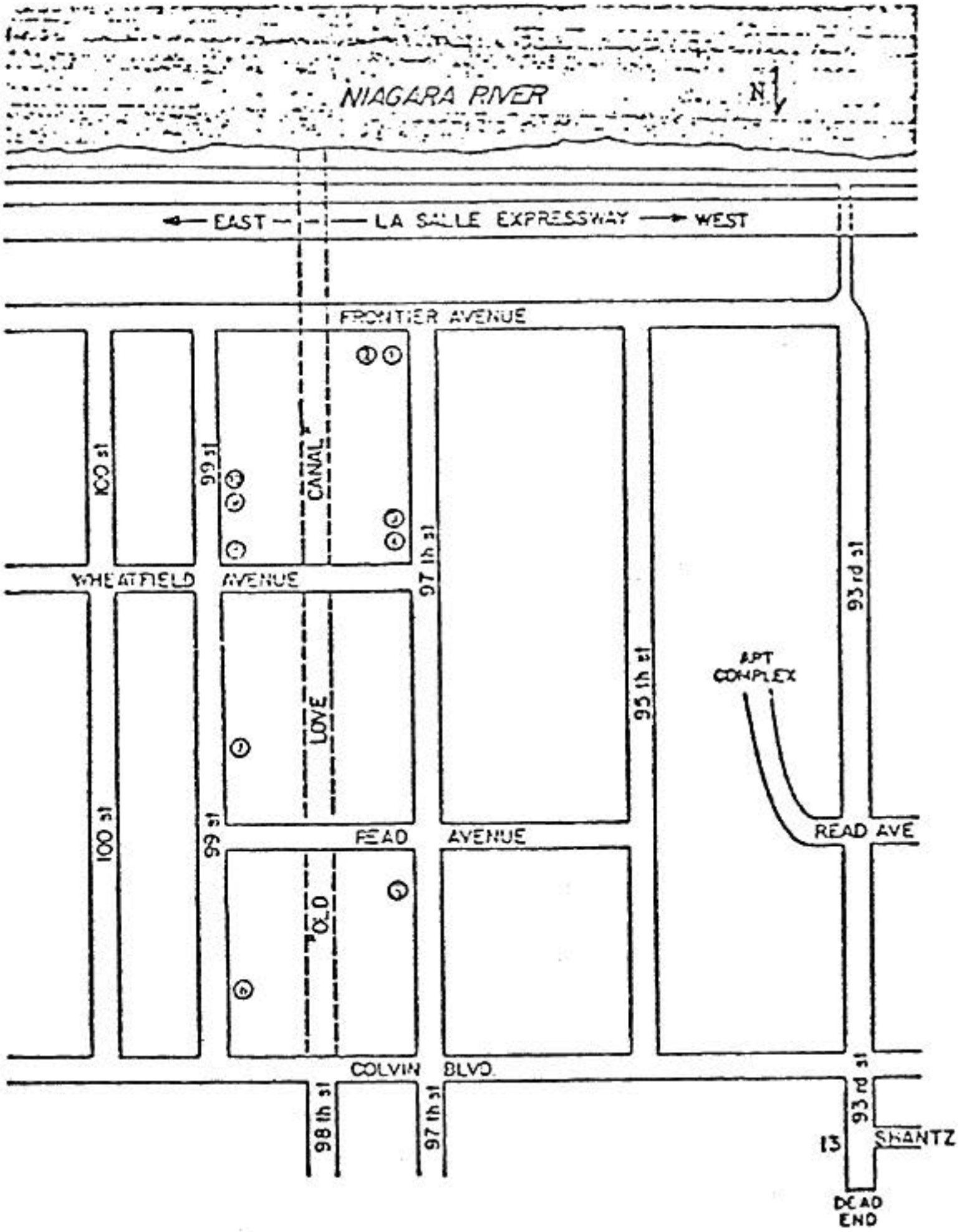


Figure 1. Map of "Old Love Canal" area of Niagara Falls, NY - Sampling locations for ambient air outside of homes.

A chain of custody record was maintained from the time that the sampling cartridges were prepared to the time the data was returned to the Principal Investigator for inclusion into the final report. As the chain of custody changed hands from one investigator to another for each step of the procedure, signatures were required to document this transfer. A copy of a typical chain of custody for a sample is given in Appendix B.

3.0 Results and Discussion

On July 6 and 7 of 1978, RTI personnel took ambient air samples on and near the Old Love Canal area. This sampling trip was also coordinated with another program which was interested in the human body burden for halogenated hydrocarbons (which were identified in the household air basement in February of 1978).

The sampling protocol required RTI to take concurrent upwind downwind samples of 8 to 12 hour duration. Samples at each location were taken in duplicate. During the sampling, winds were primarily out of the south-southwest at approximately 3 kilometers per hour during July 6 and was calm on July 7.

The estimated levels of halogenated compounds in ambient air outside the homes of Old Love Canal and Niagara, New York are given in Table 3. The halogenated compounds which were selected in addition to those required by the scope of work for this contract were substances which were identified in previous air samples taken from the basements of homes from this site. In many cases, each of the compounds which had been identified and detected in samples from the sampling conducted during February of 1978 were also detected in July.

Table 3. ESTIMATED LEVELS OF HALOGENATED COMPOUNDS IN AMBIENT AIR OUTSIDE HOMES OF "OLD LOVE CANAL", NIAGARA, NY[a]

Compound	Location										
	1	2	3	4	5	6	8	9	10	93rd[e]	99th[e]
Chloroform	15,846	105,461	70,308	30,231	1,385	51,692	1,050	19,692	55,923	51,350	1,700
Carbon tetrachloride	2,000	3,692	2,923	1,615	2,231	1,000	1,000	T[b]	-	T	T
1,1-dichloroethane	-	-	-	-	-	-	-	-[c]	-	-	-
1,2-dichloroethane	-	-	-	-	T	-	NQ[d]	T	-	-	-
1,1,1-trichloroethane	2,111	5,444	2,222	1,778	4,222	1,444	2,667	1,667	-	840	975
Trichloroethylene	-	-	-	-	285	-	-	611	-	-	T
Tetrachloroethylene	591	714	735	14,000	647	400	750	2,111	122	320	389
Chlorobenzene	-	119	-	T	T	T	T	-	-	T	T
Dichlorobenzene (2 isomers)	-	190	206	T	353	T	350	444	-	-	T
1,2-dichloropropane	-	-	-	-	-	T	T	-	-	-	-
Chlorotoluene (2 isomers)	T	T	1,235	647	T	-	2,750	T	T	-	-
Chlorobenzaldehyde isomer	-	-	-	-	-	-	-	-	-	-	-
Dichlorotoluene (3 isomers)	T	-	-	648	T	T	500	T	T	-	-
Chloronapthalene isomer	T	-	-	T	-	-	T	T	T	-	-
Bromotoluene isomer	-	-	-	-	-	-	-	-	T	-	-
Dichlorobenzaldehyde isomer	-	T	-	-	T	T	-	-	-	-	-
Trichlorobenzene (3 isomers)	-	T	-	T	T	T	-	T	T	-	-
1,2-Dibromoethane	-	T	-	-	T	T	T	-	-	-	-
Trichlorotoluene (5 isomers)	T	T	T	T	T	T	T	T	T	-	-
Tetrachlorotoluene isomer	-	T	T	-	-	T	-	-	-	-	-
Bromochlorotoluene isomer	-	-	-	-	-	T	-	-	-	-	-
Chlorobenzodichlorofluoride isomer	-	-	-	-	-	-	-	-	-	-	-

(CONTINUED)

Table 3 (cont'd)

Compound	Location										
	1	2	3	4	5	6	8	9	10	93rd[c]	99th[e]
Chlorobenzotrifluoride (2 isomers)	-	-	-	-	-	-	-	-	-	-	-
1,2-bis-(trifluoromethyl)benzene	-	-	-	-	-	-	-	-	-	-	-
Pentachlorobenzene	-	-	-	-	-	-	-	-	-	-	-
Tetrachlorobenzene (3 isomers)	-	-	-	T	T	T	300	T	T	-	-
1,3-hexachlorobutadiene	-	-	T	-	-	T	-	-	T	-	-
1,2-dichloroethylene	-	-	-	T	-	-	T	-	T	-	-
Benzene	1,863	2,214	1,765	3,176	2,059	1,680	2,411	4,111	4,041	-	-

[a]Values are ng/mg^3, location No. 1 was "upwind".

[b]Trace.

[c]Not detected.

[d]Not quantitated.

[e]Elementary schools.

