UTILITY OF SOLID SORBENTS FOR SAMPLING ORGANIC EMISSIONS FROM STATIONARY SOURCES

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UTILITY OF SOLID SORBENTS

FOR SAMPLING ORGANIC EMISSIONS

FROM STATIONARY SOURCES

by

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ABSTRACT

This report presents the results of a study designed to assess the utility of porous polymer adsorbents as a means for sampling and concentrating trace organic emissions from stationary sources. Emissions were sampled from two industrial field sites employing Tedlar bags. The bags, in turn, were sampled employing small porous polymer sampling tubes backed up by a cryogenic thermal-gradient sampling system to assess the efficiencies of adsorption of the trace organic species. In addition to the experimental results, conclusions and recommendations, a detailed statement of the problem of sampling trace organics in industrial emissions is presented in the Appendices. This later discussion includes a presentation of (1) the characteristics of stationary sources emitting organic species; (2) an assessment of present sampling techniques for trace organic emissions; (3) a review of the use of porous polymer adsorbents in sampling; and (4) the characteristics of porous polymer sorbents and their potential limiting properties.

It is concluded that the use of porous polymer adsorption tubes can serve as a convenient means for concentrating a range of higher boiling (B.P. >120°C) trace organic emissions in a highly portable field sampling unit which is readily interfaced with gas-chromatographic or tandem-coupled GC/mass-spectrometric instrumentation for thermal desorption and subsequent quantitation in the laboratory. Alternatively, the porous polymer tubes can be extracted with liquid solvents for subsequent analysis.

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SECTION I

CONCLUSIONS

The objective of this study was to investigate the utility
of solid adsorbents, and specifically porous polymers, as
media for sampling organic emissions from stationary sources.
While the limited quantity of data collected during the study
does not permit a definitive statement as to the utility of
porous polymers as sampling media, the results demonstrate
that with knowledgeable use, porous polymer adsorption tubes
represent a convenient, highly portable means for semi-
quantitative and even quantitative sampling of stationary
sources characterized by a wide range of trace organic
emissions. The degree of success in employing porous polymer
media to concentrate trace organic species in emissions is
dependent upon the proper selection of the porous polymer(s)
to be employed in a given sampling program. For best results,
this selection must be based upon a knowledge of both the
polymer media physical and chemical properties and the
emission characteristics of the source.

One drawback in the use of porous polymer adsorbent media
for sampling of trace organic emissions is their inability
to efficiently retain low molecular weight or highly volatile
species such as C_1 to C_3 hydrocarbons, ethers etc., when
sampling at ambient temperatures. These lighter organic
species must be sampled by other means (e.g., cryogenic
trapping) in order to be quantitated.

In the use of porous polymer media, care must be taken to assure that the total capacity of the porous polymer adsorbents are not exceeded in field sampling. Some knowledge of the level of total organics from the source and the retention capacity of the polymers is required to assure that breakthrough does not occur due to sampling of excessive total volumes of emissions. Equally important is the control of sampling volume flow rate since excessive sampling rates can lead to inefficient adsorption.

When the above precautions are observed, the use of small porous polymer adsorption tubes can serve as a convenient means for concentrating a range of trace organic emissions in a highly portable field sampling unit which is readily interfaced in the laboratory with gas-chromotographic and on tandem-coupled GC/mass-spectrometric instrumentation for quantitation of emissions.

Based on the above, it should be stated that porous polymer adsorption tubes do not represent a panacea for solution of all trace organic emissions sampling problems. Each of the polymers possess characteristic adsorption properties that can be tailored to a given source emission sampling problem depending upon the anticipated composition of the trace organic emissions. A generalized sampling procedure employing ambient-temperature porous polymer sampling tubes is not feasible due to inefficiencies in adsorbing low boiling trace organic materials. In cases where the concern is primarily with higher boiling species (>120°C), the sampling procedure employing Tenax GC as a sorbent should represent a convenient and accurate solution to this problem.

SECTION II

RECOMMENDATIONS

The successful application of porous polymers as adsorption
media for sampling of trace organic emissions requires proper
selection of the solid substrate and a matching of its
chemical and physical properties with that of the source
emissions. The following laboratory and field experimental
approaches can assist in assuring an acceptable data quality
in field sampling efforts using porous polymers.

• Laboratory testing of porous polymer adsorption capa-
  cities should be conducted employing a dynamic system
  for generation of known standards of trace organics
  in air.

• When there is no pre-knowledge of the emissions levels
  of total organics at a given field site either one of
  two approaches can be employed to assure that break-
  through of the polymer media will not occur: (1) a
  field measurement of the total hydrocarbon concentra-
  tion by flame ionization detection, along with an esti-
  mated average molecular weight of organic emissions, will
  serve to estimate appropriate sampling times, or (2)
  several porous polymer tubes can be employed to sample
  over different time lengths (e.g., 5, 10, 15 min.), with
  subsequent laboratory analysis permitting a decision
  as to the optimum sampling time for reporting purposes.

•The coupling of two or more porous polymer sampling
 tubes in series will often yield excellent results.
 An example of this approach would be the use of Tenax
 GC followed by Chromosorb 102 or Porapak Q. In this
 case the Tenax GC demonstrates a high efficiency for
 adsorption of trace organic species above 6 carbons
 in chain length. The lower molecular weight organics
 would be adsorbed more efficiently in the second ad-
 sorption tube.

An alternative sampling method for low boiling trace organic
emissions is suggested based on the use of the thermal-gradient
sampling tube used in this study. Two major drawbacks in
use of this system in its present state of refinement are
(1) in sampling of emissions high in water vapor content a
means for condensation of water before the cryogenic trap
must be devised, and (2) the present system of delivering
liquid-nitrogen-cooled nitrogen to the thermal-gradient tube
is excessively cumbersome in weight and size for field
sampling operations. It is recommended that a study be
conducted to redesign the existing thermalgradient approach
into a more portable system and to evaluate its performance
as a potentially attractive general method for sampling of
both low- and high-boiling trace organic emissions in the
field.

SECTION III

INTRODUCTION

A pressing need exists for a general method for sampling organic emissions from stationary sources for purposes of source assessment or source inventory of manufacturing plants which produce organic chemicals or employ them in manufacture of other products. These sources are frequently characterized as emitting a large number of individual organic species of varying potential health hazard. The alternative to development of a general method is the development of specific approaches for each emission component where extreme care must be taken to assure that interferences from structurally similar emissions do not occur. This alternative is impractical from both a technical and an economic viewpoint.

The objective of this task study was to investigate the utility of solid sorbents, and specifically porous polymer beads, as media for sampling organic emissions from stationary sources. While sampling tubes containing porous polymers have been employed in the sampling of trace organics in ambient air, limited systematic studies of the various polymers have been conducted for ambient air applications, and only limited experience has been gained in the use of porous polymer bead adsorbents for sampling of industrial stationary source emissions.

A more complete understanding of the scope of the problem of developing a general sampling method for organic emissions will be obtained by reading the material contained in the

Appendices to this report. Appendix A summarizes the charac-
teristics of stationary sources emitting organic species in
a unit process format. This listing includes composition,
humidity, acid content, temperature, pressure, and flow rate.
Also included are listings of organic species identified as
pollutants and a listing of industrial sources of organic
emissions. Appendix B presents an assessment of techniques
that are commonly employed for sampling of organic emissions.
Appendix C presents a historical review of the use of porous
polymers in sampling while Appendix D discusses the charac-
teristics of these materials and their potential limiting
properties as adsorbent media for concentration of trace
organic emissions.

SECTION IV

EXPERIMENTAL APPROACH

The purpose of this task study was to investigate the utility
of solid sorbents for sampling organic emissions from sta-
tionary industrial sources. This information was required
for development of general sampling and analysis procedures
for assessing emissions from industrial sources which produce
organic chemicals or employ them in manufacture of products.
The long-range objective of the study was to develop infor-
mation which might lead to the design of a portable sampling
technique for trace organic emissions that would require
minimal support equipment and would be readily interfaced
with laboratory analytical systems.

The utility of porous polymer bead materials as adsorbent
media for concentrating organic emissions was studied employ-
ing actual gaseous emissions from two industrial stationary
sources. While controlled laboratory studies of adsorption/
desorption efficiency and break-through or capacity measure-
ments on porous polymers would be of interest, few industrial
emission sources can be simulated accurately in a laboratory
evaluation. The use of actual process emissions was con-
sidered to be a more realistic and practical approach to
evaluation of the porous polymer media.

The original intent in the study was to sample source emis-
sions under field conditions in the process of scheduled
sampling efforts under the Source Assessment Program (EPA
68-02-1874). When difficulties were encountered in obtaining
plant cooperation for this effort, the approach was altered.

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Samples were collected in the field employing Tedlar bags which were subsequently sampled in the laboratory under ambient temperature conditions. This latter approach resulted in sampling of only the more volatile organic species which did not condense on the surface of the bag and limited the concentration of water vapor to its partial pressure at room temperature. The conditions under which the porous polymer media were tested were therefore significantly less adverse than originally planned since source characteristics of high temperature and high humidity were not simulated.

Since the composition of the organics in the Tedlar bags was unknown, an independent measure of the true value for organic emissions was required in order to assess the efficiencies of the porous polymers as adsorbent media. This was accomplished by backing up the porous polymer tubes with a cryogenically-cooled thermal-gradient tube patterned after that described by R. E. Kaiser (Ref. 1). The thermal-gradient tube was employed to isolate organic emissions that eluted from the primary sampling tube.

The performances of the porous polymer tubes were quantitated by subsequent laboratory analysis of the collection tubes and the thermal-gradient tubes employing gas chromatographic and tandem-coupled GC/mass spectrometric techniques.

SECTION V

SAMPLING AND ANALYSIS TECHNIQUES

A. SAMPLING TRAIN

The sampling train employed in the porous polymer performance tests is shown schematically in Figure 1. An evacuated cylinder was used as a sampling gas driving force. The valve and rotometer upstream of the tank was used to adjust flow rate in the general region of 150 cc/minute. Sampling was conducted over a 20-minute period for a total sampled volume of about 3 liters of gas. The cryogenic thermal-gradient tubes fitted with thermocouples and the porous polymer adsorption tubes are constructed of stainless steel and standard Swagelok fittings.

Some details of the sampling system are included as follows:

-The evacuated cylinder was a 0.42 cu.ft. Freon tank fitted with a thermometer and a 3-in. vacuum gauge to permit calculation of total volume sampled.

-The liquid nitrogen dewar was a four-liter Nalgene dewar flask (Cat. #4150) constructed of double-walled highly crosslinked polyethylene.

