

AN ABSTRACT OF THE THESIS OF

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Title: A COMPARISON OF POROUS POLYMERS USED IN COLLECTING ORGANIC VOLATILES IN FOODS

Abstract approved: \_\_\_\_\_  
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Porapak Q, Chromosorb 102, and Tenax GC, three porous polymers commonly used as adsorbents in headspace analyses were investigated. The retention times of various low-boiling compounds relative to water were measured on the collection columns to determine which compounds would be lost during the water removal step employed after sampling aqueous materials. Compounds eluted fastest from Tenax GC precolumns and slowest from Porapak Q, with retention times on Chromosorb 102 generally intermediate. Thus, loss of low-boiling compounds relative to water was greatest on Tenax GC and limited the use of this polymer for quantitative study of samples containing low-boiling volatile compounds. The residual water in Porapak Q precolumns employed in the usual procedure for collection of volatile materials by entrainment from aqueous systems, could be completely eluted in 15 min with a N<sub>2</sub>

purge of 30 ml/min at 55° C. without appreciable loss of collected organic compounds.

Retention times of high-boiling organic compounds were determined on the precolumns, and those containing Tenax GC had shorter times than Chromosorb 102 or Porapak Q. Under conditions employed for unloading trapped compounds from precolumns, fewer compounds remained on Tenax GC precolumns. Thus, Tenax GC appeared to be the trapping polymer of choice in investigations involving high-boiling compounds. Back flushing of Porapak Q, Chromosorb 102, and Tenax GC precolumns during unloading was essential in order to recover the trapped organics within the time allotted for unloading at 135° C. At 280° C back flushing on Tenax GC was not necessary to insure unloading since retention times were well within the unloading period.

The recovery of n-undecane from the precolumns after simulated water removal conditions was found to be 98.5% for Tenax GC, 99.5% for Porapak Q, and 100.0% for Chromosorb 102.

A Comparison of Porous Polymers Used in Collecting  
Organic Volatiles in Foods

by

Alayne Linda Boyko

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# A COMPARISON OF POROUS POLYMERS USED IN COLLECTING ORGANIC VOLATILES IN FOODS

## INTRODUCTION

Porous polymers are being used extensively in flavor and pollution research as trapping agents in the gas chromatographic (gc) analyses of organic volatile compounds. The advantages of these materials in such analyses include: 1. preliminary separation of H<sub>2</sub>O from organic compounds, 2. ease of sample handling, 3. relatively short analysis times, 4. lack of water vapor interference, 5. reproducibility, and 6. sensitivity. A number of porous polymers are available commercially, however additional retention time and elution data are needed to allow selection of the best polymer for a particular application. We attempted to characterize Porapak Q, Chromosorb 102, and Tenax GC by examining retention and recovery data obtained with various high and low-boiling compounds on these polymers.

Our general method for collecting volatile organic compounds on porous polymers follows. Using a headspace technique, vapors were entrained from the sample with prepurified nitrogen at flow rates of 30 to 60 ml/min and collected on a porous polymer precolumn maintained at 55° C. At the end of the entrainment period, the

sample vessel was disconnected, and the removal of residual water from the polymer trap was accomplished by continuing the nitrogen flow for 45 to 60 min. The organic compounds were back-flushed from the precolumn at 135° C for 45 min with the flow rate reduced to 12 ml/min. The organic compounds were trapped in a capillary U-tube cooled in a Dry-Ice-2-methoxyethanol slurry and were thus ready for development on an analytical column.

Prior to this investigation, trial and error was the main approach used in establishing optimum conditions for an application. We have attempted to establish some optimum conditions and some of the limitations of the porous polymer trapping technique by examining the following:

1. Retention times of various compounds relative to water
2. Losses of trapped organic compounds during water removal
3. Retention times of some high-boiling compounds on polymers
4. Advantages of reversing the precolumn prior to unloading
5. Recovery of n-undecane using Poropak Q, Chromosorb 102, and Tenax GC as trapping agents

In summary, the purpose of this investigation was to increase our information regarding the use of Poropak Q, Chromosorb 102, and Tenax GC as trapping materials.

## REVIEW OF LITERATURE

### Brief History of Porous Polymers

A new area of gas chromatographic (gc) analysis began to develop in 1963, when Baum successfully evaluated various classes of compounds using microporous polyethylene as a low temperature support. However microporous polyethylene received little attention in the area of gc due to relatively low temperature limitations, difficulty of handling, and poor efficiency. The use of Teflon powders also went unnoticed.

Synthesized porous polymers resulted in an upsurge in liquid chromatography. This was largely due to the ability of these polymers to separate large molecules by the gel permeation technique. Porous polymers were later adopted for use in gc and were immediately accepted for separating and analyzing small polar molecules. Today a variety of porous polymers are commercially available.

### Synthesis of Porous Polymers

Porous polymers are synthesized by either of two techniques. In bulk polymerization, the polymerized material is fractured, ground, and separated into particle sizes suitable as column

packing material for use in gas or liquid chromatography. The second technique, bead polymerization, leads to small spherical particles. In this case polymerization occurs at the microdrop level making the preferred uniform particles.

### Types of Porous Polymers

Several types of porous polymers used extensively in chromatography have been discussed by Hollis (1973). One type is a cross-linked linear polymer such as "Sephadex". Hollis (1973) states that by controlling the concentration and molecular weight of the linear polymer and the concentration of the crosslinking agent, the porous structure of these gels can be modified. One disadvantage is that some of the gels shrink or swell as the eluting solvent is changed, and thus column efficiency is destroyed. These gels have seen very limited use in gc.

Another type of polymer not used in gc is a linear copolymer, formed when a monovinyl compound is copolymerized with a fixed amount of crosslinker. The porous structure collapses upon drying, making this polymer useless for gc analysis.

A third type of porous polymer is made by a heterogeneous crosslinking polymerization. This process eliminates many of the problems associated with the other types of polymers. Heterogeneous polymers are widely used in gel permeation chromatography

and are the main type used in gc. Examples of this type are Porapak Q, Chromosorb 102, and Tenax GC.

### Physical Structure and Properties

The method of synthesis has a profound effect on the physical structure of a polymer and thus on its behavior as a chromatographic support. For example, permanent porosity upon complete drying depends on the amount, kind, and solvent properties of the inert solvent and the amount and kind of crosslinker used during synthesis. This porosity in turn greatly affects retention time and other properties such as rigidity, surface area, and average pore diameter. Dave (1969) has observed that the speed of a chromatographic analysis increases with increasing pore diameter. He recommends a pore diameter less than 100 angstroms for separating low-boiling gases and one greater than 100 angstroms for high-boiling substances. Some physical properties are summarized in Table 1.

Table 1. Properties of porous polymers.<sup>a</sup>

Polymer	Surface Area M <sup>2</sup> /g	Average Pore Diameter Å	H <sub>2</sub> O Affinity	Isothermal Temperature Limit °C
Porapak Q	840	85	Hydrophobic	250°
Chromosorb 102	300-400	74.8	Hydrophobic	250°
Chromosorb 103	15-25	3500	Hydrophobic	250°
Tenax GC	30	60/80, 35/60 <sup>b</sup>	Hydrophobic	375 to 450 <sup>c</sup>

<sup>a</sup> From Dave (1969) and Geiss, *et al.* (1972)

<sup>b</sup> Mesh size

<sup>c</sup> Reports vary

The microstructures of polymers have been studied with electron microscopes. With a better understanding of the effects of synthesis and physical structure on chromatographic behavior, polymers of the future may be engineered for specific uses.

### Temperature Limits

Each polymer has an upper temperature limit. Above this temperature, thermal degradation and column bleed occur. The upper limit for Tenax GC ranges from 375 to 450<sup>o</sup> C. (van Wijk, 1970, Applied Science Laboratories Inc., Bulletin 24). Porapak Q and Chromosorb 102 both have an upper limit of 250<sup>o</sup> C (Dave, 1969). Krumperman (1972) detected artifacts when Porapak Q was heated at 170<sup>o</sup> C. Thus, use of Tenax GC permits rapid separations at high temperatures and reconditioning at higher temperatures for short periods without polymer breakdown.

### Chemical Structure and Properties

Hollis (1973) states that relatively little is known about the effect of chemical structure of stationary phases on the efficiency of separation in liquid chromatography. However, these effects are better understood in the area of gas chromatography. By choosing polymers with different chemical compositions, the order of elution of various polar and nonpolar compounds can be altered.

The hydrophobic nature of these polymers is evidenced by rapid elution of water in symmetrical peaks. Since residual water usually interferes with subsequent analyses, the low affinity of porous polymers for water is a major advantage. If mass spectrometry is to be used in conjunction with gas chromatography for identification of compounds, a low concentration of water vapor in the sample is imperative.

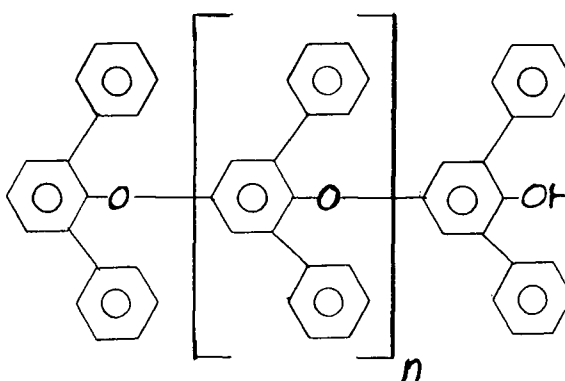
Harris et al. (1974) investigated the use of crosslinked porous polymer packed columns for use in a direct aqueous injection gas chromatograph-mass spectrometer (gc-ms) procedure. The ion source potentials and electron multiplier voltage were not applied and analysis was not begun until the rapid elution of water was complete. The procedure was found to be a valuable supplement for the detection of volatile compounds that are not found with solvent extraction.

If the chemical structure of a commercial polymer is not known, an infrared analysis will give a good rapid indication of its chemical composition (Hollis, 1973). Table 2 lists the monomer components of several porous polymers.

