## The Utility of Porous Polymer Sorbents in Chemically-Active Environments

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# The Utility of Porous Polymer Sorbents in Chemically-Active Environments

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Porous polymer adsorbents used for combustion source sampling have the potential for alteration by reacting with components of the stream being sampled. Two potential problems, alteration of capacity and selectivity by sulfonation and nitration and the creation of a thermally-induced blank are examined in this report.

The effect of sulfonation and nitration on the porous polymers Tenax-GC and XAD-2 was examined by gas-solid chromatography. Variation in capacity and selectivity between native and altered sorbents was determined by construction of plots of log $V'_R$ versus $1/T \times 1000$. A series of five solutes representing a range of polarities was used. Surface area measurements were used in conjunction with these plots to make generalizations about the potential effects of alteration of the sorbents.

The thermal blank from XAD-2 resin was examined by using the resin in a simulated sampling scheme where the resin temperature was varied. The XAD-2 was then carried through a standard workup procedure designed to characterize collected components. Specific components were identified by GC/MS.

KEY WORDS: Porous polymer adsorbents, alteration of capacity and selectivity, thermal blank determination.

## INTRODUCTION

Porous polymers have been used extensively for the preconcentration of organic materials in air and water systems. As a collection sorbent XAD-2, a polystyrene-divinylbenzene copolymer, has the advantage of high

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surface area while Tenax-GC, a polyphenylene oxide polymer, exhibits greater upper temperature stability. Zlatkis[1] collected trace organic materials on a Tenax-GC cartridge, and after thermal desorption separated them by gas chromatography. Others have used similar techniques to concentrate high molecular weight[2] and hazardous organic compounds in air[3,4] on Tenax-GC. Low molecular weight substances[5] and other volatile materials[6] have been collected from drinking water using a combination of headspace sampling, sorption onto Tenax-GC, and analysis by gas chromatography. Burnham[7] found that XAD-2 extracts many non-ionic organic materials, particularly aromatic compounds, from drinking water with high efficiency. Ryan and Fritz[8] used an experimental version of XAD-4, a porous polymer similar to XAD-2, to collect trace organics from water. These materials were thermally desorbed onto a Tenax-GC cartridge, where they were then volatilized and injected into a gas chromatograph for further analysis. Recently, these two polymers have been utilized as a component of source monitoring traps used to sample stationary sources. Parsons[9] used a Tenax-GC cartridge to sample stack gases, with subsequent thermal desorption and gas chromatographic analysis. Jones[10] collected polycyclic aromatic hydrocarbons on a highly efficient Tenax-GC sorption trap and after desorption by pentane extraction and concentration by evaporation, the materials were analyzed by gas chromatography/mass spectroscopy. XAD-2 is currently employed in the United States Environmental Protection Agency's Source Assessment Sampling System (SASS) to collect a broad range of volatile organic materials from gaseous streams.[11] We report here the results of two studies which examine possible problems with these porous polymers related to their use in chemically hostile environments.

The first part of this study deals with the effect of chemically-active species upon the capacity and selectivity of XAD-2 and Tenax-GC. When these polymers are used for source sampling, chemically-active species such as reactive gases and their acids could be adsorbed by the resins and react with the polymer backbone and side chains.[12] This potential for sorption raises the question of its effect on the capacity and selectivity of the resin for various classes of compounds. Both of these materials sulfonate upon exposure to sulfuric acid, and XAD-2 can be nitrated by reaction with nitric acid. Sulfonation and nitration are not unlikely situations to be encountered in source monitoring traps especially since such traps are often operated at or near the dew points of the respective acids of $SO_x$ and $NO_x$. If porous polymer sorbent traps are operated to breakthrough, capacity and selectivity are even more important considerations since the *relative* distribution of materials could be distorted, making source to source comparisons difficult. This portion of the study

deals with the effect of varying degrees of sulfonation and nitration on the gas chromatographic retention capacity and selectivity of XAD-2 and Tenax-GC. Comparisons were made between native and altered sorbents by observing changes in the specific retention volumes of a series of standard solutes as a function of temperature. From these data some generalizations can be made about the possible effects of reactive species on the collection of various classes of compounds.