-The porous polymer tube is a 7-inch length of 1/4-in. 304 stainless steel tube fitted with Swagelok fittings and plugs.
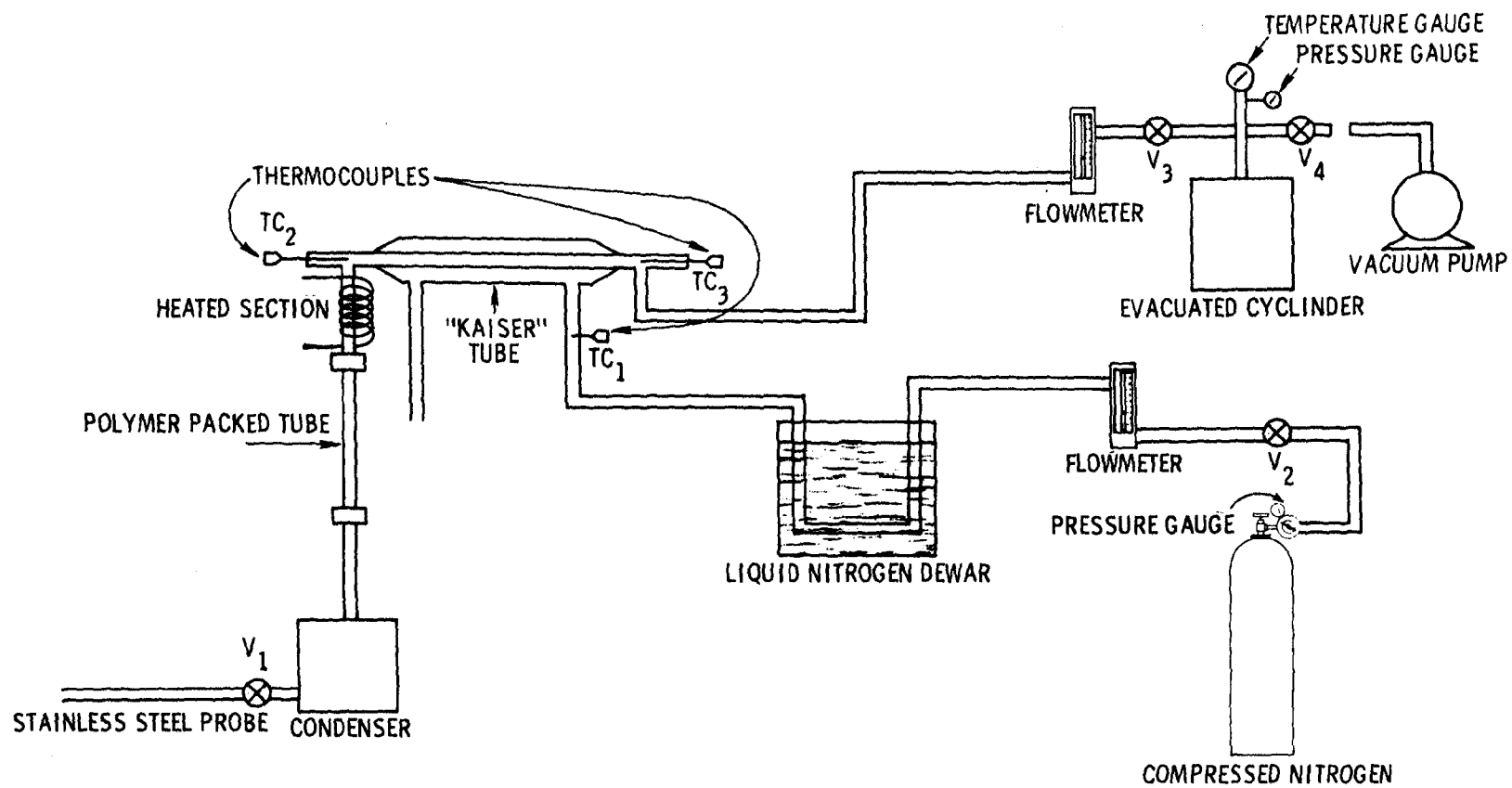
Figure 1. Porous polymer sampling train

A photograph of the thermalgradient tube is shown in
Figure 2. The inner tube of the concentric heat exchanger is
a 20 cm length of 304 SS tube (0.180 in. OD; 0.149 in. ID;
0.015 wall). The outer tube is a 9 cm length of 5/16 in. OD
by 0.020 wall 304 stainless steel tubing. These dimensions
were selected based on the recommendations of R. E. Kaiser
(Ref. 1). The thermocouples are type K (1/16 in. x 6 in.
probe length, Thermoelectric #SK 1110L). The thermocouple
tip penetrates to an area of the inner tube at the center of
the 3/8 in. stainless steel Swagelok tee nitrogen entrance
(and exit). The inner tube is filled with a solid absorbent.
One-quarter inch Swagelok tees serve as the sample gas inlet
and outlet. Above and beyond the cost of stainless fittings
and thermocouples, approximately $40 per Kaiser trap was
required for welding the inner/outer tube and for assembly.

1. Operation of Sampling Train

To prepare for a sampling run, the train was assembled and
leak checked via vacuo with the valve after the sampling
probe closed. The flow of nitroben through the jacketed
thermogradient tube is adjusted so that the entering nitro-
gen flow is near liquid nitrogen temperature. In earlier
work, Kaiser (Ref. 1) employed nitrogen flow rates of from
1200 liter/hour to 2000 liter/hour to maintain the lowest
temperature of the gradient tube at about 160°C. Under his
conditions, about 200 grams of liquid nitrogen was consumed
in a 20 minute sampling period. An initial setting on the
rotometer of 50 ft^3/hr (ca. 1500 ℓ/hr is recommended. After
thermal equilibrium has been attained (e.g., TC_2 and TC_3
register about 160°C), the sample run is initiated by
closing V_4 and opening V_1 and V_3. V_3 should be adjusted to
a flow of about 150 cc/minute (0.3 cfm). The nitrogen flow
rate is quickly adjusted so that TC_3 registers -160°C.
Under these conditions TC_2 will register about -100°C when

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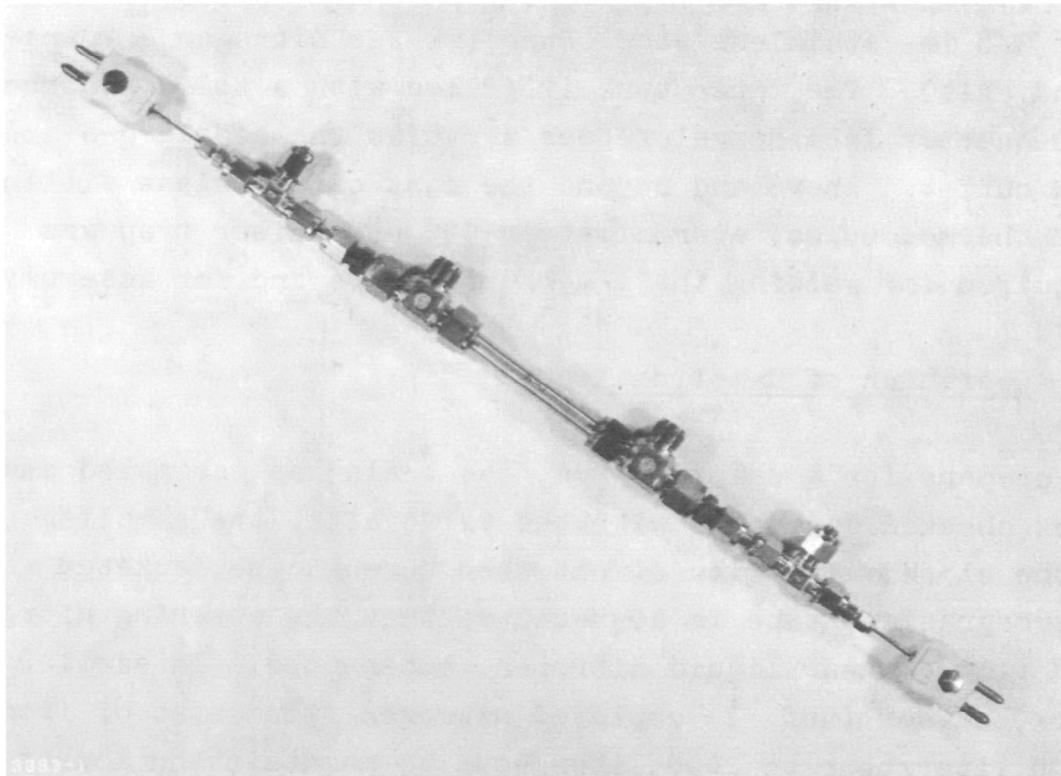
Figure 2. Thermal-Gradient Tube Design.

a 2-ft, 1/4-in. heated "U"-tube is upstream of the thermal-gradient tube. After the 20-minute run, V_1 is closed, the temperature and pressure of the tank is noted and the porous polymer tube and the cryogenic thermalgradient tube are disconnected, sealed with Swagelok caps and stored in a dry-ice chest. Normal precautions should be taken so that liquid nitrogen does not come in contact with the skin.

B. LABORATORY ANALYSIS

The contents of collectors and thermalgradient tubes were analyzed using a GC/MS system consisting of a CEC 21-104 mass spectrometer with an Infotronics digital readout system coupled to an F&M Model 700 gas chromatograph. The chromatograph was modified by the addition of an F&M 1609 flame ionization detector and the injection port was altered to directly accept either the 0.25 in. diameter collectors or Kaiser tubes. Collectors were desorbed by heating in a small tube furnace (E. H. Sargent Co.), the temperature of which was controlled by means of an F&M Scientific Corp. power proportioning temperature programmer/controller. This latter unit was also used to control the temperature output of a laboratory heat gun (Masters Appliance Corp.) which was used in desorbing the thermal-gradient tubes. A flow of hot air from the heat gun was directed through the outer jacket of the tube from the inlet end. The inlet thermocouple was used as the sensing couple for the temperature controller.

Collectors containing Tenax GC or polyimide packings were desorbed at 220°C, while those containing Porapak or Chromosorb 100 series packings were desorbed at 180°C. Compounds were flushed from the collectors into the chromatograph by a flow of helium in a direction opposite of that used in

sampling. A splitter located before the FID detector was used to direct a portion of the effluent to the mass spectrometer.

A 7.5-ft x 0.25-in. stainless steel column packed with Tenax GC was used as an analytical column.

SECTION VI

EXPERIMENTAL RESULTS

Emissions from two plants (A and B) were collected in Tedlar bags and returned to the Laboratory for sampling.

A.   PLANT A RESULTS

Table 1 presents the combinations of porous polymer tube packings and the solid adsorbent employed in the thermal gradient tube for Plant A samples. Tenax GC and Dexsil 300 on Chromosorb W (AW, HMDS) were employed as the thermal gradient tube packing while Chromosorb 102, Chromosorb 103, Porapak Q, Tenax GC, and an experimental polyimide were the porous polymers under study. The sampling data for Plant A emissions are presented in Table 2. The equation employed for calculation of sample volume is:

$$V_s = 17.71 \ V_c \left(\frac{P_f}{T_f} - \frac{P_i}{T_i} \right)$$

where: V_s = Sample volume at 70°F and 29.92-in. Hg
         V_c = Cylinder volume, cu.ft.
          P = Barometric pressure-cylinder pressure, in. Hg
          T = Temperature, °F +460
      i,f = initial and final conditions

Analysis of the collector tubes was performed as presented in Section V.

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Table 1. COMBINATIONS OF POROUS POLYMER AND
THERMAL GRADIENT TUBE PACKINGS EMPLOYED
FOR PLANT A SAMPLING

| Porous Polymer | Thermal Gradient Tube Packing | |
	Tenax GC	Dexil 300
Chromosorb 102	x	x
Chromosorb 103	xx	–
Porapak Q	x	x
Tenax GC	x	x
Polyimide[a]	–	xx

[a]Polyimide – Crushed polyimide foam – Monsanto
Research Corporation experimental sample.

Table 2.   SAMPLING DATA - PLANT A

Porous Polymer	Thermal Gradient	Cylinder Pressure in. Hg, Vacuum		Temperature, °F		Sampling Time, sec.	Sample Volume, SCF[a]
		Initial	Final	Initial	Final		
Chromosorb 102	Dexil 300	27.8	19.5	69	72	1775	0.116
Tenax GC	Tenax GC	28.1	19.9	73	75	1165	0.114
Chromosorb 103	Tenax GC	28.8	20.6	73	75	1083	0.114
Poropak Q	Dexil 300	27.5	19.3	73	74.5	1215	0.114
Polyimide	Dexil 300	25.5	20.3	70	72	1085	0.115
Chromosorb 103	Tenax GC	28.5	20.3	69	71	1156	0.115
Chromosorb 102	Tenax GC	28.5	20.3	69	73	1276	0.115
Tenax GC	Dexil 300	27.5	19.4	74	75	970	0.114
Polyimide	Dexil 300	27.0	18.8	75	76	1325	0.114
Porapak Q	Tenax GC	28.4	20.2	75	76	1026	0.114

[a]SCF at 70°F and 29.92 in. Hg.

Sampling Conditions:
    Nitrogen Flow = 50 cfh
    Cylinder Volume = 0.421 cu.ft.
    Barometric Pressure = 29.52 in. Hg first 4 runs
                          29.28 in. Hg last 6 runs

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The chromatographic column used in analysis was temperature programmed from 30°C to 300°C at 10°C/min. Low molecular weight hydrocarbons of the same carbon number were insufficiently separated to allow measurement of the mass of each specie. However, the spectral data in each case indicates that the alkene is by far the more predominant component.