APPENDIX A

SAMPLING AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

SAMPLING AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

1.0 Principle of Method

Volatile organic compounds are concentrated from ambient air onto Tenax GC in a short glass tube (1-3). Recovery of the volatile organics is accomplished by thermal desorption and purging with helium into a liquid nitrogen cooled nickel capillary trap (1,2,4) and then the vapors are introduced into a high resolution glass gas chromatographic column where the constituents are separated from each other (2,5). Characterization and quantification of the constituents in the sample are accomplished by mass spectrometry either by measuring the intensity of the total ion current signal or mass fragmentography (2,6). The collection and analysis systems are shown in Figure A-1.

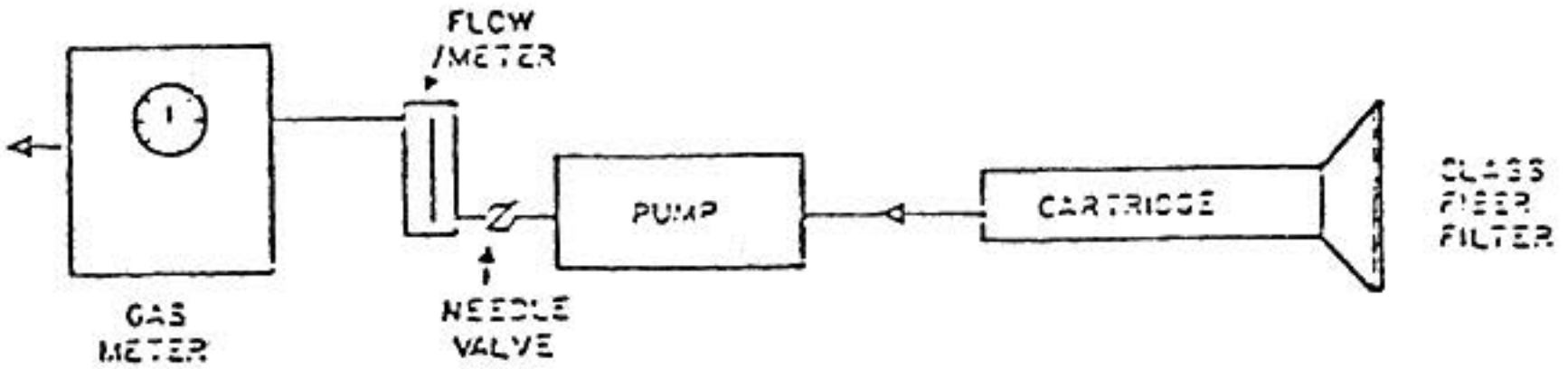
2.0 Range and Sensitivity

The linear range for the analysis of volatile organic compounds depends upon two principal features. The first is a function of the breakthrough volume of each specific compound which is trapped on the Tenax GC sampling cartridge and the second is related to the inherent sensitivity of the mass spectrometer for each organic (2,7). Thus, the range and sensitivity are a direct function of each compound which is present in the original ambient air. The linear range for the quantitation on the gas chromatograph/mass spectrometer/computer (GC/MS/COMP) is generally three orders of magnitude. Table A1 lists the overall theoretical sensitivity for some examples of volatile organics which is based on these two principles (7).

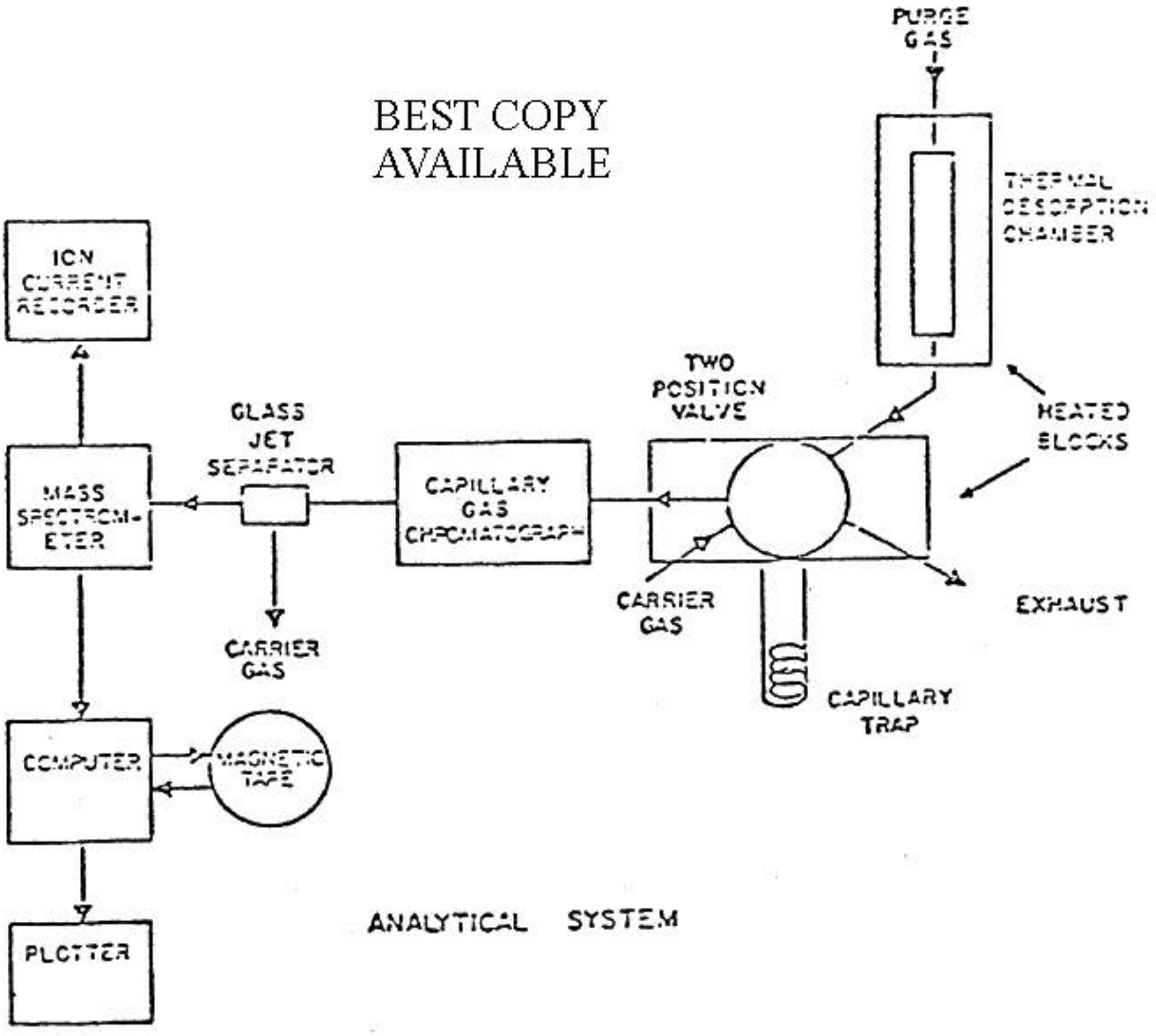
The sensitivity of this technique for the very volatile organic compounds (C_1 to C_5 alkanes) is inadequate for the purpose of this study. Alternate methods for their collection and analysis are suggested (11).

3.0 Interferences

The potential difficulties with this technique are primarily associated with those cases where isomeric forms of a particular substance cannot be resolved by the high resolution chromatographic column and when the mass cracking patterns of each of the isomers are identical. An example of such a problem is seen with the C_5-alkyl aromatics of which



VAPOR COLLECTION SYSTEM



ANALYTICAL SYSTEM

Figure A1. Vapor collection and analytical systems for analysis of organic vapors in ambient air.

Table A1. OVERALL THEORETICAL SENSITIVITY OF HIGH RESOLUTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY/COMPUTER ANALYSIS FOR ATMOSPHERIC POLLUTANTS

Chemical Class	Compound	Estimated Detection Limit[a]	
		ng/m^3	ppt
Halogenated hydrocarbon	Vinyl bromide	250	57
	Bromoform	0.340	0.03
	Bromodichloromethane	1.300	0.22
	Dibromochloromethane	0.667	0.07
	1-Bromo-2-chloroethane	1.00	0.67
	Allyl bromide	5.00	1.04
	1-Bromopropane	5.200	1.06
	1-Chloro-3-bromopropane	0.150	0.01
	1-Chloro-2,3-dibromopropane	~0.100	<0.01
	1,1-Dibromo-2-chloropropane	~0.100	<0.01
	1,2-Dibromoethane	0.530	0.07
	1,3-Dibromopropane	~0.100	~0.01
	Epichlorohydrin (1-Chloro-2,3-epoxypropane)	9.600	2.50
	Epibromohydrin (1-Bromo-2,3-epoxypropane)	0.300	0.05
	Bromobenzene	0.100	0.02
	Methyl bromide	500	135
	Methyl chloride	2000	1000
	Vinyl chloride	800	333
	Methylene chloride	700	200
	Chloroform	200	420
	Carbon tetrachloride	250	400

(continued)

Table A1 (cont'd).

