APPENDIX B

NEIC AIR AND WATER SAMPLING AND ANALYTICAL PROCEDURES

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ATTACHMENT 2 - [Air] Volatile Organic Pollutant Analysis, Permeation Tube Preparation and Calibration, January 1980

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ATTACHMENT B

Volatile Organic Air Pollutant Analysis
Sample Trap Preparation
January 1980

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 110 mm. Pyrex 9825 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 Dessicator. Glass dessicator with activated charcoal adsorbant.

2.8 Quart paint cans with pressure fit lids.

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 at least 6 hours.

3.2 Dry the resin under vacuum for at least 4 hours.

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 dessicator containing activated carbon.

4.0 Trap and Container Cleanup

4.1 Wash new and used glass sampling traps and culture tubes with lab soap and hot tap water. Rinse at least three times with organics free water (Millipore or equivalent). 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 dessicator containing activated carbon.

4.3 Wash glass wool with methanol, air dry and bake in an oven at 220°C for at least 1 hour. Remove from the oven and store in a dessicator containing activiated charcoal.

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

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

5.0 Trap Preparation

5.1 Pack about a 1 cm plug of glass wool into the trap followed by 6 cm of cleaned Tenax GC. Lightly tap the trap on the bench to pack the resin. Add another 1 cm glass wool plug to hold the resin in place.

5.2 Condition each trap at 270°C with 20-30 ml/min helium flowrate for 30 minutes.

5.3 Remove the hot trap and place into a culture tube with a glass wool plug to cushion the trap. Immediately cap the tube with a teflon lined septum cap. Store the tubes in batches of 7 traps in quart paint cans.

6.0 Quality Control

6.1 Prior to sending traps to the field, remove one trap from each paint can and analyze it for contaminants. If the traps are clean, the batch is acceptable for use. Mark the trap "Field blank - label and return" and replace it in the can.

6.2 Prior to sending traps to the field, remove one trap from each paint can and spike with known amounts of chemicals from the permeation tube system. Mark the trap "Field spike - label and return" and replace it in the can.

7.0 Options

7.1 Traps with longer resin beds may be packed in order to increase the retention volumes of pollutants.

8.0 References

8.1 "Selection and Evaluation of Sorbant Resins for the Collection of Organic Compounds", EPA-600/7-77-044, April 1977.