The second portion of this study involved examining the blank observed when XAD-2 resin is used in a sample collection scheme such as that outlined by the USEPA.[11] One of the requirements for a material used for preconcentration of species from a stream is that the material introduce as small a blank value as possible in relation to the sample collected. The use of XAD-2 in operations such as stack sampling, where the resin could be exposed to above ambient temperatures for extended periods of time, could lead to the formation of an otherwise unmeasured blank due to the thermal instability of the resin. If this blank is of sufficient size, both qualitative and quantitative determination of the trapped species becomes difficult. The thermal blank was examined as a function of temperature, using the procedure outlined in the EPA Level I analysis methodology.[11] Identification of the kinds of species present in the thermal blank makes recognition of this blank possible when the resin is used in an actual sampling procedure.

## EXPERIMENTAL

Tenax-GC and XAD-2 (Applied Science Laboratories. State College, PA, U.S.A.) were sulfonated to various extents by reaction with a 100-fold volumetric excess of concentrated sulfuric acid for 1–6 hours at 60–95°C. Prior to sulfonation, XAD-2 was washed with 500 ml deionized water and additionally in some cases, with 150 ml each of pentane, methylene chloride, and methanol, and 750 ml deionized water. After sulfonation and dilution of the acid, the resins were washed with 500 ml deionized water, 500 ml each of 2 N NaCl and 2.4 N HCl in alternating portions, and 750 ml deionized water. After the sorbents were Soxhlet extracted with deionized water for 24 hours and air-dried, total exchange capacity in meq $H^+$/g of sorbent was determined by titration of the acidic resin in an excess of standard NaOH with standard HCl (for sulfonated XAD-2) and by titration in 1 N NaCl with standard base after $H^+$ exchange with $Na^+$ (for sulfonated Tenax-GC).

Nitrated XAD-2 was prepared by heating XAD-2 at 60°C for two hours in a 20-fold excess of 40:60 v/v concentrated nitric and sulfuric acids. After dilution of the acid and thorough washing with water, the nitro

content of XAD-2 $NO_2$ in weight percent $NO_2$ was determined by titanous chloride reduction.[13]

After 24 hours of Soxhlet extraction with deionized water, each native, sulfonated, and nitrated resin was vacuum dried in a pistol drying apparatus at 116°C (native and sulfonated materials) or 56°C (nitrated XAD-2). The polymers were packed into 3.1 mm o.d. stainless steel columns ranging in length from 2 m for native resins to 0.3 m for highly sulfonated and nitrated sorbents. The weight of sorbent in each column was carefully determined after packing. Gas-solid chromatographic studies were performed on a Varian Series 3700 gas chromatograph at highest FID sensitivity. Prior to analysis, each column was conditioned at 162°C for 12 hours under low He flow. Retention times were obtained for the five solutes (pentane, 2-propanol, benzene, acetonitrile, and acetone) at various temperatures using vapor samples. All retention data are reported as specific retention volumes, $V'_r$, where $V'_r = jF_c(t_r - t_0)/g$ ($j$ = gas compressibility factor, $F_c$ = measured helium flowrate in ml/sec, $t_r$ = retention time of solute in seconds, $t_0$ = retention time of methane, and $g$ = number of grams of sorbent in the column).

Surface areas ($m^2/g$), cumulative pore desorption volume (cc/g), and their distributions vs. average pore diameter (Å) were obtained by BET and nitrogen desorption respectively for native and selected sulfonated sorbents.