Figure 1 shows the chemical structures of Tenax GC (van Wijk, 1970) and several other porous polymers. Junk and Svec's (1973) diagram of a styrene-divinylbenzene (DVB) polymer assumes a ratio of four styrene molecules to one divinylbenzene. The actual



Tenax GC: poly-p-2,6-diphenyl-phenylene oxide



XAD-2, XAD-4, Chromosorb 102, Porapak Q: styrene-divinylbenzene polymers

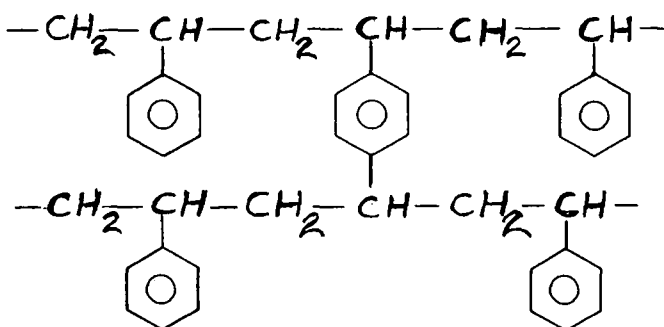


Figure 1. Structures of porous polymers.

ratio is known only by the suppliers of XAD-2, XAD-4, Chromosorb 102, Porapak Q, and other DVB polymers.

Table 2. Chemical components of polymers.<sup>a</sup>

Polymer	Monofunctional Agent	Crosslinking Agent	Use
Porapak Q	ethylvinylbenzene	divinylbenzene	GC, LC
Chromosorb 102	styrene	divinylbenzene	GC, LC
Tenax GC	2,6-diphenyl-para-phenylene oxide	divinylbenzene	GC
XAD-2	styrene	divinylbenzene	GC, LC

<sup>a</sup> From Hollis (1973) and Junk and Svec (1973).

Porapak Q is synthesized and marketed by Waters Associates; Chromosorb 102, by Johns-Manville; and Tenax GC is produced by AKZO Research Laboratories and is distributed by Applied Science Laboratories, Inc. A variety of information regarding polymer structure and applications is available from these companies.

### Mechanisms of Separation

The exact mechanisms involved in separations on porous polymers are in question at this time. Dave (1969) stated that porous polymer beads act in both a gas-solid and a gas-liquid sense with adsorption, diffusion, and partitioning all contributing to the effectiveness of the material. Hollis (1966) suggested that the solubility of the compounds being separated in the polymer is most important

in determining the order of elution and that boiling point is of little consequence. Smith and Waddington (1968) refuted this by reporting that within a class of compounds there exists a linear relationship between the logarithm of the retention time and the boiling point of the compounds eluted.

Novak et al. (1965) discussed some theoretical aspects of sorption and the influence of concentration of impurities. Physiochemical fundamentals of chromatographic retention on Porapak Q and T are dealt with by Zado and Fabecic (1970). They noted that Porapak Q shows repulsion or weak interaction with a hydroxyl, ether or ketone oxygen, but strongly interacts with the hydroxyl hydrogen. Total adsorption energies of a series of organic compounds were calculated and the corresponding functional group values were derived using the incremental energy equation. In spite of the controversies, it is apparent that various properties of porous polymers will affect the mechanisms involved in separation.

### Retention Data

Literature from the polymer suppliers and the vendors of gc instruments and accessories provide a source of retention data. Dave (1969) compiled extensive retention data for a wide variety of compounds on the Chromosorbs and Porapaks. The organic compounds investigated covered a wide range of polarity. He predicted

the retention time of succeeding members of a homologous group by plotting the retention indices of the known homologues as a function of increasing molecular weight. Dave also investigated class separations on several polymers.

Supina and Rose (1969) presented retention times of n-paraffins on various Porapak and Chromosorb polymers. Retention times for n-paraffins were useful for estimating the relative speed of analysis. To compare the relative "polarity" of the polymers, they listed the retention indices for a number of compounds.

Burger (1968) looked at the retention times of 90 organic compounds on Porapak Q. A linear relationship was found between the logarithm of the adjusted retention time and the logarithm of the molecular weight of the compound. Molecular weights were estimated within 20% from retention times.

Novotny et al. (1974c) stated that the dynamic capacity of Tenax GC has not been evaluated for various classes of compounds, even though retention data are known for some compounds. Additional retention data was calculated and other properties of Tenax GC were investigated by Daemen et al. (1975).

Depending on retention times and separating properties, certain polymers are better suited for work with particular classes of compounds. Thus, the compounds of interest in a study will help

determine which polymer is to be used. More complete retention and separation data would aid in choosing the polymer.

### Reproducibility

Reproducibility of retention times on porous polymers has been discussed extensively. Hollis (1973) commented on the very poor batch to batch quality of commercial polymers. Variations greater than 50% occurred in the relative retention volumes for water, even after thorough conditioning. In spite of the problems of poor reproducibility, porous polymers have found broad use because of their utility. Better synthesis and cleanup procedures and use of high purity starting materials should improve reproducibility in the future.

### Conditions Detrimental to Porous Polymers

Porous polymers may be destroyed or damaged by the following conditions (Hollis, 1973):

1. Contact with oxidizing atmospheres especially at elevated temperatures
2. Presence in samples of very heavy molecular weight organic molecules which may modify the polymer
3. Deposition of salts on the polymer from aqueous samples
4. Use at excessive temperatures

Salts and heavy organics may be washed out with appropriate solvents

much in the manner of conditioning new batches of polymer. Care must be taken to avoid detrimental treatment of polymers.

### Applications in Flavor and Pollution Research

Porous polymers have been used as trapping agents in flavor research and pollution analyses. The concept of a "flavor profile" which has been used to characterize food flavors has more recently found application in pollution research. This advancement has been intimately tied with analytical techniques involving collection on porous polymers of organic compounds from entrained vapors.

What common factors in flavor and pollution work make porous polymers applicable? In both cases one is often dealing with trace quantities of compounds. They may be compounds with low thresholds in foods or trace (ppb) organic contaminants in air or water. A prior concentration step is necessary before most analyses can be carried out. Besides often being time consuming, these techniques have major limitations. Mieure and Dietrich (1973) briefly discussed some of the problems associated with solvent scrubbing trains, collecting on charcoal, and condensing with cold traps. Porous polymers circumvented some of these problems. By using porous polymers for collecting trace organic compounds, there was no interference from solvents or losses during the evaporation of solvents. Since polymers have a lower affinity for water than for most organic

compounds, there was no problem from water vapor interference. This was especially advantageous in sampling dilute aqueous systems. Porous polymers offered a very convenient and time saving method for handling a wide variety of samples.

Tassan and Russel (1974) mentioned that headspace sampling was not a widely used technique prior to the development of porous polymers. This was due to the low concentration of volatiles and the large amount of water which may be present in the samples. Suitable sampling and sufficiently sensitive analyses of headspace vapors will detect both quantitative and qualitative changes in sample composition, since the volatile constituents in the headspace will be in concentration proportional to their respective partial pressures. Nawar (1971) and Buttery et al. (1969) discussed some of the variables affecting the composition of headspace aroma. The picture has changed considerably, and headspace technique using porous polymer sampling traps, has seen many applications.

Morgan and Day (1965) developed a simple on-column trapping procedure for gas chromatographic analysis of flavor volatiles. An entrainment technique was used where nitrogen was bubbled through an agitated sample held at the desired entrainment temperature. The volatiles were then trapped in a U at the head of the analytical column. The U was cooled in 2-methoxyethanol and Dry Ice. Upon analysis a variety of compounds were found with relatively good sensitivity.

By maintaining a slow collection rate and keeping the total volume of entrainment gas low, they did not find it necessary to remove water from the entrained volatile compounds.

Novak, Vasak, and Janak (1965) devised a system for concentrating trace impurities in the atmosphere and other gases. They used an adsorbent (such as Polyethylene glycol 400) or a support wetted with a liquid of low volatility to absorb the impurities from the sample. These compounds were heat desorbed and introduced into the gc. They concluded that the method was applicable to estimation of trace (ppb) impurities in the air and that quantitation could be attained. Judicious selection of the packing material in the sampling tube made possible the selective concentration of compounds of interest and suppression of others.

In their early work on porous polymer columns, Hollis and Hayes (1966) noted that water eluted very rapidly with an excellent peak shape. They then used such columns to determine trace amounts of water in hydrocarbons, alcohols, oxides, glycols, chlorinated hydrocarbons, ammonia, and hydrogen-chloride-containing samples. They noted that the retention of water increased with polymer polarity. Because of their low, linear adsorption for water and other hydroxyl-containing compounds, quantitation was possible. Hollis and Hayes (1966) believed there was little if any loss of water by adsorption on the column. They stated that many sample systems were now



analyzed routinely by this technique. These water retention characteristics led to the application of the polymers to headspace sampling.

Papers appeared combining a sampling technique such as entrainment or other headspace methods with collection of the volatiles on porous polymers. Schultz et al. (1971) investigated the problem of separation of organic volatile compounds from water vapor prior to gc-ms analysis of vapors entrained from fresh orange juice with sample sizes up to 2 liters. They used a pre-column packed with various polystyrene column packings followed by a cold trap immersed in liquid nitrogen. The juice was swept with nitrogen and the entrained volatile organic compounds were trapped on the precolumn. After sampling, nitrogen flow was continued for 30 min. to remove the remaining water from the precolumn. The trapped organic compounds were eluted from the precolumn, condensed in the cold trap, and then flushed onto the analytical gc column. At first various dessicants were used in place of the precolumn in an attempt to remove water. While most of the water was adsorbed, so were varying amounts of the orange volatile compounds. Precolumns containing Chromosorb 101 were used with satisfactory results. The following problems were encountered:

1. adsorption effects,
2. chemical instability in the precolumn,
- and 3. column bleed.

The authors believed that modifications in method would reduce these problems.

Dravnieks and O'Donnell (1971) employed a similar approach using Chromosorb 102 as the collector. They noted that the temperature of the polymer must be maintained above the dew point of water to prevent in-line condensation. After collection, the volatile compounds were removed by reverse flushing into a special injector. Subsequent development was performed on two consecutive columns of differing polarity in a modified commercial gc without an intermediate trapping step. In conjunction with observing the odor of effluents, these techniques resulted in information indicating which species were the most odor-relevant.