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

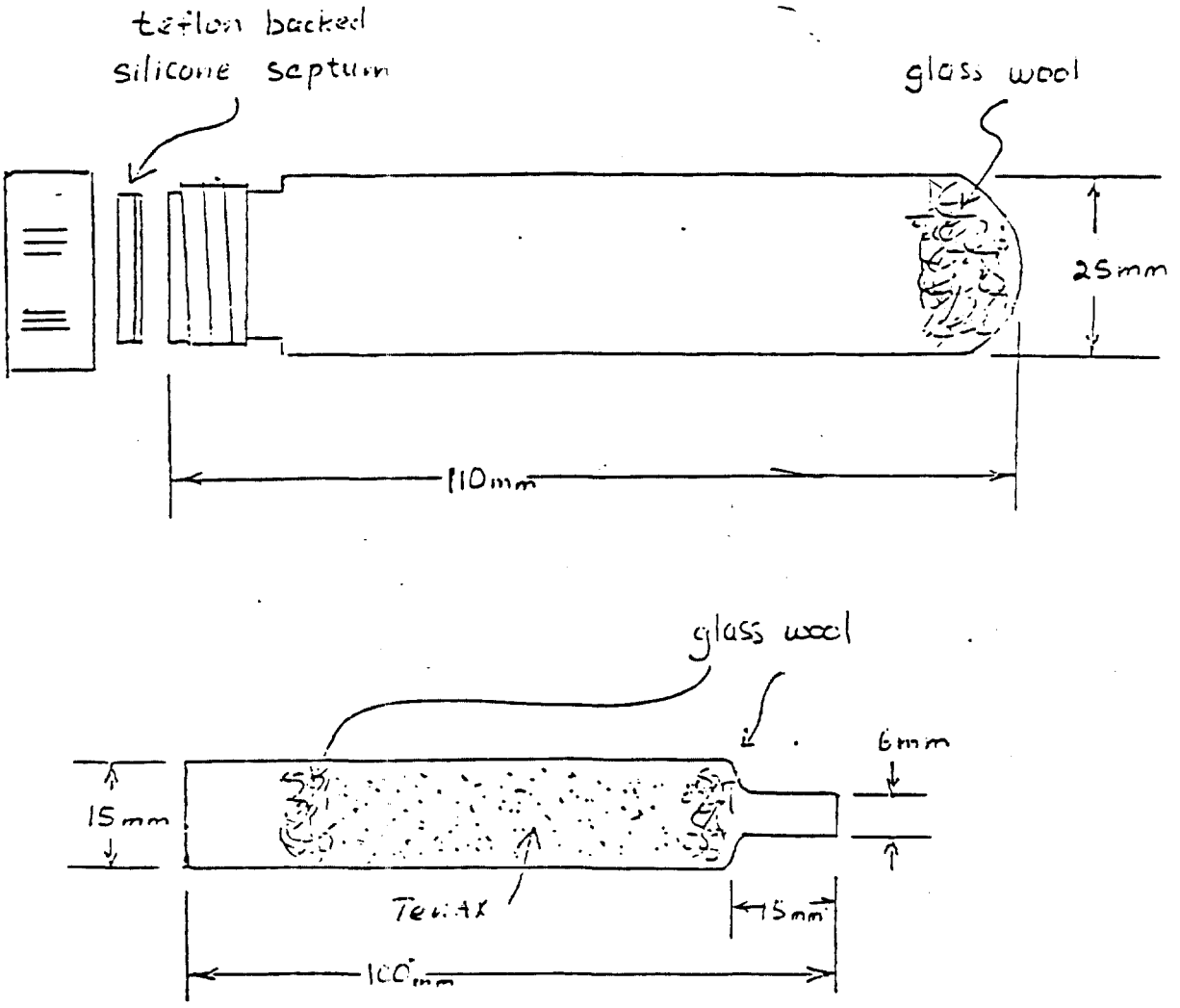

figure 1. Sampling trap and culture tube holder design.

ATTACHMENT 5
Volatile Organic Air Pollutant Analysis
Permeation Tube Preparation and Calibration
NEIC - January 1980

1.0 Introduction

1.1 Quantitative analysis of organic air pollutants requires sampling traps, identical to those used in the field, be loaded with known amounts of chemicals. Thse standards are most easily prepared by sampling the effluent gas stream from a chamber containing calibrated permeation tubes.

1.2 Permeation tubes are generally Teflon tubes containing a pure chemical and 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 several orders of magnitude.

2.0 Tube Materials

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

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

2.3 Teflon Rod. Kel-F roc 3/16" o.d.

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

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

3.0 Permeation Chamber

3.1 Temperature bath. Recirculating heating/cooling water bath capable of maintaining a temperature of 30 +- 0.1 deg. C.

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

3.3 Flow limiter. Stainless steel capillary tube capable of delivering 40 cc/min of N_2 from a 20 psig supply.

3.4 Switching valve. Teflon 2-way solenoid valve.

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

4.0 Tube Preparation

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

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

4.3 Fill the tube to about 75% capacity of the active length. CAUTION: Some chemicals may be carcinogenic, toxic or hazardous., Research its toxic effects and take the necessary precautions.

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

4.5 Visually inspect the tube for signs of leaking.

4.6 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.

5.0 Tube Calibration

5.1 Maintaining the tubes at constant temperature with about 40 ml/min N_2 flowing over them, measure changes by weighing the tubes weekly. Use a balance with +- 0.1 mg accuracy.

5.2 Before every weighing, weigh a standard weight and record its value. Changes greater than +- 0.2 mg requires correction of the balance calibration.

5.3 Record weight changes for each tube on the form in Figure 1. Calculate the permeation initial rate from the week to week weight changes (see section 6.1). After the rates stabilizes, the tube is ready for routine use.

5.4 Monitor the weight changes of calibrated tubes every 2 to 4 weeks for the life of the tube.

6.0 Calculations

6.1 Average Rate

6.1.1 Weekly rate:

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

6.1.2 Typically weight change is less than 10 mg and time between weighings is about 10000 minutes (about 1 week).

6.1.3 Average the weekly rates.

6.2 Regression Rate

6.2.1 Tabulate the weight of the tube vs. time from the point the weekly rate stabilized.

6.2.2 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.