Weights of components in micrograms are given in Table 3. Calculated molar responses (Ref. 2) served as a basis for these calculations and are given in Table 4. These are in excellent agreement with reported values for these compounds (Ref. 3). To aid in calculating weights of the various components, molar response factors were converted to weight responses, also given in Table 4. In cases where hydrocarbons were unresolved, an average response value was used. (Responses are very similar and either value could actually have been used.)

An instrument response factor was established for n-heptane. This allowed the absolute instrument response to any of the components to be determined. All calculations are based on integrated peak areas.

B. PLANT B RESULTS

Table 5 presents the combinations of porous polymer tube packings and solid adsorbents employed in the thermal gradient tubes for Plant B samples. The sampling data for Plant B emissions are presented in Table 6.

The procedure for desorption and analysis of the collector tubes was identical to that employed for Plant A samples. The chromatograms obtained for collector tube components

Table 3.   ANALYSIS RESULTS - PLANT A COLLECTOR TUBES

Collector Pairs (Ambient Temperature Collector/ Thermal Gradient Tube)	Micrograms Collected [a]						
	Ethane/ Ethylene	Propane/ Propylene	Acetal- dehyde	Butane/ Butene	Acrylo- nitrile	Methacrylo- nitrile	Benzene
Chromosorb 102/	0.07	14	1.2	6.0	0.4	0.01	6.7
Dexil 300	0.4	60	0.8	0.2	-	-	-
Chromosorb 102/	0.09	15	1.3	5.3	0.4	0.5	6.0
Tenax GC	b	24.3	0.2	1.8	0.09	0.1	0.2
Porapak Q/	1.0	33	2.9	6.1	-	1.0	-
Dexil 300	- c	4.9	-	0.1	-	-	-
Porapak Q/	1.4	22	1.2	9.6	0.4	0.2	7.6
Tenax GC	0.3	33	-	0.9	0.09	0.2	0.04
Tenax GC/	-	35	2.0	10	0.3	0.4	5.1
Dexil 300	-	0.2	0.01	0.7	-	-	-
Tenax GC/	0.2	0.4	-	-	-	-	-
Tenax GC	0.008	0.02	-	-	-	-	-
Chromosorb 103/	0.6	19	2.3	10	0.4	0.7	5.8
Tenax GC	0.3	46	-	1.1	-	0.08	-
Chromosorb 103/	0.9	0.8	1.8	1.0	0.1	0.1^{5}	0.5
Tenax GC	-	49	-	0.7	-	-	-
Polyimide/	0.1	2.8	0.4	0.2	0.7	-	0.03
Dexil 300	0.002	0.08	0.004	0.04	0.03	0.23	0.2
Polyimide/	-	1.4	0.1	0.08	0.08	-	0.02
Dexil 300	-	2.4	0.3	0.4	0.1	0.7	1.2

[a] Normalized for 0.114 SCF sample.

[b] Not analyzed.

[c] Not detected.

Table 4. RESPONSE OF FID TO VARIOUS COMPOUNDS

Compound	Relative Molar Response[a]	Relative Weight Response
Ethane	191	6.37
Ethylene	186	6.64
Propane	293	6.66
Propylene	288	6.86
Acetaldehyde	96	2.18
Butane	394	6.79
Butene	389	6.95
Acrylonitrile	210	3.96
Methacryonitrile	305	4.55
Benzene	600	7.69
Heptane	700	7.00

[a]Relative to 700 for heptane

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Table 5. COMBINATIONS OF POROUS POLYMER AND
         THERMAL GRADIENT TUBE PACKINGS EMPLOYED
         FOR PLANT B SAMPLING

| Porous Polymer | Thermal Gradient Tube Packing | |
	Tenax GC	Dexil 300
Chromosorb 102	x	x
Chromosorb 103	x	x
Porapak Q	x	x
Tenax GC	x	x
Polyimide[a]	-	x

[a]Polyimide - Crushed polyimide foam - Monsanto
Research Corporation experimental sample.

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Table 6. SAMPLING DATA - PLANT B

Porous Polymer	Thermal Gradient	Cylinder Pressure in. Hg, Vacuum		Temperature, °F		Sampling Time, sec.	Sample Volume, SCF
		Initial	Final	Initial	Final		
Chromosorb 102	Dexil 300	28.6	20.2	65	67	1091	0.119
Tenax GC	Tenax GC	28.8	20.6	65	67	1214	0.116
Chromosorb 103	Dexil 300	28.5	20.3	66	68	1151	0.116
Poropak Q	Dexil 300	28.6	20.4	65	68	1117	0.116
Chromosorb 103	Tenax GC	28.6	20.4	64	67	1143	0.116
Chromosorb 102	Tenax GC	28.6	26.9	66	67	639	0.024[a]
Tenax GC	Dexil 300	28.8	20.6	67	68	1199	0.116
Polyimide	Dexil 300	28.7	20.5	63	65	1256	0.116
Porapak Q	Tenax GC	28.7	20.5	63	65	1137	0.116

[a]Collection tube partially plugged.

Sampling Conditions:

    Nitrogen Flow = 50 cfh
    Cylinder Volume = 0.421 cu.ft.
    Barometric Pressure = 29.53 in. Hg first 4 runs
                        29.14 in. Hg last 6 runs

were extremely complex. In most instances, a broad envelope
of unresolved peaks was obtained which was similar to those
experienced in the case of hydrocarbon fuels, excepting that
the present samples cover a much larger range of compound
types. GC/MS analysis was performed without the benefit of
samples for development of analytical conditions. A single
column for the adequate separation of these components,
which range in boiling points from -88°C to nearly 200°C,
might not have been available anyway.

The identification of all compounds present in the samples
was not accomplished. Major compounds present within various
areas of the chromatographic trace have been established,
however.

The total weight of each group of such compounds has been
estimated using peak areas. No specific correction has been
applied for the various compound types. Estimates, however,
are probably accurate to within the one significant figure
reported.

Groups of compounds and their identifying letters are:

A - Ethane, formaldehyde
B - Propane, methanol, carbonylsulfide
C - Butene, butane, sulfur dioxide, ethanol
D - Acetaldehyde
E - Furan, acrolein, propionaldehyde
F - Pentane, pentene, other C_5's
G - Butyraldehyde
H - Hexane, hexene, C_6's, methacrolein
I - Methyl furan
J - Dimethylfuran, C_7 hydrocarbons

K - Benzene
L - C_8 hydrocarbons
M - C_9 hydrocarbons
N - Toluene
O - C_{10} hydrocarbons
P - Xylenes

Table 7 presents the milligrams of organics found in each compound group.

Table 7. ANALYSIS RESULTS - PLANT B COLLECTOR TUBES

Collector Pairs (Ambient Temperature Collector/ Thermal Gradient Tube)	Estimated Weight (mg) in Compound Groups[a]															
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Chromosorb 102/	0.06	0.2	0.9	0.03	2.0	0.5	0.1	0.6	0.9	0.6	1.5	-	0.3	0.9	0.3	0.3
Dexil 300	0.007	0.4	1.4	-	-	0.2	-	0.2	0.2	0.1	-	-	-	-	-	-
Chromosorb 102/	0.05	0.5	0.4	0.05	1.9	1.9	0.5	1.4	1.9	1.9	1.9	-	1.4	1.9	1.9	1.9
Tenax GC	0.20	1.9	1.0	-	-	2.9	-	1.0	1.0	0.5	-	-	-	-	-	-
Porapak Q/	.0.2	0.6	2.4	0.1	1.1	1.0	0.4	0.4	0.6	0.5	0.9	0.1	0.06	0.06	0.6	0.4
Dexil 300	-	0.8	0.2	0.08	0.2	0.05	-	0.09	-	-	-	-	-	-	-	-
Porapak Q/	0.2	1.2	3.0	0.3	0.9	0.9	0.3	0.4	0.3	0.3	0.6	0.2	0.1	0.1	0.5	0.3
Tenax GC	0.004	0.3	0.08	0.06	0.3	0.02	-	-	-	-	-	-	-	-	-	-
Tenax GC/	0.03	0.2	0.6	0.3	0.7	0.6	0.06	0.3	0.1	0.4	0.5	0.3	0.1	0.4	-	0.3
Dexil 300	0.08	0.04	0.8	-	-	-	-	-	-	-	-	-	-	-	-	-
Tenax GC/	0.04	0.4	0.6	0.2	0.5	0.6	0.1	0.4	0.5	0.4	0.5	-	0.3	0.4	-	0.3
Tenax GC	0.2	0.6	0.8	-	-	-	-	-	-	-	-	-	-	-	-	-
Chromosorb 103/	0.05	0.2	0.9	0.5	0.4	0.5	0.2	0.6	0.5	0.6	1.2	0.5	0.4	0.5	0.3	0.3
Dexil 300	0.02	0.4	0.5	0.01	0.3	0.2	-	0.1	0.2	-	0.1	-	-	-	-	-
Chromosorb 103/	0.03	0.3	1.0	0.6	0.6	0.6	0.3	0.6	0.6	0.6	1.1	0.6	0.4	0.4	0.3	0.2
Tenax GC	0.02	0.3	0.6	-	0.2	0.3	-	0.2	0.2	-	0.1	-	0.1	-	-	-
Polyimide/	0.2	0.7	-	-	0.2	-	-	-	-	0.2	-	-	0.1	0.1	0.2	0.3
Dexil 300	0.2	0.8	0.8	0.3	0.3	0.8	-	0.8	0.1	0.9	1.0	0.3	0.9	1.0	0.5	1.0

NOTE: Higher hydrocarbons in the C_{11} to C_{14} range were detected above group P.

[a] Normalized for 0.116 SCF sample.

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SECTION VII

ANALYSIS OF DATA AND DISCUSSION

Since the thermal-gradient tube was designed to sample trace
organic material that was not absorbed by the ambient col-
lector tube, the total weight of organics in each collector
pair was examined.

It would be expected that the sum of the individual species
concentrations found in the paired tubes and that of the
total hydrocarbons would be equal for all combinations of
ambient temperature collector and thermal gradient tube.
Tables 8 and 9 present the summed data as pairs by individual
species and total hydrocarbons for Plants A and B, respec-
tively.

Examination of the data in Table 8 indicated that the total
hydrocarbon results from samples 6, 9, and 10 were not with-
in 2σ of the mean total hydrocarbon value for all collector
pairs. After discarding these runs, the error for total
hydrocarbons in the remaining seven sampling runs was 24%
at the 95% confidence limit.

A similar analysis of the data from Plant B indicated that
run 2 should be disqualified as an outlier. This pair of
collection tubes became plugged during sampling and sampling
was discontinued with only 21% of the desired sample volume.
For Plant B, the error at the 95% confidence limit for total
hydrocarbons collected was found to be 19%.

For organic emission compositions as complex as those charac-
teristic of the two sources sampled, the performance of the
dual adsorber system appears to be quite adequate.

