ADSORPTION CAPABILITIES OF ADSORBENTS FOR SELECTED TOXIC AIR POLLUTANTS

BY

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ABSTRACT

The relative adsorption capacities of seven toxic, volatile organic air pollutants of either proven or suspected carcinogenic potential were tested on various adsorbents. Tests were run at flow velocities similar to those set in field sampling. This allows for extrapolation of test results to actual ambient air sampling systems. Experimentation was performed using a gas chromatograph (G.C.) equipped with a flame ionization detector. Sample introduction was carried out using the "displacement method" where the sample is introduced to the adsorbent cartridge as a plug.

Incipient elution volumes (V_N), normalized for bulk adsorbent packing volume, were obtained at various temperatures. Plots were drawn of the ln V_N vs. $10^3/T$ (^oK) for each adsorbate-adsorbent combination. The plots all show good linearity. From the plots, results indicate that Spherocarb is by far the strongest adsorbent for the volatile organics tested while Tenax is the weakest. XAD-2 is very close to Tenax in retentiveness, but retains CCl_4 at the experimental flow velocity whereas Tenax does not. Porapak-T has adsorption capabilities consistently above Tenax and below Spherocarb, while Silica Gel shows a very strong retention of high boiling and water soluble compounds.

APPROVAL OF THESIS

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PREFACE

In April, 1978, I began doing research work at the New Jersey Institute of Technology Air Pollution Research Laboratory. At the time, ambient air samples were being taken at various New Jersey locations in an attempt to quantify concentrations of selected volatile organics. Tenax was being used as the trapping adsorbent in the air sampling system, and analyses were being performed on a capillary gas chromatograph (G.C.). Following initial quantitation results, it was perceived that vinyl chloride and possibly some of the other volatile organics might be breaking through the adsorbent cartridge before sampling was completed. It was suggested that the use of other adsorbents might be a viable solution to this problem. Since I was looking for a thesis topic at this time, it seemed timely that I should do an elution analysis of the most volatile of the targeted organics on Tenax and on other possible adsorbents.

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I. INTRODUCTION

The rapidly increasing control that government, both state and federal, is placing on industrial emissions of toxic and harmful chemicals has created a very large need for quantitatively accurate atmospheric sampling and analysis procedures. Examples of these governmental regulations are seen in the Clean Air Act and its Amendments(1) and the Toxic Substances Control Act of 1976.(2) In New Jersey the high incidence of cancer has prompted governmental officials to survey ambient air in industrial areas for pollutant levels, targeting specific organic chemicals which are either proven or suspected carcinogens, as based on mammalian and bacterial bioassays. The seven organic compounds studied here were chosen because they are all highly volatile, toxic substances with either proven or suspected carcinogenic potential, and are produced in very large quantities in this country.

One of the most difficult parts of ambient air sampling for selected organics is the field collection of these species and subsequent recovery from the sampling device or apparatus.(3) There are numerous methods that can be employed in sampling. The efficiency of these methods is a function of many factors, one of which is sample quantity. Since the quantity of a given substance contained in a measured volume of ambient air is likely to be extremely small, some of the methods are more attractive than others. In addition, sample quantity dictates whether analysis can be performed in situ, or whether samples have to be transported back to a laboratory for analysis by more sophisticated equipment. At the present time, there is a highly expensive, sophisticated, mobile ambient air sampling system available called TAGA which uses the principle of mass spectrometry and can detect component concentrations down to the ppt range.(4) However, most in situ measuring devices can only measure component concentrations down to a few ppm. Since ambient carcinogen concentrations are usually in the sub-ppb range, in-situ testing is insufficient.

To determine ambient concentrations of carcinogenic or toxic substances, samples are collected and transported to a laboratory where they are analyzed. For volatile organic compounds the standard instrument is the gas chromatograph (G.C.). The G.C. is a highly efficient, quantitative instrument which has a large degree of operational flexibility due to various detection options. Relatively inexpensive ($10,000)(5), the G.C. is reliable and easy to operate. Alternatively, to expand the precision of sample analyses quantitatively and qualitatively, the gas chromatography-mass spectrometry system (G.C./M.S.) can be used. Interfaced to the G.C., the M.S. is a very expensive ($100,000)(6), operationally complex instrument that must be treated delicately and constantly maintained. Use of the G.C./M.S. system for identification and quantitation of organic air pollutants has been covered by several researchers.(7)(8)(9)(10)

The various methods employed in sample collection for volatile organics in air can be categorized according to the following groups: container collection, solvent absorption, and solid adsorption.

Container Collection

The types of containers used in ambient air sampling include glass bulbs, flexible plastic bags, and stainless steel cylinders. Glass bulbs have their limitations in that the large volumetric flasks required for low concentration components are awkward to transport. Plastic bags have an advantage over bottles in that they are light, less expensive, and easier to transport.(11) Problems with bags arise from contamination of the bag sampling inlet system which usually consists of an aspirator assembly or a pump and some flexible tubing.(12) The inlet system can either adsorb or desorb organics and can distort results. Also, the walls of the bags themselves will adsorb and desorb contaminating organics. It has been shown that component concentrations in bags varies with the time following sampling. Therefore, bags have been designed to minimize these effects. Such bags include Mylar, Saran, Teflon, Scotchpak, etc.(13) These bags, however, do not work satisfactorily for a wide range of compounds at low (sub-ppb) concentrations.

In both glass and plastic bag collection, the fact that only a few liters can be collected limits analysis to those components which are close to ppm concentrations. Thus, bottle and bag collection is insufficient for ambient, organic carcinogen sampling.

One additional method of container sample collection is through the use of stainless steel canisters. Usually reserved for sampling of high pressure sources, stainless steel canisters can be used for ambient air sampling with an effective pumping system. The advantages are that by compressing the sample into a canister to 10 atmospheres pressure, a much larger sample volume, and subsequently, a much larger amount of component, can be obtained. Some limitations of this system are the cost and portability of the pumping system and the adsorption and desorption effects of the pump and the stainless steel. Other problems include the effects on the components of interest, e.g., catalytic decomposition of reactive species and wall adsorption. These effects can be minimized at a substantial cost by using electropolished stainless steel canisters. However, the overall cost of the system and its awkwardness, coupled with the present lack of information on the efficiency and operational drawbacks of the system, dictates that it not be used at the present time.(14)

Solvent Absorption

Absorption is accomplished by passing vapors through a liquid in which they are soluble or one that contains reactive chemicals which will react and hold the substance being sampled. Many different absorption vessels have been designed, ranging from simple bubblers made by inserting a piece of tubing beneath the surface of a liquid to rather complex gas-washing devices which are designed to increase the length of time the air and liquid are in contact with each other. An immediate problem in an absorption system is that the best systems only achieve about a 90% air-liquid contact efficiency, indicating constant component loss. In addition, for multi-component sampling at low contamination levels, absorption is unsuitable. This is because a required solvent would have to dissolve all the desired constituents, recovery from the solvent would have to be high, and the solvent would have to be of extremely high purity so that impurities at the ppt level would not interfere with sample analysis. Because of these strict criteria, liquid absorption is not used for ambient sample collection. At the present time, formaldehyde is the only organic contaminant currently measured in the atmosphere that relies on the principle of absorption. Here, colorimetry rather than G.C. analysis is used.(15)

Solid Adsorption

Solid adsorption sample collection involves passing an air stream through a solid-adsorbent material packed in a cartridge of some design and collecting the desired contaminants in the pores and on the outer surface of the adsorbent by mutual adhesion forces. The cartridge is then transported back to the laboratory where the contaminants are recovered by either solvent or thermal desorption. In solvent desorption, carbon disulfide (CS_2) is most widely used when a flame ionization G.C. is employed for analysis, as a flame ionization detector (FID) does not respond to CS_2 and thus cannot introduce analytical errors.(16) Conventionally, activated carbon is used along with CS_2 as the solid adsorbent. The failing of any solvent desorption system is that solvent contaminants are present in sufficient quantity to introduce a large error in analysis of any components present in amounts less than a few ppm.