Miller et al. (1972) used Porapak Q to collect the volatile compounds entrained from ground muscle tissue of canary rockfish stored in ice. After collecting and water removal procedures, the precolumn was reversed to aid in rapid elution and cold trapping of higher boiling compounds. Many compounds were recovered and identified. Using the same techniques, Miller et al. (1973) investigated volatile compounds produced in sterile fish muscle by Pseudomonas perolens.

Analysis of the vapor in the headspace over alcoholic beverages was conducted by Jennings et al. (1974). Ethanol was the dominant volatile and produced a large tailing peak covering a portion of the chromatogram and seriously limiting the size of the injected sample. The use of Porapak Q, which exhibits short retention times for water

and the lower alcohols, was investigated. An all-glass system was used consisting of a sampling vessel connected to a precolumn. After collecting the volatile compounds and purging with nitrogen to remove water and ethanol, the column was reversed and the volatile compounds were eluted into a glass cold trap. Upon analysis, they concluded this method could be used on a variety of alcoholic beverages having complex aromas, and that the method was sufficiently sensitive to differentiate between them. Withycombe and Lindsay (1972) looked at six flavor compounds naturally occurring in beer and concluded the polymer trapping procedure was reproducible to  $\pm 7.6\%$ . Reproducibility was established by comparing the average deviation of six observations to their mean total area. Temperature control was shown to be extremely important in quantitative sampling. Additional investigations were made on beer flavor by Withycombe and Lindsay (1973a, 1973b).

The compounds trapped on Porapak Q were divided into the following groups by Jennings et al. (1972): 1. those compounds exhibiting shorter retention times on the precolumn than the time used in column development, 2. compounds whose retention times on the precolumn exceeded the development time, but were less than the combined times for entrapment and development, and 3. compounds whose retention times exceeded the combined times of entrapment and development. Thus whether a compound was lost, partially

recovered, or fully retained, depended on its retention volume and the volumes of gas used in entrapment and development. Optimum conditions for analysis were obtained by modifying the trapping and development conditions.

Several studies have been made on the volatile compounds produced by ripening fruit. Using Porapak Q, Tressl and Jennings (1972) examined volatiles in the ripening banana and found it desirable to include three internal standards in such work. They stated that it would be advantageous to follow changes in a single fruit, since a group of fruits may be in several stages of ripening simultaneously. Jennings (1974) looked at changes in volatile constituents of ripening cantaloupes. The headspace volatiles were collected on Porapak Q and analyzed with a computerized gc-ms system. A technique of sampling a single fruit was discussed and results obtained by both methods were similar.

In a paper by Bergstrom (1973), a modified gc was described in which a separation column and a precolumn tube were arranged so volatile compounds in the tube were transferred to the separation column by degassing and trapping. An enfleurage technique was also used where objects such as flower parts were placed in direct contact with a porous polymer coated with silicone high vacuum grease. The adsorbent was placed in the precolumn tube and degassing continued as usual. Labial gland of bumble-bees, orchids,

and wing scales of butterflies were analysed as examples of applications of this system.

Dravnieks and Watson (1973) modified a technique that showed that gc patterns of headspace volatiles of dry corn could be correlated through use of computerized stepwise discriminant analysis to the odor quality of corn. By using Chromosorb 105 as a trapping agent at ambient temperature, the technique was shortened and adapted for routine use.

The volatile substances associated with Cheddar cheese aroma were identified by Manning and Robinson (1973) by sampling distillates from Cheddar cheese using both a 15 m Apiezon surface coated open tubular (SCOT) column and a 1.5 m glass column packed with Porapak Q. The capacity of the Porapak Q column was much greater than that of the SCOT column. More emphasis was placed on the results obtained from the Porapak Q column. A study on coffee beverage volatiles by Tassen and Russel (1974) also used Porapak Q for headspace analysis. Seasonal variations in the volatile constituents of black tea were investigated by Gianturco et al. (1974).

Dravnieks et al. (1971) used Chromosorb 102 for the extraction of organic species from air and essentially contamination-free transfer of the sample to a gc.

Zlatkis et al. (1973a) described a new procedure for the sampling, transfer, and analysis of trace volatile organics in gases and

biological fluids. This method was also amenable for investigation of volatile organic compounds involving air and water pollution, flavor, and aroma analyses. After evaluating Porapak P, Carbosieve, and Tenax GC, the latter was chosen as the adsorbent since it could sustain the high temperatures needed for desorption. A glass trapping chamber was designed as an insert for a modified injection port. The trap-insert was attached to a condenser which in turn was attached to a 500 ml sample container. A sample of urine was placed in the container, heated, and swept with helium; the volatile compounds were collected on the trap-insert. When air or breath was sampled, a vacuum was drawn through a similar system. Several trap-inserts could be used simultaneously when multiple injections were required. These traps could be stored without loss of sample. After collection of the sample, the trap-insert was placed in the modified injection port. The sample was purged at 300° C for 20 min at 20 ml/min and collected in a cold trap. Chromatography was begun by transferring the sample to the analytical column. Because of its simplicity and reproducibility, this method lent itself to routine analyses.

Zlatkis et al. (1973b, 1973c) using the technique described above, studied the profiles of volatile metabolites in urine of both normal and diabetic individuals. They noted that the analytical conditions must be constant for long term comparisons and that the

possibility of artifact production must be considered. Simpler chromatographic profiles were obtained by use of selective detectors and subtractive techniques. Novotny et al. (1974b) concentrated trace volatile constituents of human urine, serum, and cerebrospinal fluid on a porous polymer precolumn and resolved them with high-efficiency glass capillary columns.

Various techniques used for concentrating highly diluted samples such as organic volatile compounds in air pollution were discussed by Bertsch et al. (1974a, 1974b). They described a sampling system for air-borne chemicals essentially the same as the one used in urine sampling, mentioned previously. Under sampling considerations, they listed the following problems in obtaining a representative sample:

1. Losses of low boiling compounds and irreversible adsorption resulting in failure to collect quantitatively
2. Chemical changes of sample constituents after collection due to oxidation and polymerization
3. Capability of completely regenerating the substances sampled for analysis
4. Difficulty in relating the sample to the original source
5. Time requirements sufficient to detect short term changes in composition

The optimum sampling conditions depended on the type of information needed and on the analytical procedure itself.

Bertsch et al. (1974a) chose Tenax GC as an adsorbent after examining its properties. Tenax showed selectivity toward certain classes of compounds and retained high molecular weight more easily than low molecular weight compounds. They stated that for quantitative use, its limits in respect to trapping efficiency and recovery needed to be established. Compounds eluting before benzene were partially lost. Benzaldehyde and acetophenone could not be retained quantitatively, but other compounds were trapped and recovered in better than 90% yields.

Lindsay et al. (1972) compared various gc methods for applications in beer flavor analyses. The direct injection, head-space, and carbon disulfide-porous polymer extraction quantitative procedures were found to be simple and of acceptable precision.

Mieure and Dietrich (1973) used short collection columns, 4 to 6 inches long, containing porous polymer beads to sample both air and water. After collection, these columns were directly coupled to the head of the analytical column and then temperature programmed. No loss of analytical column resolution was observed. If the pre-column and analytical column were in the same gc oven, the same porous polymer was used in both. The procedure restricted the analysis to those compounds with boiling points less than 300° C because of long retention times. This was not considered a serious disadvantage, however, as most air pollutants have boiling points



below 300° C. If the stationary phase of the analytical column was different from the collection column, the collection column was heated separately as an injection port insert. The authors knew of no column packing capable of quantitatively releasing all volatile organic pollutants. They used a combination of three types (Chromosorb 101, Chromosorb 105, and Tenax GC) to characterize an unknown air sample. Sampling time varied, with the retention volume of the earliest eluting components of interest defining the maximum volume of air which could be sampled quantitatively. The following experiments verified quantitative collection and recovery:

1. Sampling of constant sources was continued for varying lengths of time. Sampling time was proportional to the weight of compound collected.
2. When two columns were placed in series, the test compound was detected in the second column only after the retention volume of the first was exceeded.
3. Essentially identical results occurred with simultaneous samplings of a source using a column and a solvent scrubbing train.

The above procedure was used to characterize new car smell, volatiles evolved from vinyl films and other coatings, stack gases, coffee aroma, and other substances.

The same paper discussed other techniques for sampling water. One utilized headspace analysis and was very similar to that discussed above. Another involved sampling water directly with porous

polymers. Water samples were pulled through packed columns by vacuum at the rate of 5 ml/min. Some problems were caused by residual water on the polymer.

Junk and Svec (1973) extracted organic compounds from water by passing it through XAD-2 (a styrene-divinylbenzene polymer) and eluting with an appropriate solvent. Gc analyses were run after preconcentration. The recoveries on spiked water samples were acceptable and suggested the method may be acceptable for all nonionic and slightly soluble organics. Fritz and Chang (1974) characterized XAD resins.

A multidetection unit for the analysis of organic micropollutants in environmental samples was assembled by Geiss et al. (1972). Sampling was effected on a porous polymer adsorption column followed by thermal elution. For water, both adsorption columns and direct solvent extractions were being considered. Tenax GC was chosen for several reasons, one being its thermal stability. After conditioning, the column bleed at 250<sup>o</sup> C was below flame ionization detector (FID) detection limits even when the column was subjected to thermal shocks. Quantitative adsorption and desorption data were obtained for a variety of compounds in air. The desorption recoveries were 90% or better for the various compounds. Separation in this system was done on glass capillary columns coated with different stationary phases. These columns were coupled to a ms via a glass

jet separator. The analytical data produced by this unit came from three to four gc detectors and the ms. Thus a computer was used for compound identification or structure approximation. Novotny et al. (1974a) discussed computer-aided data evaluation.

### Problems Related to the Use of Porous Polymers

Porous polymers received more attention in recent years as trapping agents for organic volatile compounds. Although these techniques have been useful, problems were noted. Richardson and Mocek (1972) investigated the production of artifacts when beer headspace was sampled with extended incubation at various temperatures. They found a variation in the volatile sulfur components in the headspace related to analytical procedure selected, and recommended caution when choosing conditions for analysis.