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Table 8.   STATISTICAL ANALYSIS OF TOTAL COLLECTION BY PAIRS - PLANT A

Collector Pairs (Ambient Temperature Collector/ Thermal Gradient Tube)	Micrograms Collected							
	Ethane/ Ethylene	Propane/ Propylene	Acetal- dehyde	Butane/ Butene	Acrylo- nitrile	Methacrylo- nitrile	Benzene	Total Hydrocarbons
1. Chromosorb 102/Dexil 300	0.47	74	2.0	6.2	0.4	0.01	6.7	89.78
2. Chromosorb 102/Tenax GC	0.09	39.3	1.5	7.1	0.49	0.6	6.2	55.28
3. Porapak Q/Dexil 300	1.0	37.9	2.9	6.2	-	1.0	-	49.00
4. Porapak Q/Tenax GC	1.7	55	1.2	10.5	0.49	0.4	7.64	76.93
5. Tenax GC/Dexil 300	-	35.2	2.01	10.7	0.3	0.4	5.1	53.71
6. Tenax GC/Tenax GC	0.21	0.42	-	-	-	-	-	0.63
7. Chromosorb 103/Tenax GC	0.63	65	2.3	11.1	0.4	0.78	5.8	86.01
8. Chromosorb 103/Tenax GC	0.90	49.8	1.8	1.7	0.1	0.15	0.5	54.95
9. Polyimide/Dexil 300	0.1	2.88	0.4	0.24	0.73	0.2	0.23	4.78
10. Polyimide/Dexil 300	-	3.8	0.4	0.48	0.18	0.7	1.22	6.78

Table 9. STATISTICAL ANALYSIS OF TOTAL COLLECTION BY PAIRS - PLANT B

Collector Pairs (Ambient Temperature Collector/ Thermal Gradient Tube)	Estimated Weight (mg) by Compound Groups																
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	THC
Chromosorb 102/Dexil 300	0.067	0.6	2.3	0.03	2.0	0.7	0.1	0.8	1.1	0.7	1.5	-	0.3	0.9	0.3	0.3	11.70
Chromosorb 102/Tenax GC	0.25	2.4	1.4	0.05	1.9	4.8	0.5	2.4	2.9	2.4	1.9	-	1.4	1.9	1.9	1.9	28.00
Porapak Q/Dexil 300	0.2	1.4	2.6	0.18	1.3	1.05	0.4	0.49	0.6	0.5	0.9	0.1	0.06	0.06	0.6	0.4	10.84
Porapak Q/Tenax GC	0.204	1.5	3.08	0.36	0.12	0.92	0.3	0.4	0.3	0.3	0.6	0.2	0.1	0.1	0.5	0.3	9.28
Tenax GC/Dexil 300	0.12	0.24	1.4	0.3	0.7	0.6	0.06	0.3	0.1	0.4	0.5	0.3	0.1	0.4	-	0.3	5.82
Tenax GC/Tenax GC	0.24	1.0	1.4	0.2	0.5	0.6	0.1	0.4	0.5	0.4	0.5	-	0.3	0.4	-	0.3	6.84
Chromosorb 103/Dexil 300	0.07	0.6	1.4	0.51	0.7	0.7	0.2	0.7	0.7	0.6	1.3	0.5	0.4	0.5	0.3	0.3	9.48
Chromosorb 103/Tenax GC	0.05	0.6	1.6	0.6	0.8	0.9	0.3	0.8	0.8	0.6	1.2	0.6	0.5	0.4	0.3	0.2	10.25
Polyimide/Dexil 300	0.4	1.5	0.8	0.3	0.5	0.8	-	0.8	0.1	1.1	1.0	0.3	1.0	1.1	0.7	1.3	11.70

The performance of the individual ambient temperature porous polymer tubes varies according to the volatility and polarity of the emitted species. This subject is addressed more completely in Appendix D of this report. As is evident from the data in Tables 3 and 7 the ambient collector tubes do not exhibit a high efficiency in all cases. The failure of the porous polymers to concentrate the hydrocarbons efficiently is especially evident for the case of propane/propylene analysis from Plant A (Table 3) and for the lower molecular weight compound groups from Plant B (Table 7). In the later case, for groups D through P the efficiencies of the ambient collectors appear to be improved, with little organic emissions breaking through to the thermal-gradient tube.

In both sources sampled non-oxygenated hydrocarbon emissions predominated. Based on total hydrocarbons adsorbed by the ambient temperature media, it is apparent that the experimental polyimide performed very poorly. The performance of the commercial porous polymers varied for the two plants. For Plant A emissions, the first Tenax GC adsorption tube (see Table 3) exhibited a higher total organics collection followed by Porapak Q, Chromosorb 103 and Chromosorb 102. In the case of Plant B emissions the decreasing order for total organics collection was Porapak Q > Chromosorb 102 > Chromosorb 103 > Tenax GC. The reversal of efficiency for concentration of organics for Plants A and B by Tenax is indicative of the variation in adsorption performance due to the nature of the emissions composition.

SECTION VIII

REFERENCES

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2. David, D.J. Gas Chromatographic Detectors, Wiley - Interscience, New York, New York, 1974, pp. 67-68.
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APPENDICES

APPENDIX A

CHARACTERISTICS OF STATIONARY SOURCES
EMITTING ORGANIC SPECIES

The use of porous polymer packed adsorption tubes seems to be an
attractive approach to field sampling of organic emissions. How-
ever, the potential utility of these tubes depends on the ability
of the polymer materials to withstand the adverse conditions char-
acteristic of industrial sources emitting the organic materials.
Table 1 presents a matrix of industrial processes which could
serve as point sources of organic emissions. The emission char-
acteristics are presented in terms of composition, humidity, acid
content, temperature, pressure and flow rate. While this table
presents only a cursory view of the emission sources, it can serve
as a frame of reference to identify potential problems in the
application of porous polymer-packed sampling tubes. Sources
that exhibit reactive emissions (NO_x, SO_2, acids, oxidizing atmos-
pheres), elevated temperatures, and high water loadings would
have to be approached with caution to assure that the final analyses
were indicative of the trace composition of the organic emissions.

A partial list of organic emissions which have been identified as
pollutants (Ref. 1 and 2) is presented in Table 2. Industrial
operations which have been identified as sources of organic con-
taminants (Ref. 3) are presented in Table 3. These latter two
tables are presented solely to point out the magnitude of the
overall problem and underline the need for a relatively simple
but accurate sampling and analysis technique for organic emissions.

The successful application of solid sorbents for sampling and
analysis of organic emissions depends upon a knowledgeable appli-
cation of selected sorbents to each specific source. To accomplish
this, detailed knowledge of the sorbent limitations must be com-
bined with accurate engineering knowledge of the source charac-
teristics.

TABLE 1

CHARACTERISTICS OF POTENTIAL ORGANIC EMISSION SOURCES

Potential Organic Emission Sources	Composition					Humidity (% RH)	Acid Content	Temperature, °F	Pressure, psig	Flow Rate, scfm
	Part.	NO_x	SO_x	CO	HC					
Storage Tanks					X	0-20	X	-54 - 300	0-2	<100
Unloading Facilities					X	0-20	X	-54 - 200	0-2	<100
Chemical Reactors										
Non-Catalytic				X	X	0-20	X	-20 - 1000	0-1500	100-10,000
Catalytic										
Fluidized Bed	X			X	X	0-20	X	0 - 300	0-50	100-10,000
Fixed Bed	X			X	X	0-20	X	0 - 300	0-50	100-10,000
Moving Bed	X			X	X	0-20	X	0 - 300	0-50	100-10,000
Distillation Column				X	X	0-98	X	80 - 250	0-50	100-10,000
Flash Separator				X	X	0-98	X	-48 - 300	0-50	100-10,000
Filters										
Pressure Leaf Filters	X				X	0-98	X	70 - 150	0-10	100-10,000
Rotary Vacuum Filters	X				X	0-98	X	70 - 150	0-20	100-10,000
Nutsche Filters	X				X	0-98	X	70 - 150	0-10	100-10,000
Horizontal Plate Filters	X				X	0-98	X	70 - 150	0-10	100-10,000
Tubular Filters	X				X	0-98	X	70 - 150	0-10	100-10,000
Bag Filters	X	X	X	X	X	0-98	X	70 - 150	0-10	100-10,000
Mixers					X	0-20		32 - 90	0-2	100-10,000
Grinders	X				X	0-20		32 - 90	0-2	100-10,000
Crushers	X				X	0-20		32 - 90	0-2	100-10,000
Scrubbers		X	X	X	X	80-95	X	60 - 150	0-10	>10,000
Dryers										
Counter-Current Dryer	X	X	X	X	X	0-95	X	100 - 300	0-20	100-10,000
Rotary Drum Dryer	X	X	X	X	X	0-95	X	100 - 300	0-20	100-10,000
Vacuum Rotary Dryer	X	X	X	X	X	0-95	X	100 - 300	0-35	100-10,000
Spray Dryers					X	0-95	X	100 - 300	0-20	100-10,000
Screeners	X				X	0-20		32 - 100	0-2	100-10,000
Vacuum Jets		X	X		X	95-99	X	270 - 390	25-200	>10,000

TABLE 1 (Cont'd)

CHARACTERISTICS OF POTENTIAL ORGANIC EMISSION SOURCES

Potential Organic Emission Sources	Part.	NO$_x$	SO$_x$	CO	HC	Humidity (% RH)	Acid Content	Temperature, °F	Pressure, psig	Flow Rate, scfm
Waste Incinerators	X	X	X	Y	X	40-95	X	500 - 1500	0-5	>10,000
Utility Boilers	X	λ	Y	X	X	40-95		500 - 1500	0-5	>10,000
Pneumatic Conveyors	X				X	10-30	X	40 - 90	0-20	>10,000
Conveyor Belts	X				X	0-20		32 - 90	0-2	<100
Extruders		X	X	X	X	0-20		100 - 350	0-2	<100
Pelletizers					X	0-20		100 - 200	0-2	<100
Paint Spray Booths	X				X	0-20		60 - 100	0-5	>10,000
Ovens	X	X	X	X	X	0-50		500 - 1500	0-2	>10,000
Blenders	X				X	0-20		32 - 90	0-2	100-10,000
Cyclones	X				X	0-20		70 - 150	0-20	10,000
Extraction Towers					X	0-90	X	70 - 300	0-50	100-10,000
Flares	X	X	X	X	X	40-95		1500 - 3000	0-2	>10,000
Baggers	X				X	0-20		100 - 200	0-2	<100
Loading Facilities	X				X	0-20	X	-54 - 300	0-2	<100
Cooling Towers					X	40-95		32 - 100	0-2	100-10,000
Settling Ponds					X	40-95	Y	32 - 80	0-2	100-10,000
Evaporators					X	0-95	X	100 - 200	0-50	100-10,000
Leaching Vat					X	0-95	X	100 - 200	0-2	100-10,000
Cookers	X	X	X	X	X	0-95	X	100 - 300	0-2	100-10,000
Refrigeration Machines						0-10		-50 - 32	50-300	<100

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TABLE 2

ORGANIC SPECIES IDENTIFIED AS POLLUTANTS

A. OLEFINS

ethylene
propylene
1-butene
isobutene
1-pentene
2-methyl-1-butene
3-methyl-1-butene
1-hexene
2-ethyl-1-butene
2-methyl-1-pentene
2,3-dimethyl-1-butene
3,3-dimethyl-1-butene
1-heptene
2-methyl-1-hexene
1-octene
trans-2-butene
cis-2-butene
trans-2-pentene
cis-2-pentene
2-methyl-2-butene
trans-2-hexene
trans-3-hexene
trans-4-methyl-2-pentene
cis-4-methyl-2-pentene
2,3-dimethyl-2-butene
2-methyl-2-pentene
trans-2-heptene
trans-3-heptene
2-methyl-2-hexene
3-ethyl-2-pentene
2,3-dimethyl-2-pentene
trans-4-octene
2-methyl-2-heptene
pinene
2,3-dimethyl-2-hexene
cyclopentene
1-methylcyclopentene
cyclohexene
1-methyl cyclohexene
1,2-dimethyl cyclohexene
1,3-butadiene
2-methyl-1,3-butadiene

B. AROMATICS

benzene
toluene
p-Xylene
o-Xylene
m-Xylene
Ethyl benzene
1,2,4-trimethylbenzene
1,2,3-trimethylbenzene
1,3,5-trimethylbenzene
isopropylbenzene
1,3-methylethylbenzene
t-butylbenzene
1,2-diethylbenzene
1,4-diethylbenzene
1,3-diethylbenzene
1,2,3,4-tetramethylbenzene
1,2,3,4,5-pentamethylbenzene
styrene
cumene
methylstyrene

C. ALKANES

methane
ethane
propane
n-butane
isobutane
2,2-dimethylpropane
n-pentane
isopentane
n-hexane
2-methylpentane
3-methylpentane
2,2-dimethylpentane
2,3-dimethylpentane
n-heptane
2,4-dimethylpentane
n-octane
3-methylheptane
isooctane
n-nonane
2,2,5-trimethylhexane
cyclopentane
methylcyclopentane
cyclohexane

TABLE 2 (Cont'd.)