The thermal blank from XAD-2 resin (Lot 2-9154, Rohm and Haas, Philadelphia, PA) was determined by the method outlined in the EPA Level I procedure[11] for the determination of Total Chromatographable Organic (TCO) content. The TCO analysis quantitates all materials with boiling points in the range 100° to 300°C by a gas chromatographic procedure. This analysis is applied to all samples that might contain compounds in this volatility range collected in a SASS train operation. A Varian Model 1700 gas chromatograph equipped with flame ionization detectors was used. The columns were 1.8 m long and 3.1 mm o.d. stainless steel packed with 10% DC-200 on Chromosorb 750 (100/120 mesh). Determinations were carried out by operating the chromatograph isothermally at 40°C for 6 minutes and then temperature programming at 20°/min to a final temperature of 250°C. Elution time limits corresponding to the temperature limits of the determination were calibrated by the peak maxima for $n$-heptane (bp 98°C) and $n$-heptadecane (bp 303°C). In this case, the upper elution temperature limit was determined by interpolation between the retention maxima of $n$-$C_{16}$ and $n$-$C_{18}$ hydrocarbons. The response was calibrated with a solution containing normal $C_8$, $C_{10}$, and $C_{12}$ hydrocarbons in concentrations similar to those of the TCO materials in the samples. Injection volumes were no larger than $5 \mu l$. A blank

methylene chloride injection was run along with each TCO determination to account for background signal due to column bleed. This background signal was subtracted from the extraction chromatogram before quantitative TCO determination by the cut and weigh method.

Samples of XAD-2 for use in thermal blank determinations were cleaned by successive Soxhlet extraction with deionized water and methanol for 48 hours each. The resin was then extracted with fresh methylene chloride at 24 hour intervals. The total volume of each of these extracts was reduced to 10 ml by rotary evaporation, and a 5 μl sample of this concentrate was examined by GC and compared to a blank methylene chloride injection. When the concentrated sample showed no measurable material in the TCO range, the resin was determined to be clean. It was then air-dried and stored until needed. All glassware used in the resin cleaning process was washed in alcoholic KOH, rinsed, and heated to 600° in an oven for 2–4 hours to rid it of any adsorbed organic material.

Resin samples of approximately 40 ml volume were heated in the apparatus shown in Figure 1. The column consisted of three pieces of Pyrex tubing 150 mm long and 25 mm i.d. joined with appropriate clamps. Section B contained glass beads of 5 mm diameter which served to preheat the air before contact with the resin. Section C contained the clean resin separated from Section B by a wire mesh and glass wool. Air from a compressed air tank was passed through a tube containing anhydrous calcium sulfate and admitted into Section A at a rate of 300 ml/min. The temperature of the resin bed was monitored with two thermometers inserted to varying depths in the resin. For runs above 140°C; decomposing rubber gaskets in the clamps contaminated the resin, so another all
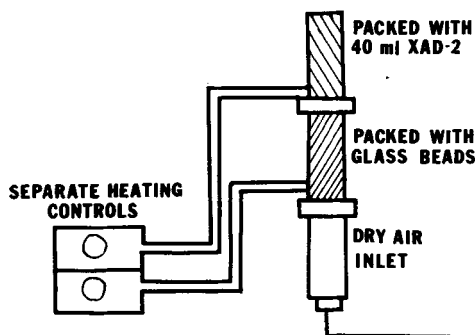


FIGURE 1   Apparatus for heating XAD-2 resin under air flow.

glass column (300 mm long and 25 mm i.d.) was used for these experiments. Air (or in certain cases, nitrogen) flow was applied as the resin samples were brought up to the desired temperature. After heating, the resin samples were Soxhlet extracted with methylene chloride for 24 hours. The bulk of this extract was then concentrated by rotary evaporation to a final volume of 10 ml before analysis.

The GC/MS data were obtained with a Hewlett–Packard 5992A GC/MS system and the infrared spectra were taken on a Perkin–Elmer 297 infrared spectrometer.

## RESULTS

Table I contains surface area ($m^2/g$) and cumulative pore volume (cc/g) data for several sorbents. Sulfonation of Tenax-GC has little effect on these two properties. However, the distribution of pore volume versus pore size shifts slightly towards an increase in larger pores. For XAD-2, sulfonation substantially reduces surface area and pore volume and shifts the pore distribution towards an increase in larger pores.