In thermal desorption the adsorbent is simply heated for a period of time at a high temperature. During heating, contaminants can either be flushed into an injection cartridge or transferred to a sample injection loop connected to the G.C. inlet valve. The use of the injection cartridge is favored if replicate samples are desired, if a separate, non-interfaced M.S. is used, or if the G.C. cannot be tied up for the amount of time required for thermal desorption. Using a desorption apparatus separate from the G.C., the sample cartridge is heated while a pressure head of displacement gas is applied. Desorbed contaminants are swept into a cold, dead-end injection cartridge, which after a time, is further pressurized, then sealed off. This pressurized injection cartridge can then be used for multiple sample injections by a simple release of some pressure.

Thermal desorption directly into the G.C. sample inlet valve is effectively used in G.C./M.S. interfaced systems. Here, the desorbed sample must be concentrated into a small plug prior to injection to produce high component peak resolution. Pellizzari, et al.(17) accomplished this through use of a six-port, two-position, low-volume injection valve. As the adsorbent cartridge is heated, a purge gas flushes contaminants into a cooled capillary coil connected to the injection valve. Liquid nitrogen or solid carbon dioxide-isopropanol is used as the coolant. Pollutants condense in the capillary coil as the purge gas is vented out. Once thermal desorption is complete, the sample valve is switched to the inject position while the capillary trap is rapidly heated (to about 175°C), revaporizing the condensed contaminants and flushing them into the G.C. column. A disadvantage of this system is that replicate runs cannot be performed.

Comparing the two desorption-injection systems, in direct injection, use of a constantly flowing purge gas will yield high desorption efficiencies, but there is also the possibility of losing sample through the cold capillary coil. In the dead-end injection system, while no sample is lost, the efficiency of desorption may be somewhat less than for direct injection, and introduction of contaminants through cartridge transfer and connection to an instrument may be significant. As of yet, no study has been performed on the relative efficiencies of these two thermal desorption-G.C. injection systems.

At the present time, solid adsorption coupled with thermal desorption and G.C. analysis is the accepted method of quantifying organic air pollutant concentrations. Using either the G.C. or the G.C./M.S. system, component concentrations can be effectively determined down to the sub-ppb level. The analytical methods and criteria for evaluating air pollutants using this system have been reported by Dietrich et al.(18), and Melcher et al.(19)

Many investigators have performed tests on the use of different adsorbents for trapping specific air pollutants. Pellizzari et al.(20) found that Tenax, Porapak Q, Chromosorb 101, and Chromosorb 104 were ≥ 90% efficient in trapping vapors of epoxides, β-lactones, sulfonates, sultones, N-nitrosamines, chloroalkyl ethers, aldehydes, and nitro compounds from synthetic air-vapor mixtures at a sampling rate of 0.25 l/min. Tenax and Chromosorb 101 were also evaluated at sampling rates up to 9 l/min and were found to maintain collection efficiencies of ≥ 90%. Bertsch et al.(21) found that volatile hydrocarbon compounds containing less than five carbon atoms were not efficiently trapped by Tenax, while aromatics were. Holzer et al.(22) reported that Tenax could only be used effectively for trapping organic vapors in the C_7 range. Also, carbon adsorbents and carbon molecular sieves proved far too reactive for sampling, while Ambersorb XE-340, having properties intermediate to polymeric and carbonaceous adsorbents, showed promise in trapping n-alkanes in the C_4 region.

Murray[(23)] studied the adsorption capacity of Tenax and Chromosorb 102, 105, and 106 for volatile components generated from several food and beverage processes. He reported that Chromosorb 102 was found to be unacceptable for trapping volatile constituents as it gave high and erratic background readings due to thermal or oxidative breakdown during cartridge loading procedures. Tenax showed a lower adsorption capacity than either Chromosorb 105 or 106, and thus was suggested for use with stable, high molecular weight compounds (e.g., PNAs) where high recovery temperatures for thermal desorption were required. Chromosorb 105 showed no evidence of any chemical reactivity or catalytic activity or specific adsorptive properties. This apparent inertness, coupled with high retentive capacity and relative ease of recovery of volatiles at moderate temperatures indicated Chromosorb 105 to be a very versatile adsorbent. Chromosorb 106 also appeared to be a possible alternative to Chromosorb 105, although insufficient tests were performed to verify this.

Of the numerous industry-produced air pollutants that are present in the troposphere, only a small percentage have been tested in adsorbent trapping capacity studies. Much additional research is needed on specific adsorbate-adsorbent retention capabilities before a precise adsorbent inventory can be developed for specific contaminant sampling. In light of this, an analysis was performed on relative adsorption capabilities of adsorbents for selected adsorbates.

Method Basis

At the New Jersey Institute of Technology Air Pollution Research Laboratory, a G.C. system was employed in determination of targeted carcinogenic air pollutant concentrations. Tenax was initially used as the sorbent media based on the work performed by Pellizzari et al.(24) where it was shown that Tenax could be used effectively for trapping and desorbing a large range of compounds. However, as Pellizzari et al. also indicated, volatile hydrocarbons containing less than five carbon atoms were not efficiently trapped by Tenax. Therefore, as it was perceived that some of the light targeted carcinogens might be breaking through the Tenax adsorbent bed, an analysis was performed on the more volatile ones, comparing their relative retention volumes on Tenax with those obtained on other adsorbents.