ORGANIC SPECIES IDENTIFIED AS POLLUTANTS

D. ALCOHOLS

methanol
ethanol
D-butyl alcohol
isopropanol
n-butyl alcohol
isooctyl alcohols
octyl decenol
2-ethyloctanol

E. ALDEHYDES

acrolein
C_8 aldehydes
crotonaldehyde
formaldehyde
acetaldehyde
propionaldehyde

F. HALOGENATED COMPOUNDS

methyl chloride
methylene chloride
chloroform
carbon tetrachloride
allyl chloride
trichloropropane
epichlorohydrin
chlorobenzene
chloroethane
dichloroethane
trichloroethane
benzyl chloride
vinyl chloride
tetrachloroethylene
phosgene
ethylene bromide
methylbromine
chlorinated camphene

G. ESTERS AND ETHERS

acetone
ethyl acetate
methyl methacrylate
diethyl ether
methyl ethyl ketone
isopropyl acetate
ethyl acrylate
n-butyl acetate
diisopropyl ether
vinyl acetate
diethyl ketone
ethyl butyrate

H. ACIDS & ANHYDRIDES

acetic acid
phthalic anhydrides
maleic acid
benzoic acid
acrylic acid
fumaric acid
butyric acid
acetic anhydride
oleic acid
lactic acid
toluenesulfonic acid

I. NITROGEN COMPOUNDS

acrylonitrile
acetonitrile
aniline
nitrochlorobenzene
toluene diisocyanate
methylene dianiline
dinitrobenzene
trimethylamine
nitrobenzene
dimethylformamide

TABLE 2 (Cont'd.)

ORGANIC SPECIES IDENTIFIED AS POLLUTANTS

J. MISCELLANEOUS

acetylene
propylene oxide
phenol
propylene glycol
nonylphenol
glycerol
hydroquinone
bisphenol A
naptha
hydrocarbons

TABLE 3

ALPHABETICAL LISTING OF ORGANIC EMISSION SOURCES

Acetaldehyde - Hydration of Ethylene
Acetic Acid - from Acetaldehyde
Acetic Acid - Carbonation of Methanol
Acetic Acid - Oxidation of Butane
Acetic Anhydride - from Acetic Acid
Acetone - from Cumene
Acetone - from Isopropanol
Acetone Cyanohydrin
Acetylene
Acrolein
Acrylic Acid - Propane Oxidation
Acrylonitrile
Acrylonitrile-Butadiene-Styrene Resins
Adipic Acid
Adiponitrile
Alcohol Sulfates - Ammonium Salt
Alcohol Sulfates - Sodium Salt
Alcohol Sulfates - Triethanolamine Salt
Alkyd Resins
Allyl Chloride
Amino Resins
Aniline
Anthelmintics
Ascorbic Acid
Asphalt Paving - Hot Mix
Asphalt Roofing
Aspirin
Benzene - Coal Tar
Benzoic Acid
Benzyl Chloride
Bis-Phenol-A
Bromomethane - Methyl Bromide
Butadiene
Butoxyethanol
n-Butyl Acetate
n-Butyl Acrylate
n-Butyl Alcohol
sec-Butyl Alcohol
t-Butyl Alcohol
Butyl Octyl Phthalate
Butylene Dimer
n-Butyraldehyde (oxo reaction)
Caprolactam - from Hydroxylamine
Carbon Black - furnace
Carbon Black - thermal
Carbon Disulfide
Carbon Tetrachloride - Chlorination of Carbon Disulfide
Carbon Tetrachloride - Chlorination of Methane
Carbon Tetrachloride - Chlorination of Propane
Cellulose Acetate
Chlorinated Camphene
Chloroacetic Acid
Chlorobenzene
2-Chloro-4-Ethylaminoisopropylamino Triazine
Chloroform
Chlorophenol
Chloroprene (from Butadine)
Choline Chloride
Coffee Roasting
Cottonseed Oil Milling
Cresol - synthetic
Cresyldiphenyl Phosphate
Cresylic Acid
Crotonaldehyde
Cumene
Cumene Sulfonate - Hydrotrope
Cumene Sulfonic Acid
Cyclohexane
Cyclohexone
Cyclohexylamine
Cyclooctadiene
Decyl Alcohols
Deep Fryers

TABLE 3 (Cont'd.)

ALPHABETICAL LISTING OF ORGANIC EMISSION SOURCES

Di Butyl Phthalate
o-Dichlorobenzene
p-Dichlorobenzene
Dichlorodifluoromethane
2,4-Dichlorophenoxyacetic Acid
2,4-Dichlorophenoxyacetic Acid, Dimethylamine Salt
Di-2-Ethylhexyl Adipate
Di-(2-Ethylhexyl) Phthalate
Diisodecyl Phthalate
Diisooctal Phthalate
Dimethylhydrazine - unsymmetrical
O,O-Dimethyl-o-p-Nitrophenyl-phosphorothioate
Dimethyl Phthalate
Dimethyl Terephthalate
Dinitrotoluene
Distilled Liquor
Dodecene
Dodecylbenzene - hard
Dodecylbenzene Sulfonic Acid
Epichlorohydrin
Epoxy Resins
Ethanol
Ethanolamine
Ethoxyethanol
Ethoxylated Nonylphenol
Ethoxylated Octylphenol
Ethoxyethyl Acetate
Ethyl Acetate
Ethyl Acrylate- Carbonylation of
  Acetylene
Ethyl Acrylate-Direct Esterification
Ethyl Benzene
Ethyl Butyrate
Ethyl Chloride- Hydrochlorination of
  Ethylene
Ethyl Chloride- Chlorination of Ethane
Ethyl Chloride- Hydrochlorination of
  Ethanol
Ethyl Ether
Ethyl Hexanol
Ethylene
Ethylenediamine
Ethylene Dibromide
Ethylene Dichloride- Ethylene
  Chlorination
Ethylene Dichloride- Oxychlorination
Ethylene Glycol
Ethylene Oxide
Ethylene - Propylene Rubber
Ethylene Propylene Terpolymer Rubber
Fish and Sea Food Canning
Food Preparation
Formaldehyde
Fruit and Vegetable Canning
Fruit and Vegetable Freezing
Fumaric Acid
Glycerin - Acrolein
Glyerin - Allyl Alcohol
Glycerin - Allyl Chloride
Glycerin - Epichlorohydrin
Glycerol, Tri - Polyoxypropylene Ether
Heptene
Hexachlorobenzene
Hexamethylenediamine - from Adiponitrile
Hexamethylenetetramine
Isocyanates
Isooctal Alcohols
Isophthalic Acid
Isoprene
Isopropanol - Direct Hydration
Isopropanol Acetate
Ketone Alcohol Oil
Leather

TABLE 3 (Cont'd.)

ALPHABETICAL LISTING OF ORGANIC EMISSION SOURCES

Linear Alcohols- Zieglar Process
Linear Alkylbenzene
Malathion
Maleic Anhydride - from Benzene
Malt Beverage Production
Meat Smokehouse
Melamine
Methanearsonic Acid - Calcium Acid Salt
Methanearsonic Acid - Dodecyl and Octyl
  Ammonium Salts
Methanearsonic Acid - Disodium Salt
Methanearsonic Acid - Monosodium Salt
Methanol
Methoxyethanol
Methyl Acetate
Methyl Chloride
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methyl Methacrylate - Cyanohydrin Process
Methylene Chloride - Chlorination of
  Methane
Methylene diphenyldiisocyanate
Mixed Linear Alcohols
Mixed Olefinite Product
Modacrylic Fibers
Monosodium Glutamate
Naphthalene - Coal Tar
Naphthonic Acid - Copper Salt
1-Naphthyl-N-Methyl Carbonate
Nitroaniline
Nitrobenzene
Nitrocellulose
Nitrochlorobenzene
Nitroglycerine
Nitroparaffins
Nonene
Nonylphenol
Nylon 6
Nylon 66
n-Octyl-n-Decyl Phthalate
Octylphenol
Oleic Acid
Oxalic Acid - Oxidation of Glucose
Oxo Mixed Linear Alcohols
Oxo Process
Paint Manufacturing
n-Paraffin Chloride
Penicillin, G, Potassium
Penicillin, G, Procaine
Pentachlorophenol
Pentaerythritol
Pentaerythritol Tetranitrate
Perchloroethylene - Chlorination of Propane
Perchloro-ethylene - from Trichloroethylene
Phenol-Cumene Process
Phenylmercuric Acetate
Phenylmercuric Oleate
Phosgene
Phthalic Anhydride - from Naphthalene
Phthalic Anhydride - from O-oxlene
Polyacrylonitrile - Solution Polmerization
Polyamide Resins
Polybutadiene
Polycarbonate Resins
Polychloroprene
Polyester Polyols
Polyester Resins
Polyethylene - High Density
Polyethylene - Low Density
Polyisobutylene - Isoprene - Butyl Elastomers

TABLE 3 (Cont'd.)

ALPHABETICAL LISTING OF ORGANIC EMISSION SOURCES

Polyisoprene
Polymethylene Polyphenyl Isocyanate
Polypropylene
Polyram
Polystyrene Resins
Polysulfide Rubber
Polyurethanes
Polyvinyl Acetate
Polyvinyl Alcohol - Hydrolysis
Polyvinyl Chloride
Polyvinylvinylidene Chloride
Printing Ink
Propionic Acid
Propylene Glycol
Propylene Oxide - Chlorohydrin Process
Propylene Rimer + Tetramer
Rayon
Saccharin-o-toluenesulfonanites
Saccharin - from Phthalic Anhydride
Salicylates - excluding Aspirin
Salicylic Acid
Soap and Detergents
Solvent Evaporation - Degreasing
Solvent Evaporation - Dry Cleaning
Solvent Evaporation - Printing and Publishing
Solvent Evaporation - Rubber and Plastic Processing
Solvent Evaporation - Surface Coating Auto Painting
Solvent Evaporation - Surface Coating - Excluding Auto Painting
Sorbitol
Styrene
Styrene - Butadiene Copolymer Resins
Sugar Processing
Sulfated Ethoxylates
Sym-Trimethylene-Trinitramine
Terephthalic Acid
Tetracycline
Tetraethyl/Tetramethyl Lead
Tobacco
Toluenediamine
Toluene Diisocyanate
Toluene Sulfonate - Hydrotrope
Toluene Sulfonic Acid
1,1,1-Trichloroethane
1,1,2-Trichloroethane - from Ethylene Dichloride
Trichloroethylene - from Acetylene
Trichloroethylene - from Ethylene
Urea
Varnish Manufacturing
Vegetable Oil Milling
Vinyl Acetate - from Ethylene
Vinyl Acetate - from Acetylene
Vinyl Chloride - from Acetylene
Vinyl Chloride - from Ethylene Dichloride
Vinylidene Chloride - from Trichloroethane
Vitamin A
Vitamin B Complexes
Wet Corn Milling
Wood Processing - Kraft or Sulfate Process
Wood Processing - Neutral Sulfite Semi Chemical
Wood Processing - Sulfite Process
m-Xylene
o-Xylene
p-Xylene
Xylene Sulfonate-Ammonium Salt
Xylene Sulfonate Potassium Salt
Xylene Sulfonate - Sodium Salt
Xylene Sulfonic Acid

APPENDIX B

ASSESSMENT OF PRESENT SAMPLING TECHNIQUES

The determination of a range of organic emissions from specific
sources is usually accomplished by sampling in the field and sub-
sequent analysis in the laboratory. Only in very special cases
is it feasible to monitor these emissions at the field site. One
case where this on-site monitoring was demonstrated was the use
of a chromatographic analyzer with flame photometric detector in
analysis of inorganic and organic sulfur species emitted from a
Kraft pulp mill (Ref. 4). However, in general, continuous or
intermittent monitoring of a range of organic species in the field
is not feasible due to the sophistication of laboratory instrumen-
tation required for analyses.