TABLE I

Surface area and cumulative pore volume data for several sorbents

| Porous polymer | Specific surface area, $m^2/g$ | Cumulative pore volume desorption, cc/g |
|---|---|---|
| XAD-2 | 366 | 0.89 |
| XAD-2S, 1.34 meq/g | 140 | 0.61 |
| Tenax-GC | 21 | 0.05 |
| Tenax-GCS, 0.37 meq/g | 22 | 0.05 |

Gas-solid chromatography is an effective tool for the study of native, sulfonated, and nitrated porous polymers. The weight capacity of a trap (the concentration of material adsorbed when all the pores in the sorbent are in use) can be measured by the breakthrough volume of the trap (the amount of air sampled before leakage occurs). A measure of this breakthrough volume can be obtained through measurement of the gas chromatographic volumetric capacity per gram of sorbent, that is, the volume of gas required to elute a low concentration of material from the sorbent by gas chromatography.[14] The volumetric capacity is simply the specific retention volume ($V'_R$) of a solute on the porous polymer sorbent, obtainable at a variety of temperatures by plots of log $V'_R$ versus $1/T$ × 1000 for the solute. When sampling, $V'_R$ of the earliest eluted compound

defines the breakthrough volume of a trap.[6] Relative values of log $V_R'$ (or intercepts of such plots) between two sorbents for the same solute indicate changes in capacity between them: an increase in the log $V_R'$ values indicates an increase in capacity and vice versa. These sorbents also possess selectivity for certain materials. The more selective a sorbent for a solute, the more its capacity changes with temperature or the greater the $\Delta H_{ADS}$ for the solute. Selectivity changes between two sorbents for a solute can be found by comparisons of slopes of log $V_R'$ versus $1/T \times 1000$. The greater the slope, the higher the selectivity of the sorbent.

Linear regression plots of log $V_R'$ versus $1/T \times 1000$ for the five solutes were constructed for XAD-2, XAD-2S 0.89, 1.80, 1.83, and 2.44 meq/g, Tenax GC, Tenax-GCS 0.27 meq/g, and XAD-2 2.5% $NO_2$. Two representative plots, pentane on XAD-2/XAD-2S, and acetonitrile on XAD-2/XAD-2S, are shown in Figures 2 and 3.

Figure 2 indicates there is little difference between native and sulfonated XAD-2 resin with respect to retention capacity and selectivity for pentane within the temperature range studied. Plots for benzene on XAD-2 and for pentane and benzene on Tenax-GC show similar results. As shown by $t$-tests between intercepts and slopes of these plots for native and sulfonated sorbents, sulfonation produces no change in capacity and selectivity for pentane or benzene on XAD-2S 1.83 meq/g and benzene on XAD-2S 2.44 meq/g. When these data are considered in conjunction with the surface area measurements, one can conclude that while sulfonation reduces the net nitrogen surface area of XAD-2, the loss of small pore structure upon sulfonation produces no change in available surface area for the sorption of hydrocarbons such as pentane, benzene, and other molecules in general. Sulfonation, rather than surface area, is therefore the main cause of capacity and selectivity changes.

Sulfonation significantly changes capacity and selectivity of both sorbents for 2-propanol. On Tenax-GC and partially sulfonated (0.83 meq/g) XAD-2, sulfonation significantly reduces capacity and selectivity for this solute. As the extent of sulfonation of XAD-2 increases to 1.83 meq/g, capacity and selectivity increase to levels statistically comparable to the native resin. At maximum obtainable sulfonation, capacity and selectivity for 2-propanol increase significantly. Evidently, XAD-2 loses capacity for 2-propanol as surface area is lost, but by increasing the extent of sulfonation, the capacity and selectivity are restored by a competing mechanism to near-native resin values.