7.0 References

7.1 Anal. Chem., 49, 1278 (1977).

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

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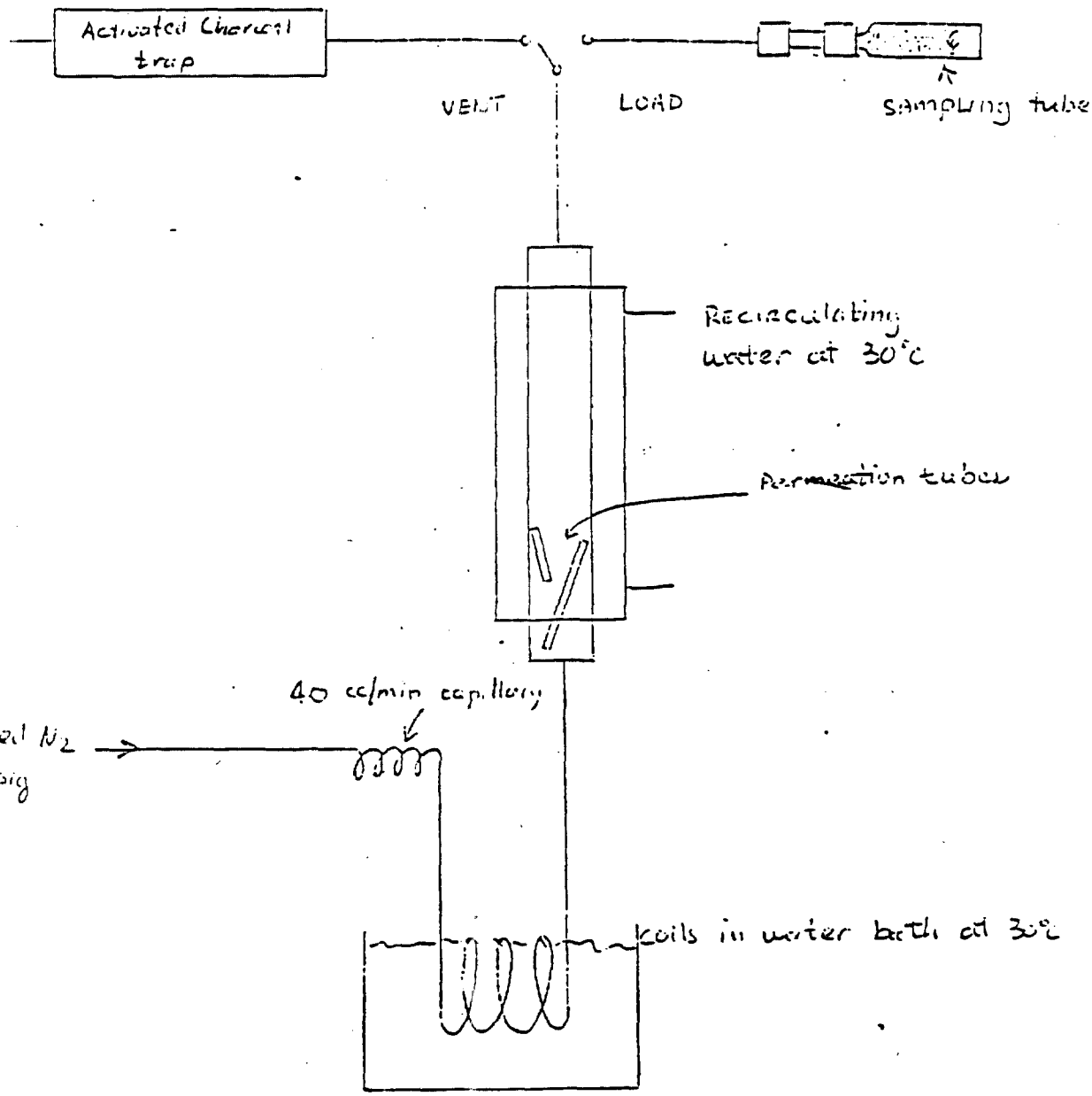


Attachment I. Permeation tube chamber schematic.

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. Air is drawn through each trap at 0.1 to 1 liter per minute using a calibrated personnel sampler. The sampler is calibrated before sampling using a mass flow meter.

2.0 Equipment

2.1 Sampler. MSA model S 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.

2.2 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 and 0 - 10 lpm.

2.3 Sample traps. Glass sampling traps packed with Tenax GC.

2.4 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.

2.5 Dummy Sampling Trap. One trap taken from the batch to be sampled.

3.0 Calibration Procedure

3.1 Attach the dummy sampling trap to the sample pump. Attach the mass flow meter over the inlet of the sample trap. Set the mass flow meter to the appropriate range and zero with no flow.

3.2 Start the sampling pump and adjust for a stable flow at the desired rate. Note the flow meter reading on the personnel sampler at the desired flow rate.

3.3 Record the mass flow meter reading and the sampler flow meter reading.

3.4 Detach the mass flow meter and the dummy trap.

3.5 Recalibrate the sample pump at the beginning of each sampling day, whenever the sample flow meter reading deviates from that at calibration or whenever necessary.

3.6 Flow rate variation between these traps is less than 5%.

4.0 Sample Collection

4.1 Using a clean tissue or wearing a nylon cloth glove, remove a sample trap from its culture tube being careful to reseal the culture tube.

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

4.3 Attach the trap to the calibrated sampler. See Figure 1.

4.4 Begin sampling noting the start time and sample pump flow meter reading. Collect sample volumes depending upon the suspected levels of contaminants. Generally:

Dumpsites: 1 lpm for 5-30 min.
Offsite: 1 lpm for 15-120 min.
Ambient: 1 lpm for 60-120 min.
or 1 lpm for 1-24 hr.

4.5 Stop sampling noting the end time and sample pump flow meter reading. Replace the trap into the culture tube being sure the glass wool cushions the trap. Reseal with the teflon lined septum cap and tag.

4.6 Replace sample traps in culture tubes into the tin can and reseal the can. Be sure to tag the "field blank" and "field spike" samples in each tin can.

5.0 Quality Control

5.1 Sample pumps are calibrated daily and any flow rate changes noted by monitoring the flow meter on the sampler.

5.2 Contamination in each sample transport container is monitored by a "field blank".

5.3 Deterioration of the samples is monitored by a "field spike".

6.0 Options

6.1 In the event of unknown atmospheres suspect of containing high levels of contaminants, two samples should be collected at flow rates of 1 and 1/10 or 1/100 rate (1 lpm and 10 ccpm for example).

7.0 Limitations

7.1 The sample traps are essentially short chromatographic columns. Retention of chemicals is dependant upon absorbtion characteristics of the chemical/resin system. Factors influencing retention include: temperature, flow rate, air volume and vapor pressure of the chemical. 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 conditons however. Table I lists breakthrough volumes for some relevant chemicals. The volumes represent the amount of air sampled where 50% of the collected chemical is lost through the trap. Data for chemicals where the sample volume exceeded the breakthrough volume represent at least that amount in the air.