The detection and quantitative measurement of trace organic sub-
stances in gas phase mixtures, particularly ambient air and mobile
or stationary emission sources, generally requires a concentration
step to attain the required detection limit. The most frequently
employed concentration techniques are solvent scrubbing, con-
densation (cryogenic trapping), adsorption on activated carbon,
chromatographic adsorption, chromatographic equilibration, and
chemical reactions.

Solvent scrubbing for organics is achieved using an impinger train
containing a solvent system which will trap the desired emissions.
The train is often held at ice temperature to enhance collection
efficiency and minimize slippage of the desired components. De-
pending on the concentration of the emission, the flow rate and
the sampling time, the solvent must be reduced in volume to con-
centrate the pollutants before analysis. Evaporation of the
solvent runs the risk of significant losses in the more volatile
components of interest.

Use of condensation techniques is the least desirable approach since (a) collection efficiencies are poor and vary significantly with physical and chemical properties of the substances being collected, (b) condensation of water with attendent trap plugging and hydrolysis of collected organics can occur, and (c) aerosols (micro-fog) can form and not be trapped unless electrostatic precipitators are used. If significant amounts of moisture are present, as is often realized in combustion, incineration or absorber vent gases, the trap will contain a two-phase system which will require special handling before analysis. Cryogenic trapping at temperatures sufficient to condense oxygen or nitrogen requires the use of special equipment to carry out analyses (Ref. 5).

Sample collecting and concentration techniques based on adsorption on activated carbon have been used extensively. Activated charcoal has been shown to quantitatively remove an extremely broad range of organic contaminants from air. The National Institute of Occupational Safety and Health (NIOSH) has promulgated a general procedure for sampling and analysis of organics in work place atmosphere (Ref. 6 and 7). This procedure is based on adsorption of the organics on activated charcoal and desorption with carbon disulfide followed by subsequent analysis by gas chromatograph. While the adsorption process is quantitative, the recovery of the collected components is usually incomplete and variable (Ref. 8). The charcoal may also serve as a catalyst to promote alternation of the sample (Ref. 9 and 10) and it is extremely subject to adsorption of water vapor which limits the adsorption capacity and can displace the desired organic components. Desorption by heating requires high temperature (up to 400°C) and is accompanied by chemical changes due to pyrolysis of the organic species and thermally enhanced reactions between the components.

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Silica gel has been used for collecting three-carbon and higher molecular weight hydrocarbons. The collection efficiency for lower hydrocarbons, such as ethylene, from air has been demonstrated to be poor even when trapping at dry ice acetone temperatures (Ref. 11).

Short lengths of packed chromatographic columns commonly used for the sepearation of hydrocarbons have been used to concentrate aliphatic hydrocarbons at liquid-oxygen or liquid-nitrogen temperatures (Ref. 12 - 16).

For specific applications, the chromatographic equilibration technique (Ref. 17 - 19) can be employed. However, the major limitation of this technique is the requirement that complete equilibrium of adsorbate and gas-phase species be attained. With the complex mixtures of source emissions, the potentially high temperatures, and the problems of selective displacement of volatile organics by less volatile species, the probability of realistically attaining an adsorption equilibrium is questionable in sampling source emissions.

GLC packings have been successfully employed for trapping and concentrating aromatic hydrocarbons and organic oxygenenated substances in ambient air on short sampling tubes (Ref. 17 - 19). This method of sampling avoids the use of cryogenic cooling and special drying methods to remove atmospheric water. Cropper and Kaminsky (Ref. 17) used a Celite 545 (30-60 mesh) support with either Silicone Elastomer E301 or polyethylene glycol 400 as stationary phases in short (1 inch) absorption tubes to concentrate a wide variety of organic substances at ambient temperature. Retention volumes were determined for a range of organic vapors to assess maximum permissable sampling times before break through of the absorption tube occurred. Novak et al., (Ref. 18 and 19),

used the identical GLC packings in 4.5 cm long tubes of 0.5 cm
diameter for sampling and subsequent GC analysis of nonpolar
(benzene, toluene and p-xylene) and polar(acetone, methanol and
toluene) mixtures in air. In this case the mean error was about
5% with concentrations from 1 to 25 ppm, and practical applica-
tions were demonstrated in the ppb range.

In certain applications, chemical reactions can be used to collect
and concentrate specific classes of chemicals and to desorb the
materials for analysis. Okita (Ref. 20) devised a field system
for sampling malodorous sulfur- and nitrogen-bearing organic gases.
Mercuric salts were used to collect mercaptans and organic sul-
fides, while sulfuric acid was used as an impregnating agent to
glass fiber filters. By using the impregnated filters, sampling
flow rates of 1 to 14.5 l/min. with 97-100% efficiencies of
collection and recovery can be used. In selected cases, sampling
rates as high as 100 l/min. can be used satisfactorily.

APPENDIX C

USE OF POROUS POLYMER ADSORBENTS IN SAMPLING

Potentially, the most attractive method for collecting and concentrating organic substances from ambient air and mobile or stationary emission sources employs the adsorption and/or partitioning properties of materials normally used in gas chromatographic analysis to retain organic substances selectively while removing the major diluent gases, such as air, nitrogen, and water vapor. By proper selection of materials which retain little water, separation of organic substances from water can be accomplished even in samples taken in humid atmospheres. Various types of chromatographic materials have been used, including carbon molecular sieves, liquid phases on solid supports, e.g., Dexil 300 GC on Chromosorb AW HMDS and Silicone Oil DC 200 on Chromosorb, and porous polymers such as Tenax GC and the Chromosorb and Porapak series.

Williams and Umstead (Ref. 21) used porous polymer beads (Porapak Q and S obtained from Waters Associates, Inc.) at room temperature for concentrating organic vapors from air. The 80-100 mesh Porapaks were contained in a 6-foot x 1/4-inch stainless steel column which was later employed as the column in a chromatograph equipped with a Dohrmann microcoulometer detector. A wide range of halogenated organic compounds were determined at air concentrations as low as 10 ppb. The data showed that the collection and analysis method was quantitative. Since the porous polymer beads do not absorb moisture and readily pass the major components of air and since they are amenable to on-column injection to the detector, this method showed great promise for analysis of organic air contaminants.

A number of workers have employed the porous polymer bead concentration approach in the last four years and have developed

performance data for ambient air, blood, and urine analyses. Aue and Teli (Ref. 22) prepared support-bonded chromatographic phases such as $(C_{18}H_{37}SiO_{3/2})_n$ on various types of Chromosorb to trap organic vapors from the atmosphere. Using the silicone support-bonded sorbents, gasoline, automobile exhaust, chlorinated hydrocarbons, and contaminated air samples were sampled. In these studies the trapped organics were extracted with pentane prior to analysis. The method was found to be limited to higher molecular weight species ($>C_6$ organics), and some difficulties arose in the occasional appearance of artifacts, possibly due to the incomplete removal of non-support-bonded silicone before sampling.

Dravnieks et al., (Ref. 23) employed Chromosorb 102, a high surface area styrene-divinyl copolymer porous polymer absorbent for high speed (4l/min) collection of organic species from air. The collection efficiencies of Chromosorb 102 for individual organic species were compared to the respective partition coefficients. In sampling from synthetic mixtures of nine components in air, the reproducibility of the GC peak areas was within ±3%.

Zlatkis et al., (Ref. 24) employed Tenax GC, a 2,6-diphenyl-p-phenylene oxide porous polymer for sampling organic contaminants in air, human breath, and urine. In these studies, the authors compared the performance of Porapak P (a porous polymer of styrene and divinyl benzene), Carbosieve (a carbon molecular sieve), and Tenax GC in trapping organic contaminants. The major drawback to the use of Porapak P is its temperature limit of 230°C. This necessitates a maximum desorption temperatures of 200°C at which temperature bleeding produced artifacts upon analysis. Carbosieve, which is prepared by thermally cracking polyvinylidene chloride, exhibited a high surface area (1000 m^2/g) and high temperature stability. Its major disadvantage is that temperatures in excess of 400°C were needed to desorb organic volatiles, and such conditions could cause pyrolysis of some organics. In such cases, desorption by solvents may be required.

Tenax GC appeares to fulfill both requirements, i.e., efficient adsorptivity and desorptivity. It can withstand temperatures as high as 375°C, permitting desorption at 300°C. The adsorption tubes can be stored for long periods of time with excellent reproducibility of data after subsequent desorption and chromatographic analysis. In a later paper (Ref. 25) Zlatkis and coworkers described use of the Tenax GC adsorption method in obtaining profiles of volatile metabolites of 150 urine samples from normal subjects and 40 samples from individuals with diabetes. Characteristic constituents in normal urines were 2-butanone, 2-pentanone, 4-heptanone, dimethylsulfide, several alkyl furans, pyrole, and carvone. For diabeties under insulin treatment, high concentrations of pyrazines, cyclohexanone, lower aliphatic alcohols, and octanols were found. These data point out the wide variety of organic structures that are trapped by Tenax GC.

R. E. Kaiser (Ref. 26) conducted environmental analyses of organic contaminants by using two different adsorption packings. Carbon molecular sieve was employed to enrich ethylene or hydrocarbons from methane to C_4. Dexsil 300 GC (5% w/w on Chromosorb AW) was used for enriching nonpolar and medium-polar impurities from C_4 to C_{15}. Kaiser employed an adsorption tube with an imposed temperature gradient (-20°C to -160°C for trapping; +250°C to +400°C for elution) which led to a concentration focusing effect that prevented chemical reaction of the enriched traces with one another. This gradient enrichment approach also prevents micro-fog production, which is a common source of error in cryogenic trapping systems.

Mieure and Dietrich (Ref. 27) employed a variety of porous polymer adsorbents for determination of trace organics in air and water. These investigators recommended Chromosorb 101 for sorption and desorption of acidic and neutral components, Chromosorb 105 for low boiling components and Tenax GC for basic, neutral and high boiling species. As was the case with earlier workers, the adsorption tube could be directly interfaced with a gas chromatograph

either as an injection port insert or as a connection directly in the GC oven. Field sampling of ambient air at two liters/minute flow rate over a 10-minute sampling interval was sufficient to measure organic components at concentrations as low as 0.5 $\mu g/m^3$ (1 ppb for a molecular weight of 100). Compound classes determined in air in the vicinity of manufacturing sites included phenols, alcohols, ketones, ethers, hydrocarbons, disulfides, sulfur heterocyclics, aromatic amines, phthalate esters, and chlorinated hydrocarbons. Corresponding classes determined in wastewater included phenols, alcohols, nitro compounds, carboxylic acids, aromatic amines, chlorinated hydrocarbons, esters, amides, hydrocarbons, aliphatic amines, ethers, anilides, heterocycles, aldehydes, ketones and sulfides.

Zlatkis and coworkers (Ref. 28 - 30) have published three recent papers concerning use of Tenax GC for analysis of urinary metabolites (Ref. 28), organic volatiles in air (Ref. 29), and trace volatile metabolites in serum and plasma (Ref. 30).

It is evident from the above survey of recent publications that the porous polymer bead adsorption sampling method shows great promise for sampling of trace organic contaminants in ambient air and is also attractive because the sampling tubes can be interfaced directly with laboratory analytical instrumentation such as a gas chromatograph or a tandem-coupled gas chromatograph/mass spectrometer system.

APPENDIX D

CHARACTERISTICS OF POROUS POLYMER SORBENTS AND POTENTIAL LIMITING PROPERTIES

As discussed in the previous section, various types of chromatographic materials have been employed for sampling and subsequent analysis of a range of organic pollutants. These include carbon molecular sieves, liquid phases on solid supports, and porous polymers.

The carbon molecular sieves (Carbosieves) can enrich ethylene or hydrocarbons from methane to C_4 from air, but suffer the same desorption limitations as noted above for activated carbon. The coated chromatographic packings lack retention capacity unless cooled to subambient temperatures. With gradient cooling, however, Dexsil 300 GC on Chromosorb AW HMDS provides sufficient retention properties to enrich nonpolar and medium polar impurities in air from C_4 up to C_{15} (Ref. 26).