Sulfonation produces large, significant increases in capacity and selectivity for acetonitrile and acetone on both sorbents. A plot of log $V_R'$ versus $1/T \times 1000$ for acetonitrile on XAD-2 and XAD-2S is shown in Figure 3. As the extent of sulfonation increases, capacity and selectivity
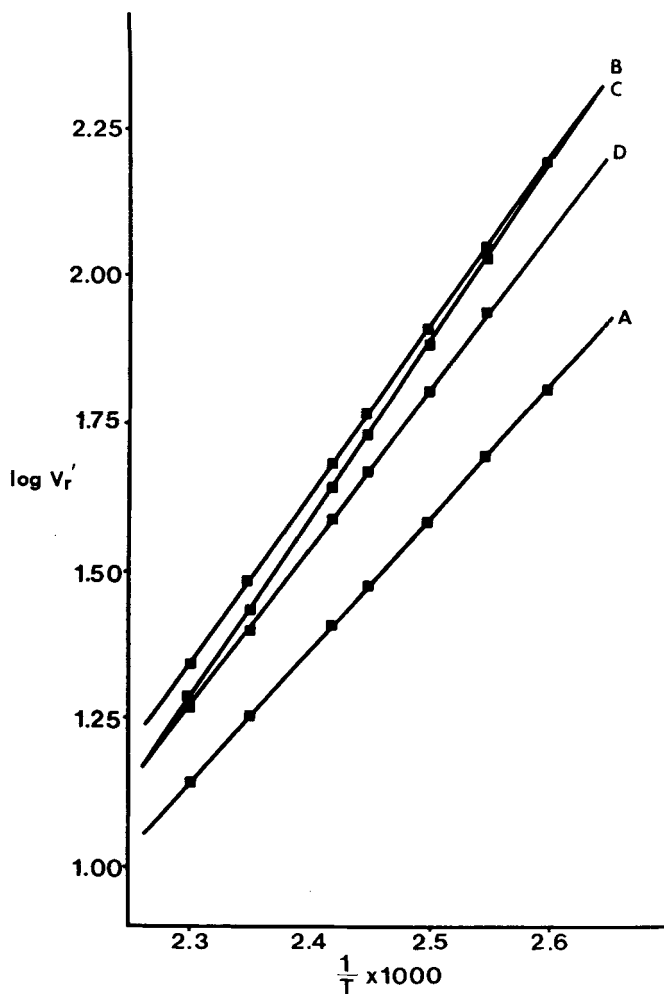
FIGURE 2    Plot of log $V_r'$ versus $1/T \times 1000$ for pentane on native and sulfonated XAD-2 resin. $A = $XAD-2, $B = $XAD-2S 0.89 meq/g, $C = $XAD-2S 1.83 meq/g, $D = $XAD-2S 2.44 meq/g.

increase. These large effects are explained by the fact that acetonitrile and acetone are both capable of acting as hydrogen bond acceptors to the sulfonic acid groups on the resin.

