NEIC

ENVIRONMENTAL PROTECTION AGENCY
NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
P.O. Box 25227 Denver Federal Center
Denver, Colorado 80225

March 1983

National Enforcement Investigations Center, Denver

U.S. Environmental Protection Agency

Office of Enforcement

ENVIRONMENTAL PROTECTION AGENCY
NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
P.O. Box 25227 Denver Federal Center
Denver, Colorado 80225

March 1983

GUIDELINES FOR ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AIR

A INTRODUCTION AND GUIDANCE FOR PLANNING FIELD STUDIES

B SAMPLE COLLECTION

C THERMAL DESORPTION AND GC/MS ANALYSIS

D PERMEATION TUBE PREPARATION AND CALIBRATION

E TENAX-GC® SAMPLE TRAP PREPARATION AND SCREENING

® *Tenax-GC is a registered trademark of Enka N.V., The Netherlands.*

A INTRODUCTION AND GUIDANCE FOR PLANNING FIELD STUDIES

This introduction to the NEIC air sampling and analysis procedures provides background information on air sampling by various means and the reasoning behind the selection of procedures for use at NEIC. Any environmental analytical data can be no better than the sampling plan and the protocols used to collect samples. This is especially true for air sampling for organic compounds. The objectives of a field study (for example: great interest in one or a few known compounds) can indicate, if not require, the use of modifications to standard sampling protocols. Stated more explicitly, air sampling and analytical methods need to be tailored to the objectives of the field study. Therefore, is is important that both field and laboratory personnel understand the basic physical processes and principles of organic air pollutant analysis.

Approaches to Air Sampling

Almost every organic analysis, including organics in air, depends on getting the sample or sample extract onto some type of chromatographic column for the actual quantitation step. (This discussion ignores *in situ* spectroscopic methods such as infrared because such methods are limited in the number of compounds which can be determined and because the potential for interferences limits their application to known atmospheres.) The most straightforward, and therefore the best, way to analyze air would be to place a measured amount of the air directly onto the chromatographic column. However, using gas chromatography limits the sample size to a few cm^3 at most, so that this direct approach does not provide the necessary sensitivity in most cases.[1] In order to increase sensitivity, three categories of methods have been employed to trap organic compounds from a stream of air to increase the effective sample size. The three types of methods are liquid sorbents, cryogenic trapping, and solid sorbents.

Liquid Sorbents

Liquid sorbents, or bubbler trains, are inconvenient to use both from a field and laboratory standpoint. Their use ought to be limited to special situations where a chemical selectivity can be achieved in the trapping step which outweighs the disadvantages of the technique.

Cryogenic Trapping

Cryogenic trapping involves drawing the air sample over a cold inert surface so that when the trap is warmed, the organics are contained in a small volume. The method works best for very volatile compounds (gases at room temperature) although it has been used for compounds as involatile as trichlorobenzene.[2] An obvious disadvantage of the method is the need for cryogenic material, such as liquid argon or liquid oxygen or dry ice at the very least, both to collect and store the samples before analysis. Other problems encountered with cryogenic trapping are plugging of the trap with frozen water vapor and reproducibly obtaining an inert trapping surface. The most extensive use of cryogenic trapping has been by a group headed by Hanwant Singh. They perform analyses in the field using a mobile laboratory to avoid problems associated with storing and shipping samples. The analyses are done by GC using classical (not mass spec) detectors. Reference 3 contains a brief description of their methods and summarizes results they have obtained in urban ambient air.

Solid Sorbents

Solid sorbents are the most applicable to general purpose air sampling because of their relative ease of use and storage and the wide range of compounds which can be sampled. Analysis can be performed either by solvent elution of the sorbent or by thermal desorption. With thermal desorption, the entire sample is analyzed giving lower detection limits than solvent elution for a given sample size. However, solvent elution allows reanalysis of the sample, which is not possible with thermal desorption. Thermal desorption and solvent elution should be thought of as complimentary techniques with a range of overlap in their applicability. Except for specialized methods, compounds compatible with solvent elution analysis are solids at room temperature, while thermal desorption can be used for liquids and more volatile solids. Compounds which are gases at room temperature can be analyzed by thermal desorption with a judicious choice of solid sorbent.

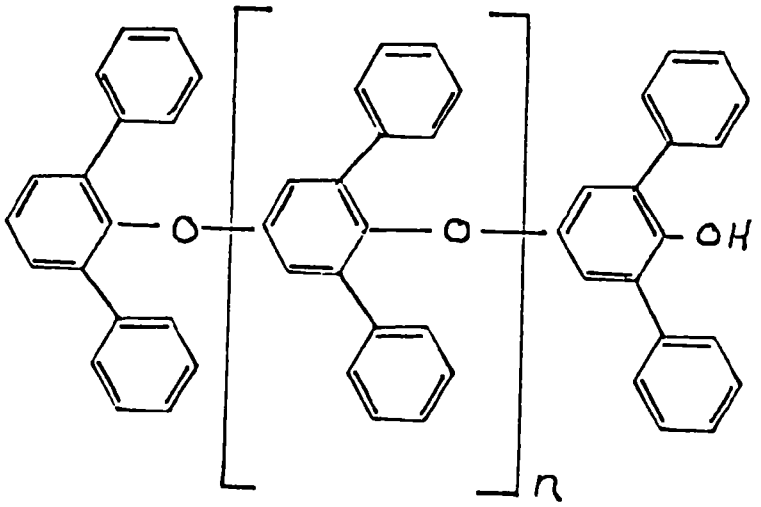
Choice of Sampling Technique

The method expected to be most applicable to NEIC needs (for example, air sampling near a hazardous waste site) is trapping on Tenax solid sorbent with analysis by thermal desorption. In situations where only relatively non-volatile compounds such as pesticides, PCBs, or benzo(a)pyrene are of interest, trapping on combination polyurethane foam (PUF)/XAD resin cartridges followed by solvent elution is recommended. The latter technique has been successfully applied to a wide variety of compounds including organophosphorous pesticides by EPA personnel at HERL-RTP.[4]

The properties of Tenax are described more completely below. Briefly, among the solid sorbents available, Tenax is applicable to the widest variety of compounds while not collecting large amounts of water. Water causes problems during the analysis because thermal desorption includes a cryogenic trapping step, and ice plugs the trap if enough water was collected with the air sample. Other materials which have been used as solid sorbents have fewer of the desirable properties possessed by Tenax. Nearly all adsorb more water. Some do not have the thermal stability of Tenax and others, such as charcoal, can irreversibly adsorb compounds limiting their range of applicability.

Properties of Tenax-GC

The structure of Tenax is shown below.



Tenax-GC is poly-p-2,6-diphenylphenyleneoxide, a porous linear polymer first used as a packing material for gas chromatography. Several properties of Tenax make it suitable for collection of organic volatiles in air. They are:

1. Excellent thermal stability. Thermal analysis methods (Differential Scanning Calorimetry) have been used to confirm the stability of Tenax. Breakdown does not occur below temperatures of 400° C.[5] This characteristic makes thermal desorption feasible and temperatures as high as 400° C. will not increase background due to breakdown of the polymer.

2. Quantitative desorption. Tenax does not exhibit losses due to irreversible adsorption as charcoal does.[6] Decomposition of sorbates on charcoal has been reported.[7]

3. Low background contamination. Virgin Tenax is Sohxlet extracted for ≅18 hours with methanol. It is then thermally conditioned at an elevated temperature (275-325° C.) for 20 to 30 minutes. Traps are easily rebaked and returned to a low background state for reuse. After solvent extraction and thermal conditioning, Tenax shows negligible background contribution. However, the sampling process exposes any solid sorbent to ozone and other oxidants which can be expected to cause artifacts. Artifacts reported from the thermal decomposition and/or reactions of Tenax include ethylene oxide[7], alkylbenzenes[8], styrene[8], benzene[8], alkylphenols[8], acetophenone[9], and benzaldehyde[9].

   In our experience at NEIC, only acetophenone and benzaldehyde have been observed as artifacts in upwind field samples.

4. High collection efficiency. Tenax collection efficiency of 100% has been reported with a wide variety of compounds[10] (when breakthrough volumes are not exceeded). Testing has also been conducted under commonly encountered analytical conditions. Results indicate that collection efficiency does not drop with repeated thermal desorption[10,11]

and that breakthrough volumes are somewhat dependent on relative humidity[12] and CO_2 concentration[12], even though no apparent decrease in collection efficiency is observed with relative humidity[10,13]. (Collection efficiency and breakthrough volume are not the same thing.)

5. Low affinity for water. Water vapor is poorly retained on Tenax[14,15], a distinct advantage. In addition to the plugging problem mentioned previously, adsorbed water presents a potential medium for hydrolysis reactions and for collecting potentially reactive gases such as NO_x and SO_2[15].

Limitations of Tenax

Although Tenax has many desirable properties, it does have limitations. Because of these limitations, it may be desirable to use other sorbents in conjunction with Tenax. Materials such as charcoal[8,16] and Ambersorb XE-340® [8] retain very volatile compounds much better than Tenax. Ambersorb XE-340 is essentially carbonized XAD resin which has the desirable adsorptive properties of charcoal, hopefully without the undesirable features such as active sites due to metals. If it is necessary to sample very volatile compounds, Ambersorb XE-340 can be used by itself or behind Tenax traps.

Breakthrough Volumes

Two terms commonly used to describe collection efficiency in air are Elution Volume and Breakthrough Volume. Due to ambiguity by early researchers, these terms were often used interchangeably[7,10]. To clarify the meaning, they are defined below.

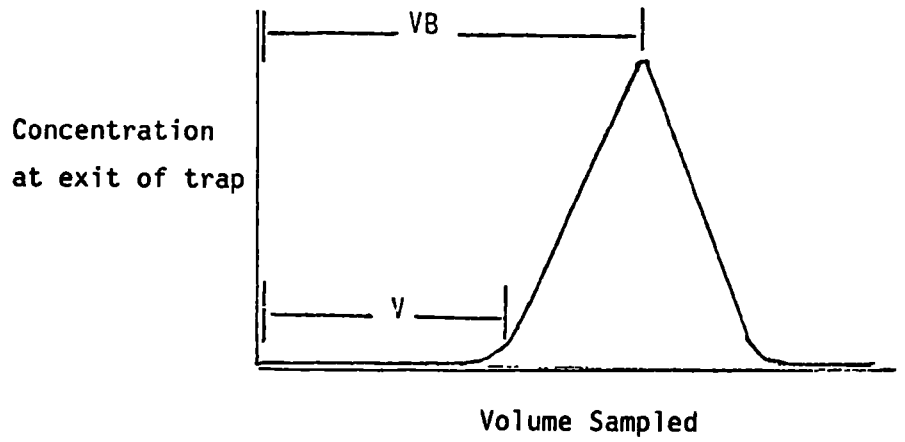
Elution Volume - The volume of air sampled which is required to move the mass transfer zone to the end of the available packing bed.

® *Ambersorb XE-340 and XAD are registered trademarks of Rohm & Haas Company.*

Breakthrough Volume - That volume of air which purged 50% of the adsorbed vapor out of the cartridge.