The retentive characteristics, varied polarity, high-thermal stability, and low affinity for water of porous polymers, suggest that these materials might be the best media for efficiently collecting and enriching organic substances in ambient air and/or from mobile or stationary emission sources. However, the varied nature of the emission sources requires an evaluation of the limiting properties before specific applications can be defined. The characteristics of typical porous polymers and their limiting properties as sorbents are discussed in the following subsections.

The use of small tubes (4, 6 or 8 inches in length) packed with porous polymer materials is an attractive approach to field sampling. However, most sampling with these sorbents has been done on ambient air, and their application to sampling stationary source emissions has not been evaluated. MRC has used the porous

polymer sampling techniques for collecting specimens and for quantitative determinations of organic emission products from a variety of major industrial paint and polymer-coating, drying or processing, ovens (see Table 4). For applications to other emission sources, which emit a more complex mixture or a more reactive (temperature, oxidant, humidity, etc.) gas stream, further evaluation is necessary.

The major problems related to the use of porous polymers as sorbents for collecting organic compounds from industrial emission sources are:

(1) Displacement of more volatile species by less volatile trace organics and/or by carbon-containing gases (CO_2, hydrocarbons) which may be the major components of the gas stream.

(2) Irreversible adsorption or poor desorption efficiencies for certain specific compounds (e.g., amines, glycols, carboxylic acids, nitriles, high molecular weight compounds).

(3) Chemical reaction of sorbates (e.g., oxidation, hydrolysis, polymerization).

(4) Change in sorption properties of sorbent due to interaction with reactive gases (e.g., NO_x, SO_x, O_2, and inorganic acids, and depolymerization).

(5) Artifact species produced by action of reactive gases and/or thermal effects.

(6) Retention capacity of the porous polymers.

(7) Thermal stability of sorbent.

(8) Sampling volume, flow rate, sampling time.

TABLE 4

ORGANIC SUBSTANCES MEASURED BY MRC FROM PAINT
AND POLYMER CURING OVENS BY POROUS POLYMER
ADSORPTION AND SUBSEQUENT GC/MASS SPECTROMETRIC ANALYSIS

Methanol	2-Ethoxyethylacetate
Ethanol	Chloroform
Isopropanol	Methylenechloride
2-Ethoxyethanol	Cyclohexane
Isobutanol	Dimethylcyclohexane
n-Butanol	Benzene
C_5 Alcohols	Toluene
n-Propanol	Xylenes
2-Methylbutanol	Styrene
Ethyleneglycol monoethyl ether	Methylstyrene
2-(2-ethoxyethoxy) ethanol	Dimethylstyrene
Formaldehyde	C_3 Alkylbenzenes
Acetaldehyde	C_4 Alkylbenzenes
Acrolein	C_4 Substituted Styrene
Acetone	Trichloroethane
Methylethylketone	Dichloroethylene
Diethylether	Carbon Disulfide
Butylacetate	Isopropylbenzene
Sat. Hydrocarbons	Phenol
	Benzaldehyde

1. PHYSICAL AND CHEMICAL CHARACTERISTICS OF POROUS POLYMER SORBENTS

A variety of porous polymers have been developed for chromato-
graphic purposes and have been used as collecting media for
organic substances. Although there are a number of variations,
the most used porous polymers are based on two or more monomer
systems, e.g., styrene or ethylvinylbenzene, divinylbenzene, and
a polar vinyl monomer. By varying the proportion of each monomer,
different polarity, thermal stability, surface area, pore size,
and retention characteristics can be obtained.

Recently, Tenax GC, a new, more polar, and more thermally stable porous polymer has become commercially available. This system is based on 2,6-diphenyl-p-phenylene oxide. Other systems that have been used in laboratory tests, but are not widely used or are not commercially available, are polyimides, polyamides, polyacrylates, and phosphonated or halogenated resins.

Four groups of porous polymers are potentially usable as sorbents for collecting and concentrating organic compounds from stack emissions. These are:

(1) Porapak series (Waters Assoc., Inc.)

(2) Chromosorb Century series (Johns-Manville Products Corp.)

(3) XAD Resins (Rohm and Haas Co.)

(4) Tenax-GC (Enka, N.V., the Netherlands)

(5) Polyimides

Note: Some XAD resins are marketed by Johns-Manville Products Corp. as the Chromosorb Century series; e.g., Chromosorb 102 is XAD-2.

A limited amount of information is available which directly compares the chromatographic properties of these materials. Retention indices obtained under similar operating conditions are reported for two groups, namely, the Porapak and the Chromosorb Century series. Compilations of chromatographic retention data (Ref. 31 - 33) for various chemical classes are reported and compared for the most used resins in the Chromosorb and Porapak series. The retention times (< 1 min to 260 min) of 90 organic compounds (MW 32 to 162) including a variety of alcohols, ethers, esters, dioxane, and dioxolanes are reported by Burger (Ref. 31) for Porapak Q (2 ft x 3/16 in.) at 163°C.

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In general, the retention characteristics of the porous polymers are influenced by both gas-solid and gas-liquid mechanisms. The pore size distribution and micropore volume, the nature of the polymer, and the surface activity all influence the adsorption, diffusion, and partitioning processes. Although specific retention indices are not available for all porous polymers, certain physical property data and a relative ranking of polarity can describe the relative retention characteristics. These data are shown in Tables 5, 6 and 7.

1.1   Chromatographic Characteristics of Porapak Resins

Porapak P

Least polar. Separates a wide variety of carbonyl compounds, glycols, and alcohols.

Porapak P-S

Surface-silanized version of "P" which minimizes tailing. Separates aldehydes and glycols.

Porapak Q

Most widely used. Particularly effective for hydrocarbons, organic compounds in water, and oxides of nitrogen.

Porapak Q-S

Surface-silanized version of "Q" which eliminates tailing. Separates organic acids and other polar compounds with minimum tailing.

Porapak R

Moderate polarity. Long retention and good resolution observed for ethers. Separates esters, and H_2O from Cl_2 and HCl.

TABLE 5

PROPERTIES OF PORAPAK SERIES POROUS POLYMERS

Porapak Type	Surface Area (m^2/g)	Ave. Pore Diam. $(\overset{\circ}{A})$	Temp. Limit ($^{\circ}$C)	Monomer Composition
P	110	150	250	STY-DVB
P-S*	-	-	250	-
Q	840	75	250	EVB-DVB
Q-S*	-	-	250	-
R	780	76	250	Vinyl pyrollidone
S	670	76	250	Vinyl pyridine
N	437	-	190	Vinyl pyrollidone
T	450	91	190	Ethyleneglyco-dimethylacrylate

*P-S and Q-S are silanized modification of P and Q, respectively

TABLE 6

PROPERTIES OF CHROMOSORB CENTURY SERIES POROUS POLYMERS

Porous Polymer Type	Surface Area (m^2/g)	Ave. Pore Diam. (Å)	Temp. Limit (°C)	Monomer Composition
Chromosorb 101	30-40	3000-4000	275 (325)*	STY-DVB
Chromosorb 102	300-400	85	250 (300)*	STY-DVB
Chromosorb 103	15-25	3000-4000	275 (300)*	Cross-linked PS
Chromosorb 104	100-200	600-800	250 (275)*	ACN-DVB
Chromosorb 105	600-700	400-600	250 (275)*	Polyaromatic
Chromosorb 106	-	-	250 (275)*	Cross-linked PS
Chromosorb 107	-	-	250 (275)*	Cross-linked acrylic ester
Chromosorb 108	-	-	250 (275)*	Cross-linked acrylic ester

STY-styrene; DVB-divinylbenzene; PS-polystyrene; ACN-acrylonitrile

*Maximum temperature for short duration

TABLE 7

PROPERTIES OF XAD RESINS

Porous Polymer	Surface Area (m^2/g)	Ave. Pore Diam. (Å)	Temp. Limit (°C)	Monomer Composition
XAD-1	100	200	200-250	STY-DVB
XAD-2	300	90	200-250	STY-DVB
XAD-4	784	50	200-250	STY-DVB
XAD-7	450	90	200-250	Acrylic Ester
XAD-8	140	235	200-250	Acrylic Ester
XAD-11	69	352	200-250	Amide

Porapak S

Separates normal and branched-chain alcohols.

Porapak N

Separates CO_2, NH_3, and H_2O, and acetylene from other C_2 hydrocarbons. High water retention.

Porapak T

Highest polarity and greatest water retention. Used for determination of formaldehyde in aqueous solutions.

1.2   Chromatographic Properties of Chromosorb Resins

Chromosorb 101

Because of its surface nature Chromosorb 101 shows no interaction; that is no tailing with oxygenated compounds, particularly hydroxyl compounds (alcohols, glycols, phenols) as well as carboxylic acids. Chromosorb 101 is very effective in separating hydrocarbons, alcohols, fatty acids, esters, aldehydes, ketones, ethers, and glycols.

Chromosorb 102

Since Chromosorb 102 has a high surface area, it performs in a manner similar to that of a conventionally packed column having a high liquid phase loading. This characteristic causes retention times on the column to be relatively high. Because of its high surface area, Chromosorb 102 can be used to separate light and permanent gases, as well as lower molecular weight compounds such as acids, alcohols, glycols, ketones, esters, hydrocarbons, etc.

Chromosorb 103

Chromosorb 103 was developed specifically for amines and for basic compounds. Fast, efficient separations are attained for amines, amides, alcohols, aldehydes, hydrazines, and ketones. Chromosorb 103 will not handle acidic materials, glycols, or other compounds

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as acidic as glycols; these are totally adsorbed. Methyl amine is easily separated from light gases such as ammonia. There is some tailing of water below 150°C.

Chromosorb 104

Chromosorb 104 is very efficient for gas analysis of various types at subambient, ambient, and higher temperatures. It is also very effective in separating isomeric xylenols, alcohols, ketones, nitriles, aldehydes, and hydrocarbons. The important characteristics of Chromosorb 104 are its effectiveness in separating sulfur-containing compounds at low levels, aqueous ammonia and hydrogen sulfide at low levels, isomeric xylenols, and gases of various types. The retention times are longer on Chromosorb 104 than other Chromosorb "Century Series" porous polymers. Chromosorb 104 has the highest polarity in the Chromosorb "Century Series" porous polymers.

Chromosorb 105

The important characteristics of Chromosorb 105 are its effectiveness in the separation of formaldehyde from water and methanol, acetylene from lower hydrocarbons, and most other classes of organic compounds of different polarity having a boiling point up to 200°C. The polarity of Chromosorb 105 is lower than that of Chromosorb 104.

Chromosorb 106

Chromosorb 106 retains benzene in relation to polar compounds and separates C_2 to C_5 fatty acids from corresponding alcohols.

Chromosorb 107

Chromosorb 107 provides efficient separation of various classes of compounds in general and formaldehyde in particular.

Chromosorb 108

Chromosorb 108 is effective for separating gases and polar materials such as water, alcohols, aldehydes, ketones, glycols, etc.

1.3   Chromatographic Properties of XAD Resins

Low molecular weight gases C_1-C_2, are moderately retained at ambient temperature on XAD resins. H_2S is more strongly retained, and sulfur dioxide, and vinyl chloride are strongly sorbed.

The more polar gases (H_2S and SO_2) are more strongly sorbed on the acrylate resins (XAD-7 and -8) and the phosphonated resin (XAD-1) than on the STY-DVB resins. Ammonia also is retained longer on the acrylates.

In a given XAD series, the retention times increase as the surface area of the resins increase (Ref. 34). These findings are contrary to those of Johnson and Barrall for a series of Porapak resins (Ref. 35). They found similar retention times for nonpolar gases on four resins and concluded that the controlling factor for separation is a function of the nature of the porous polymer, rather than its micro-pore structure.

Increased temperature reduces the retention times and sharpens the chromatographic peaks. For XAD-2 (2.5 ft x 1/4 in. with a flow rate of 20 ml/min), typical retention times are 70 min at ambient, 19.0 min at 60°C, and 4.7 min at 100°C for vinyl chloride, and 40 min at ambient, 10.6 min at 60°C, and 2.70 min at 100°C for SO_2.