8.0 References

8.1 "Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors", EPA-600/2-75-075, November 1975.

8.2 Env. Sci. Tech., 9, 556 (1975).

8.3 Pellizzari, E. D., Quarterly Report No. 1, EPA Contract No. 68-02-2262, February 1976.

8.4 Anal. Lett., 9, 45 (1976).

PREPARED 1/24/8 O.J. Logsdon Jr

Table I

Table A-2. TENAX GC BREAKTHROUGH VOLUMES FOR SEVERAL ATMOSPHERIC POLLUTANTS[1]

liters of air sampled

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 A-2 (cont'd.)

Table I cont

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
	acetopheonone	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 I cont

Table A-2 (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 I cont.

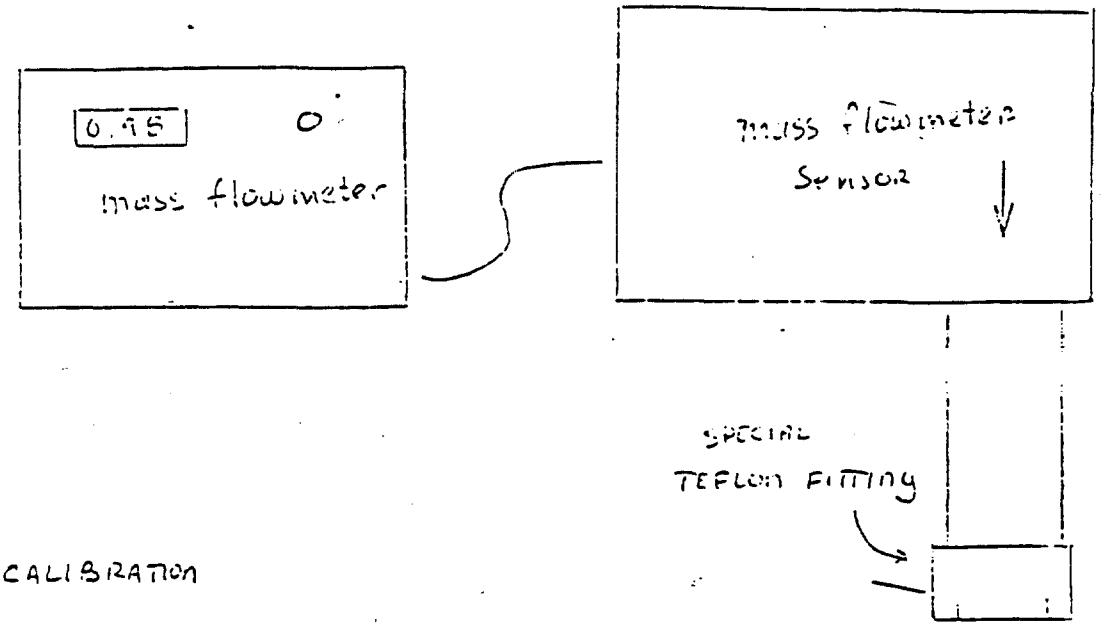
Table A-2 (cont'd.)

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.

from: EPA-560/13-79-010, September 1979
"Analytical Protocols for Making a Preliminary Assessment of Halogenated Organic Compounds in Man and Environmental Media".