The two definitions can be represented diagramatically.

FIGURE 1
ELUTION PROFILE

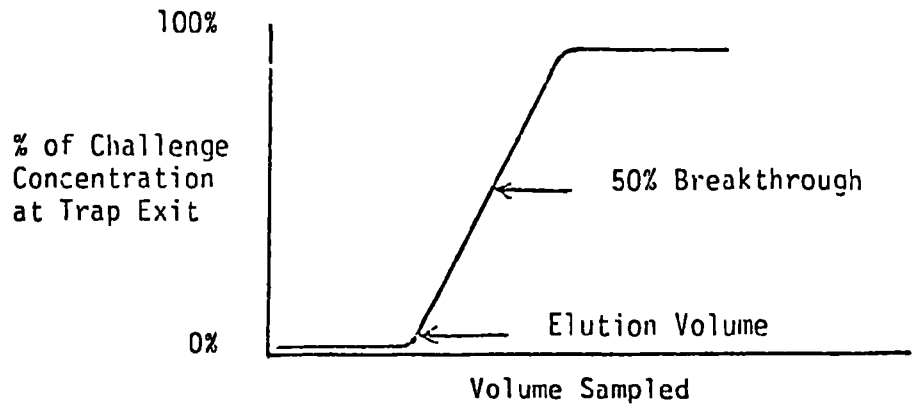


V = point where actual breakthrough of the sorbate begins (Elution Volume)

VB = 50% breakthrough (Breakthrough Volume)

Another way of visualizing this concept is shown in Figure 2.

FIGURE 2
FRONTAL PROFILE



Elution analysis entails injecting a small quantity of adsorbate onto a cartridge in a very small time. During frontal analysis, the sample injection is continuous.

In actuality, the elution volume and the 50% breakthrough volume may be very similar for compounds with low breakthrough volumes. Compounds with high breakthrough volumes will have a larger difference between the two values.

Superimposing Figures 1 and 2 will show the relationship between frontal breakthrough (Figure 2) and an elution peak (Figure 1)[11].

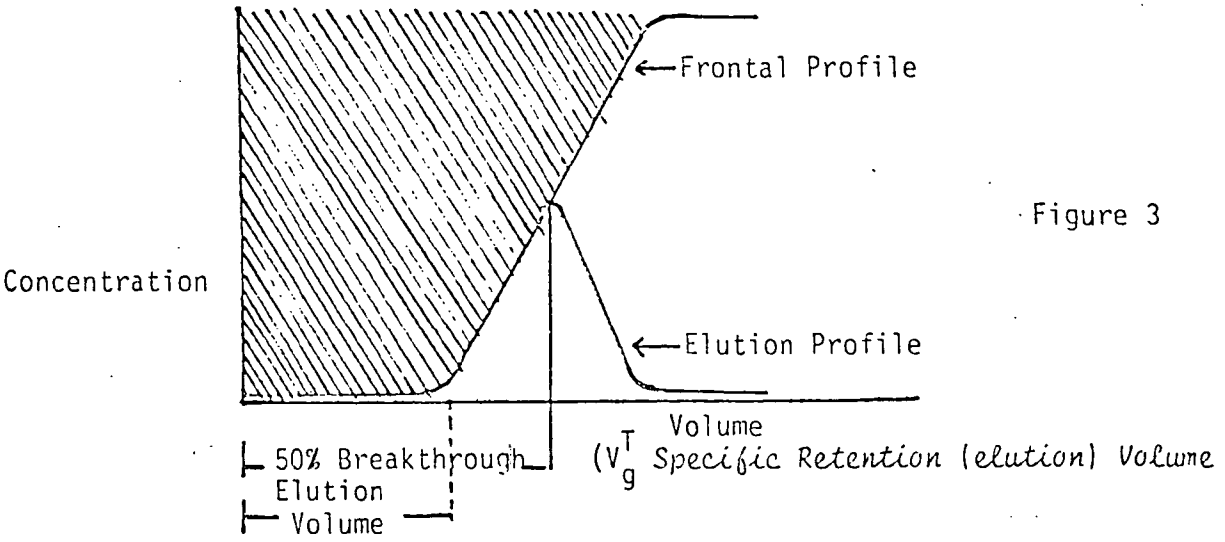


Figure 3

Factors Affecting Breakthrough Volume

Factors which affect or may affect breakthrough volume include temperature, humidity, chemical class of the sampled compound, CO_2 concentration, the total organic concentration in the sampled atmosphere or the concentration of particular compounds, and changes in the sorbent surface caused by reactions with ozone or other oxidizing species. All porous polymer sorbents

work by allowing airborne compounds to diffuse into pores within the polymer. This process requires a finite time so that collection efficiency will eventually decrease as the sample flow rate in increased.[17] This problem would probably never be encountered because the flow rates are higher than are typically used or even possible with common pumping systems. However, one should be aware of the possibility. The dependence of breakthrough volume on temperature is well known and has a theoretical basis[16, 17]; extrapolation of breakthrough volumes to other temperatures is an often used and accepted procedure. Tabulated breakthrough volumes are useful in estimating relative detection limits.

The dependence on relative humidity and CO_2 concentration has been determined empirically for selected compounds on Tenax.[12] The breakthrough volumes of four compounds decreased 22 to 43% upon going from 0 to 87% relative humidity in a laboratory situation. When CO_2 was added in addition to water, breakthrough volumes decreased by approximately an additional 25%.

C. R. McMillin and co-workers sampled indoor and outdoor air using Tenax as the first stage of a three-sorbent trapping system.[8] They found great and unexplained differences in the indoor and outdoor breakthrough volumes on Tenax (other sorbents were not tested), implying that breakthrough volumes determined in the laboratory cannot be used in quantitating field results. These differences are the observable effects of the many factors affecting breakthrough volume.

The only practical approach to obtaining quantitative field data is to avoid breakthrough by limiting sample size and to include tests for breakthrough in the quality assurance plan so that you are aware if breakthrough did occur. Tabulated breakthrough volumes or past experience can be used to set sample size, but should not be used for quantitation.

Generic Quality Assurance Plan for Air Sampling

The procedures listed are recommended as a general approach to any air sampling study. The reasons for each procedure are also listed.

1. Keep the sampling time to the minimum which will give adequate sample volume. This point depends on the objectives of the study. Presumably, you are trying to detect contributions from a particular source. The shorter the sampling time, the more stable weather (wind speed and direction) conditions will be during the sampling, resulting in better directional resolution in the data. An obvious corollary is to collect all samples as nearly simultaneously as possible.

2. Do not use a sample volume larger than necessary to give the desired detection limits. During sampling, both the solid sorbent and adsorbed compounds are exposed to ozone and other reactive species. Reactions between adsorbed compounds are also possible. These possibilities cannot be avoided, but minimizing the sample size also minimized their effects.

3. Take all samples using tandem (connected in series) sorbent tubes with a sample size chosen to avoid breakthrough on the first tube. This procedure is based on the assumption that quantitative data for more volatile compounds are given higher priority than lower detection limits for less volatile compounds. Avoiding breakthrough is necessary to obtain quantitative data; analyzing tandem tubes provides a check for breakthrough.

4. Always take duplicate samples downwind of the source as a minimum; triplicate samples are recommended. The downwind samples are the most important samples because they are most likely to show positive results; the upwind sample is the next most important because it shows background levels. Taking duplicate samples downwind helps to ensure that data will be available for the most important sampling point even if one laboratory analysis fails. (Using thermal desorption, there is only one chance at the analysis.) The duplicate or triplicate samples also serve as a check of sampling and analysis precision.

5. Take duplicate breakthrough spikes upwind of the source in addition to the upwind sample(s). A breakthrough spike consists of a tandem pair

of tubes with the first tube spiked with known amounts of target compounds. The tandem pair is then sampled over in the normal manner. A breakthrough spike is the most valid matrix spike which is practical in most air sampling projects. The results obtained from the breakthrough spike are the best performance that can be expected from the sampling and analysis procedure. If a spiked compound is not retained on a tube during sampling, it cannot be expected to be sampled reliably. The duplicate breakthrough spikes are a check of the precision and accuracy of the methodology.

6. Carry triplicate field spikes to the field. The field spikes are sample tubes which are spiked with target compounds but not sampled over. The field spikes serve to check for losses of target compounds during shipment and storage and as a check of analytical precision. At the time the spiking for the breakthrough and field spikes is performed, an additional spike is performed which is stored in the laboratory under the best possible conditions. This spike serves as a reference for the field and duplicate spikes.

7. Include a field blank in each container of sample tubes to check for contamination during storage or shipment.

8. One can expect artifacts from any sampling technique. Be aware of the artifacts which can be expected with the methodology employed.

9. Know the principles involved in air sampling methodologies and avoid situations which might cause artifacts or errors. For example, two situations to avoid would be exposing sample traps to high concentrations of organic vapor such as gasoline fumes, and exposing the traps to high temperatures during shipment or storage.

FOOTNOTES AND REFERENCES

1. Tom Spittler and co-workers in U.S. Environmental Protection Agency Region I, Boston, have very successfully employed this direct approach to monitor solvent-type compounds.

2. H. B. Singh, L. J. Salas, A. J. Smith, and H. Shigeishi, *Atmos. Environ.*, 15, 601 (1981).

3. H. B. Singh, L. J. Salas, and R. E. Stiles, *Environ. Sci. Technol.*, 16, 872 (1982).

4. R. G. Lewis and K. E. MacLeod, *Anal. Chem., 54, 310 (1982).*

5. *"Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds"*, A. D. Little, Inc., EPA/600/7-77/044, April 1977.

6. E. D. Pellizzari, B. H. Carpenter, J. E. Bunch, and E. Sawicki, *Environmental Science and Technology,* 9, 556 (1975).

7. *"Development of Method for Carcinogenic Vapor Analysis in Ambient Atmospheres"*, Research Triangle Institute, EPA-650/2-74-121, July 1974.

8. *"Potential Atmospheric Carcinogens, Phase 2/3, Analytical Technique and Field Evaluation"*, Monsanto Research Corp., EPA-600/2-81-106, June 1981.

9. *"Artifact Problems in Atmospheric Analysis of Organic Compounds and Strategies for Minimization,"* R. E. Sievers, presented at National Symposium on Monitoring Hazardous Organic Pollutants in Air, Raleigh, N.C., April 28 to May 1, 1981. Also by NEIC experience.

10. *"Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors"*, Research Triangle Institute, EPA-600/2-75-076, November, 1975.

11. *"Characterization of Sorbent Resins for Use in Environmental Sampling"*, Research Triangle Institute, EPA-600/7-78-054, March 1978.

12. *"Further Characterization of Sorbents for Environmental Sampling"*, A. D. Little, Inc., EPA-600/7-79-216, September 1979.

13. E. D. Pellizzari, J. E. Bunch, R. E. Berkley, J. McRae, *Analytical Letters,* 9, 45 (1976).

14. Dravnieks, et al., *Environmental Science and Technology,* 5, 1220 (1971).

15. *"Analysis of Organic Air Pollutants by Gas Chromatography and Mass Spectroscopy, Final Report"*, Research Triangle Institute, EPA-600/2-79-057, March 1979.