For C_1 to C_7 alcohols, an acrylic resin, XAD-7, has been used for chromatographic separation. However, the alcohols are so strongly retained that a high column temperature (programmed to 239°C) is required for elution.

1.4   Chromatographic Characteristics of Tenax GC

Tenax GC is a porous polymer that is based on 2,6-diphenyl-p-phenylene oxide. It was developed originally for chromatography of high boiling polar compounds such as alcohols, polyethylene glycol compounds, diols, phenols, mono- and diamines, ethanolamine, amides, aldehydes, and ketones. It can also be used for chromatography of lower boiling compounds such as methanol, acetonitrile, methyl ethyl ketone, benzene, styrene, etc. The resolution of these compounds is not as good for Tenax GC as for Porapak Q. However, the thermal stability resulting in reduced column bleed makes Tenax GC an excellent compromise for chromatography samples containing organic compounds with a wide distribution of boiling points. In addition, Tenax GC is more stable than most porous polymers due to its resistance to oxidation.

A recent paper by Butler and Burke (Ref. 36) discusses the relative sampling capacities for Tenax GC, Porapak, P, Q, R & T, and Chromosorb 101 and 102. Their conclusion was that Porapaks Q and R have the best overall sampling capacities and Tenax GC should be used when higher boiling compounds are to be sampled and analyzed. In addition, MRC's experience shows that the greater thermal and oxidative stability of Tenax GC, compared with the Porapaks Q and R, will result in lower levels of artifact compounds being present in the analysis.

The surface area of Tenax GC is 19 m^2/g and the temperature limitation for its use is 375°C.

1.5   Chromatographic Characteristics of Polyimide Resins

An additional porous polymer system which is not presently available commercially shows very high thermal stability (400°C) and oxidative resistance. This system is based on polyimides (Ref. 37). Two polymers of this type have been evaluated.

Polysorbimide 1, formed from the reaction of pyromellitic
dianhydride and diaminodiphenyl ether, has a surface area of
67.5 m^2/g and an average pore diameter of 2000 Å. Polysorbimide 2,
formed from the dianhydride of benzophenone tetracarboxylic acid
and diaminodiphenyl ether, has a surface area of 41.8 m^2/g and an
average pore diameter of 20,000 Å. Both are macroporous sorbents
having large pore volumes. The high thermal stability extends
both the range of the compounds desorbed and the temperature of
desorption.

Some of their retention characteristics are:

(1)   Saturated hydrocarbons, same as STY-DVB.

(2)   Unsaturated compounds are more strongly retained.

(3)   Retention of polar molecules depends on the dipole moment
      and ability of compounds to form hydrogen bonds with the
      sorbent surface.

(4)   Specificity for molecular species, which is due to the
      presence of imide and carbonyl functional groups on the
      surface of the sorbents.

(5)   Suitable for the separation of high boiling polar compounds
      such as alcohols, esters, aromatic hydrocarbons, pyrrolidones,
      aldehydes, and ketones (bp 200-300°C).

2.   POTENTIAL LIMITING PROPERTIES OF POROUS POLYMERS AS SORBENTS

2.1   Displacement of Volatile Species

The displacement of volatile organic species by less volatile
organic substances is a major problem when using porous polymers.
High molecular weight compounds are more easily retained than low
molecular weight substances. Substances eluted before benzene
can be partially or completely lost. Bertsch, et al., (Ref. 29)

have reported their inability to retain benzaldehyde, aceto-
phenone, and substances eluting before benzene on Tenax GC.

Data by Rabbani, et al., (Ref. 38) show that retention data of
different gases on porous polymers like porapak Q are influenced
by the nature of the carrier gas. Slight dependence of retention
data was observed when using gases (H_2, Ar, N_2) which are physi-
cally sorbed; however, when using carbon-containing carrier gases
(CO_2, C_2H_2, or C_3H_6), a substantial decrease in retention volumes
was observed for both hydrocarbons and nonhydrocarbon gases. At
52°C, the retention volume for C_3H_8 changed from 430 with N_2 as
carrier to 305 with CO_2 and 260 with C_2H_2.

Such differences also depend on temperature since greater dif-
ferences are found at lower temperatures, e.g., 20°C, lesser
differences at higher temperatures, e.g., 70°C, and much lesser
differences at 150°C. The effect is most critical at the lower
temperatures where the adsorption mechanism predominates, whereas
once the glass transition temperature for the polymer is reached
(~140°C), partitioning mechanism predominates. Based on these
data, when sampling CO_2 or hydrocarbon-rich emissions, some con-
sideration must be given to flushing effects when establishing
sampling times and rates.

2.2   Irreversible Adsorption or Poor Desorption Efficiencies

Supina and Rose (Ref. 33) and Dave (Ref. 32) list retention data
for a wide variety of organic compounds. Information for the
Porapak (N, P, Q, R, S, T, QS) series and the Chromosorb Century
(101, 102, 103) series is provided. As derived from these in-
formation sources and general commercial literature, the most
pertinent data to use for porous polymers as adsorbents relate
to the chemical classes that cannot be desorbed from the resins.
Generally, the adsorption characteristics of most resins are

adequate. However, some chemical classes are irreversibly adsorbed or are desorbed slowly over a relatively long period.

The resins and associated chemical classes that will provide potentially poor desorption efficiencies are as follows:

Glycols   -   Complete adsorption on Chromosorb 103
                        Some tailing on Porapak Z, R, and S.
                        Severe tailing on Porapak QS

Nitriles   -   Severe tailing on Chromosorb 103

Nitroparaffins   -   Severe tailing on Chromosorb 103

Amines and
diamines   -   Severe tailing on Chromosorb 101 and 102
                        Porapak N, P, Q, R, S, T. Some tailing
                        on Porapak QS

Anilines   -   Severe tailing on Porapak N, Q, S, T, QS
                        Some tailing on Porapak R

Carboxylic acids-   Complete adsorption on Chromosorb 103
                        Severe tailing on Porapak S. Some
                        tailing on Chromosorb 102 and Porapak Q

Alcohols   -   Some tailing on Porapak N. Branch-chain
                        broadening on Chromosorb 101, 102, 103
                        and Porapak T

A study by Hertl and Neumann (Ref. 39) established that extreme tailing of amine peaks on Chromosorb 102 is due to unreacted vinyl groups. A method was devised for removing these active sites by adding HF to the double bond of the vinyl group. This deactivation of Chromosorb 102 resulted in elimination or reduction of tailing for amine and pyridine peaks, but tailing of acetic acid was increased by apparent interaction between the carboxylic acid and surface fluoride groups.

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Peak broadening with branched hydrocarbons, alcohols, cycloalkanes, sulfides, ketones, and fatty acids are reported for Porapak P and PS, and Chromosorb 101 (Ref. 40).

Considerable irreversible adsorption difficulties can be encountered when using some porous polymers; however, also significant is the compatibility of the tubing and end plugs with the substance being collected. For example, free carboxylic acids are strongly adsorbed on metal column tubing, carbonaceous residues, as well as glass wool used as column end-plugs. Silanized glass wool is unsatisfactory; phosphoric acid appears to be the most effective acid additive for treating glass wool. Glass column tubing does not adsorb acids. Porapak Q, with added phosphoric acid to suppress tailing, and Chromosorb 101 can be used to chromatograph free acids (Ref. 41).

2.3 Chemical Reaction of Sorbates with Sorbents and Production of Artifact Species

Porapak Q and Chromosorb 102 were found to react with NO_2 (Ref. 42) and oxygen (Ref. 43). The reaction with NO_2 yields NO, water, and nitrated aromatic rings of the polymer plus the possible presence of increased olefinic unsaturation and/or oxidation of the polymer. Oxygen reacts with the resin above 100°C to depolymerize part of it to produce carbonyl compounds.

In general, polystyrene-type materials suffer from oxidation and thermal fragmentation at temperatures above 250°C.

2.4 Change in Sorption Properties of Porous Polymers

The reactions discussed above in 2.3 undoubtedly influence the sorption properties of porous polymers. The displacement phenomena indicated above in 2.1 also point out potential problems

related to physical adsorption changes at collection temperatures below 140°C, where the physical adsorption mechanism for compound retention predominates with the STY or EVB-DVB systems.

Also, problems may be experienced when using porous polymers under high-humidity, high-temperature conditions. Although Dave (Ref. 32) reports that Chromosorb 101, 102, and 103, and Porapaks N, P, Q, QS, R, S, and T are hydrophobic, and Bertsch (Ref. 29) suggests that Tenax GC has little affinity for water. Certain precautions must be considered in actual use. Steam displacement of organic substances may occur, and some changes in the surface adsorption sites (particularly with the more polar resins) may result. Even with the more hydrophobic resins, e.g., Porapak Q (EVB-DVB), some water is actually adsorbed. Porapak Q retains up to 3.4 μg H_2O/g of polymer at 110°C (Ref. 44).

At present, it is generally assumed in a qualitative sense that the interaction mechanism for adsorbates on porous polymers is a combination of both adsorption and partitioning, especially at higher temperatures. Below the glass transition temperature (T_g), absorption of organic vapors by porous polymers occurs through very complex processes. Amorphous polymers would be expected to absorb organic vapors to a much greater extent if they were in a rubbery state as opposed to a glass. Data suggest that surface adsorption should predominate for organic molecules at temperatures below 140°C.

2.5   Retention Capacity of Porous Polymers

Pore size determinations for Porapak P and Q indicate that a large proportion of very small pores exist in these resins, particularly Porapak Q. As a result, a large portion of the "N_2" surface area reported by the manufacturers may not be available to the more bulky organic molecules. Chromosorb 101 has relatively large pores compared to the Porapak P and Q.

Estimates of "available" surface area to organic molecules were made by Gearhart and Burke (Ref. 45) for Chromosorb 102, Porapak P, and Porapak Q. The basis for their estimates was the measurement of free energy changes for molecular probe-adsorbent interactions. By relating these measurements for benzene, cyclohexane, cyclohexene, hexane, hexene, methylene chloride, and chloroform, estimates of "available" surface area were computed. Chromosorb 101 was used as a norm for comparison since it probably has the greatest proportion of available surface area. The apparent surface areas for Chromosorb 102, Porapak P, and Porapak Q are 95, 37, and 133 m^2/g, respectively. These estimates represent 33.7%, 27.1%, and 20.2% of the manufacturer's reported surface areas.

2.6 Thermal Stability of Sorbent

Thermal stability of the porous polymer sorbent is critical principally from the standpoint of the optimum temperature for desorption. If relatively high molecular weight materials (e.g., MW 140) are to be measured, desorption temperatures as high as 290-300°C may be required. Obviously, lower molecular weight materials will be desorbed at lower temperatures. The choice of sorbent for a particular sorbate will depend in large part on the temperature needed for desorption.

2.7 Sampling Volume, Flow Rate, and Sampling Time

The sampling volume and sampling times will depend largely on the concentration of species, the retention characteristics of the sorbent, the gas stream temperature, and the composition of the gas stream with reference to potential displacement mechanisms.

The choice of sampling flow rate will depend on the retention characteristics and volatility of the species being collected.

Flow rates of 20-30 ml/min are preferred, but 50 to 200 ml/min can be used as a compromise between time requirement and sample loss. The volatile compounds, e.g., benzene, C_9 and lower aliphatic or olefinic hydrocarbons, are only partially adsorbed at high flow rates (200-1000 ml/min).

APPENDIX E

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16. ABSTRACT The report gives results of a study to assess the utility of porous polymer adsorbents as a means of sampling and concentrating trace organic emissions from stationary sources. Emissions from two industrial field sites were sampled, using small porous polymer sampling tubes backed up by a cryogenic thermal-gradient sampling system to assess the efficiencies of adsorption of the trace organic species. In addition to experimental results, conclusions, and recommendations, a detailed statement of the problem of sampling trace organics in industrial emissions is presented in the Appendices. This later discussion includes: the characteristics of stationary sources emitting organic species; an assessment of present sampling techniques for organic matter; a review of the use of porous polymer adsorbents in sampling; and the characteristics of porous polymer sorbents and their potential limiting properties.

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