The plots for the five solutes on nitrated XAD-2 yield the following effects on capacity and selectivity: pentane—no change, benzene—no change in capacity but a slight gain in selectivity, 2-propanol, acetonitrile and acetone—large gains in both categories.
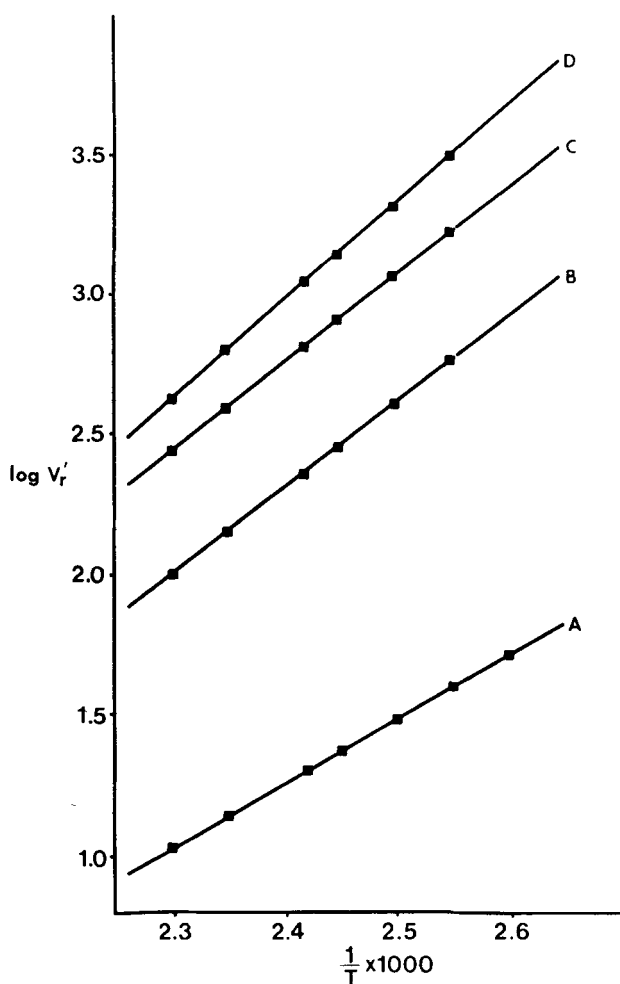
FIGURE 3   Plot of log $V_r'$ versus $1/T \times 1000$ for acetonitrile on native and sulfonated XAD-2 resin.   $A$ = XAD-2,   $B$ = XAD-2S   0.89 meq/g,   $C$ = XAD-2S   1.80 meq/g,   $D$ = XAD-2S 2.44 meq/g.

Studies of the methylene chloride extract of untreated XAD-2 resin indicated the need for extensive cleaning prior to use in order to obtain a nearly zero blank value in the TCO range. Up to 144 h of extraction with methylene chloride were necessary to remove measurable amounts of extracted material. In the first 24 hour extract resolved peaks in the TCO range were observed superimposed on a broad unresolved background signal. This background signal remained for several more washings.

Examination of this initial extract by GC/MS indicated the presence of naphthalene, one or more substituted decalins, ethylstyrene, and various butyl or diethyl benzenes. The magnitude of the blank from the unheated resin appears to be time dependent as well. A sample of clean XAD-2 which had been stored under methanol for 14 months was also examined. The results of a GC/MS study on a concentrated sample of this methanol demonstrated the presence of 1,2-diethyl benzene, ethylstyrene, naphthalene, and low molecular weight polystyrene fragments. Evidently these components were formed by a slow desorption or decomposition process. Avoiding this type of blank can be easily accomplished by cleaning the resin just prior to use in sampling.

Clean XAD-2 samples were heated over the temperature range 85°–183°C while under air or nitrogen flow. The calculated TCO values for 400 ml resin samples as used in a SASS train are shown in Figure 4. It is obvious from the graph that above a threshold temperature, the TCO value rises very rapidly. This emphasizes the importance of keeping the resin cooled during sampling operations, for if the resin is heated much above ambient temperature, the measured blank from an unused resin sample will not be indicative of the true blank. The same pattern of peaks was observed in the TCO range for most samples, indicating that the same process of decomposition/desorption is taking place in each case, with the major variable being the amount of material produced. Resin samples heated above 120°C took on a characteristic yellow-brown color which intensified with increasing temperature and remained after methylene chloride extraction.

To determine whether atmospheric oxygen has an effect on the amount of TCO material produced, a resin sample was heated to 183°C under nitrogen flow of 30 ml/min for 24 hours. As noted from Figure 4, the extrapolated TCO value for this run falls below the curve outlined for the samples heated in air. A possible explanation for this phenomenon is that oxygen may be taking part in the decomposition process by attacking the polymer and initiating an "unzipping" process where the polymer systematically breaks down into small pieces. If oxygen is present in low concentrations, the number of sites of attack are low and thus the overall rate of decomposition is lowered. This is not to suggest that oxygen attack is the primary mode of decomposition, but rather that it is one of several possible mechanisms.