16. K. J. Krost, E. D. Pellizzari, S. G. Walburn, and S. A. Hubbard, *Anal. Chem.*, 54, 810 (1982).

17. *"Characterization of Sorbent Resins for Environmental Sampling," A. D. Little, Inc.*, EPA-600/7-78-054, March 1978.

B SAMPLE COLLECTION

ENVIRONMENTAL PROTECTION AGENCY
NATIONAL ENFORCEMENT INVESTIGATION CENTER
Box 25227 Denver Federal Center
Denver, Colorado 80225

Volatile Organic Air Pollutant Analysis
Sample Collection
March 1983

1.0 Introduction

1.1 This procedure describes the collection of air samples on sampling tubes containing a solid sorbent. Tenax-GC® is the most commonly used sorbent. Adsorbed organic compounds are detected by thermal desorption of the sorbent onto a gas chromatograph column for GC/MS analysis. The procedure presented here was designed to perform reasonably well on a wide range of compounds. In general, those organic compounds that are liquids at room temperature are well suited for analysis using this method and Tenax as an adsorbent. If only compounds of a narrow volatility range are of interest, it is probable that the sample size and/or sorbent material could be changed to yield superior performance for the compounds of interest. For example, compounds as low in volatility as benzo(a)pyrene have been analyzed by similar procedures. Although this procedure was specifically designed for the use of Tenax sorbent, other sorbents can be used.

2.0 Limitations

2.1 The sample traps are essentially short chromatographic columns. Retention of chemicals is dependent upon adsorption characteristics of the chemical/resin system. Factors influencing retention include: temperature, flow rate, air volume, vapor pressure of the chemical, and sample matrix. Volatile species like vinyl chloride are only moderately retained while other chemicals like chlorobenzene are retained very well. All chemicals will experience breakthrough under the correct conditions. Table I lists breakthrough volumes for some relevant chemicals. The volumes represent the amount of air sampled when 50% of the collected chemical is lost through the trap. This data was compiled by Pellizzari in Reference 9.7. Data for chemicals where the sample volume exceeds the breakthrough volume represent minimum concentrations. The data in Table 1 can be used to estimate an appropriate sample size. When doing this, one must decrease the volumes shown in Table 1 by the factor $\frac{8}{22}$ because the NEIC sample traps contain 0.8g of Tenax rather than 2.2g. In general, the sample size should be 25 liters or less.

® *Registered Trademark of Enka N.V., The Netherlands; appears hereafter without the ®.*

Table 1

Tenax GC Breakthrough Volumes for Selected Compounds at Various Temperatures
Data Taken From Reference 9.7

Chemical Class	Compound		Temperature (°F)					
			50	60	70	80	90	100
		b p (°C)	Breakthrough Volumes for 2.2 g Tenax (liters)					
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
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
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
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
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
Ethers	Diethyl ether	34.6	29	21	15	11	8	5
	Propylene oxide	35	13	9	7	5	4	3
Halogenated Ethers	2-Chloroethyl ethyl ether	108	468	336	241	234	124	89
	Bis-(chloromethyl)ether	-	995	674	456	309	209	142
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	
	4-Chloro-1-butene	75	47	36	27	20	15	12
	1-Chloro-2-butene	84	146	106	77	56	40	29

Table 1 (cont.)

Tenax GC Breakthrough Volumes for Selected Compounds at Various Temperatures
Data Taken From Reference 9.7

Chemical Class	Compound		Temperature (°F)					
			50	60	70	80	90	100
		b.p. (°C)	Breakthrough Volumes for 2 2 g Tenax (liters)					
Halogenated hydrocarbon (cont.)	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
	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
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-Diemthylpentane	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
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
Nitrogenous hydrocarbons	Nitromethane	101	45	34	25	19	14	11
	Aniline	184	3,864	2,831	2,075	1,520	1,114	817
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
	Acetopheonone	202	3,191	2,382	1,778	1,327	991	740
	b-Propiolactone	57	721	514	366	261	186	132
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

2.2 The accuracy of the data produced from the analysis of samples obtained using this procedure depends on the care with which sampling is performed. Particular attention must be given to the calibration of pumps, checking to demonstrate that the sampling rate was constant, and to the handling of sample tubes to avoid contamination. The sampling tubes should be kept in sealed culture tubes except for the time required for set up and sampling. The tubes should never be handled without using nylon gloves or tissues to prevent contamination by body oils.

2.3 The data in Table 1 show that the effects of temperature on sample breakthrough volume are significant. For many of the compounds listed in Table 1, the breakthrough volume at 90° F is only 20 to 25% of the breakthrough volume at 50° F.

2.4 In order to check for sample breakthrough, each sample is taken using a tandem tube arrangement. If a particular compound is detected on the first tube but none is seen on the second tube, then that compound did not experience breakthrough.

3.0 Equipment

3.1 Sampler - DuPont model P4000 or equivalent personnel sampler. Capable of adjusting and monitoring the flow over the range of 0.1 to 1 liter per minute (ℓpm) with a trap in place.

3.2 Mass flow meter - Portable unit equipped with a teflon fitting to measure the flow through a sampling trap. It should have a range of 0-2 ℓpm.

3.3 Sample traps - Glass sampling traps packed with the selected sorbent. See the procedure "Tenax Sample Trap Preparation and Screening".

3.4 Sampling line - 2-5 feet of 1/4" o.d. tygon tubing with a teflon fitting at one end to attach to the sampling traps.

3.5 Swagelok - 5/8" union.

4.0 Calibration Procedure

4.1 A mass-flow meter is used in line between the pump and the adsorbent traps to calibrate the pump before sampling begins at each station. The pump is rechecked with the mass-flow meter after the sampling period is complete.

5.0 Sample Collection

5.1 Sample tubes are packaged inside screw cap culture tubes placed in metal cans with a compression fit closure for transport to the field. The NEIC employs virgin paint cans for packaging. Using a clean tissue or wearing a nylon cloth glove, remove a numbered sample trap from its culture tube, and reseal the culture tube.

5.2 Inspect the trap for damage such as broken glass, loose glass wool plugs, or spilled resin. If the trap is damaged, replace in the culture tube and return to the laboratory unused.

5.3 Attach the tandem traps to the calibrated sampling pump. See Figure 1.

5.4 Begin sampling, noting the start time and sample pump flow meter reading. Select sample volumes so as to avoid breakthrough of target pollutants from the first trap to the second. For most purposes a 25-liter sample collected at 0.5-1.0 liters per minute is desirable.

5.5 Record the weather conditions occurring during sampling including temperature, wind speed and direction, humidity, and barometric pressure.

5.6 Stop sampling, noting the end time and sample pump flow meter reading. Replace the trap into a culture tube. Reseal with the teflon-lined septum cap and tag. Note on the tag the trap number and whether the trap was the front or back of the tandem pair. The front trap is the one sampled air passes through first.

5.7 Return culture tubes containing sample traps to the paint can and reseal the can. Be sure to tag the "field blank" sample in each can and any field spikes (will be total of at least three).

6.0 Quality Control

6.1 Sample pumps are calibrated daily. During sampling any flow rate changes are noted by monitoring the flow meter on the sampler. Changes in flow up to 10% are acceptable. If the change is greater than 5%, the beginning and ending flow rates are averaged to give the flow rate.

6.2 Triplicate samples indicate the reproducibility of the overall sampling and analysis. Triplicate samples will be collected at least at one sampling station. The triplicate sample station (or one of the duplicate sample locations) should be that station most directly downwind of the source being sampled. The triplicates should be collected at the same place, at the same flow rate and at the same time. It is very important to have the sampling as identical as physically possible.

6.3 Breakthrough spikes give an indication of which compounds would have broken through under the field conditions of the sampling. A breakthrough spike [Figure 2] consists of a tandem pair of traps, the front trap having been spiked with a standard set of compounds in the laboratory. A sample is then collected in the normal manner using the tandem traps. Duplicate breakthrough spikes should be sampled at the same time and rate as the regular field sample at the sample station most directly upwind of the source being sampled.

FIGURE 1: Tandem Air Sample Traps

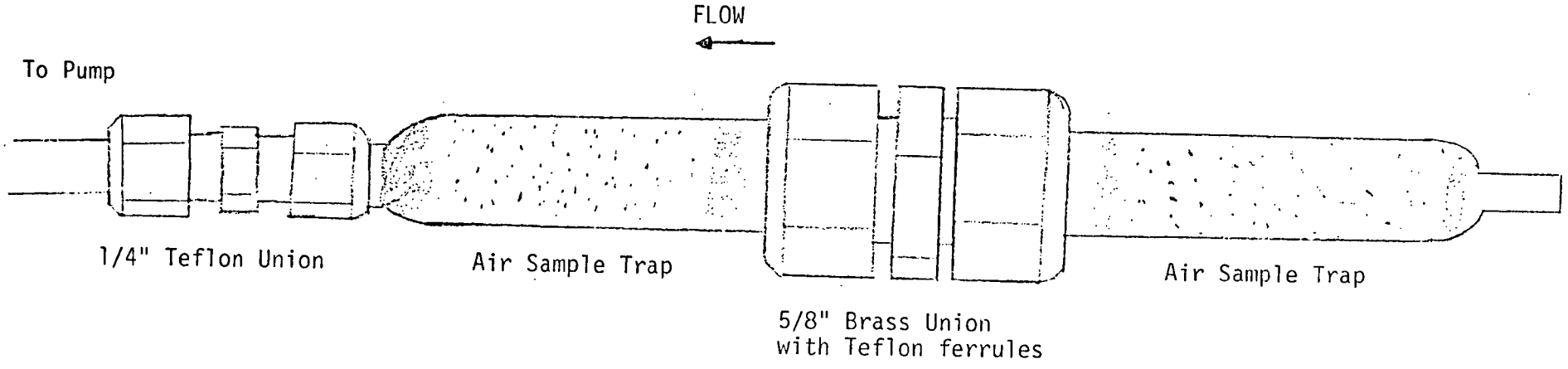


Figure 1. Tandem Air Sample Traps

FIGURE 2: Breakthrough Spike

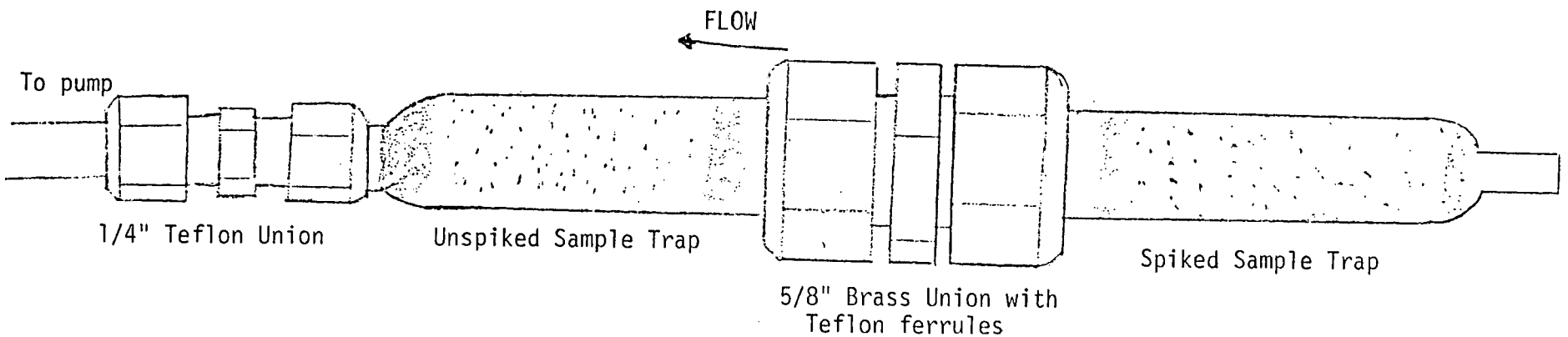


Figure 2. Breakthrough Spike

6.4 Contamination in each sample transport container (paint can) is monitored by a "field blank". A field blank is a sample trap which is not sampled. It is transported and stored the same as the samples. Field personnel designate the trap to be used as the field blank.