Loss of flavor compounds in gc columns because of decomposition or adsorption was the concern of McGugan and Howsam (1972). A simple method was described for recovering the sample from the gc effluent and comparing it to the original aroma of the unchromatographed sample. The odor of Cheddar cheese volatiles was markedly changed by columns packed with Carbowax 20M on Chromosorb W-HP, uncoated Porapak Q, and FFAP on Porapak T. The aromas recovered from two other columns were essentially unchanged. The importance of column selection was stressed.

Ottenstein and Bartley (1971) in a study of the separation of free acids  $C_2$  to  $C_5$  on various columns, noted that when porous polymers were contained in stainless steel or aluminum columns no acids were eluted. Acids were, however, eluted from glass columns. Thus it was established that metal columns were highly adsorptive of free acids under those conditions. The use of glass polymer traps should be considered over metal columns.

Water adsorption by porous polymer beads was studied by Gough and Simpson (1972), and it was confirmed that both water and alcohol were irreversibly adsorbed by Porapak columns. Given a satisfactory batch, they stated that the material was suitable for quantitative analysis of samples in which the portion of water was at least as low as 1%. If a porous polymer packed column was to be used for quantitation, it should be chosen to minimize irreversible adsorption. Patzelova and Volkova (1972) studied the interactions of water and methanol at various temperatures with Porapak R. Because of the increased mobility of molecules on the surface of the adsorbent, the adsorbent-adsorbate interaction decreased with temperature for a given partial pressure of the adsorbate. Using the highest practical temperature for collecting should minimize irreversible adsorption of polar compounds.

Various reactions of compounds with Porapak Q have been discussed. Trowell (1971) found that  $NO_2$  reacted with Porapak Q or

Chromosorb 102 to produce NO, water, and nitration of the aromatic rings of the polymer. Upon injecting NO<sub>2</sub> into a packed glass column, a blue-green band moved down the packing leaving a light tan discoloration behind. Upon heating the band turned brown and the remaining packing darkened.

Alpha-hydrogen exchange of ketones on Porapak Q columns was investigated by Barta and Gordon (1970). At temperatures greater than 170<sup>o</sup> C. the exchange was significant and limited the possibility of using Porapak Q for isolating deuterated compounds for label analyses. The authors stated that residues of polymerization catalysts probably were the reactive groups. The possibility of reactions with porous polymers should be considered when using these materials.

A study by Hertl and Newman (1971) showed that the extreme tailing of amine peaks on Chromosorb 102 was caused by the unreacted vinyl groups on the polymer. They devised a method for deactivating these sites using HF. Supina and Rose (1969) also found that acids tailed on Chromosorb 102. Zado and Fabecic (1970) concluded that interactions of free electron pairs with the surface probably caused specific interactions. Better understanding of the reactive sites should lead to methods of producing totally unreactive porous polymers. Ottenstein (1973) discussed tailing.

Another problem associated with porous polymers has been the peak broadening effects of certain classes of compounds. Ackman (1972a, 1972b) discussed the peak broadening of ketones and low molecular weight fatty acids with single methyl branched structures on Chromosorb 101. Guha et al. (1973) examined the branched-chain peak broadening effect and rationalized it as being caused by restricted intraparticle diffusion and the relative affinities of the various adsorbates for the polymer. Better understanding of these processes will lead to more efficient polymers.

Rabbani et al. (1968) noted that the retention times of various compounds and their sequences were changed depending on the carrier gas used. The flow of He, Ar, and CO<sup>2</sup> through a Porapak S column at 273<sup>o</sup> K was studied by Czubryt and Gesser (1970), and they found that in order to explain some of the anomalies noted in this study, certain mechanisms had to be postulated. Studies of such problems will aid in better understanding porous polymers.

## MATERIALS AND METHODS

Procedure for Collecting Volatile Compounds  
on Porous Polymers

Although porous polymers have been used as trapping agents in many applications, the techniques employed remain essentially the same. Our technique for collecting organic compounds on porous polymers was as follows: samples, contained in screw-capped vials or bottles, were purged with nitrogen (30 to 60 ml/min) at 60°C. The compounds were collected on polymer-containing precolumns held at 55°C (102 by 3 mm I. D.) by continuing the nitrogen flow for 30 to 60 min. Residual water was then removed from the precolumn at 55°C with nitrogen flowing at 30 ml/min. up to 1 hr. The precolumn was then reversed and heated to 135°C, and the organic compounds eluted with nitrogen flowing at 12 ml/min for 30 to 45 min. The eluted compounds were collected in an open tubular trap (150 by 1.25 mm I. D.) immersed in a slurry of Dry Ice and 2-methoxyethanol. The organic compounds were flashed onto an analytical column in the manner described by Scanlan *et al.* (1968). As mentioned before, these conditions were varied as the experimental situation dictated. The above technique was considered as the reference method in this study.

### Preparation of Precolumns

Sections of stainless steel tubing, 102 by 3 mm I. D., were cleaned with dichloromethane and thoroughly dried. A plug of silanized glass wool was tamped into one end of the tubing. The following porous polymers were firmly packed into individual tubes:

Porapak Q 100-120 mesh

Chromosorb 102 100-120 mesh

Tenax GC 60-80 mesh

The open end was then plugged with silanized glass wool and the ends were marked either no. 1 or no. 2. Prior to packing, the polymers were washed with acetone on a coarse sintered glass funnel.

### Conditioning of Precolumns

Prior to use, the precolumns were conditioned as follows: Porapak Q and Chromosorb 102 were heated for 12 hr. at 200° C, and then for 48 hr at 100° C. The minimum nitrogen flow rate was maintained throughout at 30 ml/min. Because of its greater thermal stability, Tenax GC was conditioned at 260° C. for 1 hr under a minimum nitrogen flow of 30 ml/min. After each subsequent use of a precolumn, it was reconditioned in the same manner before reuse.



### Water Removal from Precolumns after Sampling

To determine the length of time necessary to eliminate water from the precolumns, distilled water was sampled under the following sets of conditions. The surface of 50 ml of distilled water, contained in a screw-cap bottle maintained in a 60° C water bath, was swept with prepurified N<sub>2</sub> at a flow rate of 33 ml/min for 30 min. Maintained between the gas cylinder and sampling bottle were a cold trap immersed in a Dry Ice 2-methoxyethanol slurry and an Oxy-Trap (Alltech Associates) heated to 250° C. These precautions were followed to remove contaminants and oxidants which may be present in the N<sub>2</sub>. The entrainment assembly (Figure 2) was attached to end no. 1 of a precolumn during a 30 min sampling interval. Samples were collected on Porapak Q, Chromosorb 102, and Tenax GC precolumns.

Samples were also collected on the same assembly by bubbling prepurified N<sub>2</sub> through 100 ml of distilled water for 30 min under identical conditions. Again the three porous polymer precolumns were tested.

Under normal sampling procedure, the needle assembly would have been disconnected, the gas line reconnected to end no. 1 of the precolumn, and gas flow continued for an additional 60 min at 30 ml/min to remove water. However to determine the time necessary

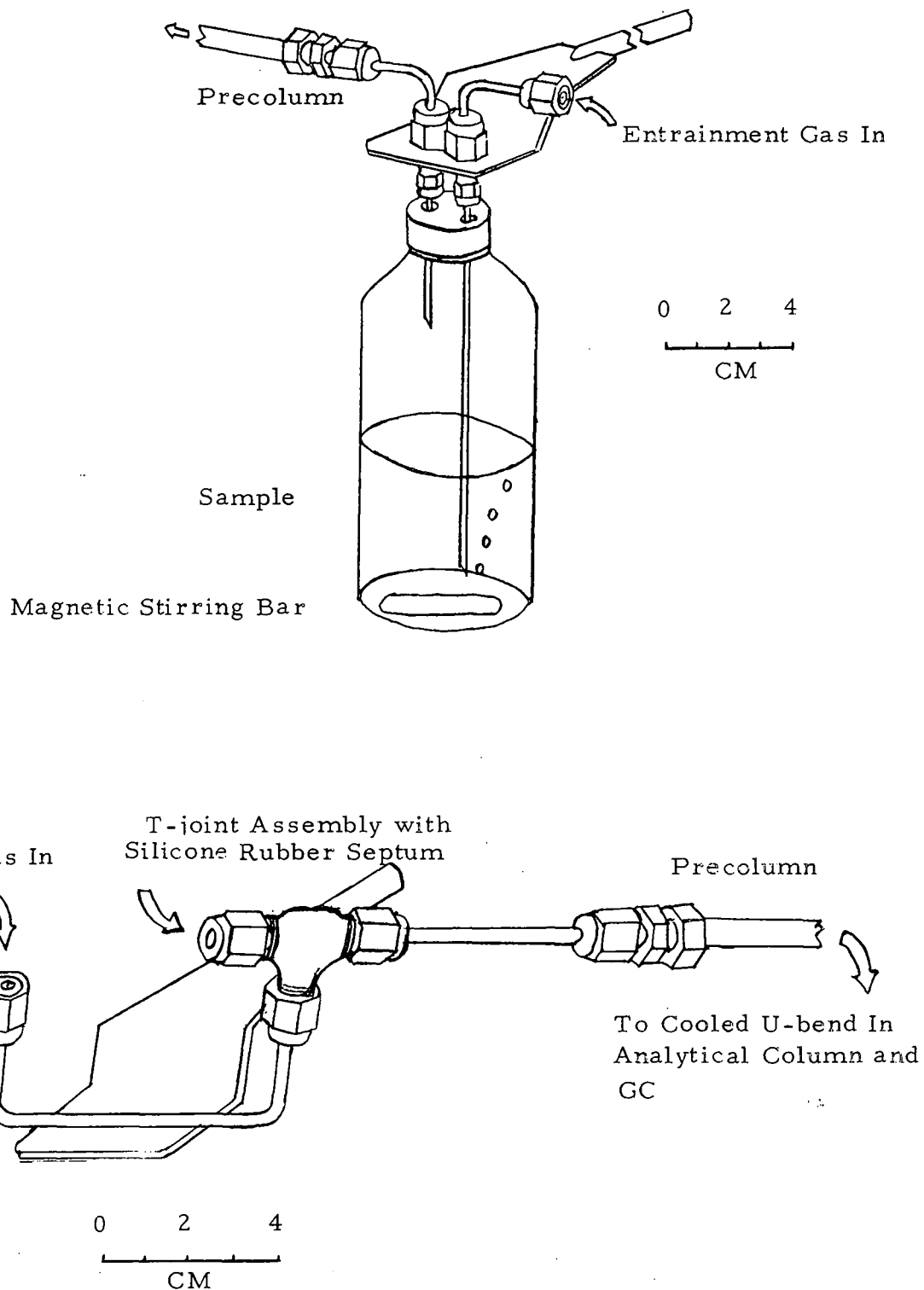


Figure 2. Entrainment assembly (top) and on-column trapping arrangement (bottom).

to remove the water, the precolumn was attached to the detector side of an Aerograph 90 P3 gc with Swagelok fittings. A piece of tubing 1 mm I. D. by 12 cm connected end no. 1 of the precolumn to the injection port.