Sample extracts were examined by GC/MS for component identification. The major components exhibited some or all of the ion pattern 77, 91, 105, 119, 133, etc., characteristic of alkyl benzenes. None of the major components in the TCO range appeared to contain oxygen. Several of the spectra indicated unsaturation in the alkyl chain portion of some of the
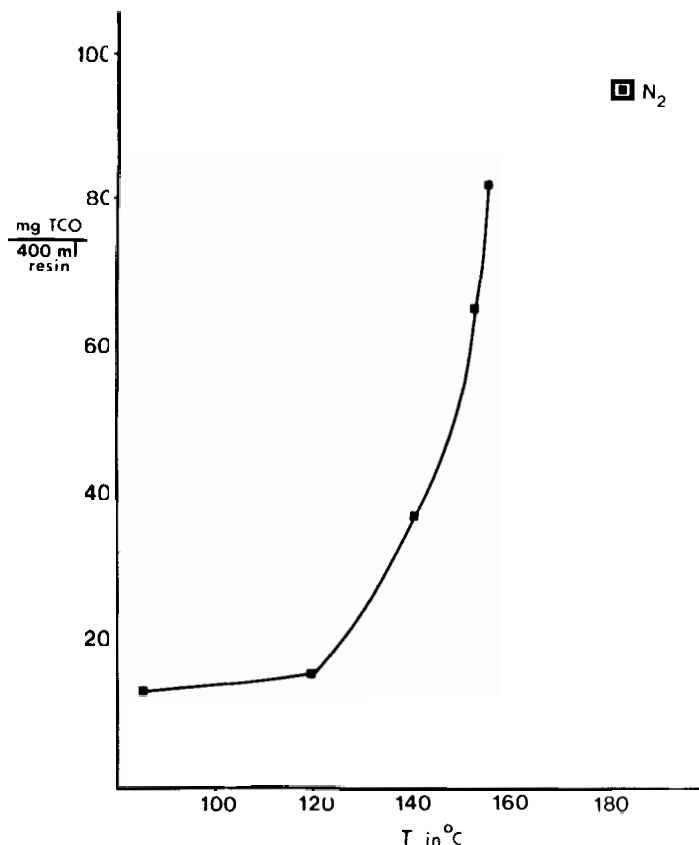
FIGURE 4 Plot of mg Total Chromatographable Organic content per 400 ml of XAD-2 versus temperature.

species formed. All of the components in the TCO range contained only one benzene ring, while some of the material eluting beyond the upper limit of the range appeared to contain two or more. Because of incomplete resolution by the GC, some of the peaks may have consisted of two or more geometrical isomers, thus making positive structure assignment difficult. Compounds containing oxygen were detected in the IR spectra of the extract residues after total evaporation of the solvent. Absorption above $3100 \, cm^{-1}$, a strong peak at $1700 \, cm^{-1}$, and a series of peaks between 1350 and $1100 \, cm^{-1}$ all indicate the presence of oxygen, possibly as an acid. Due to the nonvolatility of organic acids and the fact that they do not "chromatograph" well, these acids would not be detected by GC/MS.

## CONCLUSIONS

While porous polymers have utility for collection of organic species from gaseous streams, they also have the potential to be altered by components of those streams. These alterations can have a substantial effect upon the composition of the sample collected relative to the composition of the source. Reactive species such as $SO_x$ and $NO_x$ and their respective acids are capable of altering the capacity and selectivity of these resins, particularly for electron-rich species. Even the presence of a non-reactive gas can cause the formation of an otherwise unmeasured blank from XAD-2 with a resulting loss of quantitative analysis data accuracy. The primary components of this blank are alkyl benzenes and other products of polymer decomposition. Recognition of these potential problems prior to use in an actual sampling situation allows one to treat the resulting data in a logical manner.

### Acknowledgement

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