6.5 Deterioration of the samples is monitored by a "field spike". A field spike is a sample trap which is spiked in the laboratory prior to going out to the field. The field spike is stored and transported alongside the samples.

6.6 At the time laboratory personnel prepare the field and breakthrough spikes, they will prepare a reference spike which remains in the laboratory.

6.7 Samples can be stored in a dark, organic vapor-free area at -20° C for up to four weeks before analysis according to Reference 9.10.

7.0 Options

7.1 In the event of unknown atmospheres suspected of containing high levels of contaminants, two samples could be collected, one at the normal sampling rate, and another at one tenth the normal rate.

7.2 If specific compounds are of special interest, flow rates and sampling times may be changed (e.g., a compound with a high breakthrough volume, suspected in low concentrations might be sampled at 1 liter per min for 100 minutes).

7.3 If particulate matter may provide an unwanted contribution to sampled organics, filters are available which will prevent particulate greater than 0.5 um in size from reaching the sorbent traps (and thus being thermally desorbed when the trap is analyzed). Any filter must be used with the realization that organic compounds may be stripped from particulates on a filter by the sampled air flow, so that a total elimination of the contribution of organics from particulate is not possible. However, compounds stripped from particulates by the sampling process would have to be considered readily available for volatization, and would probably be of interest.

7.3.1 The filters used are sold commercially as filters for liquid chromatography solvents. The filters are Millex®-SR, Millipore Corp., Bedford, MA, Catalog #SLSR025NS, 0.5 um PTFE (polytetrafluoroethene). The PTFE filter itself is encased inside a hard plastic holder equipped with leur fittings. Other filter pore sizes are available.

7.3.2 The filters can be connected to sample traps by forcing one end of the plastic case directly into the quarter-inch end of the glass trap.

8.0 Sample Analysis

8.1 Samples are analyzed by the procedure *"Thermal Desorption and GC/MS Analysis of Air Samples"* (see Section C).

9.0 References

9.1 Bertsch, Wolfgang, Chang, Ray C. and Albert Zlatkis, *"The Determination of Organic Volatiles in Air Pollution Studies: Characterization of Profiles"*, Journal of Chromatographic Science, Vol. 12, pp 175-182, April 1974.

9.2 Pellizzari, Edo D., *"Development of Method for Carcinogenic Vapor Analysis in Ambient Atmospheres"*, EPA-650/2-74-121, July 1974.

9.3 Pellizzari, Edo D., Bunch, John E., and Ben H. Carpenter, *"Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres: Technique for Evaluating Concentration of Vapors by Sorbent Media"*, Environmental Science and Technology, Vol 9, pp 552-553, 1975.

9.4 Pellizzari, Edo D., *"Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors"*, EPA 600/2-75-076, November 1975.

9.5 Pellizzari, Edo D., *"The Measurement of Carcinogenic Vapors in Ambient Atmospheres"*, EPA 600/7-77-055, June 1977.

9.6 Pellizzari, Edo D., *"Analysis of Organic Air Pollutants by Gas Chromatography and Mass Spectroscopy: Final Report"*, EPA 600/2-79-057, March 1979.

9.7 Pellizzari, Edo D., *"Ambient Air Carcinogenic Vapors: Improved Sampling and Analytical Techniques and Field Studies"*, EPA 60012-79-081, May 1979.

9.8 *"Volatile Organic Air Pollutant Analysis - Permeation Tube Preparation and Calibration"*, NEIC, March 1983.

9.9 *"Volatile Organic Air Pollutant Analysis - Tenax Trap Preparation and GC Screening"*, NEIC, March 1983.

9.10 Pellizzari, Edo D., *"Analytical Protocol: Personal Monitoring of Vapor Phase Organic Compounds in Ambient Air (RTI)"*.

C THERMAL DESORPTION AND GC/MS ANALYSIS

ENVIRONMENTAL PROTECTION AGENCY
NATIONAL ENFORCEMENT INVESTIGATION CENTER
Box 25227, Denver, Colorado 80225

Volatile Organic Air Pollutant Analysis Using Tenax GC®, Thermal Desorption and GC/MS Analysis of Air Samples

March 1983

1.0 Introduction

This method describes the GC/MS analysis of the organic components of air samples collected on Tenax traps. The analysis depends on proper procedures for the preparation of Tenax traps, and for the collection of samples. Those procedures are documented as the NEIC methods "Volatile Organic Air Pollutant Analysis - Tenax Trap Preparation and GC Screening" and "Volatile Organics Air Pollutant Analysis - Sample Collection".

2.0 Summary of Method

Samples are collected by drawing a known volume of air through an adsorbent resin which traps organic components. The resin traps are analyzed by thermal desorption of the organics into a cryogenic trap which is subsequently flash-heated to transfer the compounds onto a GC column for GC/MS analysis.

3.0 Detection Limits

Detection limits for air samples depend on sample size, retention characteristics on Tenax, and the individual sample matrix, among other things, but can generally be expected to be in the range of 5 to 50 $\mu g/meter^3$ for a 25-liter sample size. Table 1 lists minimum amounts of representative compounds detectable by this thermal desorption/GC/MS procedure.

4.0 Limitations

4.1 Often, standard reference materials are not available and only tentative identifications of unknowns can be achieved.

4.2 Because of the long time required to prepare accurate permeation tube quantitation standards, a limited number of chemicals can be quantitated.

4.3 Quantitation may not be possible if breakthrough occurs during sampling. The sample traps are essentially short chromatographic columns. Retention of chemicals is dependent upon adsorption

---

® *Registered Trademark of Enka N.V., The Netherlands; appears hereafter without®.*

Table 1

GC/MS RESPONSE FACTORS AND DETECTION LIMITS FOR SELECTED COMPOUNDS

Compound	Spiking Level (ng)	Average Response Factor	%RSD*	Lower Limit of Detection (ng)
Hexafluorobenzene (IS)	2500	1.000	-	-
d_5-bromoethane (IS)	2500	0.867	6.4	-
Bromochloromethane (SU)	380	2.494	16.3	200
Bromopentafluorobenzene (SU)	1000	2.101	15.7	300
Benzene	630	3.668	16.4	200
Carbon Tetrachloride	1000	0.890	14.2	400
Chlorobenzene	400	3.146	18.3	100
1,2,4-trichlorobenzene	100	0.959	29.1	NA**
1,2-dichloroethane	900	1.056	17.5	300
1,1,1-trichloroethane	270	1.333	18.2	100
1,1-dichloroethane	620	2.431	18.3	200
1,1,2-trichloroethane	150	1.489	20.5	50
1,1,2,2-tetrachloroethane	160	1.694	26.4	200
Bis(2-chloroethyl)ether	75	1.548	23.8	20
Chloroform	1600	1.273	23.8	800
1,1-dichloroethane	2000	1.280	16.4	600
1,2-transdichloroethylene	4000	0.644	17.8	1000
1,2-dichloropropane	270	1.816	18.0	60
Ethylbenzene	160	5.024	15.0	20
Bromoform	100	0.643	16.2	NA
Tetrachloroethene	990	1.114	17.7	300
Toluene	320	4.694	16.6	100
Acetone	1000	1.076	21.4	700
Hexane	510	0.548	12.1	90
Trichlorofluoromethane	1600	1.139	15.3	500
n-Octane	50	6.549	19.6	NA
2-Chlorotoluene	70	4.595	20.7	NA

* *%RSD = Percent Relative Standard Deviation* = $\frac{STD\ DEV}{Average} \times 100\%$

** *Not Available*

characteristics of the chemical and the resin system. Some factors influencing retention include: temperature, flow rate, volume of air sampled, vapor pressure of the chemical, chemical class, presence of other chemicals, and batch-to-batch variation in the sorbent resin. Due to the many variables involved, predicting breakthrough is very difficult. Tandem tubes and breakthrough spikes are used in the field to determine if breakthrough has occurred. The sample size should be chosen to try to avoid breakthrough.

The breakthrough volume is defined as the amount of air which causes 50% of the collected chemical to be lost through the trap. Table 1 of the procedure "Sample Collection" lists breakthrough volumes compiled by Pellizzari in Ref. 12.8. The temperature was the only factor varied.

5.0 Equipment and Reagents

5.1 Thermal Desorber. Nu-Tech 320 or equivalent desorber with the following important features:

5.1.1 Capable of desorbing resin traps at 200-270° C.

5.1.2 Nickel cold trap able to be cooled to liquid nitrogen temperature (-196°) and then rapidly heated to 150-250° C. The upper temperature limit on the heated trap should be reached in less than 2 minutes.

5.1.3 Heated transfer line between nickel trap and GC oven.

5.2 Gas Chromatograph. Varian 3700 or equivalent equipped with linear temperature programmer, cryogenic cooling (liquid carbon dioxide or liquid nitrogen), and capillary column capability.

5.3 Capillary Column. 15M fused silica, DB-5 thick film (1 micron) column. Other capillary columns yielding the desired chromatographic separations may be used.

5.4 Packed Column (optional). 6' x 2 mm I.D. glass column packed with 60/80 mesh Carbo-pak C coated with 1% SP1000. Condition overnight at 220° C with 20 mℓ/min flow rate. Other packed columns may be used if chromatographic separation is satisfactory for the compounds of interest.

5.5 Mass Spectrometer capable of scanning from 35-350 a.m.u. in 1 second or less and with open-split or direct interface for capillary.

5.6 Data System. Finnigan INCOS or equivalent capable of acquiring and storing continuous repetitive mass spectra from the mass spectrometer. The system must be able to match unknown spectra to the EPA/NIH/MSDC mass spectral library and integrate

ions for quantitation. Automated processing of the data is desirable.

5.7 Culture Tubes. Pyrex glass screw cap tubes 25 mm x 150 mm. Pyrex 9825 or equivalent washed, dried, baked and fitted with Teflon-backed butyl rubber septa as described in Reference 12.10.

5.8 Pyrex glass wool. Prepared as in Reference 12.10.

5.9 Calcium sulfate or sodium sulfate. Anhydrous, non-indicating. Baked at 220° C for at least 1 hour prior to use.

5.10 5/8" Teflon Rod with ¼" drilled hole. Sized to hold Resin traps securely against septa of culture tubes.