Gc conditions were adjusted prior to analysis to simulate water removal conditions. The helium flow rate was adjusted to 30 ml/min, column temperature to 55° C, and detector temperature to 190° C. A Carle micro thermal conductivity detector was set at attenuation X5 and the baseline zeroed with an appropriate conditioned precolumn in place in the gc oven.

After the 30 min sampling period, the precolumn was detached from the entrainment system and connected to the gc maintaining the same direction of gas flow. The recorder and detector were then activated and the time for the recorder pen to return to the baseline after elution of the water peak was measured.

#### Determination of the Retention Times of Low-Boiling Compounds Through the Precolumns

To measure the retention times of water and low-boiling compounds on the packed precolumns, the following arrangement was constructed in an Aerograph 90 P3 gc. The precolumn was directly connected to the inside of the injection port. Swagelok fittings were used to connect the precolumn to the detector with 0.7 mm I. D.

capillary tubing ca 15 cm long. The precolumn and capillary tubing were maintained at oven temperature. The elution of test compounds was detected with a Carle micro thermal conductivity detector and was recorded on a model H, Leeds and Northrup recorder. The complete elution of the test compounds was taken as the point at which the recorder pen returned to the baseline.

One  $\mu$ l of water and low-boiling compounds were individually injected into the injection port with a Hamilton syringe, and chromatograms were developed under the following conditions: column 55<sup>o</sup> C, injection port 120<sup>o</sup> C, and detector 150<sup>o</sup> C. Two helium flow rates were studied: 12 ml/min and 45 ml/min. The time recorded for elution of each substance tested was the uncorrected residence time on a particular porous polymer precolumn. The classes of compounds tested included alcohols, aldehydes, ketones, esters, carboxylic acids, mercaptans, and sulfides. These compounds are representative of flavor compounds commonly occurring in foods.

#### Determination of the Retention Times of High-Boiling Compounds Through the Precolumns

A similar arrangement was used to measure the retention times of high-boiling compounds on the precolumns under unloading conditions. A Varian Aerograph 1400 gc was used because of the relatively rapid temperature equilibration of the oven. The

precolumn was attached to the injection port with a piece of tubing (1 mm I. D. by 4 cm). A second piece of tubing (1 mm I. D. by 8 cm) connected the precolumn to the flame ionization detector.

One  $\mu\text{l}$  samples were individually injected into the injection port and the retention times of the compounds recorded. The precolumns were reconditioned between each sample. The following gc conditions were used: column temperature  $135^{\circ}\text{C}$ , injection temperature  $300^{\circ}\text{C}$ , detector temperature  $230^{\circ}\text{C}$ , and flow rate 36 ml/min. These conditions were typically used in our laboratory for unloading volatile compounds from the porous polymer precolumns.

Retention times for high-boiling compounds on Tenax GC were also investigated at higher temperatures. The column temperature was  $280^{\circ}\text{C}$ , the injector temperature  $300^{\circ}\text{C}$ , the detector temperature  $255^{\circ}\text{C}$ , and the flow rate was 45 ml/min. At this column temperature, polymer degradation would have occurred in Chromosorb 102 and Porapak Q.

### Precolumn Reversal

To examine the effect of precolumn reversal prior to unloading organic compounds on the qualitative recovery of high-boiling compounds, the setup described above utilizing the Varian Aerograph 1400 gc was combined with the following procedure: End no. 1 of the

porous polymer precolumn was attached to the injection port. End no. 2 was left open to the atmosphere. A 1  $\mu$ l sample was injected into the injection port (300<sup>o</sup> C) and subjected to the conditions employed for residual water removal, flow rate 30 ml/min at 55<sup>o</sup> C for 1 hr. The carrier gas was then shut off and the precolumn reversed and connected to the injection port and detector. The column temperature was raised to 135<sup>o</sup> C, and the carrier gas turned on. The times required to elute the test compounds from the reversed precolumns were compared to elution times of the same compounds when the precolumns were not reversed. Only high-boiling compounds were tested as low-boiling compounds would have been lost through the precolumn during simulation of water removal.

#### Quantitation: Recovery of n-Undecane

##### Preparation of Standard Solutions

Standard solutions of n-undecane in the range of 0.5 to 1.5  $\mu$ g/ml were prepared. Appropriate amounts of n-undecane were weighed into 1-ml volumetric flasks, and the flasks were brought to volume with n-hexane.

##### Conditions and Selection of the Analytical Column

After experimentation with various analytical columns, a 3 m

by 3 mm O. D. Carbowax 1500 column was found to give good separation of n-undecane and hexane with reasonable retention times and peak shapes. A 3373B Hewlett Packard electronic integrator used according to the manufacturer's instructions was employed to determine peak areas. Optimum conditions for developing the analytical column were found essentially by trial and error. They were: column temperature  $50^{\circ}\text{C}$ , injection temperature  $200^{\circ}\text{C}$ , detector temperature  $260^{\circ}\text{C}$ , and a flow rate of 24 ml/min. All subsequent runs were developed at these conditions.

#### Preparation of Standard Curves

Standard curves were prepared by injecting varying amounts of the same standard solution onto the analytical column. Micrograms of n-undecane were plotted against peak area calculated as electronic integrator counts. A line was drawn through the experimental points using the technique of least squares.

Periodically the same standard solution was checked against the standard curve to detect possible changes in concentration due to evaporation or deterioration. Several other standard solutions were prepared and checked against the standard curve to insure the accuracy of the solutions.

### The On-Column Trapping System

A variation of the on-column trapping procedure described by Morgan and Day (1965) was employed. Prior to an analysis, with the analytical column in place in the gc oven, the carrier gas flow rate, oven temperature, attenuation, recorder baseline, and integrator were adjusted.

The carrier gas was then turned off and the head of the analytical column in which a 10 cm U-bend had been made was disconnected from the injection port and connected to a conditioned precolumn which in turn was connected to an 1/8 inch Swagelok T supported externally to the gc oven (Figure 2). The T was connected to a tank of prepurified nitrogen through a flow meter. An 1/8 inch nut containing a silicone rubber septum was screwed onto the remaining leg of the T. The U-bend in the column was immersed in a slurry of Dry Ice and 2-methoxyethanol. The precolumn was maintained at the desired temperature with a hooded heat gun controlled by a variable transformer.

Extreme care was taken to prevent and detect leaks in order to prevent loss of sample. Stainless steel fittings were found to be less prone to leaks than brass fittings and lasted longer before scoring.

Each sample on Porapak Q, Tenax GC, and Chromosorb 102 was subjected to the following procedure with conditions kept constant



The prepurified nitrogen was adjusted to a flow rate of 12 ml/min and the T-joint and connecting tubing were attached to the end no. 1 of the precolumn. End no. 2 of the precolumn was left open to the atmosphere. To prevent condensation in the line, the T-joint and connecting tubing were heated at 135° C. (62 volts) for 5 min. prior to injecting a known amount of n-undecane in hexane through the septum. Injections were made using the same method as used in preparing the standard curves. Heating was continued for 5 more minutes. The heat gun was then turned down to 55° C and moved to the packed precolumn. With the gas still flowing at 12 ml/min the precolumn was subjected to these water removal conditions for 30 min. Next the precolumn was reversed with end no. 2 attached to the T-joint assembly and end no. 1 attached to the cooled head of the analytical column. All joints were carefully checked for leaks. The heat gun was again placed on the precolumn and turned on at 135° C (62 volts). Heating was continued for 10 min with the same gas flow (12 ml/min). The volatile compounds were trapped on-column and were ready for analysis. The analytical column was disconnected from the assembly and attached to the injection port of the Varian Aerograph 1400 gc. Oven temperature was brought to 50° C, the gas flow turned on, and the gc and recorder started. This column was developed under the same conditions as used in preparation of the standard curve. The 3373B Hewlett Packard

electronic integrator was used to measure peak area. Peak areas were compared to the areas on the standard curve for the appropriate quantity of injected n-undecane.

### Recovery Calculations

Recoveries were calculated as follows:

(Integrator counts per  $\mu\text{g}$  of sample) / (Integrator counts off standard curve per  $\mu\text{g}$  of sample) X 100 = % Recovery

The precolumns were reconditioned (conditions given earlier) after each run. Using this procedure, we attempted to determine the quantitative recovery from Porapak Q, Tenax GC, and Chromosorb 102 traps.

## RESULTS AND DISCUSSION

### Behavior of Water on the Polymers

The low affinity of porous polymers for water permits simultaneous elimination of water and collection of volatile organic materials from aqueous vapor systems. However to make intelligent use of such properties it is necessary to know the exact behavior of water on these trapping agents under various conditions.

As indicated in Table 4, water was first detected at 0.63 min eluting from Porapak Q and Chromosorb 102 precolumns and elution was complete at 6.0 min. In both cases sharp symmetrical peaks were observed with little tailing. This indicated little loss of water due to irreversible adsorption on the porous polymer. The water eluted faster from Tenax GC under the same conditions. It was first detected at 0.25 min. and last detected at 5.5 min. Again a symmetrical peak was observed. Thus the water was retained approximately 6 min. on all precolumns.