Chemical Class	Compound	Estimated Detection Limit[a] ng/m^3	ppt
Halogenated hydrocarbon (cont'd)	1,2-Dichloroethane	32	8.15
	1,1,1-Trichloroethane	66	12.45
	Tetrachloroethylene	2.5	0.38
	Trichloroethylene	10	1.92
	1-Chloro-2-methylpropene	62	21.5
	3-Chloro-2-methylpropene	62	21.5
	3-Chloro-1-butene	83	28.8
	Allyl chloride	83	28.8
	4-Chloro-1-butene	38	13.2
	1-Chloro-2-butene	13	4.5
	Chlorobenzene	2.10	0.47
	o-Dichlorobenzene	1.00	0.06
	m-Dichlorobenzene	0.75	0.01
	Benzylchloride	0.65	0.01
Halogenated ethers	2-Chloroethyl ethyl ether	4.15	0.97
	Bis-(chloromethyl)ether	1.0	1.10
Nitrosamines	N-Nitrosodimethylamine	5.0	1.67
	N-Nitrosodiethylamine	3.0	0.74
Oxygenated hydrocarbons	Acrolein	~100	56.5
	Glycidaldehyde	~59	9.5
	Propylene oxide	~60	25.5

(continued)

Table A1 (cont'd)

Chemical Class	Compound	Estimated Detection Limit[a] ng/m^3	Estimated Detection Limit[a] ppt
Oxygenated hydrocarbons (cont'd)	Butadiene diepoxide	~20	6.7
	Cyclohexene oxide	~10	2.5
	Styrene oxide	2	0.415
	Acetophenone	~2	~0.415
	β-Propiolactone	~3	~1.2
Nitrogenous Compounds	Nitromethane	8	~2.4
	Aniline	3.0	0.78
Sulfur Compounds	Diethyl sulfate	~50	-
	Ethyl methane sulfate	~5.0	-

[a]Limits are calculated on the basis of the breakthrough volume for 2.2 g of Tenax GC (at 70°F), capillary column performance and sensitivity of the mass spectrometer to that compound in the mass fragmentography mode of most intense ion.

there are 53 isomers. As the number of carbon atoms increases in the hydrocarbons and aromatics, the number of potential isomers becomes increasingly large and difficult to completely resolve by gas chromatography and/or by their corresponding mass cracking patterns. However, differentiation between the hydrocarbons, that is, alkanes, alkenes, aromatics, oxygenated, etc., can be accomplished.

4.0 Reproducibility

The reproducibility of this method has been determined to range from ±10 to ±30% of the relative standard deviation for different substances when replicate sampling cartridges are examined (5). The inherent analytical errors are a function of several factors: [1] the ability to accurately determine the breakthrough volume for each of the identified organic compounds; [2] the accurate measurement of the ambient air volume sampled; [3] the percent recovery of the organic from the sampling cartridge after a period of storage; [4] the reproducibility of thermal desorption for a compound from the cartridge and its introduction into the analytical system; [5] the accuracy of determining the relative molar response ratios between the identified substance and the external standard used for calibrating the analytical system, [6] the reproducibility of transmitting the sample through the high resolution gas chromatographic column; and [7] the day-to-day reliability of the MS/COMP system (1-8).

The accuracy of analysis is generally ±30% but depends on the chemical and physical nature of the compound (2,8).

5.0 Advantages and Disadvantages of the Method

The gas chromatograph/mass spectrometer interfaced with a glass jet separator is extremely sensitive and specific for the analysis of many volatile organic compounds in ambient air. High resolution gas chromatographic separation provides adequate resolution of the substances found in ambient air for their subsequent quantification. The combination of the high resolution gas chromatographic column and the selection of specific or unique ions representing the various compounds of interest identified in the air samples yields a relatively specific assay method for these compounds (1-8).

Collected samples can be stored up to one month with less than 10% losses for most of the chemical classes (2,8). Because some of the compounds of interest may be hazardous to man, it is extremely important to exercise safety precautions in the preparation and disposal of liquid and gas standards, cleaning of used glassware, etc. in the analysis of air samples.

Since the mass spectrometer cannot be conveniently mobilized, sampling must be carried out away from the instrument.

The efficiency of air sampling increases as the ambient air decreases (i.e., sensitivity increases) (8).

The retention of water by Tenax is low; its thermal stability is high; and its background is negligible allowing sensitivity analysis (1,2,5,8).

6.0 Apparatus

6.1 Sampling Cartridges

The sampling tubes are prepared by packing a ten centimeter long by 1.5 cm i.d. glass tube containing 6 cm of 35/60 mesh Tenax GC with glass wool in the ends to provide support (2,5). Virgin Tenax (or material to be recycled) is extracted in a Soxhlet apparatus for a minimum of 18 hours each time with acetone and hexane prior to preparation of cartridge samplers (2,5). After purification of the Tenax GC sorbent and drying in a vacuum oven at 100°C for 3 to 5 hours at 28 inches of water, all the sorbent material is meshed to provide a 35/60 particle size range. Cartridge samplers are then prepared and conditioned at 270°C with helium flow at 30 ml/min for 30 min. The conditioned cartridges are transferred to Kimax® (2.5 cm x 150 cm) culture tubes, immediately sealed using Teflon-lined caps and cooled. This procedure is performed in order to avoid recontamination of the sorbent bed (2,5).

Cartridge samplers with longer beds of sorbent may be prepared using a proportionally increased amount of Tenax in order to achieve a larger breakthrough volume for compounds of interest, and thus increasing the overall sensitivity of the technique (8).

6.2 Gas Chromatographic Column

A 0.35 mm i.d. x 100 m glass SCOT capillary column coated with SE-30 stationary phase and 0.1% benzyltriphenylphosphonium chloride is used

for effecting the resolution of the volatile organic compounds (5). The capillary volume is conditioned for 48 hrs. at 245° at 2.25 ml/min of helium flow.

A glass jet separator on a Varian MAT CH-7 GC/MS/COMP system is employed to interface the glass capillary column to the mass spectrometer. The glass jet separator is maintained at 240°C (2,5).

6.3 Inlet Manifold

An inlet manifold for thermally recovering vapors trapped on Tenax sampling cartridges is used and is shown in Figure A1 (1,2,4,5).

6.4 Gas Chromatograph

A Varian 1700 gas chromatograph is used to house the glass capillary column and is interfaced to the inlet manifold (Figure A1).

6.5 Mass Spectrometer/Computer

A Varian MAT CH-7 mass spectrometer with a resolution of 2,000 equipped with a single ion monitoring capability is used in tandem with a gas chromatograph (Figure A1). The mass spectrometer is interfaced to a Varian 620/L computer (Figure A1).

7.0 Reagents and Materials

All reagents used are analytical reagent grade.

8.0 Procedure

8.1 Cleaning of Glassware

All glassware, sampling tubes, cartridge holders, etc. are washed in Isoclean/water, rinsed with deionized distilled water, acetone and air dried. Glassware is heated to 450-500°C for 2 hours to insure that all organic material has been removed prior to its use.

8.2 Preparation of Tenax GC

Virgin Tenax GC is extracted in a Soxhlet apparatus for a minimum of 18 hours with acetone or methanol prior to its use. The Tenax GC sorbent is dried in a vacuum oven at 100°C for 3-5 hours and then sieved to provide a fraction corresponding to 35/60 mesh. This fraction is used for preparing sampling cartridges. In those cases where sampling cartridges of Tenax GC are recycled, the sorbent is extracted in a Soxhlet apparatus with acetone or methanol as described for the virgin material, but the sorbent is further extracted with a non-polar solvent,

hexane, in order to remove the relatively non-polar and non-volatile materials which might have accumulated on the sorbent bed during previous sampling periods.

8.3 Collection of Volatile Organics in Ambient Air

Continuous sampling of ambient air is accomplished using a Nutech Model 221-A portable sampler (Nutech Corp., Durham, NC, see Figure A1, Reference 2). Flow rates between 1-10 ℓ/min are available with this sampling system. Flow rates are generally maintained at 1 ℓ using critical orifices and the total flow is monitored through a calibrated flow meter. The total flow is also registered by a dry gas meter. Concomitant with these parameters the temperature is continuously recorded with a Meteorological Research, Inc. Weather Station since the breakthrough volume is important in order to obtain quantitative data on the volatile organics. This portable sampling unit operates on a 12 volt storage battery and is capable of continuous operation up to a period of 24 hours. However, in most cases at the rates which are employed in the field, the sampling period is generally 1-3 hours. This portable sampling unit is generally utilized for obtaining "high volume" samples. Duplicate cartridges are deployed on each sampling unit utilizing a sampling head as shown in Figure A2.