5.11 Resin traps as described in Reference 12.10.

6.0 Instrument Conditions

6.1 Desorber

6.1.1 Block Temperature 220° C - 270° C. 220° is the usual operating temperature.

6.1.2 Desorber flow rate 15 mℓ/min helium.

6.1.3 Cold trap temperature -190° C (Reads approximately 160 on Nu-tech Model 320 thermal desorber).

6.1.4 Cryogenic trap desorb temperature 180° C.

6.1.5 Transfer line temperature 180° C.

6.2 Gas Chromatograph (fused silica capillary column).

6.2.1 Carrier (helium) pressure 14 psig.

6.2.2 Initial temperature -20° C.

6.2.3 Initial hold time 2 minutes.

6.2.4 Program rate 5° C/min.

6.2.5 Final temperature 220° C.

6.2.6 Final hold time 15 min.

6.2.7 GC/MS separator oven 240° C.

6.2.8 Make-up gas flow (for open split) 30 mℓ/min.

6.3 Gas Chromatograph (packed column)

6.3.1 Carrier (helium) flow rate 30 mℓ/min.

6.3.2 Initial temperature 60°.

6.3.3 Initial hold time 4 minutes.

6.3.4 Program rate 8° C/minute.

6.3.5 Final temperature 220° C.

6.3.6 Final hold time 15 minutes.

6.3.7 GC/MS separator oven 240° C.

6.4 Mass Spectrometer

6.4.1 Source temperature 220° C.

6.4.2 Mass Range 35 to 350. Other higher mass ranges may be used.

6.4.3 Scan time 0.95 seconds up, 0.05 seconds hold at the bottom of the scan.

6.4.4 Electron energy 70 eV.

6.4.5 Emission current 1.5 mA.

6.4.6 Line-of-sight inlet 230° C.

6.5 Sample Introduction Timing Sequence

6.5.1 Before sample introduction the desorber valve is in the desorb mode, the cold trap is at liquid nitrogen temperature and the sample desorbtion chamber is at operating temperature. Time zero is the time at which the GC temperature program is started.

6.5.2	t = -8 min 0 sec	Insert Resin trap into thermal desorber.
6.5.3	t = -0 min 15 sec	Turn on Ionizer.
6.5.4	t = 0 min 0 sec	Start GC oven program. Begin mass spectral data acquisition. Remove liquid nitrogen bath from the cold trap.
6.5.5	t = 0 min 30 sec	Begin heating nickel cold trap and switch to inject mode on desorber.

6.5.6	t = 2 min 30 sec	Turn off heat on nickel cold trap. Return desorber valve to desorb mode.
6.5.7	t = 65 min 0 sec	Analysis complete.

7.0 Procedure

7.1 At least 16 hours before analysis of a sample, traps should be dried. In an organic vapor free area, transfer Tenax resin traps to cool, clean culture tubes containing approximately 10 g anhydrous sodium sulfate or calcium sulfate. The desiccant should be held in place with clean glass wool. Securely cap the culture tube. This removes water adsorbed onto the Tenax during sampling. The culture tubes should be stored in a desiccator with activated charcoal adsorbent at room temperature. This step may be omitted if the humidity was less than 20% during sampling. Other drying techniques may be necessary with different resins which adsorb water more strongly.

7.2 Set up instrument conditions as described in Section 6.

7.3 Spike the trap with surrogate standards. See Section 9.

7.4 Spike the trap with 20 µℓ Internal Standard. See Section 9.

7.5 Begin analysis. Use the procedure described in 6.5.

7.6 After analysis is complete, output, and evaluate data.

8.0 Storage and Holding Times

8.1 Samples prior to the drying step are stored in a dark organic-free area and held at -20° C or less. (Ref.12.12).

8.2 The samples should be analyzed within 4 weeks of collection. (Ref.12.12).

9.0 Standards

9.1 Internal Standard (Static)

9.1.1 To a clean 300-mℓ glass gas sampling bulb prepurged with inert gas add 9.3 µℓ hexafluorobenzene and 10.3 µℓ d_5-bromoethane.

9.1.2 Maintain the bulb in a water bath at 30° ±0.1° C. The bulb should be in the water bath for at least 1 hour before sampling.

9.1.3 Withdraw 20 µℓ aliquots using a gas-tight syringe. Slowly inject into the center of the sample or standard trap. This injects 1000 ng of each compound. See calculations 9.1.3.1 and 9.1.3.2.

9.1.3.1 Hexafluorobenzene has a density of 1.607 g/mℓ or 1.607 mg/μℓ.

$$\frac{1.607\ mg}{\mu\ell} \times \frac{9.3\ \mu\ell}{300\ m\ell} \times 20\ \mu\ell \times \frac{10^{-3}\ m\ell}{\mu\ell} =$$

$$1.0 \times 10^{-3}\ mg = 1000\ ng$$

9.1.3.2 Bromoethane has a density of 1.4606 g/mℓ.

$$\frac{1.4606\ mg}{\mu\ell} \times \frac{10.3\ \mu\ell}{300\ m\ell} \times 20\ \mu\ell \times \frac{10^{-3}\ m\ell}{\mu\ell} =$$

$$1.0 \times 10^{-3}\ mg = 1000\ ng$$

9.2 Surrogate Standards (Dynamic)

9.2.1 Prepare permeation tubes of bromochloromethane and bromopentafluorobenzene using the procedure outlined in Reference 12.9.

9.2.2 Spike surrogates onto sample and standard tubes immediately prior to analysis. This is done by connecting the Tenax trap to the gas exit flow from the permeation chamber. Time to the nearest second the length of time that the trap has flow from the permeation chamber going thru it. This time (min) multiplied by the permeation rate (ng/min) gives the amount (ng) of each compound on the Tenax trap. The usual time is 3 min.

9.3 Mass Intensity Standard (Static)

9.3.1 A static standard of octafluorotoluene is prepared the same as the internal standard (Section 9.1). Use a 250 mℓ gas-sampling bulb and 7.5 μℓ octafluorotoluene. Injecting 20 μℓ of the gas from the bulb places 1000 ng of octafluorotoluene on the trap. See calculation 9.3.2.

9.3.2 Octafluorotoluene has a density of 1.663 mg/μℓ

$$\frac{1.663\ mg}{\mu\ell} \times \frac{7.5\ \mu\ell}{250\ m\ell} \times 20\ \mu\ell \times \frac{10^{-3}\ m\ell}{\mu\ell} =$$

$$1.0 \times 10^{-3}\ mg = 1000\ ng$$

9.4 Quantitation Standards (Dynamic)

9.4.1 Prepare permeation tubes of compounds to be quantified as in Sec. 9.2.1.

9.4.2 Spike standards onto blank resin traps for analysis using the procedure described in 9.2.2. Add surrogate standard and internal standard before beginning analysis.

9.4.3 The amount of material spiked onto the traps is controlled by how long the outflow from the permeation tubes is allowed to flow through the resin trap. This is a linear, reproducible relationship to times at least down to 1 min. Figure 1 shows the linearity typically achieved between FID area response and sampling time.

10.0 Quantification

10.1 Chemicals identified from their mass spectra may be quantified by comparison of the responses of the unknowns to the responses of known amounts of pure standards. The preferred method is the use of relative responses and internal standards.

10.2 Calibration is performed by analyzing a mixture of chemicals at known concentrations containing an internal standard (hexafluorobenzene for example) added at a fixed concentration. The instrument responses for selected ions are measured and compared for each component. A response factor is calculated for each component by:

Resp. fact. = Area x Ref. Amt/(Ref. area x amt.) (Eq. 1).
Where: (Resp. fact. = response factor)

Area = area of ion in component
Ref. Area = area of ion in internal standard
Ref. Amt. = amount of internal standard added
Amt. = amount of component

10.3 Quantification of identified chemicals is done by determining the areas of the appropriate ions and calculating the amount from equation 1 re-arranged:

Amt = Area x Ref. amt/(Ref. area x amt.) (Eq. 2).

11.0 Quality Control

11.1 A laboratory blank spiked with the surrogate and internal standards is run daily before the analysis of samples. If there is a response change between the surrogate and internal standard compounds the cause is investigated and corrected before analysis of samples. There should not be peaks in the blank which might interfere in the analysis. Tenax traps are easily contaminated by solvents and other volatile organics.

11.2 Octafluorotoluene is run daily before the analysis of samples as a check of mass-intensity calibration. (May be combined with laboratory blank.) Mass-intensity criteria for 1000 ng of octafluorotoluene are given on page C-10.

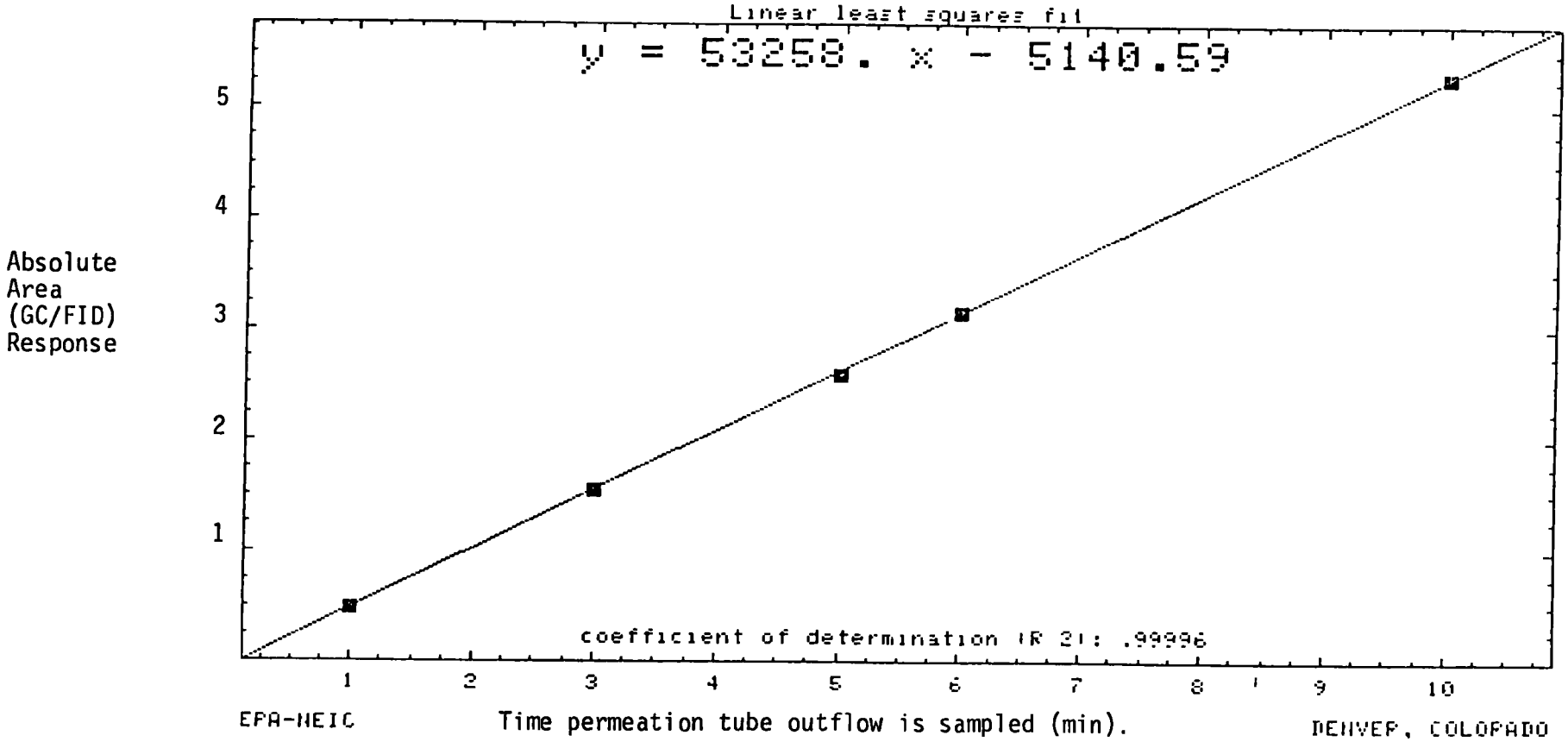


Figure 1. Typical linearity curve (area vs time)

m/Z	% Relative Abundance
69	30-60
79	5-15
93	10-30
117	40-65
167	10-25
186	55-85
217	100
236	60-85

11.3 Calibration of response factors is done daily at a mid-range concentration. Linearity is determined at least once during a set of analyses.