Under the same gc conditions but with the flow rate increased to 45 ml/min, of course the water eluted faster. On Porapak Q it was first detected at 0.3 min. and last detected at 2.0 min; on Chromosorb 102, first at 0.2 min. and last at 2.0 min; and on Tenax GC, first at 0.12 min. and last at 1.5 min. Symmetrical peaks were again observed with little tailing.

Under both sets of gc conditions 1  $\mu$ l of water eluted from these polymers within 6 min. Hollis and Hayes (1966) stated that little if any water was irreversibly adsorbed by porous polymer columns. Thus these porous polymers offered a simple and rapid means of removing interfering water from samples and of sampling dilute aqueous systems with minimal water vapor interference.

The short retention time of 1  $\mu$ l of water on the polymers suggested that a water removal period of 1 hr which had been used in our laboratory, was excessive and was probably contributing to loss of low-boiling compounds in the sample. After bubbling N<sub>2</sub> through the water or sweeping the surface of the water for 30 min (1000 ml/30 min) with N<sub>2</sub>, the time for water to be removed from the precolumns under simulated water removal conditions was measured and depicted in Table 3.

Table 3. Water removal times under various conditions.

Porous Polymer	Minutes to Remove Water	
	Surface swept with N <sub>2</sub>	N <sub>2</sub> bubbled through sample
Porapak Q	10	21
Chromosorb 102	12	23
Tenax GC	8	15

The information in Table 3 indicates that removal of the residual water from the precolumn took twice as long when the entrainment technique involved bubbling  $N_2$  through the sample as when the surface of the sample was merely swept with the gas.

To prevent water condensation in the precolumn at the beginning of sampling, the precolumn was heated to  $55^\circ C$  before gas and vapor were allowed to flow through it. Failure to do so, required excessive time periods of 1 hr. or greater to remove residual water. With careful control of temperature and flow rate, water removal was complete within 15 min. for  $N_2$  swept samples and 30 min. for  $N_2$  bubbled samples.

#### Losses During Water Removal

The question arose as to which compounds or classes of compounds were lost during water removal. Table 4 summarized the retention data collected on several classes of compounds compared to that of water. In all cases the time at which a compound was first detected and its uncorrected retention time were recorded. If the time that the compound was first detected was shorter than or near the time the water was last detected, then partial or complete loss of the compound would occur upon water removal. A variety of compounds often found in flavors were investigated. They included

Table 4. Retention times on precolumns under simulated loading and water removal conditions.<sup>a</sup>

Compound	BP °C <sup>b</sup>	Retention time (Min)								
		Porapak Q			Chromosorb 102			Tenax GC		
		First Det <sup>c</sup>	TR	Last Det	First Det	TR	Last Det	First Det	TR	Last Det
Water	100	0.63	1.44	6.0	0.63	1.38	6.0	0.25	1.0	5.5
Methanol	64.6	2.13	3.36		1.25	2.13		0.44	0.75	
Ethanol	78.5	8.5	11.63 <sup>d</sup>		5.25	7.0 <sup>d</sup>		1.12	1.5 <sup>d</sup>	
Formic acid	100.7	14.63	20.0 <sup>e</sup>		12.0	15.75 <sup>e</sup>		2.0	3.25 <sup>d</sup>	
Acetic acid	118.1		>34					8.25	10.0 <sup>e</sup>	
Acetaldehyde	21	3.63	5.0 <sup>d</sup>		2.13	3.0 <sup>d</sup>		0.5	0.75	
Propanal	48.8	18.0	22.75 <sup>e</sup>		12.0	15.0 <sup>e</sup>		2.0	2.63 <sup>d</sup>	
N-butanal	75.7							5.5	6.5 <sup>e</sup>	
Isobutanal	61.5							4.5	6.0 <sup>e</sup>	
Methyl mercaptan	7.6	3.0	3.75 <sup>d</sup>		5.13	6.75 <sup>d</sup>		1.25	1.88	
Ethyl mercaptan	34.7	23.5	29.13 <sup>e</sup>		10.75	13.75 <sup>d</sup>		1.75	2.5 <sup>d</sup>	
Isobutyl mercaptan	98							8.5	12.5 <sup>e</sup>	
Dimethyl sulfide	37.5	23.63	28.5 <sup>e</sup>		17.0	21.0 <sup>e</sup>		1.69	2.13 <sup>d</sup>	
Diethyl sulfide	92							14.38	17.38 <sup>e</sup>	
Methyl formate	31.5	6.5	8.63 <sup>d</sup>		3.5	4.5 <sup>d</sup>		0.81	1.25	
Ethyl formate	54	33.0	37.0 <sup>e</sup>		16.5	19.25 <sup>e</sup>		2.0	3.38 <sup>d</sup>	
Methyl acetate	57.5				17.0	20.5 <sup>e</sup>		2.5	3.38 <sup>d</sup>	
Ethyl acetate	77.2							7.38	9.0 <sup>e</sup>	

<sup>a</sup> Precolumn conditions:

Column temperature 55° C

He flow rate 12 ml/min

Injection port temperature 120° C

Detector temperature 160° C

<sup>b</sup> From Handbook of Chemistry and Physics. Cleveland: Chemical Rubber Publishing Co. 1960.<sup>c</sup> Det = Detected<sup>d</sup> Moderate tailing<sup>e</sup> Extreme tailing

low-boiling alcohols, carboxylic acids, aldehydes, ketones, mercaptans, sulfides, and esters.

Table 4 showed that all compounds had a shorter retention time on the Tenax GC precolumns than on the other two precolumns. Since water was retained on the Tenax GC precolumn approximately 6 min, total or partial loss of all listed compounds except acetic acid, n-butanal, isobutyl mercaptan, diethylsulfide, and ethyl acetate would occur under these conditions. If water removal conditions were continued longer than 6 min, losses in the above compounds would also have occurred. Considerable losses of low-boiling compounds would result if Tenax GC precolumns were used according to the standard procedure.

The longest retention times for the compounds investigated were on Porapak Q. Losses occurred during the 6 min water removal period for the following compounds: methanol, acetaldehyde, and methyl mercaptan. Under these conditions considerably fewer low-boiling compounds were lost upon water removal with Porapak Q precolumns as compared to the Tenax GC precolumns. However under a 30 min water removal process, some loss would have occurred in all compounds tested, as was the case with Tenax GC and Chromosorb 102.

Retention times on Chromosorb 102 were generally intermediate between those on Porapak Q and Tenax GC. Losses occurred during

the water removal time of 6 min. in the following compounds: methanol, ethanol, acetaldehyde, methyl mercaptan, and methyl formate. Although losses on Chromosorb 102 were slightly greater than those on Porapak Q, the performance of Porapak Q and Chromosorb 102 was quite similar. As mentioned before, losses in all these compounds would have occurred with a 30 min. water removal treatment.

Table 5 listed the retention times of some representative compounds under slightly different water removal conditions than used for Table 4. The only change was an increase in flow rate to 45 ml/min. The same trends were followed under the modified flow rate. Water was removed from all precolumns in approximately 2 min. Tenax GC had the shortest retention times; Porapak Q, the longest; and Chromosorb 102, intermediate. If 2 min were allowed for water removal, losses would have occurred from all compounds tested on Tenax GC precolumns. Porapak Q would have lost methanol, and Chromosorb 102 would have lost both methanol and methyl mercaptan. A 30 min water removal treatment would have resulted in increased losses at the faster flow rate.

An indication of the degree of tailing on the various porous polymers is reported in Tables 4, 5, and 6. Moderate or extreme tailing may suggest that conditions could be improved or that another column could do a better job. These notations were included to give



Table 5. Retention times on precolumns under simulated loading and water removal conditions.<sup>a</sup>

Compound	BP °C <sup>b</sup>	Porapak Q			Chromosorb 102			Tenax GC		
		First Det	TR (Min)	Last Det	First Det	TR (Min)	Last Det	First Det	TR (Min)	Last Det
Water	100.0	0.31	0.66	2.0	0.21	0.42	2.0	0.12	0.38	1.5
Acetone	56.5	7.5	8.5 <sup>c</sup>		3.2	3.63 <sup>c</sup>		0.5	0.75	
Methanol	64.6	1.0	1.25		0.5	0.75		0.16	0.44	
Methyl mercaptan	7.6	2.12	2.75 <sup>c</sup>		0.44	1.0		0.12	0.5	

<sup>a</sup> Precolumn conditions:

Column temperature 55° C He flow rate 45 ml/min

Injection port temperature 120° C

Detector temperature 160° C

<sup>b</sup> From Handbook of Chemistry and Physics. Cleveland: Chemical Rubber Publishing Co. 1960.

<sup>c</sup> Moderate tailing

Table 6. Retention times on precolumns at unloading conditions without reversal of precolumns.<sup>a</sup>

Compound	BP °C <sup>b</sup>	Retention time (Min)		
		Porapak Q	Chromosorb 102	Tenax GC
Acetone	56.5	0.5	0.38	0.25
2-pentanone	101.7	1.75 <sup>c</sup>	1.0	0.38
2-octanone	173.5	>69	11.25 <sup>d</sup>	0.50
2-nonanone	195.3	>90	>80	0.75
Hexanol	157.2	9.0 <sup>d</sup>	3.63 <sup>c</sup>	0.31
1-octen-3-ol		>120	8.25 <sup>d</sup>	0.44
γ-decalactone		>85	>100	>96
Diethyl phthalate	296.1	>80	>74	>74

<sup>a</sup> Precolumn conditions:

Column temperature 135° C N<sub>2</sub> flow rate 36 ml/min

Injection port temperature 300° C

Detector temperature 230° C

<sup>b</sup> From Handbook of Chemistry and Physics. Cleveland: Chemical Rubber Publishing Co., 1960.

<sup>c</sup> Moderate tailing

<sup>d</sup> Extreme tailing

an indication of compound behavior on a particular precolumn.