In addition to the Nutech samplers, DuPont personnel samplers are also used to acquire "low volumes" of ambient air as well as long-term integrated samples (12-36 hrs). Identical Tenax GC sampling cartridges are employed in this case, and the sampling is conducted in duplicate. The flow rate is balanced between duplicate cartridges using critical orifices to maintain a rate of 25-100 ml/min per cartridge.

For large sample volumes, it is important to realize that a total volume of air may cause the elution of compounds through the sampling tube if their breakthrough volume is exceeded. The breakthrough volumes of some of the volatile organics are shown in Table A2 (2,4,7,8). These breakthrough volumes have been determined by a previously described technique (2). The breakthrough volume is defined as that point at which 50% of a discrete sample introduced into the cartridge is lost. Although the identity of a compound during ambient air sampling is not

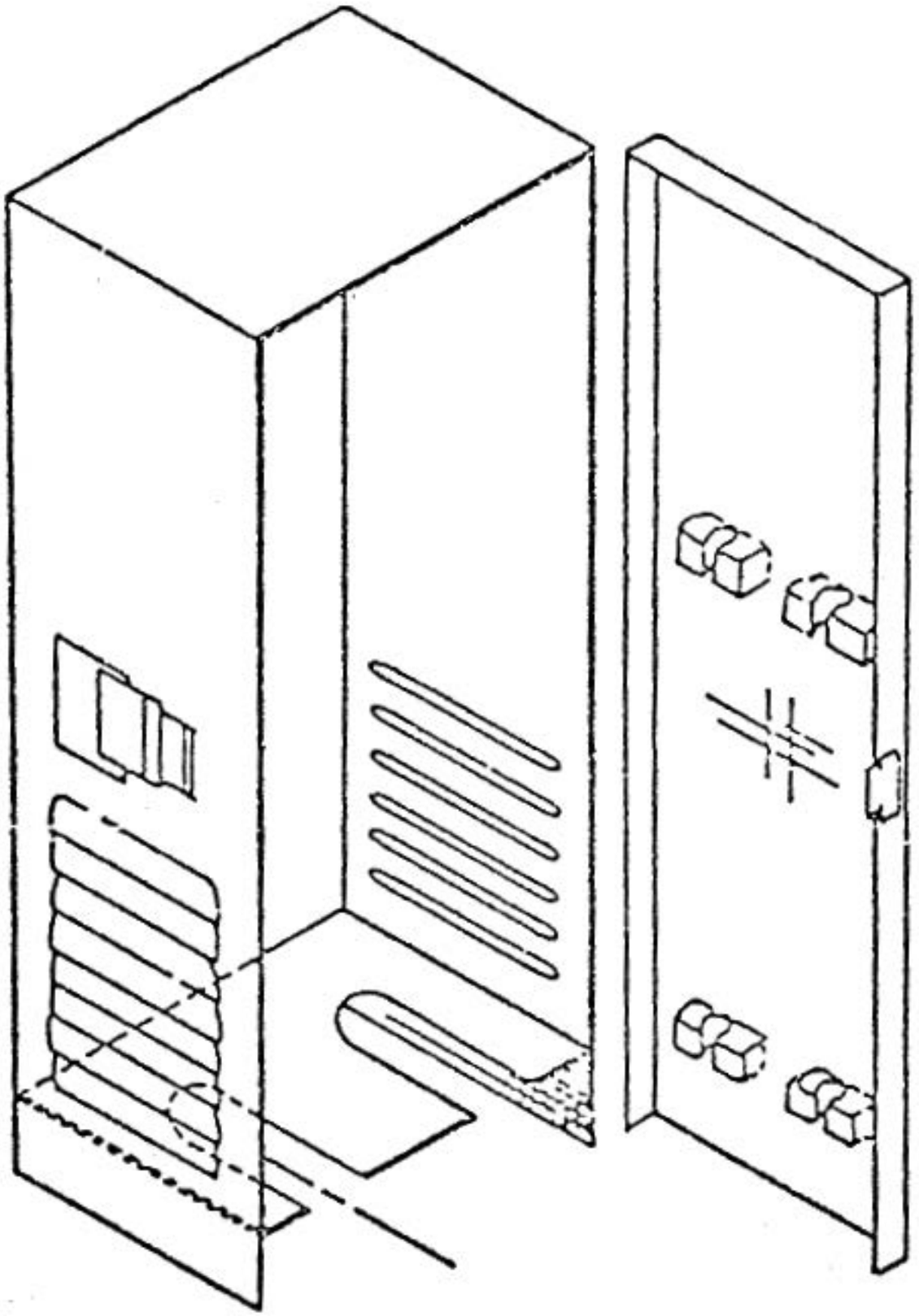


Figure A2. Sampling head for housing cartridge sampling train.

Table A2. TENAX GC BREAKTHROUGH VOLUMES FOR SEVERAL ATMOSPHERIC POLLUTANTS[a]

Chemical Class	Compound	b.p. (°C)	Temperature (°F) 50	60	70	80	90	100
Halogenated hydrocarbon	methyl chloride	-24	8	6	5	4	3	2.5
	methyl bromide	3.5	3	2	2	1	1	0.9
	vinyl chloride	13	2	1.5	1.25	1.0	0.8	0.6
	methylene chloride	41	11	9	7	5	4	3
	chloroform	61	42	31	24	18	13	10
	carbon tetrachloride	77	34	27	21	16	13	10
	1,2-dichloroethane	83	53	41	31	23	18	14
	1,1,1-trichloroethane	75	23	18	15	12	9	7
	tetrachloroethylene	121	361	267	196	144	106	78
	trichloroethylene	87	90	67	50	38	28	21
	1-chloro-2-methylpropene	68	26	20	16	12	9	7
	3-chloro-2-methylpropene	72	29	22	17	13	10	8
	1,2-dichloropropane	95	229	162	115	81	58	41
	1,3-dichloropropane	121	348	253	184	134	97	70
	epichlorohydrin (1-chloro-2,3-epoxypropane)	116	200	144	104	74	54	39
	3-chloro-1-butene	64	19	15	12	9	7	6
	allyl chloride	45	21	16	12	9	6	5
	4-chloro-1-butene	75	47	36	27	20	15	12
	1-chloro-2-butene	84	146	106	77	56	40	29
	chlorobenzene	132	899	653	473	344	249	181
	o-dichlorobenzene	181	1,531	1,153	867	656	494	372
	m-dichlorobenzene	173	2,393	1,758	1,291	948	697	510

(continued)

Table A2 (cont'd)

Chemical Class	Compound	b.p. (°C)	Temperature (°F)					
			50	60	70	80	90	100
Halogenated hydrocarbons (cont'd)	benzyl chloride	179	2,792	2,061	1,520	1,125	830	612
	bromoform	149	507	386	294	224	171	131
	ethylene dibromide	131	348	255	188	138	101	74
	bromobenzene	155	2,144	1,521	1,079	764	542	384
Halogenated Ethers	2-chloroethyl ethyl ether	108	468	336	241	234	124	89
	Bis-(chloromethyl)ether	-	995	674	456	309	209	142
Nitrosamines	N-nitrosodimethylamine	151	385	280	204	163	148	107
	N-nitrosodiethylamine	177	2,529	1,836	1,330	966	700	508
Oxygenated hydrocarbons	acrolein	53	19	14	10	8	6	4
	glycidaldehyde	-	364	247	168	114	77	52
	propylene oxide	34	35	24	17	11	8	5
	butadiene diepoxide	-	1,426	1,009	714	506	358	253
	cyclohexene oxide	132	2,339	1,644	1,153	811	570	400
	styrene oxide	194	5,370	3,926	2,870	2,094	1,531	1,119
	phenol	183	2,071	1,490	1,072	769	554	398
	acetophenonone	202	3,191	2,382	1,778	1,327	991	740
	β-propiolactone	57	721	514	366	261	186	132
Nitrogenous Hydrocarbons	nitromethane	101	45	34	25	19	14	11
	aniline	184	3,864	2,831	2,075	1,520	1,114	817
Sulfur Compounds	diethyl sulfate	208	40	29	21	15	11	8
	ethyl methane sulfate	86	5,093	3,681	2,564	1,914	1,384	998

(continued)

Table A2 (cont'd)