11.4 The response of the surrogate standards is monitored relative to the internal standard. Any significant deviation is investigated and proper corrective action is taken before other samples are run. It is very important to monitor this and correct problems immediately, since it is not possible to re-run a sample.

11.5 Air sample traps are easily contaminated. One sample trap per shipping container taken to the field will be tagged in the field as a field blank and returned with the samples to the laboratory for analysis.

11.6 Field spikes are air sample traps which have been spiked in the laboratory, taken to the field, tagged and returned to the laboratory. These spikes indicate sample deterioration due to shipping, handling and storage. Three field spikes or a number equal to 10% of the field sampling points, whichever is greater, will be analyzed.

11.7 Breakthrough spikes are air sample traps which have been spiked in the laboratory and subsequently sampled over in the field with a clean sample trap as the back-up in the tandem sampling arrangement [see Figure 2]. This spike indicates whether breakthrough of spiked compounds has occurred under field conditions. The breakthrough spike is done in duplicate at the upwind sampling point.

11.8 Table 1 lists typical response factors, percent relative standard deviations, and lower limits of detection.

11.9 Figure 3 is a typical chromatogram obtained using the 15 M DB5 capillary column.

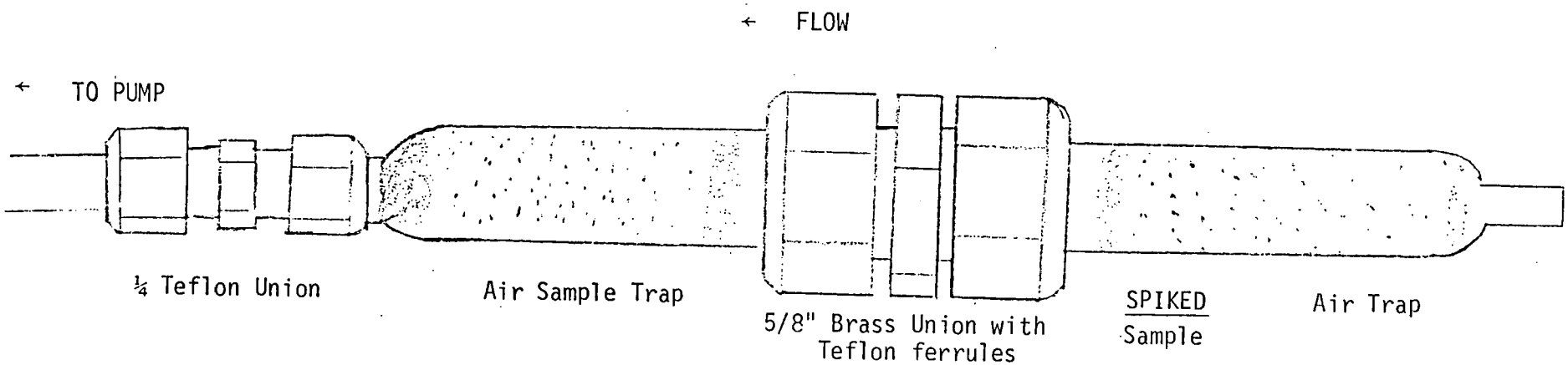


Figure 2. Breakthrough Spike

Table 2

IDENTITIES AND CONCENTRATION OF PEAKS IN FIGURE 3

Peak #	Compound	Amount (ng)
1	Carbon dioxide	***[1]
2	Trichlorofluoromethane	600
3	Acetone	980
4	trans-1,2-Dichloroethene	4000
5	Dichloromethane	***[2]
6	1,1-Dichloroethene	2000
7	1,1-Dichloroethane	620
8	Hexane	510
9	Hexafluorobenzene	2500
10	Tetrahydrofuran	***[2]
11	1,2-Dichloroethane	870
12	1,1,1-Trichloroethane	270
13	Octafluorotoluene	***[2]
14	Benzene (coelutes)	610
14	Methylcyclopentene (coelutes)	***[2]
15	Carbon tetrachloride	1000
16	Cyclohexane	***[2]
17	Methylhexane	***[2]
18	1,2-Dichloropropane	260
19	1,1,2-Trichloroethane	150
20	Toluene	380
21	Tetrachloroethene	950
22	Octane	***[2]
23	Chlorobenzene	380
24	Ethylbenzene	150
25	o-Chlorotoluene	***[2]
26	1,2,4-Trichlorobenzene	70
HC	Unidentified alkane/alkene	***

1 Carbon dixode is an artifact of the analysis. Identification is based on spectra and that it is an unretained compound.

2 New permeation tube; not calibrated.

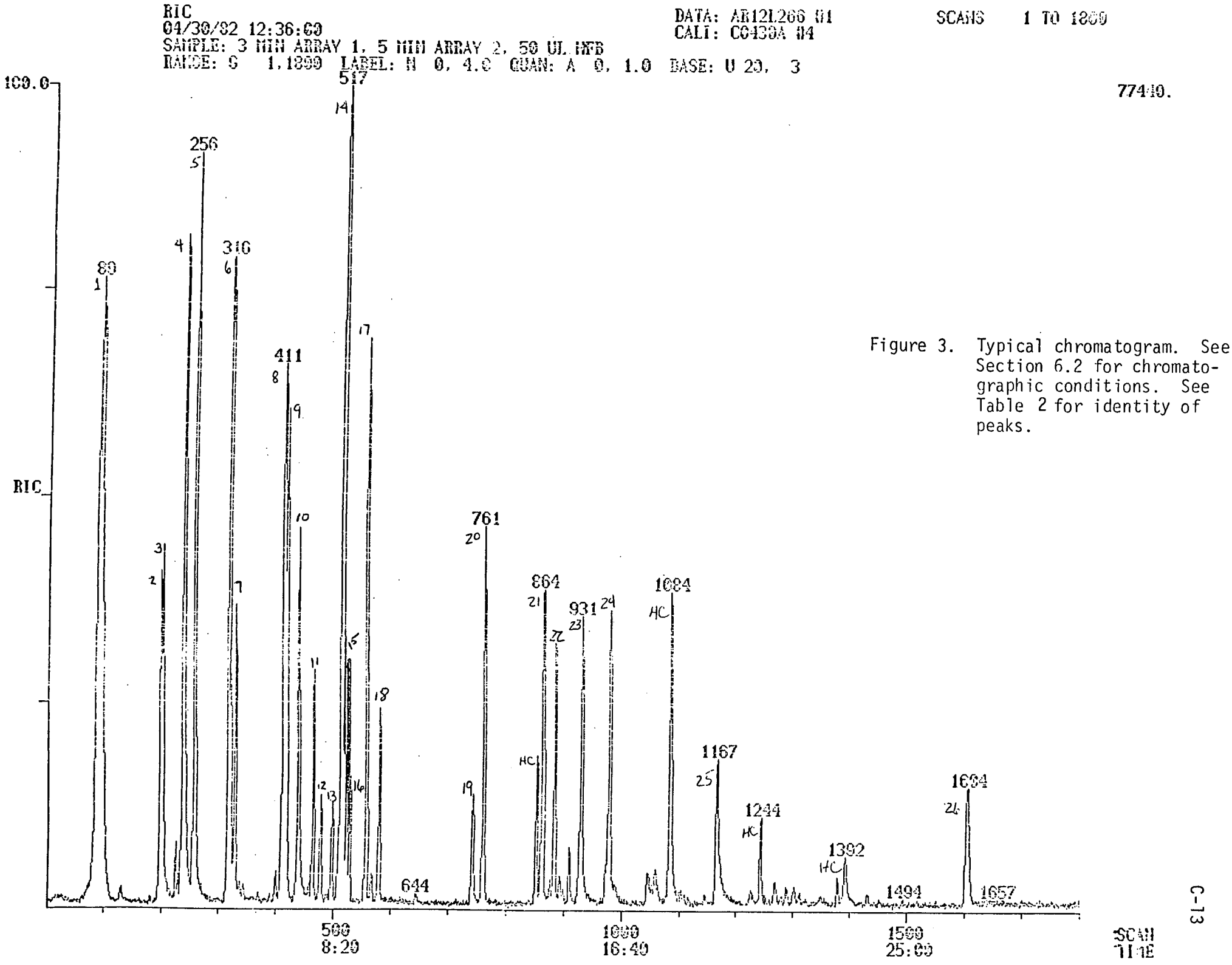


Figure 3. Typical chromatogram. See Section 6.2 for chromatographic conditions. See Table 2 for identity of peaks.

12.0 References

12.1 Bertsch, Wolfgang, Chang, Ray C. and Albert Zlatkis, *"The Determination of Organic Volatiles in Air Pollution Studies: Characterization of Profiles"*, Journal of Chromatographic Science, Vol. 12, pp 175-182, April 1974.

12.2 Pellizzari, Edo D., *"Development of Method for Carcinogenic Vapor Analysis in Ambient Atmospheres"*, EPA-650/2-74-121, July 1974.

12.3 Pellizzari, Edo D., Bunch, John E., and Ben H. Carpenter, *"Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres: Technique for Evaluating Concentration of Vapors by Sorbent Media"*, Environmental Science and Technology, Vol 9, pp 552-553, 1975.

12.4 Ibid, pp 556-560.

12.5 Pellizzari, Edo D., *"Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors"*, EPA 600/2-75-076, November 1975.

12.6 Pellizzari, Edo D., *"The Measurement of Carcinogenic Vapors in Ambient Atmospheres"*, EPA 600/7-77-055, June 1977.

12.7 Pellizzari, Edo D., *"Analysis of Organic Air Pollutants by Gas Chromatography and Mass Spectroscopy: Final Report"*, EPA 600/2-79-057, March 1979.

12.8 Pellizzari, Edo D., *"Ambient Air Carcinogenic Vapors: Improved Sampling and Analytical Techniques and Field Studies"*, EPA 60012-79-081, May 1979.