There are two laboratory methods commonly employed in elution characterization studies: the "displacement" or elution method and the frontal method. In the displacement method, a small quantity of sorbate is introduced to the sorbent in a short time (a plug). In the frontal method, the sorbent is continually "challenged" with a steady state concentration of sorbate. While ambient air sampling more closely mimics the frontal method, the elution method approach alone was chosen as it is much easier to experimentally perform and also because the parameter of importance, incipient component elution, is the same for both methods.(25)

The objective of this thesis is to compare the adsorption capacities of various light organic compounds for different adsorbents. More specifically, the intent of this thesis is to present knowledge that will help to better understand and to improve solid sorbent ambient air sampling techniques. With this intent, two important factors not conventionally associated with adsorption studies were studied. The first, incipient elution, was deemed of paramount importance because this is the point at which sample first begins to be lost, causing an under-estimation of component concentrations. Incipient elution is a function of many parameters such as flow rate, temperature, amount of adsorbent used, geometry of the cartridge, etc. While the data in this paper is only reproducible if all the above parameters are the same, the results give a good indication of relative parameter effects and adsorbent-adsorbate combination capabilities. The second factor of importance is the cartridge volume occupied by the adsorbent (including the void volume). Frequently, the weight of the adsorbent is used as the normalizing parameter to relate adsorption capabilities. However, this is a major failing when relating adsorption to air sampling because while two different adsorbents can have the same weighted adsorption capacity, they can have greatly different packing densities. For example, for two adsorbents having equal adsorption capacities, if one adsorbent has half the packing density of the other, it will only be able to retain half the amount of sample when packed into the same size cartridge. Thus, in conclusion, by analyzing incipient elution capabilities normalized for bulk adsorbent volume, it is possible to review and improve ambient air field sampling techniques.

On the basis of previous studies and possible alternatives,(26)(27)(28)(29) the following adsorbents were chosen for sample collection of the selected highly volatile, toxic vapors: Tenax, XAD-2, Porapak-T, Silica Gel, and Spherocarb. Results show that Spherocarb is by far the strongest adsorbent for these organics and Tenax is the weakest. Porapak-T and XAD-2 are consistently above Tenax and below Spherocarb in retentiveness while Silica Gel shows a very strong effect on high boiling and water soluble compounds.

FOOTNOTES - CHAPTER I

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FOOTNOTES - CHAPTER I (CONTINUED)

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II. APPROACH

At the time when elution analyses strategies were being developed, ambient air sampling was being performed by the N.J.I.T. Air Pollution Laboratory personnel using 1/4-inch diameter by 6-inch long adsorbent-packed cartridges. Field samples were being taken for 20 minutes at flow rates ranging from 700 to 1200 ml/min. It was decided that chromatographic elution studies would be most advantageous if performed at conditions close to those that were run in the field. Unfortunately, the field flow rates were from 14 to 25 times too large for the G.C. detector to handle.

It was, therefore, decided that incipient elution analysis could be approximated to field conditions by means of cartridge scale-down, using the parameter of linear velocity through the packed bed as the scale-down criterion. This meant that the ambient sampling velocity (from 70 to 120 cm/sec) would be only 2.3 to 4 times as large as the maximum 30.3 cm/sec (50 ml/min) velocity which the G.C. could handle. While the correlation between field sampling elution and experimental scale-down elution has yet to be proven, the G.C. elution data presented here is still significant in that it gives relative adsorbent-adsorbate performance capability values.

In this study, the chromatographic method of displacement through the cartridge(1) was used where the sample was injected into the column in the form of a plug. The six adsorbate liquids used were syringe injected into a heated sampling port where they were immediately volatilized and swept into the cartridge. Vinyl chloride, the only vapor, was directly injected into the G.C. by means of a gas sampling valve. For each adsorbate, a ~~maximum~~ minimum of four temperatures was selected, from which normalized incipient elution volumes (V_N) were recorded. This allowed for development of ln V_N vs. $10^3/T$ (^oK) plots, from which adsorbent-adsorbate interactions could be analyzed. Note that an equal volume of packed adsorbent was used as the elution volume normalization parameter rather than the conventional adsorbent weight quantity (refer to the previous section for an explanation). In addition to the above analysis, a brief study was performed on the effects of humidity and sample injection size on incipient elution.

Footnote:

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[1] Lloyd R. Snyder, Principles of Adsorption Chromatography, Marcel Dekker, Inc., New York, 1968, p. 35.

III. THEORY

Adsorption Mechanisms

When a molecule of mobile gas hits a solid surface, it will either ricochet elastically or it will adhere to the surface for a certain time and then fly away. The latter case (non-elastic collision) predominates as the normal behavior of molecules.(1) If a large number of these gaseous molecules continually strike upon the surface and are retained for a certain time before re-evaporating, there will be a higher concentration of gas at the surface than in the bulk of the gas.(2) At the solid surface, where the solid atoms are usually subject to unbalanced forces of attraction normal to the surface plane, the balance of forces becomes partially restored by the adhesion of gas molecules.(3) This is the phenomenon of adsorption.

Adsorption processes may be classified as physical or chemical, depending on the nature of the forces involved. In physical adsorption, the energies involved are generally small, and adsorption and desorption are instantaneous.(4) However, when fine pore adsorbents are used, diffusion of the gas into the adsorbent mass is often slow, particularly at low pressure.(5) The intramolecular forces responsible for physical adsorption are the van der Waals forces which hold non-ionic molecules together.(6) In chemical adsorption, termed "chemisorption," an actual covalent or ionic bond is formed between adsorbate molecules and the outermost layer of adsorbent atoms; that is, a new chemical compound is formed.(7)(8) The energy of chemisorption is generally large, i.e., similar in magnitude to bond formation energies. The adsorption-desorption process is frequently slow because an appreciable activation energy is often required for desorption.(9)

Physical adsorption will occur with any gas-solid system provided that the conditions of temperature and pressure are suitable. A physically adsorbed layer may be removed by simply reducing the pressure, although the process may be slow due to diffusion effects. In contrast, the removal of a chemisorbed layer often requires much more forceful conditions such as high temperatures or positive ion bombardment. Under suitable conditions of temperature and pressure, physically adsorbed layers several molecular diameters thick are frequently found. In contrast, chemisorption is complete once a monomolecular layer is built up, although physical adsorption may occur on top of the chemisorbed layer.(10)

Adsorption-desorption of a plug of material is best viewed as an equilibrium state which progresses along a length of tubing packed with an adsorbent. There are two basic mechanisms involved in this migration of physically desorbed molecules. First, numerous collisions at or near the adsorbent surface cause continual energy transfer between molecules. Second, these collisions also cause vibrations which lead to fluctuations of binding energy.(11) When some adsorbed molecules absorb more energy than the energy of adsorption, they will gain momentum. These molecules will then either exit from the surface via an approximately perpendicular path or they will migrate along the adsorbent surface. Chemisorbed adsorbate molecules are also capable of this type of surface migration if a very high temperature for desorption is provided.(12)