Chemical Class	Compound	b.p. (°C)	Temperature (°F)					
			50	60	70	80	90	100
Amines	dimethylamine	7.4	9	6	4	3	2	1
	isobutylamine	69	71	47	34	23	16	11
	t-butylamine	89	6	5	4	3	2	1
	di-(n-butyl)amine	159	9,506	7,096	4,775	3,105	2,168	1,462
	pyridine	115	378	267	189	134	95	67
	aniline	184	8,128	5,559	3,793	2,588	1,766	1,205
Ethers	diethyl ether	34.6	29	21	15	11	8	5
	propylene oxide	35	13	9	7	5	4	3
Esters	ethyl acetate	77	162	108	72	48	32	22
	methyl acrylate	80	164	111	75	50	34	23
	methyl methacrylate	100	736	484	318	209	137	90
Ketones	acetone	56	25	17	12	8	6	4
	methyl ethyl ketone	80-2	82	57	39	27	19	13
	methyl vinyl ketone	81	84	58	40	28	19	14
	acetophenone	202	5,346	3,855	2,767	2,000	1,439	1,037
Aldehydes	acetaldehyde	20	3	2	2	1	0.9	0.7
	benzaldehyde	179	7,586	5,152	3,507	2,382	1,622	1,101
Alcohols	methanol	64.7	1	1	0.8	0.6	0.4	0.3
	n-propanol	97.4	27	20	14	10	7	5
	allyl alcohol	97	32	23	16	11	8	6

(continued)

Table A2 (cont'd)

Chemical Class	Compound	b.p. (°C)	Temperature (°F)					
			50	60	70	80	90	100
Aromatics	benzene	80.1	108	77	54	38	27	19
	toluene	110.6	494	348	245	173	122	86
	ethylbenzene	136.2	1,393	984	693	487	344	243
	cumene	152.4	3,076	2,163	1,525	1,067	750	527
Hydrocarbons	n-hexane	68.7	32	23	17	12	9	6
	n-heptane	98.4	143	104	75	55	39	29
	1-hexene	63.5	28	20	15	11	8	6
	1-heptene	93.6	286	196	135	93	64	44
	2,2-dimethylbutane	49.7	0.5	0.4	0.3	0.2	0.2	0.1
	2,4-dimethylpentane	80.5	435	252	146	84	49	28
	4-methyl-1-pentene	53.8	14	10	8	6	4	3
	cyclohexane	80.7	49	36	26	19	14	10
Inorganic gases	nitric oxide	-	0	0	0	0	0	0
	nitrogen dioxide	-	0	0	0	0	0	0
	chlorine	-	0	0	0	0	0	0
	sulfur dioxide	-	0.06	0.05	0.03	0.02	0.02	0.01
	water	100	0.06	0.05	0.04	0.03	0.01	0

[a]Breakthrough volume is given in ℓ/2.2 g Tenax GC used in sampling cartridges.

known (therefore, also its breakthrough volume), the compound can still be quantified after identification by GC/MS/COMP once the breakthrough volume has subsequently been established. Thus, the last portion of the sampling period is selected which represents the volume of air sampled prior to breakthrough for calculating concentration. For cases in which the identity of a volatile organic compound is not known until after GC/MS, the breakthrough volume is subsequently determined.

Previous experiments have shown that the organic vapors collected on Tenax GC sorbent are stable and can be quantitatively recovered from the cartridge samplers up to 4 weeks after sampling when they are tightly closed in cartridge holders and placed in a second container that can be sealed, protected from light and stored at 0°C (1,2).

8.4 Analysis of Samples

The instrumental conditions for the analysis of volatile organics on the sorbent Tenax GC sampling cartridge is shown in Table A3. The thermal desorption chamber and the six port Valco valve are maintained at 270° and 240°, respectively. The glass jet separator is maintained at 240°. The mass spectrometer is set to scan the mass range from 25-350. The helium purge gas through the desorption chamber is adjusted to 15-20 ml/min. The nickel capillary trap on the inlet manifold is cooled with liquid nitrogen. In a typical thermal desorption cycle, a sampling cartridge is placed in the preheated desorption chamber and the helium gas is channeled through the cartridge to purge the vapors into the liquid nitrogen capillary trap [the inert activity of the trap has been shown in a previous study (5)]. After the desorption has been completed, the six-port valve is rotated and the temperature on the capillary loop is rapidly raised (greater than 10°/min); the carrier gas then introduces the vapors onto the high resolution GC column. The glass capillary column is temperature programmed from ambient to 240°C at 4°C/min and held at the upper limit for a minimum of 10 min. After all the components have been eluted from the capillary column, the analytical column is then cooled to ambient temperature and the next sample is processed (2).

Table A3. OPERATING PARAMETERS FOR GLC/MS/COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber	270°C
valve	220°C
capillary trap - minimum	-195°C
maximum	+250°C
thermal desorption time	4 min
GLC	
100 m glass SCOT SE/30	25-240°C, 4°C/min
carrier (He) flow	~3 ml/min
transfer line to MS	240°C
MS	
scan range	m/z 20 → 300
scan range, automatic-cyclic	1 sec/decade
filament current	300 μA
multiplier	6.0
ion source vacuum	~4 x 10^{-6} torr

An example of the analysis of volatile organics in ambient air is shown in Figure A3 and the background from a blank cartridge is shown in Figure A4. The high resolution glass capillary column was coated with SE-30 stationary phase which is capable of resolving a multitude of compounds to allow their subsequent identification by MS/COMP techniques; in this case over 120 compounds were identified in this chromatogram.

8.4.1 Operation of the MS/COMP System (Figure A5)

Typically the mass spectrometer is first set to operate in the repetitive scanning mode. In this mode the magnet is automatically scanned exponentially upward from a preset low mass to a high mass value. Although the scan range may be varied depending on the particular sample, typically the range is set from m/z 25 to m/z 300. The scan is completed in approximately 1.8 seconds. At this time the instrument automatically resets itself to the low mass position in preparation for the next scan, and the information is accumulated by an on-line 620/L computer and written onto magnetic tapes or the dual disk system. The reset period requires approximately 2.0 seconds. Thus, a continuous scan cycle of 3.8 seconds/scan is maintained and repetitively executed throughout the chromatographic run. The result is the accumulation of a continuous series of mass spectra throughout the chromatographic run in sequential fashion.

Prior to running unknown samples, the system is calibrated by introducing a standard substance, perfluorokerosene, into the instrument and determining the time of appearance of the known standard peaks in relation to the scanning magnetic field. The calibration curve which is thus generated is stored in the 620/L computer memory. This calibration serves only to calibrate the mass ion over the mass scanning range.

While the magnet is continuously scanning, the sample is injected and automatic data acquisition is initiated. As each spectrum is acquired by the computer, each peak which exceeds a preset threshold is recognized and reduced to centroid time and peak intensity. This information is stored in the computer core while the scan is in progress. In addition, approximately 30 total ion current values and an equal number of Hall

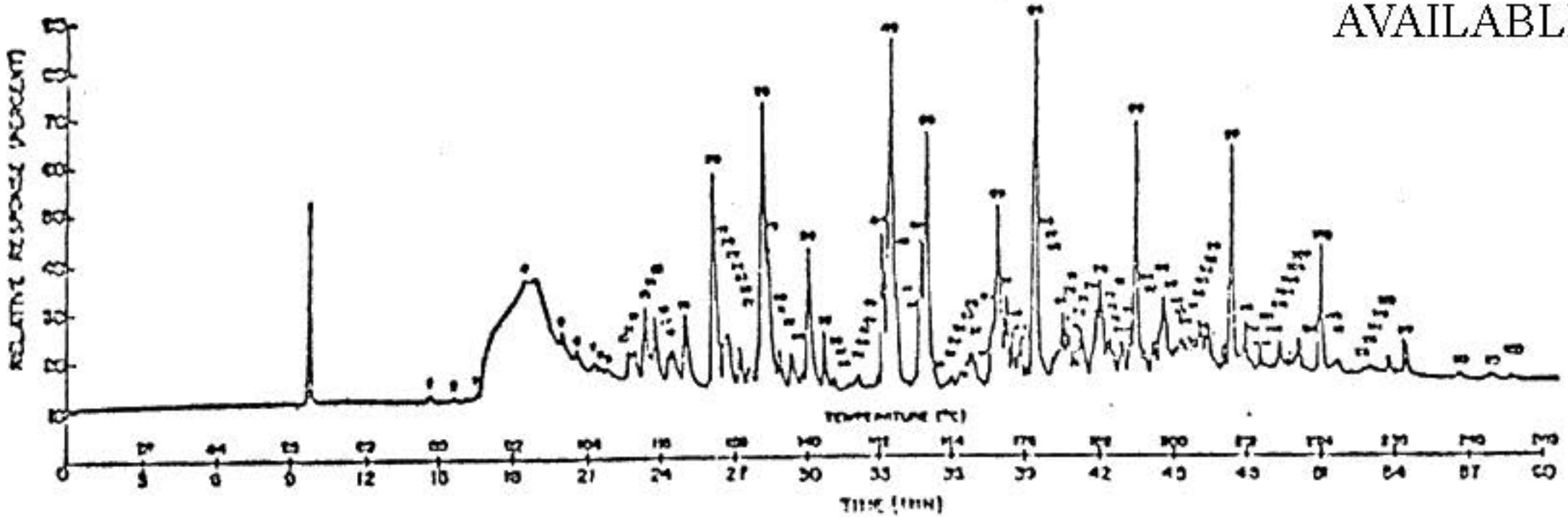


Figure A3. Profile of ambient air pollutants for Wood River, IL using high resolution gas chromatography/mass spectrometry/computer.