Sample Collection



CALIBRATION

SAMPLING

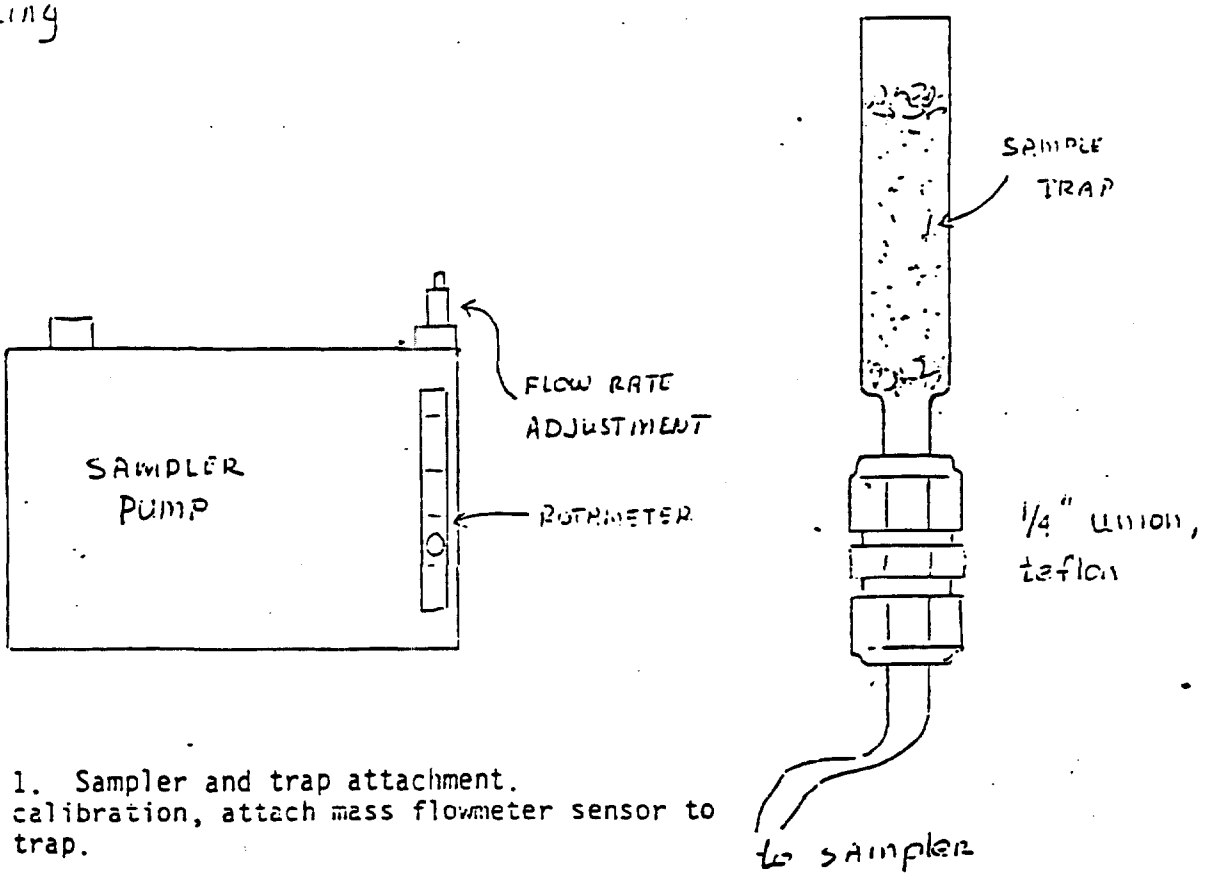


figure 1. Sampler and trap attachment.
During calibration, attach mass flowmeter sensor to top of trap.

ATTACHMENT 6
Volatile Organic Air Pollutant Analysis
GC/MS Analysis
January 1980

1.0 Introduction

1.1 Resin traps from field sampling are thermally desorbed using the technique described by Pellizzari into an analytical system consisting of a gas chromatograph (GC), mass spectrometer (MS) and computerized data system (DS).

1.2 Pollutants trapped on resin traps are thermally transferred to a nickel trap held at liquid nitrogen (LN_2) temperature. After transfer to the cold trap, the pollutants are rapidly transferred to the analytical GC column for analysis. Eluting GC peaks are analyzed by mass spectrometry. The spectra of the unknown GC peaks are compared to computer libraries of known spectra. Evaluation of spectra then leads to identification of unknowns. Identified chemicals are quantified by intergrating specific ions and referencing the response of standards of known concentrations.

2.0 Limitations

2.1 Often, standard reference materials are not readily available and only tentative identifications of unknowns can be determined.

2.2 Because of the long time required to prepare accurate quantification standards, a limited number of chemicals can be measured. The number of chemicals available shall increase as more standards are prepared and verified.

3.0 Equipment and Reagents

3.1 Thermal Desorber. Nutech 320 or equivalent desorber capable of describing sample traps at 200 to 300°C onto a nickel cold trap at LN_2 temperature (-196°C). Then capable of desorbing the cold trap at 150-250°C onto a GC column. See figure 1.

3.2 Gas Chromatograph. Varian 3700 or equivalent equipped with a linear temperature programmer and capability for packed and/or capillary columns.

3.3 Packed Column. 6' x 2 mm I.D. column packed with 60/80 mesh Carbopack C coated with 1% SP1000. Condition overnight at 220°C with 20 ml/min flowrate. Other packed columns yielding the desired separations may be used.

3.4 Capillary Column. 25 to 100 meter glass or metal SCOT (support coated open tubular) column coated with OV-101, SP-1000, CW-20M or SE30. Other phases yielding the desired chromatographic sep-

aration may be used.

3.5 Mass Spectrometer. Varian MAT-112S or equivalent (quadrupole mass spectrometers may be used as well) mass spectrometer capable of scanning from 35 to 350 amu in 3 seconds or less.

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

3.7 Culture tubes. Pyrex glass screw cap tubes 25 mm x 150 mm. Pyrex 9825 or equivalent washed, dried, and baked as described in reference (10.5).

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

4.0 Instrument Conditions

4.1 Desorber.

4.1.1 Block Temperature 220°C - 270°C
4.1.2 Desorb flowrate 15 ml/min
4.1.3 Cold Trap temperature -190°C (-150° on meter)
4.1.4 Trap desorb temperature 150°C

4.2 Gas Chromatograph (Packed Column)

4.2.1 Carrier (helium) flowrate 30 ml/min
4.2.2 Initial temperature 60°C
4.2.3 Initial hold time 4 minutes
4.2.4 Program rate 8°C/minute
4.2.5 Final temperature 220°C
4.2.6 Final hold time 15 minutes
4.2.7 GC/MS separator oven 230°C

4.3 Mass Spectrometer

4.3.1 Source temperature 220°C
4.3.2 Source pressure $\approx 4 \times 10^{-5}$ torr
4.3.3 Mass range 35-350 amu
4.3.4 Scan time 3 seconds
4.3.5 Electron energy 70 ev
4.3.6 Emission current 1.5 ma.