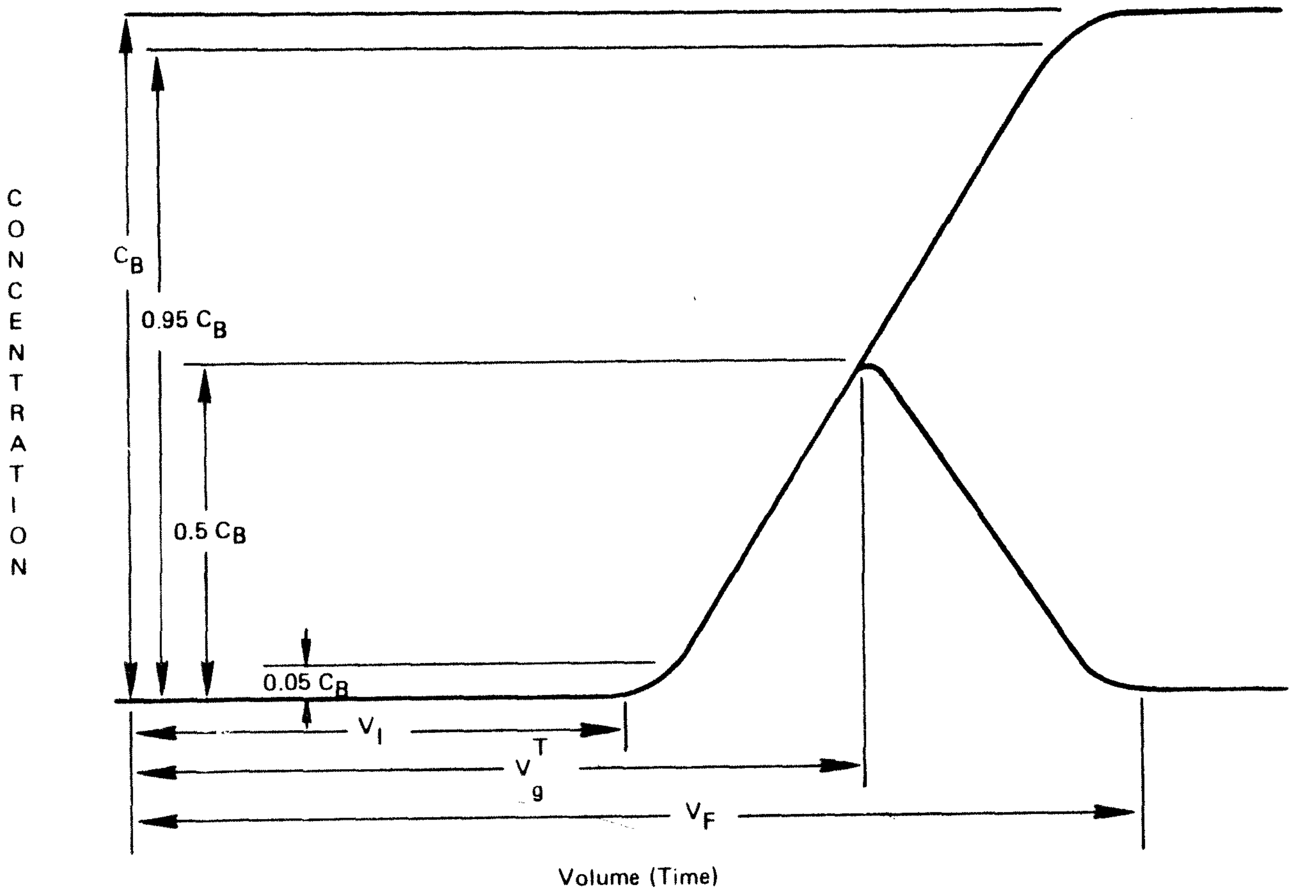
Chromatographic Adsorption Methods

In chromatographic breakthrough (elution) studies two sample introduction techniques, the frontal method or the displacement ("elution") method, can be employed. In the frontal method the sample is continuously fed to a column of adsorbent; whereas in displacement the total sample is injected as a plug into the carrier gas stream. The mode of sample introduction in no way affects the appearance of the frontal boundary curve, but the elution profiles are different as pictured in Figure 1.(13) In most chromatographic testing experiments either the peak maxima or the time to reach a pre-set "challenge" concentration is desired, depending upon the injection method. For both of these methods equilibrium adsorption coefficients are desired. In ambient air sampling, however, it is more imperative to know when incipient elution occurs (V_i), for once this condition takes place, increased sampling time will yield erroneously low component capture values for the adsorbate.

One factor that must be considered in elution studies is the purity or cleanliness of the adsorbent. Many adsorbents act tenaceously towards certain compounds because of chemisorption. For these adsorbents such rigorous cleaning treatments as long-term thermal stripping have yielded limited results. Here, the total time for an elution run becomes extensive because of the required cleaning time. When using adsorbents of low purity, it should be realized that elution volumes will be lower since there is less surface area for adsorption due to the continuing occupancy on the adsorbent by the contaminant.

FIGURE 1 (13)

ELUTION VOLUME LOCATIONS



C_B - challenge concentration

V_i - incipient elution volume

V_g^T - displacement method peak retention volume

V_F - frontal method challenge concentration volume

In analyzing adsorbent retention capabilities, the parameter of importance is usually the volume of carrier gas eluted to the point of desired component elution per weight of adsorbent. This parameter is very misleading, however, in that while one adsorbent might have a greater weight capacity, because of adsorbent size, density, porosity, and surface area, it might retain less component when packed into a set cartridge volume. Thus, a more representative parameter is carrier gas volume to incipient elution per packed cartridge volume (V_N). Note that the packed cartridge volume includes the volume occupied by the adsorbent plus the void volume. In this study, a normalization volume of 1 ml was used, although the actual adsorbent-occupied cartridge volume was 0.512 ml.

Adsorption Profiles

To visualize how component migration takes place in an adsorbent bed (or cartridge), the Craig distribution model of Keulmans is useful. Keulmans likened a chromatographic column to a Craig distribution apparatus, consisting of a series of interconnected, but distinct, bed sections or theoretical plates. The following parameters are included in Keulmans' model:

N_n = number of theoretical plates in the bed

N_i = numbered plate

W/N_n = weight of adsorbent in each plate

V^o/N_n = free volume (void volume) in each plate

X = a particular sample compound

X_a = equilibrium concentration of adsorbed X

X_u = equilibrium concentration of unadsorbed X

n = number of solvent transfers

K = equilibrium distribution coefficient = X_a/X_u

The total sample is assumed to be contained initially in volume V_o/N_o. Passage of carrier gas through the bed is visualized as progressing in steps. In each step the carrier gas plus any unadsorbed sample in plates N_o, N_1, N_2 ... N_n shifts over to the next plate and fresh carrier gas enters plate N_o. After each transfer the contents of each plate are assumed to equilibrate, with redistribution of sample between adsorbed and solvent phases according to the distribution coefficient K.(14)

Table 1(15) and Figure 2(16) illustrate the above case for K = 1.0; that is, at equilibrium one-half of the sample will be adsorbed

(15)

TABLE 1

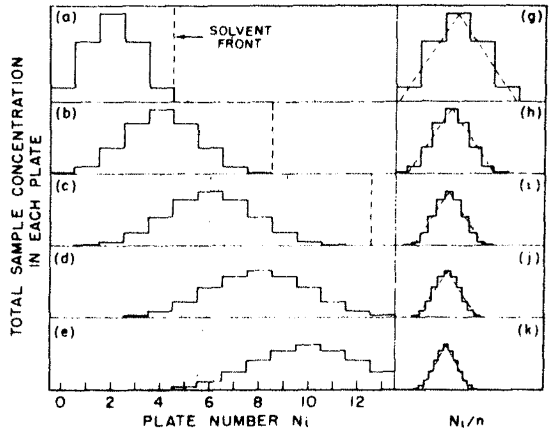
MIGRATION OF SAMPLE X IN CRAIG DISTRIBUTION MODEL

Transfer	Total amount of **X** in each plate after solvent transfer						Amount of **X** transferred from each plate during following transfer					
number	N_0	N_1	N_2	N_3	N_4	N_5	N_0	N_1	N_2	N_3	N_4	N_5
0	1	0	0	0	0	0	1/2	0	0	0	0	0
1	1/2	1/2	0	0	0	0	1/4	1/4	0	0	0	0
2	1/4	2/4	1/4	0	0	0	1/8	1/4	1/8	0	0	0
3	1/8	3/8	3/8	1/8	0	0	1/16	3/16	3/16	1/16	0	0
4	1/16	4/16	6/16	4/16	1/16	0	1/32	1/8	3/16	1/8	1/32	0
5	1/32	5/32	10/32	10/32	5/32	1/32	1/64	5/64	5/32	5/32	5/64	1/64