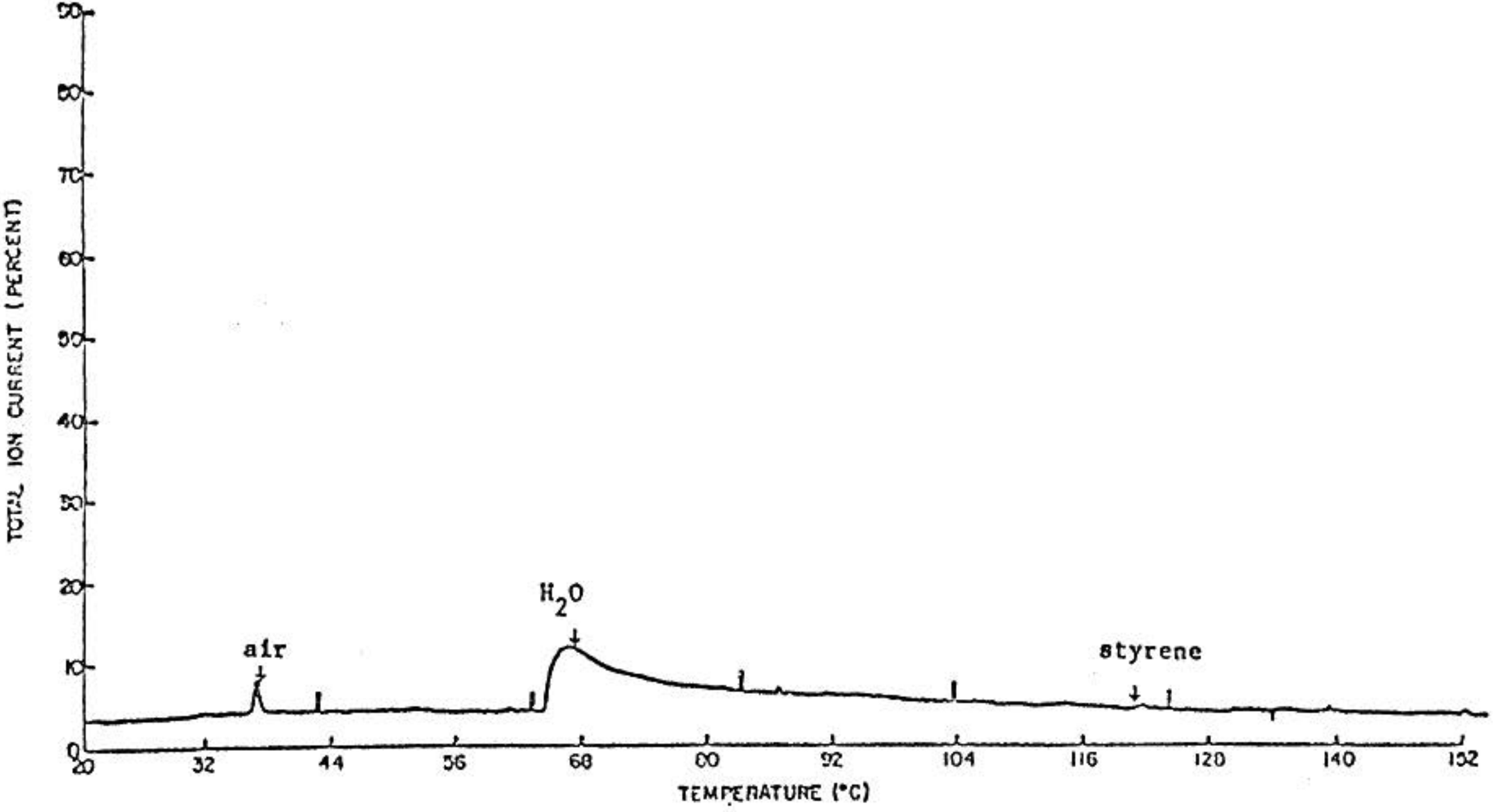


Figure A4. Background profile for Tenax GC cartridge blank.

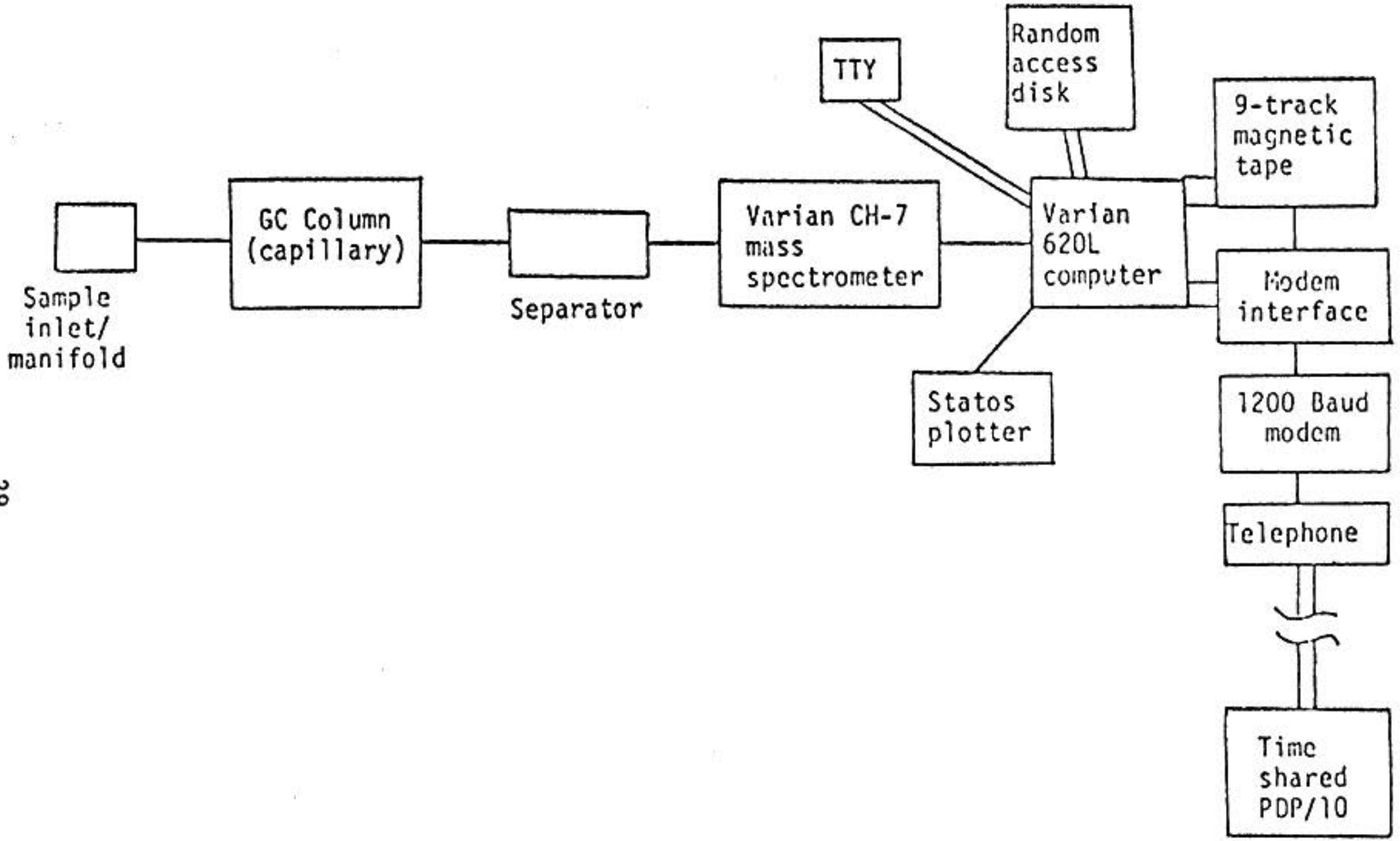


Figure A5. Schematic diagram of GC/MS/Computer system.

probe signals are stored in the core of the computer as they are acquired. During the two-second period between scans this spectral information, along with the spectrum number, is written sequentially on disks, and the computer is reset for the acquisition of the next spectrum.