12.9 *"Volatile Organic Air Pollutant Analysis - Permeation Tube Preparation and Calibration"*, NEIC, July 1982.

12.10 *"Volatile Organic Air Pollutant Analysis - Tenax Sample Trap Preparation and Screening"*, NEIC, March 1983.

12.11 *"Volatile Organic Air Pollutant Analysis - Sample Collection"*, NEIC, March 1983.

12.12 Pellizzari, Edo D., *"Analytical Protocol: Personal Monitoring of Vapor Phase Organic Compounds in Ambient Air (RTI)"*.

D PERMEATION TUBE PREPARATION AND CALIBRATION

Volatile Organic Air Pollutant Analysis
Permeation Tube Preparation and Calibration
NEIC July 1982

1.0 Introduction

1.1 Primary standards are necessary to quantitatively analyze organic air pollutants. Standards are prepared by loading sampling traps with known amounts of chemicals from permeation tubes. This is accomplished by passing the effluent gas stream from a chamber containing calibrated permeation tubes onto sampling traps identical to those used in the field.

1.2 Permeation tubes are generally Teflon tubes containing a pure chemical, plugged to form gas tight seals at each end. The organic chemical then permeates through the Teflon tubing at a rate dependent upon the temperature and length of the tube. The rates are also dependent upon the chemical and vary over serveral orders of magnitude. The permeation rate is determined gravametrically.

2.0 Safety

2.1 Many of the compounds of interest in air analysis are toxic and/or carcinogenic. They are also volatile which increases the potential for exposure to the compounds. Persons preparing permeation tube standards must be aware of the hazards of the individual compounds handled, and use appropriate safety precautions. All permeation tubes should be prepared in a hood, in extreme cases other precautions may be necessary.

2.2 The permeation tubes slowly emit the standard compounds. The effluent from the permeation tubes should be routed through a charcoal trap and into a fume hood. When weighing the tubes, the analyst should keep handling to a minimum and avoid breathing fumes from the tubes.

3.0 Tube Materials

3.1 FEP Teflon Tubing. Fluorinated ethylene and propylene polymer tubing 1/4" o.d. and 0.03" wall.

3.2 TFE Teflon Tubing. Tetrafluoroethylene polymer tubing 1/4" o.d. and 0.03" wall.

3.3 Teflon Rod. Del-F rod 3/16" o.d.

3.4 Crimp band. 5/16" o.d. and 0.028" wall 316 stainless steel band 3/16" long.

3.5 Crimp tool. Nicopress 31-CJ tool to crimp to 1/4" o.d.

4.0 Permeation Chamber

4.1 Temperature bath. Recirculating heating/cooling bath capable of maintaining a temperature of 30 ± 0.1 deg. C.

4.2 Water Jacket. Glass water jacketed tube with Teflon screw-in plugs at ends. Typical dimensions 3 cm i.d. x 20 cm long.

4.3 Flow limiter. Stainless steel capillary tube capable of delivering 40-60 cc/min of N_2 from a 30 psig supply.

4.4 Switching valve. Teflon 2-way solenoid valve.

4.5 Charcoal Trap. Low back pressure trap filled with about 100 grams of charcoal.

5.0 Tube Preparation

5.1 Based on the data in Table I or experimental data, select tubing and cut to the desired active permeation length plus 2 cm.

5.2 Plug one end with 1 cm of FEP rod and crimp a metal band over it. Label the band with the chemical to be used.

5.3 Fill the tube to about 75% capacity of the active length. CAUTION: Some chemicals may be carcinogenic, toxic or hazardous. Toxic effects must be determined and all necessary precautions observed.

5.4 Insert another 1 cm FEP plug in the open end and crimp a band in place.

5.5 Visually inspect the tube for signs of leaking.

5.6 Place the tube in the permeation chamber and maintain at a constant temperature (typically 30°C). Condition for 2 weeks before beginning the calibration procedure.

6.0 Tube Calibration

6.1 Maintain the tubes at constant temperature with about 40-60 ml/min N_2 flowing over them, Measure changes by weighing the tubes every 2-4 weeks. Use a balance with ± 0.1 mg accuracy.

6.2 Before every weighing, weigh a class S standard weight and record its value. Changes greater than ± 0.2 mg require correction of the balance calibration and/or repair.

6.3 Record time, weight (g), weight change (g), elapsed time from last weighing (min) and rate (ng/min) for each tube in a permanent notebook. Calculate the permeation rate from biweekly weight changes (see section 7.1).

6.4 The rate has stabilized when 3 or more serial weighings have a percent relative standard deviation (see section 7.3) less than or equal to 10%. When the rate has stabilized, the tube is ready for routine use.

6.5 Monitor the weight changes of calibrated tubes every 4-6 weeks for the life of the tube.

7.0 Calculations

7.1 Average Rate

7.1.1 Rate:

$$\text{Rate} = \frac{\text{weight change (ng)}}{\text{minutes between weighings}}$$

7.1.2 Typically weight change is less than 10 mg and time between weighings is 20000-40000 minutes (2-4 weeks).

7.1.3 Average the last 5 stable rates.

7.2 Regression Rate

7.2.1 Tabulate the weight of the tube vs. time from the point the rate stabilized, or for the last 20 stable weighings.

7.2.2 Using least squares techniques, calculate the slope of the weight vs. time data. The slope is the permeation rate. Also calculate the correlation coefficient as an indication of the stability of the calibration data.

7.3 Percent Relative Standard Deviation (%RSD)

7.3.1 $\%RSD = \frac{\text{Standard Deviation}}{\text{Average}} \times 100\%$

7.3.2 The percent relative standard deviation should be 10% or less for stable tubes.

8.0 Other Permeation Devices

For special applications, other permeation devices may be used such as microbottles[1], permeation bags[2] or drilled rod[3].

9.0 References

1. O'Keefe, Andrew, Ortman, Gordon, C, Analytical Chemistry, 39, 1047 (1967).

2. Andrew, P., Wood, R., Chemistry and Industry, Dec. 28, 1968, 1836.

3. Scaringelli, Frank P., O'Keefe, Andrew E., Rosenberg, Ethan, Bell, John P., Analytical Chemistry, Vol. 42, 871 (1970).

4. Analytical Chemistry, 49, 1278 (1977).

5. "Measurement of Carcinogenic Vapors in Ambient Atomspheres", EPA-600/7-77-055, June 1977.

TABLE I

Compound	Cas #	Tube Type	Rate/length* ng/min/cm
Acetone	67-64-1	TFE	64
Acrylonitrile	107-13-1	TFE	88
Benzene	71-43-2	TFE	40
Bis(2-chloroethyl)ether	111-44-4	TFE	2
Bromochloromethane	74-97-5	FEP	25
Bromoethane-d_5	Not Available	TFE	170
Bromoform	75-25-2	TFE	4
Bromopentafluorobenzene	344-04-7	FEP	71
Carbon tetrachloride	56-23-5	TFE	20
Chlorobenzene	108-90-7	TFE	25
Chloroform	67-66-3	TFE	110
1,4-Dichlorobutane	110-56-5	TFE	4
1,1-Dichloroethane	75-34-3	TFE	40
1,2-Dichloroethane	107-06-2	TFE	58
1,1-Dichloroethene	75-35-4	FEP	64
1,2-trans-Dichloroethene	156-60-5	FEP	150
Dichloromethane	75-09-2	TFE	320
1,2-Dichloropropane	78-87-5	TFE	8
Ethylbenzene	100-41-4	TFE	10
Hexane	110-54-3	TFE	37
Tetrachloroethene	127-18-1	TFE	62
Toluene	108-88-3	TFE	26
1,2,4-Trichlorobenzene	120-82-1	TFE	4
1,1,1-Trichloroethane	71-55-6	TFE	9
1,1,2-Trichloroethane	79-00-5	TFE	9
Trichloroethene	79-01-6	TFE	200
Trichlorofluoromethane	75-69-4	FEP	100

*This should only be used as a guide. Each batch of tubing will be different.

E TENAX-GC® SAMPLE TRAP PREPARATION AND SCREENING

ENVIRONMENTAL PROTECTION AGENCY
NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
Box 25227 Denver Federal Center
Denver, Colorado 80225

Volatile Organic Air Pollutant Analysis
Tenax® Sample Trap Preparation and Screening
March 1983

1.0 Introduction

1.1 Sampling for organics in air is performed by drawing air through a glass tube packed with the porous polymer resin Tenax-GC. The traps and resin must be thoroughly cleaned before use to minimize the trap background. Clean traps ready for field use must also be carefully packed in clean glass tubes to avoid contamination during handling.

2.0 Materials

2.1 Glass sampling traps. Pyrex glass traps constructed as shown in Figure 1.

2.2 Resin. Tenax-GC, 35/60 mesh.

2.3 Glass wool.

2.4 Culture tubes. Pyrex glass screw cap tubes 25 mm x 150 mm. Pyrex 9825-20X or equivalent.

2.5 Teflon®-backed silicone septa. Pierce 12722 or equivalent.

2.6 Bakelite screw caps to fit culture tubes. Pierce 13219 or equivalent.

2.7 Desiccator. Glass desiccator with activated charcoal adsorbant.

2.8 Virgin gallon paint cans with pressure fit lids.

2.9 Polyurethane foam. Used for packaging of culture tubes to avoid breakage.

2.10 Teflon spacers made from 5/8" Teflon rod with ¼" drilled hole. Sized to hold traps securely against septa of culture tube.

3.0 Resin Preparation

3.1 Extract new and used Tenax-GC with methanol followed by pentane in a soxhlet extractor. Extract with each solvent 18 hours.

3.2 Dry the resin under vacuum for a least 6 hours.

® *Registered trademark; appears hereafter without the ®.*

3.3 Sieve the dried resin to the 35/60 mesh particle size range.

3.4 Seal the cleaned and sieved resin in a glass jar capped with a Teflon liner. Store in a desiccator containing activated carbon.

4.0 Trap and Container Cleanup

4.1 Wash new and used glass sampling traps and culture tubes with lab detergent and hot tap water. Rinse at least three times with organics-free water. Rinse with methanol and let air dry.

4.2 Bake the cleaned tubes in an oven at 220° C for at least 1 hour. Remove from the oven and store in a desiccator containing activated carbon.

4.3 Place glass wool in boiling water for 15 minutes. Remove glass wool from boiling water, drain, and place on absorbent paper towels to remove excess water. Rinse by dipping in acetone and placing in a soxhlet extractor. Soxhlet extract glass wool with methanol at least 8 hours, air dry and bake in an oven at 200° C for at least 1 hour. Spread the glass wool out in a baking dish and place in a muffle furnace at 450° C for 1 hour. Remove from the oven, cool and store in a desiccator containing activated charcoal.

4.4 Bake Teflon-backed septa in an oven at 80° C for 30 minutes. Remove from the oven and store in a desiccator containing activated charcoal.