In summary, Tenax GC precolumns exhibited the shortest retention times for water and all tested compounds at both sets of conditions. Maximum loss of low-boiling compounds was observed on this polymer. Thus Tenax GC precolumns would be a poor choice for use in a study of a mixture containing low-boiling compounds. Porapak Q or Chromosorb 102 would be preferred if a quantitative study was undertaken involving low-boiling compounds. Knowledge of the compounds or type of compounds of interest would aid greatly in selecting an appropriate porous polymer with respect to losses during water removal.

As water removal conditions were modified, retention times were also changed. Therefore it was not only important to look at the type of polymer used, but also important to note the conditions used during water removal. If interest is in a particular compound, the polymer and water removal conditions must be chosen such that none of the compound is lost in the procedure, especially if quantitation is an objective. For each trapping setup and procedure, the investigator should be aware that losses can occur during water removal.

#### Unloading Characteristics of High-Boiling Compounds

Since compounds may be lost during unloading of the

precolumns, factors which influence this situation were investigated. As previously mentioned, unloading was often carried out at 135° C. for 45 min with a flow rate of 12 ml/min. Thus if column reversal was not employed, those compounds remaining on the precolumn longer than 45 min. would be lost. Table 6 lists the retention times in minutes of various high boiling compounds on Porapak Q, Chromosorb 102, and Tenax GC precolumns.

If unloading without precolumn reversal was continued for 45 min, the following compounds would be retained and thus lost on Porapak Q: 2-octanone, 2-nonanone, 1-octen-3-ol, gamma-decalactone, and diethyl phthalate. Fewer would be lost on Chromosorb 102: 2-nonanone, gamma-decalactone, and diethyl phthalate. Only gamma-decalactone and diethyl phthalate would be retained on Tenax GC precolumns after 45 min. at these unloading conditions. Thus with no precolumn reversal prior to unloading, considerable losses of high-boiling compounds would be expected, especially on Porapak Q and Chromosorb 102.

The temperature of 135° C. was chosen as the unloading temperature because Krumperman (1972) indicated excessive column bleed occurred above that temperature. However, Tenax GC is claimed (van Wijk, 1970) to be capable of withstanding temperatures up to 375° C. Table 7 shows the retention times of some compounds on Tenax GC precolumns at 280° C and a flow rate of 45 ml/min.

The three compounds tested eluted in less than 1 min without precolumn reversal. This data indicated that Tenax GC precolumns could be used at higher temperatures for rapid unloading and without column reversal prior to unloading. Primary interest in high-boiling compounds would indicate Tenax GC as the trapping polymer of choice.

### Precolumn Reversal

To evaluate the effect of precolumn reversal prior to unloading, the following compounds were subjected to a procedure with reversal: diethyl phthalate, gamma-decalactone, 2-nononone, and 1-octen-3-ol. The data in Table 8 showed that compounds previously lost without reversal were now all recovered within 10 min when the precolumns were reversed.

Presumably the high-boiling compounds were collected at the head of the precolumn during sampling and migrated only slightly during water removal. Without precolumn reversal prior to unloading, these compounds were retained on the polymer longer than the unloading time, and were thus lost in the analysis. With precolumn reversal, the compounds were unloaded within the allotted time.

In summary, precolumn reversal on Porapak Q and Chromosorb 102 would help prevent loss of compounds due to retention on the polymer during unloading. At 135<sup>o</sup> C, reversal on Tenax GC

Table 7. Retention times on Tenax GC precolumns. <sup>a</sup>

Compound	BP °C. <sup>b</sup>	Retention time (Min)
Diethyl phthalate	296.1	0.19
γ-decalactone		0.33
Acetone	56.5	0.12

<sup>a</sup> Precolumn conditions:

Column temperature	280° C
Injection port temperature	300° C
Detector temperature	255° C
N <sub>2</sub> flow rate	45 ml/min.

<sup>b</sup> From Handbook of Chemistry and Physics. Cleveland: Chemical Rubber Publishing Co. 1960.

Table 8. Retention times on precolumns with simulated water removal (N<sub>2</sub> flow of 30 ml/min. continued for 1 hr at 55° C) and column reversal. <sup>a</sup>

Compound	BP °C <sup>b</sup>	Retention time (Min)		
		Porapak Q	Chromosorb 102	Tenax GC
Diethyl phthalate	296.1	0.75	9.63	1.50
γ-decalactone		4.50	8.00	3.38
2-nonanone	195.3	1.25	1.50	c
1-octen-3-ol		3.38	1.00	c

<sup>a</sup> Precolumn conditions:

Column temperature	135° C
Injection port temperature	280° C
Detector temperature	270° C
N <sub>2</sub> flow rate	30 ml/min.

<sup>b</sup> From Handbook of Chemistry and Physics. Cleveland: Chemical Rubber Publishing Co. 1960.

<sup>c</sup> under 1.00 min.

would also be beneficial. At 280° C, reversal of Tenax GC was unnecessary to unload the high-boiling compounds. Thus Tenax GC would be a good polymer for investigation high-boiling compounds and by using high temperatures during unloading, precolumn reversal is not necessary. When using Porapak Q or Chromosorb 102, precolumn reversal is necessary for high-boiling compounds have been collected on these precolumns. If a particular compound is of interest, one should look at its behavior on the precolumns and under the particular unloading conditions. Of course, special care must be taken to carefully control temperature, carrier gas, flow rates, and other sampling and water removal conditions.

#### Quantitative Recovery of n-Undecane

Using the procedure described in materials and methods, the present recovery of n-undecane from the three types of porous polymer precolumns was calculated. The values ( $\mu\text{g}$  n-undecane vs. integrator counts) for four samples run on Tenax GC precolumns compared to a standard curve are shown in Figure 3. Values obtained from runs on both Porapak Q and Chromosorb 102 precolumns were plotted on Figure 4. In each case, seven samples ranging between 1.0 and 3.5  $\mu\text{g}$  were used to calculate the standard curves (by the method of least squares). Accurate values for samples larger than 4.0  $\mu\text{g}$  were not obtained due to the sampling limitations

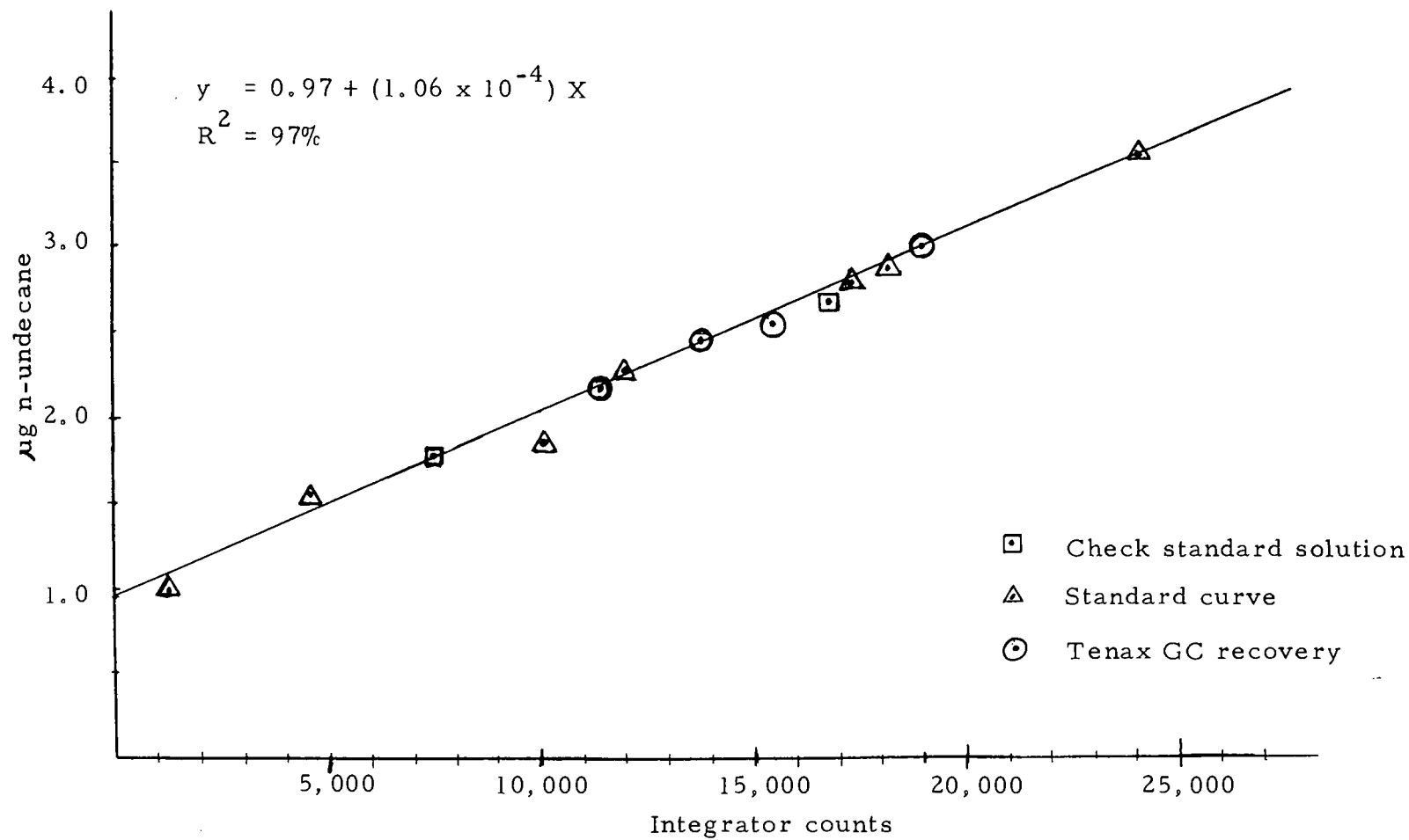


Figure 3. Standard curve with quantitative data for Tenax GC precolumns.