This procedure continues until the entire GC run is completed. By this time there are from 800-1400 spectra on the disk which are then subsequently processed. Depending on the information required, they may then either be processed immediately or additional samples may be run, stored on magnetic tape and the results examined at a later time.

The mass spectral data are processed in the following manner. First, the original spectra are scanned and the total ion current (TIC) information is extracted. Then the TIC intensities are plotted against the spectrum number on the Statos 31 recorder. The information will generally indicate whether the run is suitable for further processing, since it provides some idea of the number of unknowns in the sample and the resolution obtained using the particular GC column conditions.

The next stage of the processing involves the mass conversion of the spectral peak times to peak masses which is done directly via the dual disk system. The mass conversion is accomplished by use of the calibration table obtained previously using perfluorokerosene. Normally one set of the calibration data is sufficient for an entire day's data processing since the characteristics of the Hall probe are such that the variation in calibration is less than 0.2 daltons/day. A typical time required for this conversion process for 1,000 spectra is approximately 30 min.

After the spectra are obtained in mass converted form, processing proceeds either manually or by computer. In the manual mode, the full spectrum of scans for the GC run is recorded on the Statos 31 plotter. The TIC information available at this time is most useful for deciding which spectra are to be analyzed. At the beginning of the runs where peaks are very sharp nearly every spectrum must be inspected individually to determine the identity of the component. Later in the chromatographic run when the peaks are broader only selected scans need to be analyzed.

Identification of resolved components is achieved by comparing the mass cracking patterns of the unknown mass spectra to an eight major peak index of mass spectra (9). Individual difficult unknowns are searched by the use of the Cornell University STIRS and PBM systems. Unknowns are also submitted to EPA MSSS system for identification. When feasible, the identification of unknowns is confirmed by comparing the cracking pattern and elution temperatures for two different chromatographic columns (SE-30 and Carbowax SCOT capillaries) for the unknown and authentic compounds. The relationship between the boiling point of the identified halogenated hydrocarbon and the elution temperature on a non-polar column (the order of elution of constituents is predictable in homologous series since the SE-30 SCOT capillary separates primarily on the basis of boiling point) is carefully considered in making structure assignments.

Mass spectral search programs are operational at the Triangle Universities Computation Center (TUCC). RTI maintains twice daily service to TUCC, which is a one-quarter mile distance from the RTI campus. Additional information about each magnetic tape containing the mass spectra of halogenated hydrocarbons is entered directly into the TUCC job stream using a remote job entry processing. This is normally done at TUCC using one of the five terminals located within the Analytical Sciences Laboratory. The control information contains selected spectrum numbers with instructions to process entire GC runs. The computer program systems compare simultaneously either the entire library of 25,000 compounds or some subset of this library. The complete reports showing the best fits for each of the unknowns is produced at TUCC and printed out at the high speed terminals located on the RTI campus or TUCC. Thus, the processing of the mass spectral data obtained for the halogenated hydrocarbons in the samples collected proceeds by one of three routes. Each consists of a different level of effort. The first level is strictly a manual interpretation process which proves to be the most thorough approach. The second level is executed when the interpretation at the first level has not yielded conclusive results.

8.4.2 Quantitative Analysis

In many cases the estimation of the level of pollutants by capillary gas chromatography in combination with mass spectrometry is not feasible utilizing only the total ion current monitor (See Figure A3 for example). Since baseline resolution between peaks is not always achieved, we employ the techniques which have been previously developed under contract whereby full spectra are obtained during the chromatographic separation step and the selected ions are presented as mass fragmentograms using computer software programs which allow the possibility of deconvoluting constituents which were not resolved in the total ion current chromatogram (6). Examples are depicted in Figures A6 and A7 which represent an ambient air sample with a TIC profile as in Figure A3.

In our gc/ms/comp system, we request from the Varian 620/L dedicated computer mass fragmentograms for any combination of m/e ions when full mass spectra are obtained during chromatography; thus selectivity is obtained by selecting the unique ion for that particular organic substance and this is represented vs. time with subsequent use of that ion intensity for quantitation. Also quantitation with external standards is easily achieved using the intensity of the total ion current monitor or the use of a unique mass cracking ion in a mass spectrum of the external standard. Thus, we use mass fragmentography for the quantitation of organics in ambient air when the total ion current monitor is inadequate because of the lack of complete resolution between components in the mixture.

As described previously, the quantitation of constituents in ambient air samples is accomplished either by utilizing the total ion current monitor or where necessary the use of mass fragmentograms. In order to eliminate the need to obtain complete calibration curves for each compound for which quantitative information is desired, we use the method of relative molar response (RMR) factors (10). Successful use of this method requires information on the exact amount of standard added and the relationship of RMR (unknown) to the RMR (standards). The method of calculations is as follows:

BEST COPY
AVAILABLE

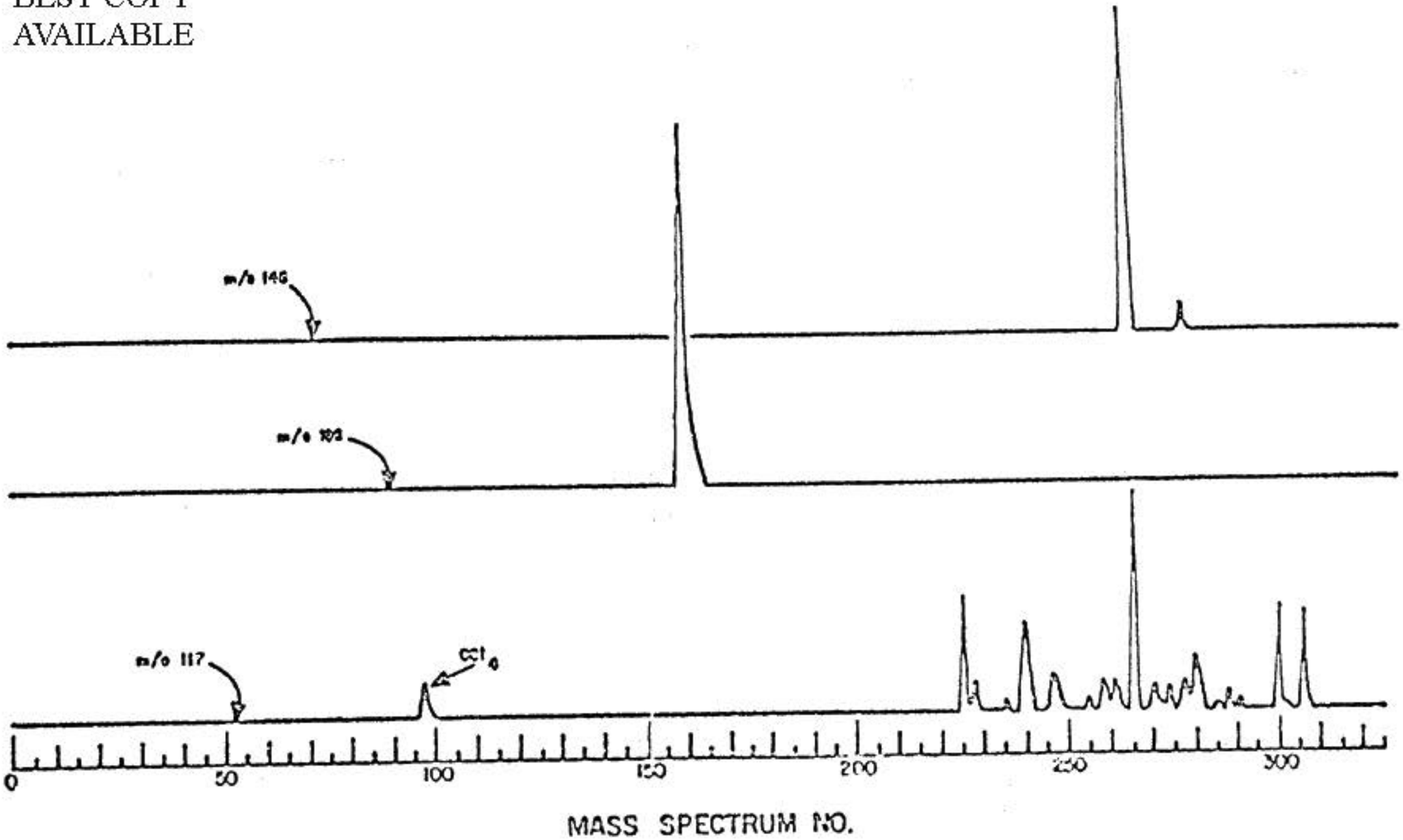


Figure A6. Mass fragmentograms of characteristic ions representing carbon tetrachloride (m/ 117), tetrachloroethylene (m/z 166) and m-dichlorobenzene (m/z 146) in ambient air.