$K = 1.0$

FIGURE 2 (16)

SAMPLE DISTRIBUTION IN THE ADSORBENT BED



Distribution of sample on the adsorbent bed after varying degrees of solvent transfer, according to the Craig distribution model: (a, g) 4 transfers; (b, h) 8 transfers; (c, i) 12 transfers; (d, j) 16 transfers; (e, k) 20 transfers.

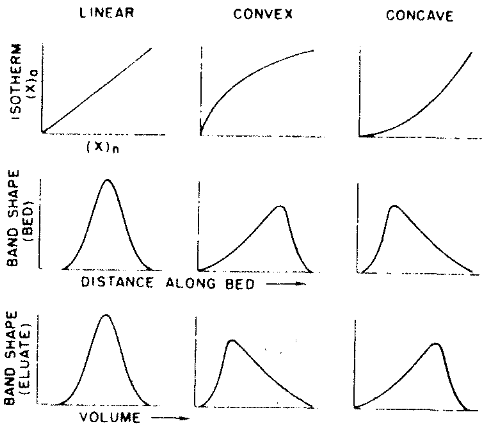
while one-half remains in the carrier gas. Figure 2 (a-e) shows the distribution of X on the adsorbent bed after 4, 8, 12, 16, and 20 transfers, respectively. As X migrates along the adsorbent bed, a symmetrical Gaussian-shaped curve is approached. Figure 2 (g-k) represents this block diagram convergence to the Gaussian shape. With an actual column containing thousands of theoretical plates and for a highly tenacious adsorbent (i.e., where K = 1,000), it can be deduced that the adsorbent will retain the adsorbate for a long period of time before incipient elution.(17)

In the preceding case, the sample distribution coefficient K was assumed to be constant throughout separation. Quite frequently, however, K varies with sample concentration. Separations where K is independent of sample concentration are referred to as linear isotherm separations; here, a plot of X_a vs. X_u at equilibrium yields a straight line.(18) (Note: Isotherms, which will be covered in the next subsection, are relationships between two variables at a constant temperature.) A non-linear sample isotherm affects both the shape of sample displacement and the rate at which the sample migrates through the adsorbent bed.(19) Figure 3(20) shows several relationships for three isotherm types at low sample concentrations. Convex isotherms are typical of adsorption chromatography, especially with dissimilar polarities in adsorbent and adsorbate. In a convex isotherm the fact that K decreases with increasing sample concentrations indicates that as sample size is decreased, the retention volume to incipient elution increases.(21) This effect becomes minimal, however, at low sample

(20)

FIGURE 3

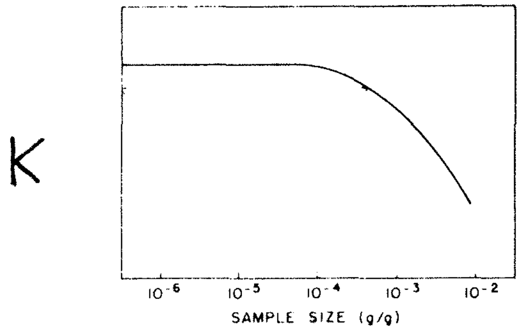
EFFECT OF ISOTHERM TYPE ON THE SHAPE AND MIGRATION OF SAMPLE AT LOW SAMPLE CONCENTRATIONS



(22)

FIGURE 4

TYPICAL RANGE OF ISOTHERM LINEARITY



Sample size in grams of sample per gram of adsorbent.

concentrations, and eventually, a point is reached where incipient elution is constant for any sample concentration below a certain value (see Figure 4).(22) One point to be added here is that while tailing is usually evidence of isotherm nonlinearity, slow desorption kinetics can also be the cause, especially when the adsorbent acts tenaceously due to strong chemisorption.(23)

Adsorption Isotherms

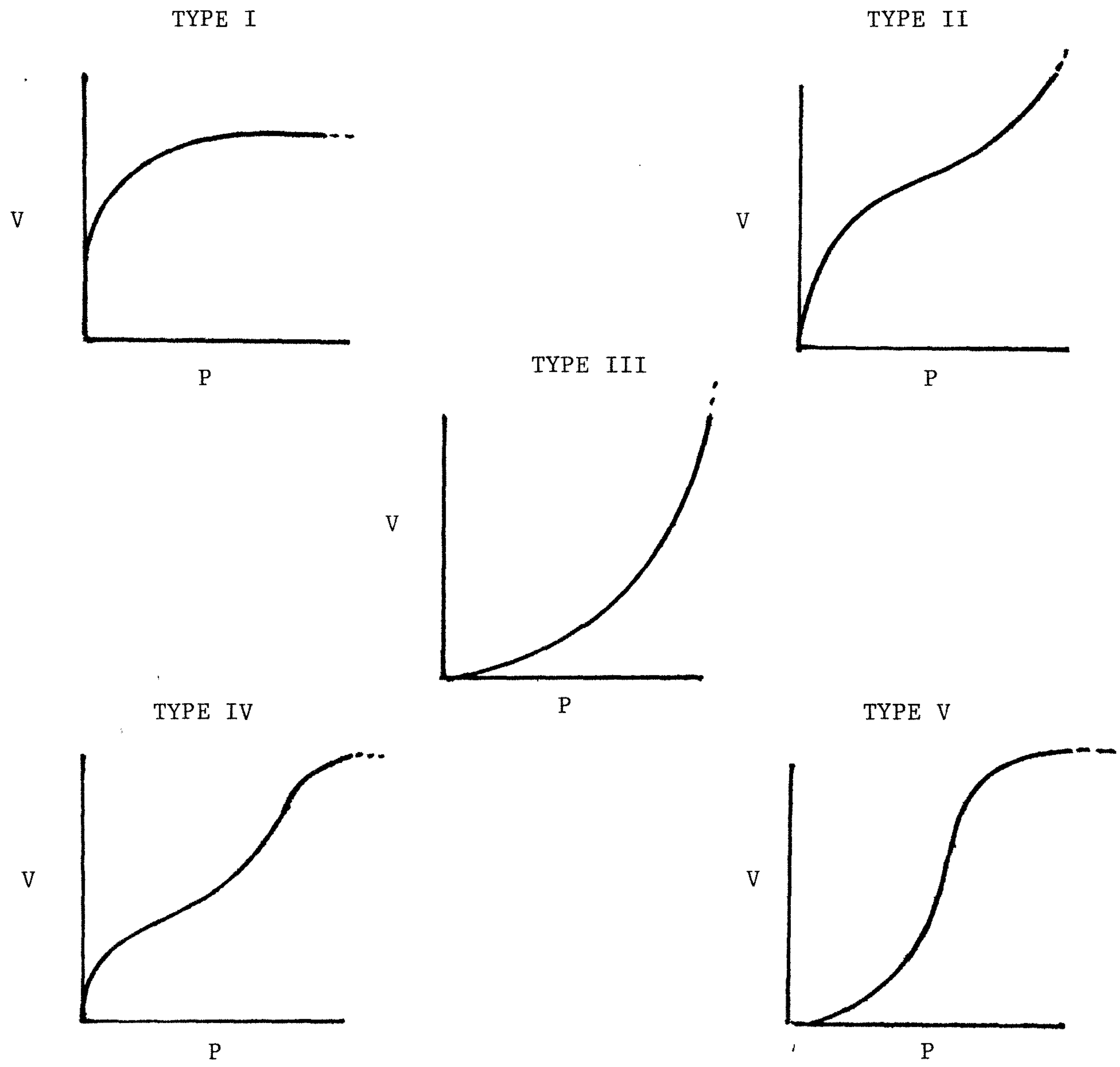
Experimental measurements of the amount of sample adsorbed, v, as a function of concentration (pressure) and temperature may conveniently be plotted in the form of adsorption isotherms. Isotherms are essentially plots of the free energy change as a function of the amount adsorbed. Their shapes can yield qualitative information about the adsorption process and a semi-quantitative measure of the fraction of the adsorbent surface covered by the adsorbate. Because they can be measured directly, isotherms are the most commonly used P-V-T plots in adsorption studies.(24)