4.4 Overall Inlet Timing

t = 0, Insert trap, LN_2 trap at -150°C

t = 8 min. Start GC program and MS
t = 8 min., 30 sec. Start desorb and switch valve to inject
t = 10 min., 30 sec. Stop desorb and switch valve to desorb
t = 11 min. Switch off diverter
t = 11 min., 30 sec. Switch on ionizer
t = 38 min. Analysis complete

4.5 All GC/MS and acquisiton timing is shown in figure 2. Timing and parameters shown are for the exact equipment configuration described here and are set up for the computer to keep track of the timing.

5.0 Procedure

5.1 At least 16 hours before analysis of sample traps, carefully transfer each trap to clean culture tubes containing about 10 grams of anhydrous calcium or sodium sulfate. Cap the culture tube with a teflon backed silicone septum and place the tube in a dessicator with charcoal adsorbant. This operation removes water absorbed onto the Tenex during sampling.

5.2 Set up instrument conditions as described in section 4.

5.3 Spike the trap with 25 ul of the internal standard as prepared in section 6.

5.4 Begin the analysis by inserting the trap into the desorber. Proceed as specified in 4.4

5.5 After the analysis is complete, proceed with data output and evaluation.

6.0 Internal Standards

6.1 Static Standard

6.1.1 To a clean 300 ml glass gas sampling bulb filled to atmospheric pressure with N_2, add 5.0 ul of perfluorobenzene.
6.1.2 Mix the contents of the bulb by shaking with glass beads inside.
6.1.3 Maintain the bulb in a waterbath at 30°C.
6.1.4 Withdraw 25 ul aliquotes using a gas tight syringe for injection onto sampling traps.
6.1.5 Perfluorobenzene has a density of 1.607 g/ml at 25°C. 5 ul = 8.035. 8.035 mg in 300 ml = 26.78 ng/ul. 25 ul times 26.78 ng/ul = 670 ng.

6.2 Dynamic Standards

6.2.1 Prepare permeation tubes for the standards of interest. After stabilization, load traps with known amounts of the

internal standards.

7.0 Standards

7.1 Static Method

7.1.1 Using the same procedure as in 5.1, prepare standards as needed. Calculate the concentrations based upon the density and amount of chemical added and the volume of the container.

7.1.2 Inject aliquots of these standards onto traps for analysis.

7.2 Dynamic Method

7.2.1 Prepare permeation tubes and calibrate as described in reference (10.6).

7.2.2 Load traps with various known amounts of these standards for analysis.

8.0 Quantifications

8.1 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.

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

Resp. fact. = Area * Ref. Amt/(Ref. area * 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.

8.3 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 * Ref. amt/(Ref. area * amt.) (eq. 2)

9.0 Quality Control

9.1 Calibration of response factors is done daily at a midrange con-

centration. Linearity of response is determined at least once during a project.

9.2 Laboratory blanks are run with each day's analysis.

9.3 The response of the internal standard is monitored from run to run. Any deviations outside past ranges are investigated and the sample re-run if possible.

9.4 Table I lists typical response, precision, and recovery data.

10.0 References

10.1 ES&T, 9 (6), 552 (1975).

10.2 ES&T, 9 (6), 556 (1975).

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

10.4 "The Measurement of Carcinogenic Vapors in Ambient Atmospheres", EPA-600/7-77-055, June 1977.

10.5 "Volatile Organic Air Pollutant Analysis", NEIC, January 1980.

10.6 "Volatile Organic Air Pollutant Analysis - Permeation Tube Preparation and Calibration", NEIC, January 1980

O.H. Langston II

Organic Air Pollutants - GC/MS Analysis

Name	Response Factors[a] Mean	% Std. Dev.	Precision[c] % difference	Recovery[d] % Recovery
Methylenechloride	0.82	11	7.4	85
Acetone	0.59	20	2.7	96
Trans-1,2-dichloroethylene	1.37	18	1.6	88
Chloroform	1.62	3.8	4.1	90
1,2-dichloroethane	1.04	3.8	4.1	88
Trichloroethylene	0.83	4.3	3.3	98
Benzene	2.33	3.2	2.7	94
Hexane	1.81	8.4	19.7	114
Toluene	2.57	3.7	5.2	92
Chlorobenzene	1.84	9.6	3.2	98
Ethylbenzene	4.13	6.4	12.2	87
Perfluorobenzene[b]	1.0	NA[e]	NA	NA

[a] Ranges as low as 5 ng to over 3200 ng

[b] Internal reference standard

[c] Measured from two injections of standards at mid range concentrations.

[d] Measured from sample trap spiked with standards, transported to field, returned and analyzed 3 weeks after spiking.

[e] Not applicable

Table I. Summary of Typical response, precision and recovery data.