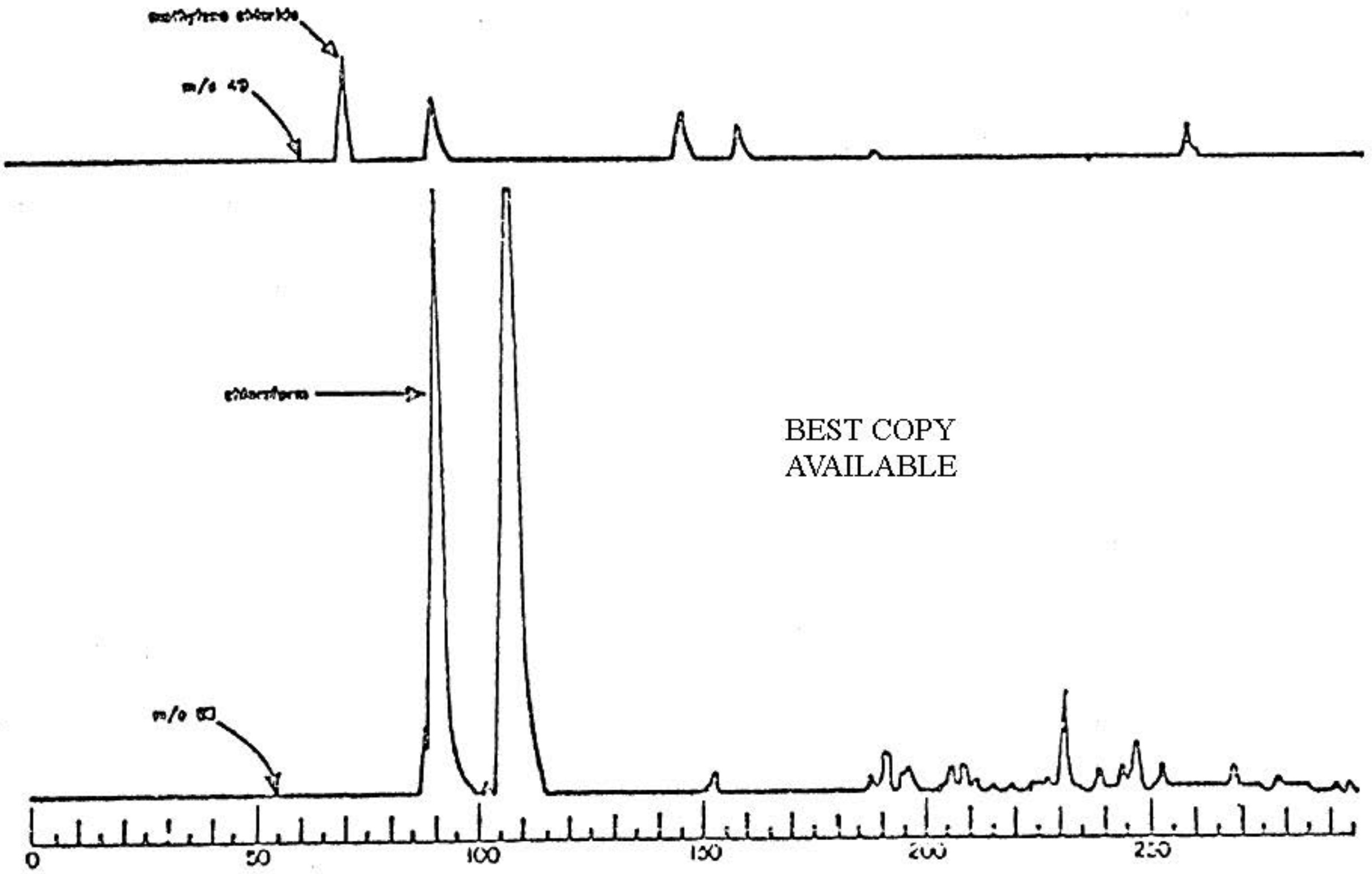


Figure A7. Mass fragmentograms of characteristic ions representing methylene chloride (m/z 49) and chloroform (m/z 83) in ambient air.

$$(1)\quad RMR_{unknown/standard} = \frac{A_{unk}/Moles_{unk}}{A_{std}/Moles_{std}}$$

A = peak area, determined by integration or triangulation.

The value of RMR is determined from at least three independent analyses.

$$(2)\quad RMR_{unk/std} = \frac{A_{unk}/g_{unk}/GMW_{unk}}{A_{std}/g_{std}/GMW_{std}}$$

A = peak area, as above
g = number of grams present
GMW = gram molecular weight

Thus, in the sample analyzed:

$$(3)\quad g_{unk} = \frac{A_{unk} \cdot GMW_{unk} \cdot g_{std}}{A_{std} \cdot GMW_{std} \cdot RMR_{unk/std}}$$

The standard can be added as an internal standard during sampling; however, since the volume of air taken to produce a given sample is accurately known, it is also possible and more practical to use an external standard where the standard is introduced into the cartridge prior to its analysis. Two standards, hexafluorobenzene and perfluorotoluene, are used for the purpose of calculating RMR's. From previous research it has been determined that the retention times for these two compounds are such that they elute from the glass capillary column (SE-30) at a temperature and retention time which does not interfere with the analysis of unknown compounds in ambient air samples.

Since the volume of air taken to produce a given sample is accurately known and an external standard is added to the sample, then the weight per cartridge and hence the concentration of the unknown can be determined. The approach for quantitating ambient air pollutants requires that the RMR be determined for each constituent of interest. This means that when an ambient air sample is taken, the external standard is added at a known concentration during the analysis. It is not imperative at this point to know what the RMR of each of the constituents in

the sample happens to be. However, after the unknowns are identified then the RMR can be subsequently determined and the unknown concentration calculated in the original sample using the RMR. In this manner it is possible to obtain qualitative and quantitative information on the same sample with a minimum of effort.

9.0 References

1. Pellizzari, E. D., Development of Method for Carcinogenic Vapor Analysis in Ambient Atmospheres. Publication No. EPA-650/2-74-121, Contract No. 68-02-1228, 148 pp., July, 1974.
2. Pellizzari, E. D., Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors. Publication No. EPA-600/2-75-075, Contract No. 68-02-1228, 187 pp., November, 1975.
3. Pellizzari, E. D., J. E. Bunch, B. H. Carpenter and E. Sawicki, Environ. Sci. Technol., 9, 552 (1975).
4. Pellizzari, E. D., B. H. Carpenter, J. E. Bunch and E. Sawicki, Environ. Sci. Technol., 9, 556 (1975).
5. Pellizzari, E. D., The Measurement of Carcinogenic Vapors in Ambient Atmospheres. Publication No. EPA-600/7-77-055, Contract No. 68-02-1228, 288 pp., June, 1977.
6. Pellizzari, E. D., J. E. Bunch, R. E. Berkley and J. McRae, Anal. Chem., 48, 803 (1976).
7. Pellizzari, E. D., Quarterly Report No. 1, EPA Contract No. 68-02-2262, February, 1976.
8. Pellizzari, E. D., J. E. Bunch, R. E. Berkley and J. McRae, Anal. Lett., 9, 45 (1976).
9. "Eight Peak Index of Mass Spectra", Vol. 1, (Tables 1 and 2) and II (Table 3), Mass Spectrometry Data Centre, AWRE, Aldermaston, Reading, RF74PR, UF, 1970.
10. Pellizzari, E. D., Quarterly Report No. 3, EPA Contract No. 68-02-2262, in preparation.
11. Pellizzari, E. D., "Measurement of Carcinogenic Vapors in Ambient Atmospheres", EPA_Contract No. 68-02-1228, Final Report, in press.

Written analytical protocol prepared 1/24/77.

APPENDIX B

CHAIN OF CUSTODY RECORD

CHAIN OF CUSTODY RECORD

Research Triangle Institute
Analytical Sciences Division
Chemistry and Life Sciences Group
Research Triangle Park, NC 27709

SAMPLE NUMBER:	SAMPLE TYPE	Number of Containers
1568-JLB-1-4-7-D4/HK-NYNFH-T1	Air	1

Relinquished By:	Received by:	Time	Date	Reason for Change of Custody
	[illegible]	1330	7/24/78	Load PFB 396ng PFT 525ng
[illegible]	DJ Smith	1330	7/24/78	Analysis
DJ Smith	K. Tome	1100	7/25/78	GC-MS Analysis
K. Tome	J. Burcy	0950	10/9/78	Data Interpretation
[illegible]	EDP	4:30	10/20	