Isotherms can be classified into five basic types, as pictured in Figure 5.(25) Type I isotherms occur when monolayer adsorption is distinctly favored over multilayer adsorption. This case will be discussed later as the Langmuir isotherm. After an initial rapid uptake of adsorbate, the surface monolayer is saturated, and further adsorption does not occur. If additional layers begin to adsorb prior to completion of the first monolayer, a Type II isotherm results. This is representative of the mechanism of physical adsorption. Type III isotherms are less common and occur when the attraction between adsorbed molecules are strong and adsorbent-adsorbate interactions are either relatively weak or are independent of surface coverage. As a result, the total attraction of the adsorbate to the already adsorbed molecules increases with sample concentration. Isotherms of Type IV and Type V are extensions of Types II and III, respectively, for highly porous adsorbents, with the eventual leveling off attributed

FIGURE 5(25)

FIVE TYPES OF PHYSICAL
ADSORPTION ISOTHERMS

V: Volume
P: Pressure



to capillary phenomena. Since capillary effects lie beyond the scope of this presentation, reference will only be made to isotherms of Type I, II, and III.(26)

The Langmuir isotherm offers an excellent starting place for a quantitative understanding of isotherm shape as it is the basis from which most theoretical forms are derived. For adsorption from the gas phase, the Langmuir isotherm takes on the equivalent form:

$$\theta = \frac{K_{th}\ P_x}{1 + K_{th}\ P_x} \quad \text{or} \quad K_{th} = \frac{\theta}{P_x\ (1-\theta)}$$

where:

θ = fractional coverage of the adsorbent surface by adsorbate X

K_{th} = the thermodynamic equilibrium constant (See Appendix A)

P_x = the partial pressure of X in the unadsorbed gas phase

The derivation of the Langmuir isotherm assumes that adsorption takes place up to the time when a monolayer is totally formed, that all surface area sites give equal adsorption energies, and that there are no interactions between adjacent adsorbed molecules. The limiting form of the Langmuir isotherm with respect to high and low sample concentrations is observed as follows. At low sample concentrations the term $K_{th}\ P_x$ becomes small relative to 1, and the equation reduces to $\theta/P_x = K_{th}$. This means that both θ/P_x and the sample coefficient K likewise become constant. Thus, the isotherm reduces to a linear form at low sample concentrations, a condition often existing in elution analysis experimentation. At very high sample concentrations the term K_{th} P_x becomes large relative to 1, and Θ approaches 1; i.e., the total concentration of X on the adsorbed surface becomes constant, indicating an adsorbed monolayer saturation.(27)

To analyze the applicability of the Langmuir isotherm based on linearity, the basic equation can be rearranged to the following form:

$$P_x/(X/m) = 1/k_1k_2 + P_x/k_2$$

where:

k_1 and k_2 are constants

X = weight of gas adsorbed

m = weight of adsorbent (See Appendix A for the derivation)

If a plot of $P_x/(X/m)$ vs. P_x yields a straight line; then the monolayer adsorption mechanism of Langmuir can be assumed to almost exclusively predominate. Also, from this plot, the adsorbent weight capacity Θ and the relative ratio of adsorption rate/desorption rate can be back calculated.(28)

Although Langmuir in 1918 attempted to generalize the ideal localized monolayer treatment to include the formation of multilayers, it was not until 1938 that the mathematical difficulties were overcome by Brunauer, Emmett, and Teller (B.E.T.). The assumptions made in the B.E.T. treatment were that each first layer adsorbed molecule serves as a site for the adsorption of a molecule onto the second layer, and so on, and that the various heat exchange rates are equal for each adsorbent layer. The simple form of the B.E.T. equation is as follows:

$$v = \frac{v_m CP}{(P_o - P) \left[1 + (C-1) P/P_o\right]}$$

where:

v = total volume of adsorbed gas

v_m = amount of adsorbate needed to form a monolayer

C = constant

P = actual component partial pressure

P_o = component saturation partial pressure

Rearranging the equation gives:

$$\frac{P}{v\ (P_o - P)} = \frac{1}{v_m C} + \frac{C-1}{v_m C} \cdot \frac{P}{P_o}$$

A plot of $P/\left[v\ (P_o - P)\right]$ vs. P/P_o should yield a straight line having a slope of $(C-1)/v_m C$ and an intercept of $1/v_m C$ if the B.E.T. theory predominates. The constant C can then be found by applying the following approximate equation:

$$C = e^{(E_1 - E_L)/RT}$$

where:

E_1 = heat of adsorption in the first layer

E_L = heat of liquefaction

$(E_1 - E_L)$ = net heat of adsorption

From this equation, the net heat of adsorption can be found. In addition, B.E.T. analysis will provide a value for the adsorbent surface area.(29)

The B.E.T. method can be used to describe either Type II or Type III isotherms depending on whether adsorbed molecule interactions are deemed important. Describing either method depends solely on whether the constant C is large or small. As C decreases, the inflection point in the Type II isotherm approaches the origin until at the critical value of $C = 2$, the isotherm reverts to Type III. This critical transition point occurs when $(E_1 - E_L)/RT \doteq 0.7$ (e.g., when the "net heat" $\doteq$ 420 cal/mole at $T = 300^oK$, or 110 cal/mole @ 80^oK). Qualitatively, this means that if $E_1 \gg E_L$, molecules will not be absorbed into the second and higher adsorbent layers until the first layer is substantially filled, and thus, the inflection point will be at $v \doteq v_m$. Because of this, the most reliable surface area values can be derived utilizing Type II isotherms.(30)

One failing of both the Langmuir and B.E.T. methods is that the adsorbent surface coverage is calculated inadequately. The failure in these methods is in the fact that adsorption does not actually occur uniformly in layers, but rather, it occurs in a Gaussian-like manner with respect to the amount of layers covered, even for low sample concentrations. This is due to varying degrees of physical adsorption and surface migration, and it can even incorporate "chemical desorption." For example, in an ambient air sampling cartridge, as some one-layer-thick physically attached adsorbate molecules are ready to elute, if the adsorbent-adsorbate relationship is not very tenacious and if the temperature is high enough, the chemisorbed monolayer existing at the adsorbent bed entrance can begin to desorb.