4.5 Bake paint cans in oven at 100° C for 1 hour.

4.6 Sohxlet extract foam in methanol for 18 hours. Drain foam and dry under vacuum for 24 hours.

5.0 Trap Preparation

5.1 Pack about a 1-cm plug of glass wool into the trap and weigh it. Add about 7 cm of cleaned Tenax-GC. Lightly tap the trap on the bench to pack the resin. Weigh the trap and adjust the weight of the Tenax to 0.8 ± 0.02 gram by adding or removing small amounts of the polymer. Add another 1-cm glass wool plug to hold the resin in place.

5.2 Condition each trap by placing it in the bakeout manifold. The manifold is an apparatus which provides flow to six traps simultaneously and can be placed in a GC oven. Connect a ¼" to 1/16" reducing filter on the top of each trap and turn on the helium flow. Measure the flow on each trap to assure it is 20-30 mℓ/minute. Set the GC for bakeout conditions of 270° for 30 minutes. Set the oven initial temperature for cooldown to 35°. After cooldown, turn off the helium flow

and place the traps in culture tubes with Teflon spacers. Cap the culture tube using a Teflon-lined septum [Figure 1]. Record the bakeout batch number on each tube label.

5.3 Tubes are stored in desiccators containing activated charcoal until ready for shipment.

6.0 Screening

6.1 Screen at least one trap from each bakeout batch on a thermal desorber system connected to an FID-GC. Thermal desorber conditions are the same as those used for GC/MS analysis. Electrometer setting is 10^{-12} amps and attenuation 32. Label each chromatogram with a GC run number and store the chromatograms by ascending number for future reference. Figure 2 shows a typical acceptable screening chromatogram.

GC Conditions	Desorber Conditions
Column:	Temperatures:
Phase: DB-5 or Equivalent	Line: 150° C
Length: 15 meter	Block: 220° C
	Trap: 180° C
Injection Temp: 110° C	Time: 0:00 min. Desorb at LN_2 Temp. on the trap.
Detection Temp: 260° C	8 min. - Start GC and Integrator and Chart and Lower LN_2 bath.
Oven: Initial Temp. 35° C	8 min-30 sec. - Valve to Inject trap switch to heat.
Initial Time: 3 min.	10 min-30 sec. - Valve to desorb trap switch to cool.
Prog. Rate: 15 deg/min.	
Final Tem: 230° C	
Final Hold: 15 min.	
Cap Pressure: 10 PSI	

6.2 Mark the label on the culture tube with the GC run number of the screening chromatogram. If the trap is clean, the batch is acceptable for use.

7.0 Packaging for Shipment

7.1 Place culture tubes containing Tenax traps in special foam inserts in 1-gallon paint cans. Insert a charcoal-filled pouch around the top of the foam insert and pour a few drops of liquid nitrogen onto the foam. After a few seconds place the lid securely on the paint can. If excessive bulging of the can occurs, immediately remove the lid to release the nitrogen gas. Secure can lids with clips. Place a label on the can lid indicating the number and types of traps inside. Indicate the type of adsorbant and whether spikes or blanks are present.

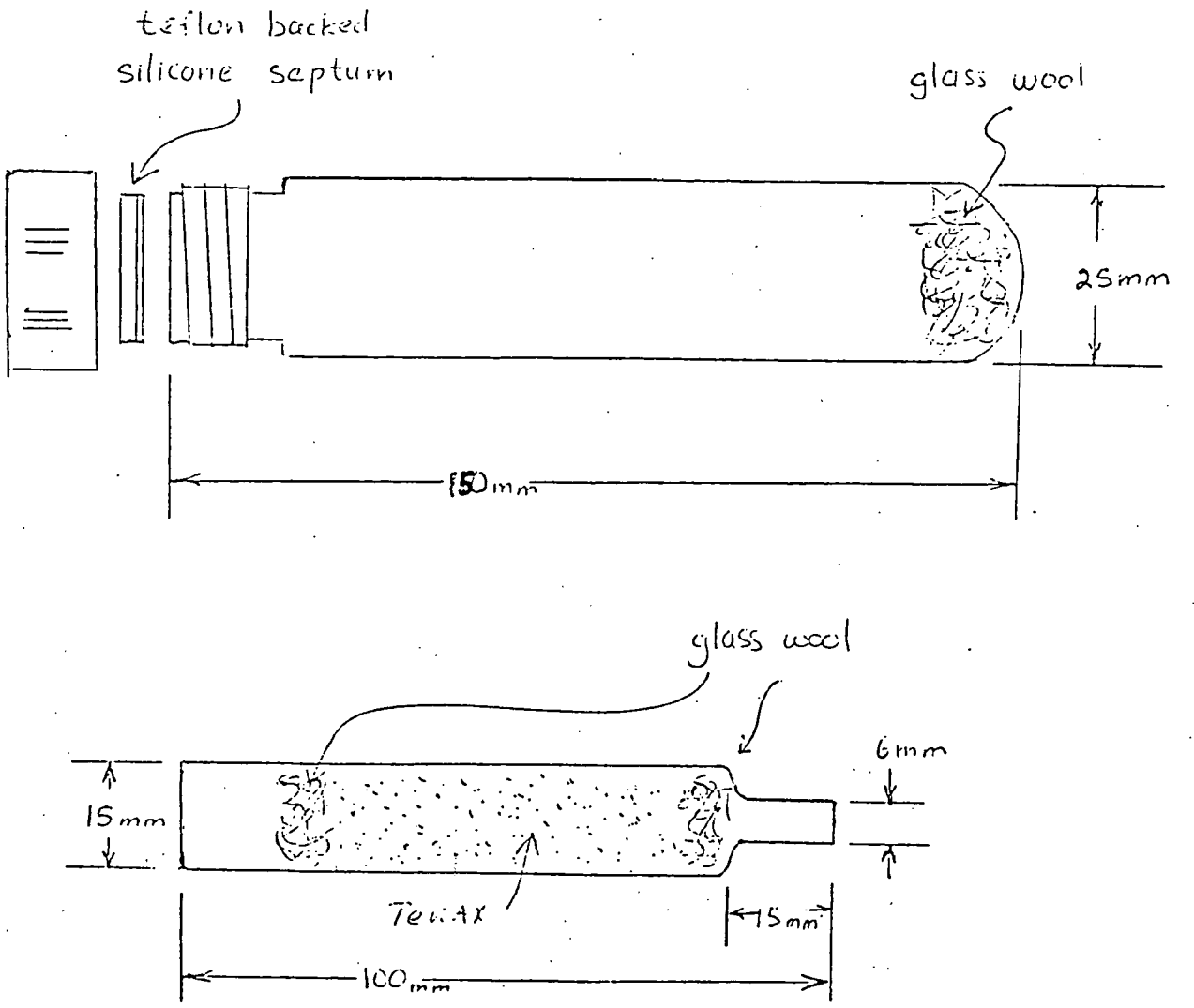
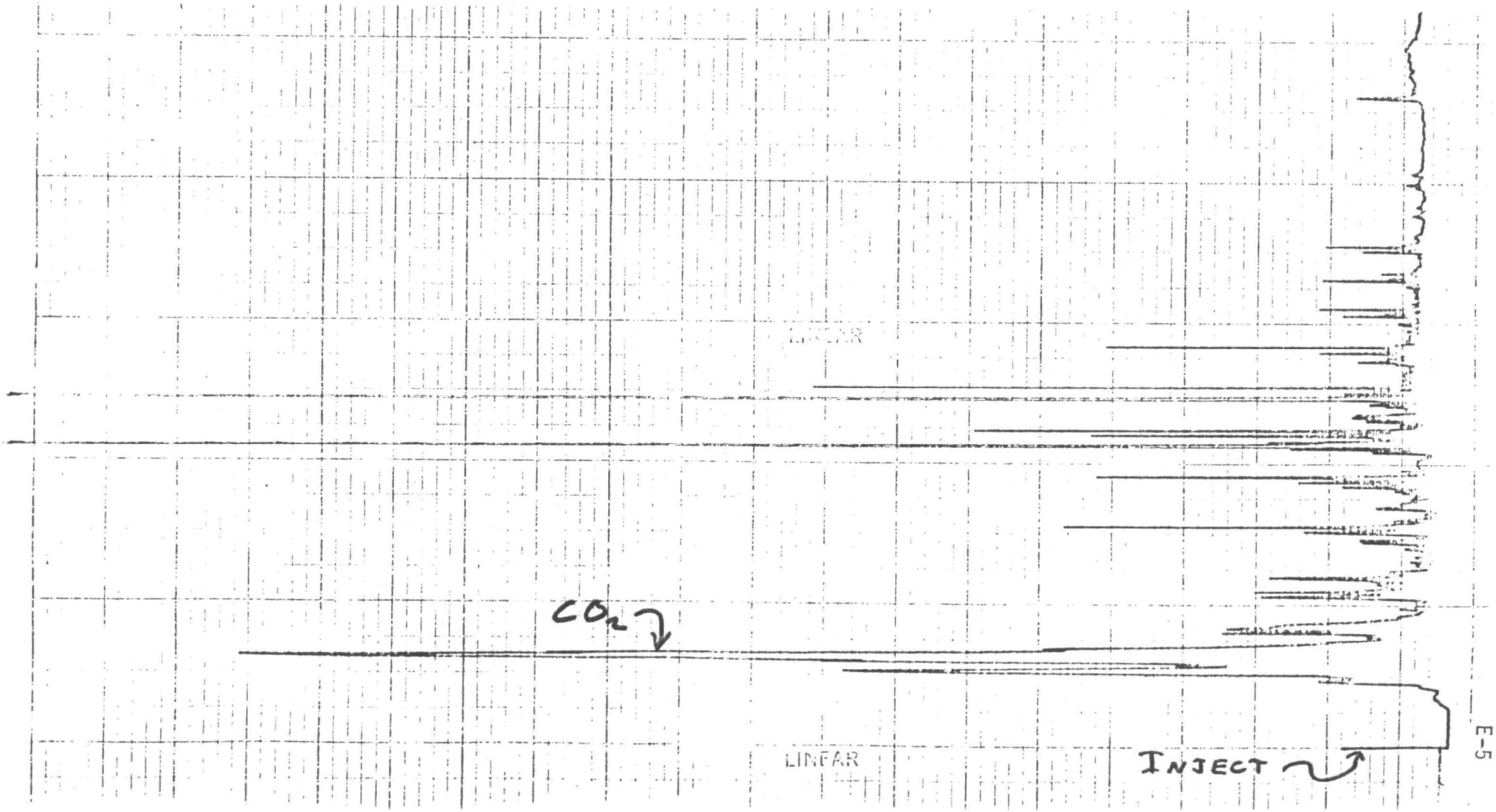


Figure 1. Sampling trap and culture tube holder design.

Figure 2. Typical FID screening of a Tenax trap after bakeout at 270°C. This result is acceptable for sample traps to be used for GC/MS analysis. Because of the difference in sensitivity between FID and MS, only the CO_2 peak would appear in an MS analyis. Chromatographic conditions are given in Sec. 6.1.



8.0 References

8.1 *"Selection and Evaluation of Sorbant Resins for the Collection of Organic Compounds"*, EPA-600/7-77044, April 1977.

8.2 *"Development of Method for Carcinogenic Vapor Analysis in Ambient Atmospheres"*, EPA-650/2-74-121, July 1974.