ATTACHMENT 5

Organic Characterization and Priority Pollutant Procedures

Sample Preparation

Water Samples - Extractables:

Samples were extracted with CH_2Cl_2 at a basic pH to extract neutrals and bases and then at an acidic pH to extract acids (phenols). The extracts were dried and filtered by passing over anhydrous Na_2SO_4 and concentrated to 5-10 ml in a Kuderna-Danish (K-D) apparatus, then concentrated to 1 ml under a gentle stream of purified air. The concentrated extracts were sealed in 1 ml serum vials and stored in a refrigerator until analysis. This procedure is in the method "Adjusted pH Extraction Technique for Organics Analysis, NEIC - January 1979". To monitor the general performance of the method, each sample was spiked with 300 ug/l of α, α, α-Trifluoro-m-cresol and 100 ug/l of D_{10}-Biphenyl. These "surrogate" spike recoveries were monitored to show the overall efficiency of the preparation procedures.

Analytical Procedures

Volatile Organics Analysis:

An aliquot of sample was purged with an inert gas and the volatile organics were then trapped on a porous polymer resin trap. The trapped organics were then thermally desorbed onto an analytical GC column. The components were separated and mass spectra were obtained as they eluted from the column. Components were identifed by comparison of their mass spectra to the spectra of standards. The specific procedure is detailed in "Volatile Organics by GC/MS, NEIC - March 1980".

Extractable Organics:

An aliquot of sample extracts, in acetone, was injected into a gas chromatographic column. The eluting components were detected by a mass spectrometer. Identifications were made by comparison of the sample mass spectra to the mass spectra of pure compounds within specific GC retention-time windows. Quantification was by measurement of the area of specific ion fragments of each component. Retention time and response references were made to the internal standard. The detailed procedure is in "Base/Neutrals, Acids, and Pesticides - Method 625", Federal Register, Monday, December 3, 1979. Starting at section 11.

Quality Control

Volatile Organics Analysis:

The precision of technique was measured using the PPG-01-01 duplicate sample. Results are in "Volatile Priority Pollutants Quality Control Report". An aliquot of the same sample was spiked with known amounts of chemicals and their recoveries measured. The same table shows the results. All the samples were screened for an additional compound (acetonitrile). The lower limit of detection was 200 ug/l.

Extractable Organics:

The precision of technique was measured using the DuPont-01-01 duplicate sample. These samples were also spiked with known amounts of chemicals and their recoveries measured. Table "Organic Priority Pollutants Quality Control Report" shows the results.

ATTACHMENT E - INORGANIC ANALYTICAL METHODOLOGY

Parameter	Methodology	Reference
CN	Manual Distillation Colorimetric	#1, Method 335.2
As, Sb, Se, Tl	HNO_3/H_2O_2 Digestion Furnace Atomic Absorption	#1, Methods 206.2, 204.2, 270.7, and 279.2
Hg	$KMnO_4/K_2S_2O_8$ Digestion Cold Vapor Atomic Absorption Spectroscopy	#1, Method 245.1
Other Elements	HNO_3/HCl Digestion Inductively Coupled Argon Plasma Atomic Emission Spectroscopy	#2

* #1: Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020.
#2: Federal Register Vol. 44, No. 233, p. 69559, Appendix IV.

0.12.1.5

ATTACHMENT 7

Vinyl Chloride in Air - Charcoal Tubes
NEIC - January 1979

1.0 Introduction

1.1 This method is applicable to the measurement of vinyl chloride monomer (VCM) in ambient and contaminated atmospheres. Other volatile organic pollutants may be measured by adjusting the sampling and analytical conditions.

2.0 Summary of Method

2.1 VCM that has been trapped on charcoal is extracted with carbon disulfide. The extract is analyzed by flame ionization detector (FID) gas chromatography (GC) and VCM identified by the GC retention time. The amount is determined by comparision of the GC peak response to the response of standard solutions of VCM.

2.2 Samples containing concentrations of VCM above about 0.005 mg/sample should be verified by GC-mass spectrometry (MS).

2.3 This method is based on the "Vinyl Chloride In Air" analytical method described by NIOSH in reference 1.

3.0 Interferences

3.1 Because routine identification of VCM is done by GC retention time, unidentified chemicals having the same GC retention time will interfere. Samples of the atmosphere being tested should be checked, prior to routine analysis for interfering peaks. Chromatographic parameters may then be optimized for the particular sample type. GC/MS verification will reduce the possibility of errors. Analysis of samples collected from an atmosphere of VCM in air yielded average contrations of 86.5 and 73.5 ppm at 0 and 100% relative humidity respectively.

4.0 Range and Sensitivity

4.1 Standard solutions of VCM were analyzed using the conditions described in this method. The measured areas were linear (correlation coefficient R greater than 0.999) over a range of 0 - 0.050 mg/sample.

4.2 Typically, no background above 25 counts is detectable near the GC retention time of VCM. Amounts as low as 0.45 ng/ul (0.00045 mg/sample) have been detected. The detection limit is thus at least 0.09 ppm in air, if 2 ℓ of air are sampled.

5.0 Apparatus

5.1 Charcoal traps: Glass tubes packed with 2 sections of activated coconut shell charcoal. Available from SKC Inc., Eighty Four, PA 15330. See reference 1 for exact specifications.