A mention should be made here that the pressure terms in both the Langmuir and the B.E.T. equations are for pure component pressures. In chromatographic studies, however, since minute amounts are injected, essentially all of the vapor stream is carrier gas. Nevertheless, pressure values for the pure sample component should still be applied.(31)

Adsorption Plots

Another method for analyzing adsorbent trapping capabilities is based on the dependence of the adsorption rate K on temperature. Values for the molar free energy ($\overline{\Delta}G_a$) and the molar enthalpy of adsorption ($\overline{\Delta}H_a$) can readily be calculated. The differential molar free energy of adsorption is given by the equation:

$$\overline{\Delta}G_a = -RT \ln K_a$$

Here, the standard state for K_a must be defined as there is no universally accepted standard state for adsorption, although several have been suggested. Since $\overline{\Delta}G_a$ primarily reflects trends in K_a (i.e., $K_a = e^{(-\overline{\Delta}G_a/RT)}$, the differential molar free energy need not be calculated as it is proportional to the retention volume V (whether V_d, V_f, or V_i), which is easily calculated.(32)

The differential molar enthalpy of adsorption is expressed as shown:

$$(1) \quad \overline{\Delta}H_a = \delta \overline{\Delta}G_a / \delta (1/T)$$

$$(2) \quad \overline{\Delta}H_a = -R\left[\delta \ln V / \delta (1/T)\right]$$

where: R is the gas law constant. A look at Equation (2) indicates that $\overline{\Delta}H_a$ values are easily obtained from plots of $\ln V_i$ vs. 1/T. One must be careful here to represent V in the proper units.(33)

In chromatographic analyses, the molar enthalpy of adsorption ($\overline{\Delta}H_a$) can be used to assess adsorbate-adsorbent interaction strengths for both the frontal and displacement sample introduction methods.

Here, the parameter "net heat of adsorption" ($\overline{H}_{na}$) comes into play. $\overline{H}_{na}$ is calculated as follows:

$$\overline{H}_{na} = \Delta H_{a(d \text{ or } f)} - \Delta H_{\ell}$$

where: ΔH_{ℓ} is the adsorbate heat of liquefaction. The larger $\overline{H}_{na}$ is, the stronger enthalpic interaction between adsorbate and adsorbent there is. For cases where $\Delta\overline{H}_{\ell} \doteq \overline{H}_{a}$, marginal interaction of the adsorbate with the resin is occurring, and the resin is merely serving as an inert surface allowing liquefaction of the adsorbate.(34)

In both displacement and frontal analysis, the peak maxima or the challenge concentrations are indicators that an equilibrium has been reached.(35) In incipient elution analysis, however, an equilibrium condition is not even closely approached. Rather, elution is dependent upon the factors influencing the dispersion of the chromatographic peak in the sorbent bed. In both cases, the factors are the same, being based on dispersion forces and specific forces (see the section on Adsorbents). Even though, whereas a large change in temperature could shift the elution peak or challenge concentration level dramatically, the incipient elution point might vary to a substantially lesser degree.

This point leads to a realization that for incipient elution, net heat of adsorption values are not indicative of adsorbate-adsorbent interaction forces. The only application for H_{na} would be to show to what degree equilibrium was being approached at the time of incipient elution by comparing the H_{na} value at incipient elution to that value obtained at either the peak maxima or challenge concentration. In any respect, the net heat of adsorption for incipient elution is not at all informative in describing adsorbent-adsorbate interactions.

For incipient elution analysis then, the only quantitative approach to viewing adsorbate-adsorbent interaction relationships is through actual chromatographic elution plots. In these plots the normalized elution volume V_N is a direct measure of adsorbent-adsorbate interaction. With the aid of additional physical data on the adsorbent and adsorbate, a qualitative assessment can be made into the nature of interactions. Such physical data would include polarizability, dipole moment, and vapor pressure for the adsorbates, and polarity, selectivity, pore size, and surface area for the adsorbents.

FOOTNOTES - CHAPTER III

1. J. H. de Boer, The Dynamic Character of Adsorption, Oxford University Press, London, 1968, pp. 1-2.

2. Ibid. p. 1.

3. D. M. Young and A. D. Crowell, Physical Adsorption of Gases, Butterworth & Co., Washington, D.C., 1962, p. 1.

4. Lloyd R. Snyder, Principles of Adsorption Chromatography, Marcel Dekker, Inc., New York, 1968, p. 40.

5. D. M. Young and A. D. Crowell, p.3.

6. Lloyd R. Synder, p. 40.

7. D. M. Young and A. D. Crowell, p. 2.

8. Lloyd R. Snyder, p. 40.

9. Ibid. pp. 40-1; D. M. Yound and A. D. Crowell, p. 3.

10. D. M. Young and A. D. Crowell, pp. 1-2.

11. J. H. de Boer, pp. 90, 95.

12. Ibid. p. 93

13. R. F. Gallant, J. W. King, P. L. Levins, and J. F. Piecewicz, Characterization of Sorbent Resins for Use in Environmental Sampling, EPA-600/7-78-054, March, 1978, p. 5.

14. Lloyd R. Snyder, pp. 12-13.

15. Ibid. p. 12.

16. Ibid. p. 13

17. Ibid. pp. 12-13.

18. Ibid. p. 22.

19. Ibid. pp. 22-23.

20. Ibid. p. 23.

21. Ibid.

22. Ibid. p. 78

FOOTNOTES - CHAPTER III (CONTINUED)

23. *Ibid*. pp. 22-24

24. D. M. Young and A. D. Crowell, pp. 3-5.

25. *Ibid*. p. 4

26. *Ibid*. pp. 3-4; Lloyd R. Snyder, pp. 53-4.

27. Lloyd R. Snyder, pp. 55-58.

28. Refer to Appendix A.

29. D. M. Young and A. D. Crowell, pp. 147-150.

30. *Ibid*. p. 152

31. Information supplied by Dr. Norendra Gangoli, Exxon Research and Engineering Company, Florham Park, New Jersey.

32. R. F. Gallant et. al., p. 121.
F.
33. *Ibid*.

34. *Ibid*.

35. *Ibid*. pp. 4, 6.