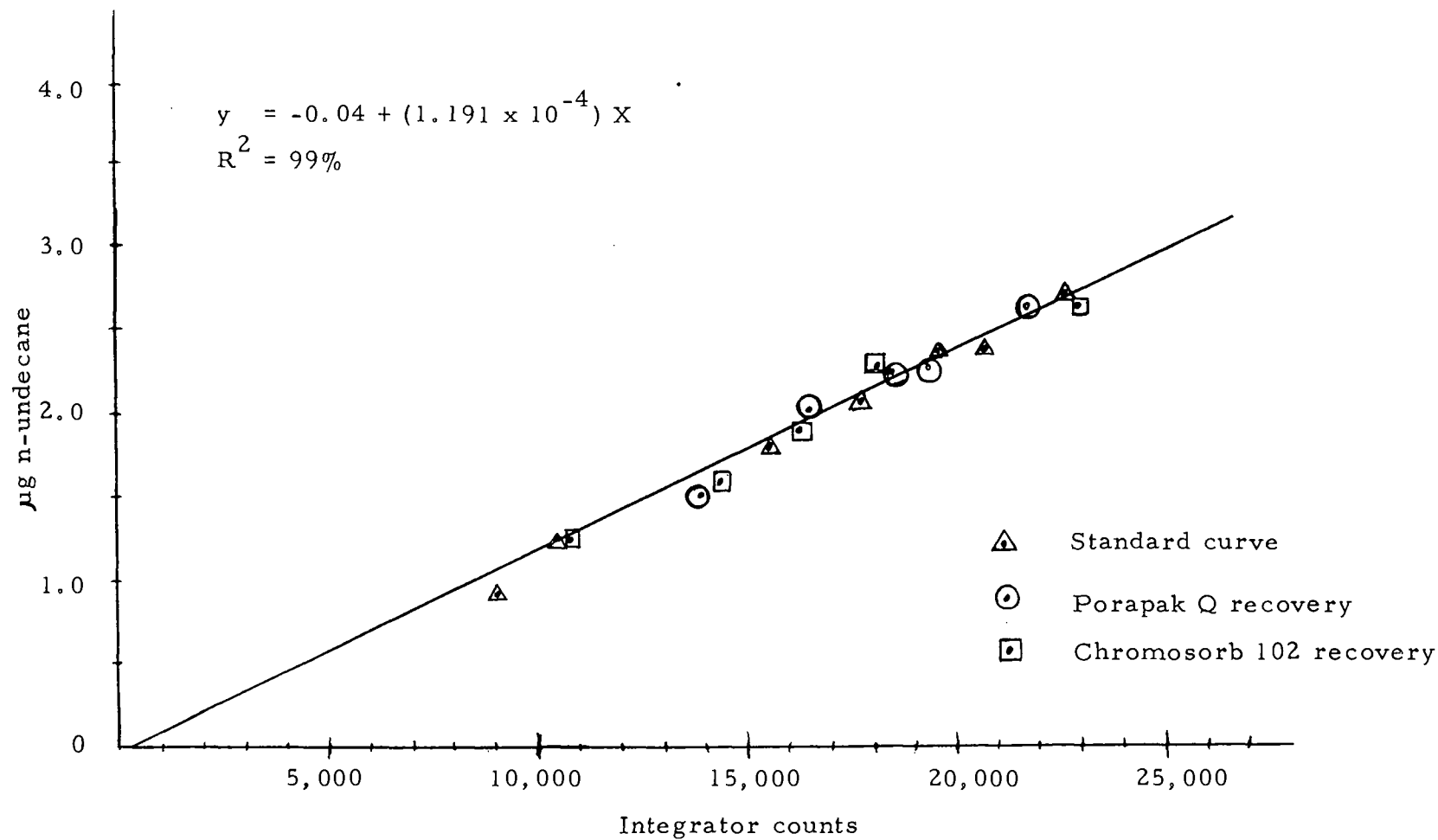


Figure 4. Standard curve with quantitative data for Porapak Q and Chromosorb 102 precolumns.



of a 10  $\mu$ l syringe. High multiple correlation coefficient ( $R^2$ ) values were observed, 97% and 99% respectively for Figures 3 and 4. These high multiple correlation coefficient values indicated that the 3373B Hewlett Packard electronic integrator was able to integrate the n-undecane peaks accurately over this range. This was expected since the peaks were sharp and uniform in shape. Percent recovery of n-undecane was calculated from Figures 3 and 4 on the various porous polymers.

Table 9 lists the percent recovery of four runs each on Tenax GC, Porapak Q, and Chromosorb 102. The averages were 98.5%, 99.5%, and 100.0%, respectively. Thus, n-undecane was essentially completely recovered from all the porous polymers tested, and any of these would be suitable for a quantitative study on this compound using the above system.

In summary, Porapak Q, Tenax GC, and Chromosorb 102 appear to adsorb and desorb n-undecane quantitatively. As indicated by this data, quantitation is successful with this porous polymer sampling method. Although some quantitative studies have been done, more work is needed with a variety of compounds before quantitation on porous polymers can be fully characterized. The question remains as to the possibility of quantitation with compounds such as ketones which have been reported to interact chemically with some polymers (Barta and Gordon, 1970). Thus for quantitative

work, the compounds of interest should be tested in the above manner to determine the recovery. In some cases, it may be found that recovery is best on a particular porous polymer. Porous polymer techniques offer the advantages of rapid qualitative and quantitative analyses.

Table 9. Recovery of n-undecane from precolumns.

Tenax GC	Porapak Q	Chromosorb 102
98.8%	102.0%	96.0%
99.5	102.0	100.0
100.6	98.0	102.0
<u>95.2</u>	<u>96.0</u>	<u>102.0</u>
98.5%	99.5%	100.0% Average

#### Color Changes in Polymers

After extended use of the polymers, varying amounts of discoloration and clumping were observed. Dave (1969) previously noted shrinking and slight discoloration after column conditioning. The Tenax GC precolumns had an even light brown discoloration, while those of Porapak Q and Chromosorb 102 had discoloration ranging from light to dark brown.

Trowell (1971) found that when  $\text{NO}_2$  came into contact with Chromosorb 102 or Porapak Q during heating, a brown color formed. The carrier gas used in our procedure was nitrogen and possibly contained  $\text{NO}_2$  as an impurity.

The effects of the discoloration and the changes in the polymers on quantitation are not known. However, the production of NO, H<sub>2</sub>O, and nitration of the aromatic rings of the polymer does occur. Hollis (1973) cites an example of porous polymer GC columns which have been in use since 1967 analyzing a sample every 15 min. with no change in retention or separation characteristics. Qualitative changes due to discoloration or other changes in polymers are not documented in the literature.

In summary, discoloration occurs in Porapak Q, Chromosorb 102, and Tenax GC. Whether this affects the performance of a pre-column is not known. However if it does, glass precolumns will give the advantage of observing changes in the polymers.

## SUMMARY AND CONCLUSIONS

This investigation was concerned with various aspects of a porous polymer trapping technique described previously. Quantitation was of special interest. Optimization of procedural parameters and characterization and comparison of Porapak Q, Chromosorb 102, and Tenax GC were other goals of this investigation.

Water eluted from the precolumns in symmetrical peaks indicating little irreversible adsorption to the porous polymers. The time for 1  $\mu$ l of water to travel through a precolumn depended on the nitrogen flow rate and column temperature. At 12 ml/min of N<sub>2</sub> at 55° C, complete elution of water required only 6 min or less, while at 45 ml/min, only about 2 min was required for the porous polymers tested. This rapid elution of water from the precolumn, prevented subsequent water interference in the analysis.

In this laboratory, the removal of water from precolumns has commonly been extended to 1 hr to insure complete water removal. This time interval appeared excessive and certainly must contribute to loss of low-boiling compounds collected from the sample. Shortening of the water removal time, depending on the conditions, would decrease overall analysis time as well as sample losses.

By comparing the retention times of various compounds to that of water under conditions usually employed in the removal of water,

it was possible to characterize some of the losses that would have occurred in this step of the procedure. The greatest losses in low-boiling compounds occurred in Tenax GC precolumns, with losses occurring in thirteen out of eighteen compounds tested. Three out of twelve were lost on Porapak Q, and five out of twelve on Chromosorb 102. Losses would have occurred in all these compounds with a 30 min water removal treatment.

If low-boiling compounds were of particular interest, Porapak Q or Chromosorb 102 would be preferred especially if quantitation was to be attempted. Under these conditions, excessive losses of low-boiling compounds would be expected on Tenax GC precolumns. More retention data on porous polymers will aid in selecting the most appropriate precolumns for various analyses.

Losses were also believed to occur during unloading where the volatile compounds were heat desorbed from the porous polymer into a cold trap. If the compound remained on the polymer longer than the unloading time allowed, it was essentially lost. Eight high-boiling compounds were subjected to unloading conditions on Porapak Q, Chromosorb 102, and Tenax GC. Five compounds were retained on Porapak Q for over 1 hr, three on Chromosorb 102, and only two on Tenax GC. Thus without precolumn reversal prior to unloading, a greater loss of high-boilers occurred on Porapak Q and Chromosorb 102. Tenax GC was therefore the porous polymer of choice for

investigating high-boiling compounds. Rapid elution and lower losses of these compounds were observed on Tenax GC at 135° C.

When Tenax GC precolumns were unloaded at 280° C, all compounds tested were eluted under 1 min. without precolumn reversal. Use of Tenax GC for high-boiling compounds would shorten total analytical time by eliminating the precolumn reversal step.

Precolumn reversal was essential on Porapak Q and Chromosorb 102, if certain compounds were to be recovered. Compounds, previously lost without precolumn reversal, were recovered within 10 min when precolumn reversal was used. Presumably the high-boiling compounds were collected at the precolumn head during sampling and migrated only a short distance during water removal. Reversal thus shortened the time necessary to elute the compound into the cold trap.

The recovery of n-undecane from precolumns of these three porous polymers was investigated and found to be quantitative within experimental error. Thus, this procedure, which included a water removal step and precolumn reversal, was practical for quantitation of n-undecane under these conditions. Full characterization of quantitation on porous polymers remains to be done. Therefore compounds of interest must be tested for quantitative recovery from

a particular polymer and system, before that system can be used routinely for quantitation.

Color changes occurred in the polymers due possibly to nitration of the aromatic rings. Although the qualitative properties of the polymers appear to be unaffected, the effects on quantitation are not known.

Additional work is needed to fully characterize the commercially available porous polymers and to improve the existing procedures and setups.

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