5.2 Gas chromatograph: Hewlett-Packard 5700 or equivalent equipped with a flame ionization detector, automatic sampler and electronic peak integrator.

5.3 GC column: 10 ft. x 1/8 in. stainless steel packed with 60/80 mesh Gas-Chrom Q coated with 10% OV101 followed by 20 ft. x 1/8 in. stainless steel packed with 80/100 mesh acid washed DMCS Chromosorb W coated with 10% FFAP. Other columns may be performing the desired separations.

5.4 Vials: 1 ml with septum seal aluminum crimp caps.

5.5 Pipet: 1.0 ml glass delivery pipet.

5.6 Syringes: 10 ul, 50 ul and 100 ul for preparation of standards.

5.7 10 cc/min air stainless steel capillary tube for delivery of pure VCM.

6.0 Reagents

6.1 Analytical Reagent Grade carbon disulfide (CS_2). Each bottle must be checked for background prior to use.

6.2 Vinyl chloride monomer, lecture bottles 99.9% purity.

6.3 Analytical Reagent grade toluene.

7.0 Standards Preparation

7.1 Concentrate - Add 5.0 ml of toluene to a 10 ml volumetric flask and weigh to the nearest 0.1 mg. Attach the stainless steel capillary tube to the VCM lecture bottle and place the open end into the toluene. Open the cylinder and bubble VCM into the toluene for about 5 minutes.

Reweigh the flask and determine the amount of VCM added from the increase in weight. Dilute the solution to 10 ml with carbon disulfide. The concentration of this solution should be about 10 mg/ml.

7.2 Diluted solutions are prepared by adding ul aliquots of the concentrate to 1.0 ml of carbon disulfide in vials.

7.3 Mark the liquid level, label and store all standards in a freezer at -20°C. The concentrated solutions should be stable at least 2 weeks.

7.4 Caution - VCM has been identified as a human carcinogen and appropriate precautions must be taken in handling the gas. See the Federal Register, Vol. 39, No. 194, Friday, October 4, 1974, pp 35390-35398.

8.0 Sample Analysis

8.1 Prepare each sample by carefully breaking open the charcoal trap above the glass wool. Remove the glass wool and carefully dump each section of the charcoal into two vials. Using a pipet, add 1 ml of CS_2 to each vial and seal. Label each vial with the sample number and F or B for front and back respectively. Shake and let stand 30 minutes before analysis. Samples should be prepared on the same day as analysis if possible. But may be stored in a freezer at -20°C overnight if necessary.

8.2 Analyze the samples by injecting 1-2 ul into the GC. Typical conditions are as follows:

1. 150°C injector temperature
2. 65°C initial column temperature
3. 4 minutes hold time
4. 10°C/min program to 180°C
5. 12 minute hold
6. 30 ml/min carrier flow rate

8.3 An automated peak identification and quantification method for the Hewlett-Packard 3353 data system is shown in Table 1.

8.4 At least 3 standards covering the range of the analysis must be analyzed to establish the standard curve. After linearity is determined, a single point calibration may be used.

Table 1 - Automatic integration parameters for HP 3353:

```
M:  VCM                  8 JAN,    79    15:29
    1,  ESTD, ME, T1,  NO,   NO,
  JG     , PROJ. 615 CHAR. TUBES
   50,   29.00, YES
   25,    .015,  0.00,  0.00
    .30,     2,     25, 0.0000E+ 0
    2
  7.32,  4.5000E+ 1,  1.1839E- 3, VINYL CHLO
 11.21,  0.0000E+ 0,  0.0000E+ 0, #SOLVENT
```

9.0 Quality control

9.1 Collection efficency: 12 samples of VCM at 94 ppm were collected in dry air at 100 ml/min sampling rate. The resultant recoveries were 104 and 81%.

9.2 Because the entire sample is used for analysis, no duplicates can be prepared. Duplicate injections can, however, be made to verify the instrument response and 10% of the injections should be repeated.

9.3 Samples containing more than about 0.005 mg/sample should be analyzed by GC/MS to verify that VCM is indeed the GC peak being measured.

10.0 Calculations

10.1 A response is calculated using two variable regression analysis or plotted on graph paper. If the responses are linear, a one point calibration in the middle of the working range may be used to determine the slope.

10.2 The total concentration (mg/sample) is the sum of the front and back trap amounts.

10.3 The air concentration may be calculated as follows:

$$mg/m^3 = \frac{mg/sample \times 1000\ l/m^3}{air\ volume\ sampled\ l}$$

Or, the concentration in ppm at standard conditions may be calculated:

$$ppm = mg/m^3 \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T+273)}{298}$$

Where: P = pressure in mm Hg during sampling
T = temperature in °C during sampling
24.45 = molar volume at 25°C and 760 mm Hg
MW = molecular weight of chemical
760 = standard pressure in mm Hg
298 = standard temperature in °C

11.0 References

(1) "Vinyl Chloride in Air", NIOSH Manual of Analytical Methods, (Volume 1), Dept. of Health, Education and Welfare, April 1977.