IV. ADSORBATES

Characterization

The seven toxic organic compounds chosen for this elution study are listed below:

Vinyl chloride
Methylene chloride
Chloroform
Carbon tetrachloride
Acetaldehyde
Diethyl ether
Ethyl acetate

The seven compounds were singled out because they are all known or suspected carcinogens which are produced in large quantities. The following pages list pertinent information about each of the seven adsorbates, including physical values, production quantities, and toxicity data. For medical terms, refer to the dictionary section in Appendix B.(1)

TABLE 2

Toxicity Ratings and Abbreviations (2)

Toxicity Ratings:

U = unknown

0 = no toxicity

1 = slight toxicity

2 = moderate toxicity

3 = severe toxicity

Local	- affects the skin or mucous membranes
Systemic	- can be absorbed into the body by inhalation, ingestion, or through the skin
Acute	- effects due to exposure of seconds, minutes, or hours
Chronic	- effects due to repeated exposures of days, months, or years

TABLE 3

Abbreviations

NBP - normal boiling point (at 1 atmosphere pressure)

LEL - lower explosive limit

UEL - upper explosive limit

BOD_5 - 5-day biological oxygen demand measured as grams of oxygen consumed per gram of adsorbate

BOD_5 - ultimate (total) biological oxygen demand

LD_{50} - lethal dose causing a 50% population death rate

LC_{50} - lowest lethal concentration

TC_{lo} - lowest toxicity causing concentration

TWA - time weighted average (chronic toxicity value set by the US OSHA)

TD_{lo} - lowest toxic dose

TLV - threshhold limit value

$t_{1/2}$ - half-life of degradation

CNS - central nervous system

Route: I.V. - intravenous (into bloodstream)

S.C. - subcutaneous (under skin)

Inh. - inhalation

I.P. - intraperitoneal (inside the abdomen covering membrane)

ppm - parts per million (volume/volume)

M - million

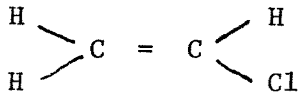
Vinyl Chloride(3)(4)(5)

Colorless liquid or gas; faintly sweet odor.

Synonyms: chloroethylene, chloroethene

Molecular Formula: C_2H_3 Cl

Structure:



Chemical Properties:

Molecular Weight: 62.50

Vapor Pressure: 2660 mm at 25°C

Normal Boiling Point: -13.4°C

Liquid Density: 0.9195g/ml at 15°C/4°C

Saturated Vapor Density: 2.15 g/l at NBP

Water Solubility: Slight (1.1 g/l H_2O)

Environmental Persistence: BOD_u = 1.28 g/g (theoretical)

Atmospheric Reactivity: Reacts with oxidizing materials

Activity towards $O_3\cdot$ $t_{1/2} < 3$ days
$RO_2\cdot$ $t_{1/2} = 1000$ days
$OH\cdot$ $t_{1/2} = 3$ days

LEL = 4%

UEL = 22%

Hazard Analysis:

Acute Local : Irritant 2

Acute Systemic : Inhalation 2

Chronic Local : Irritant 2

Chronic Systemic: Inhalation 3

Explosion and Fire Hazard:

Dangerous and severe when exposed to heat or flame. Large fires of this material are practically inextinguishable.

- No spontaneous heating
- When heated to decomposition, it emits highly toxic fumes of phosgene.

Toxicology:

In high concentrations, vinyl chloride acts as an anesthetic. It causes skin burns by rapid evaporation and subsequent freezing. Circulatory and bone changes in the finger tips were reported in workers handling unpolymerized materials.

Toxicity:

Acute Toxicity	Dosage	Animal	Route
LC	1-4 x 10^5 ppm	mouse	unknown
"	"	dog	"
"	"	cat	"
"	"	guinea pig	"

Non-lethal Acute Effects:

Cardiovascular	Dosage	Animal	Route
TC_{lo}	20 ppm	human	inhalation
Paralysis			
TC_{lo}	300 ppm	human	inhalation

Chronic Toxicity: TWA = 1 ppm

Ceiling = 5 ppm

Carcinogenicity:

LC_{lo}	250 ppm (4 hrs/260 days)	rat	inhalation

Teratogenicity: TLV: 500 ppm or 1300 mg/m^3

Mutagenicity: Positive - Ames Salmonella

Other Chronic Effects:

Liver and kidney damage

Cardiovascular damage

Thyroid and brain degeneration

Production Data:

Annual US Production - 5,088.5 Mlbs (1976)

Annual US Consumption - 4,467.6 Mlbs (1976)

Atmospheric release rate - 146.5 Mlbs/yr

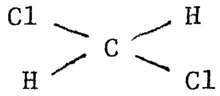
Methylene Chloride(6)(7)(8)

Colorless, volatile liquid

Synonyms: dichloromethane, methylene dichloride

Molecular Formula: CH_2Cl_2

Structure:



Tetrahedral

Chemical Properties:

Molecular Weight: 84.93

Vapor Pressure: 435.8 mm at 25°C

Normal Boiling Point: 40°C

Liquid Density: 1.3266 g/ml at 20°C/4°C

Saturated Vapor Density: 2.93 g/l at NBP

Water Solubility: Slight

Environmental Persistence: BOD_u = 0.38 g/g (theoretical)

Atmospheric Reactivity: Not very reactive towards O_3 or RO_3

$t_{1/2}$ = 1 year with OH

LEL = 15.5%

VEL = 66.4%

Hazard Analysis:

Acute Local: Irritant 2

Acute Systemic: Ingestion 2; Inhalation 3; Skin absorption 2

Chronic Local: U

Chronic Systemic: Ingestion 1; Inhalation 1; Skin absorption 1

Disaster Hazard: Dangerous; when heated to decomposition, it emits highly toxic fumes of phosgene.

Fire Hazard: None

Explosion Hazard: While none under ordinary conditions, it will form explosive mixtures in atmospheres having high oxygen content.

Toxicology: Methylene chloride is a strong narcotic, and can cause eye irritation. It also can cause dermatitis upon prolonged skin contact. Note that CH_2Cl_2 is used as a food additive (solvent). For example, it is used in the decaffeination of coffee.

Toxicity:

Acute Toxicity	Dosage	Animal	Route
LD_{50}	2136 mg/kg	rat	oral
"	1500 "	mouse	I.P.
"	6460 "	"	S.C.
LD_{100}	950 "	dog	I.P.
"	1900 "	rabbit	oral
LD_{lo}	3000 "	dog	"
"	2700 "	"	S.C.
"	200 "	"	I.V.
"	2700 "	rabbit	S.C.
"	500 ppm (2 hrs)	guinea pig	INH.

Non-lethal Acute Effects:

CNS effects - narcosis

TC_{Lo}	500 ppm (1 yr)	intermittent

Blood effects

TC_{Lo}	500 ppm (8 hr)

Chronic Toxicity: TWA - 500 ppm

Ceiling - 1000 ppm

Peak - 2000 ppm/5 min/2 hrs

Teratogenicity: TLV - 500 ppm

Other Chronic Effects:

Liver Damage

Reduced Growth Size

Production Data:

Annual US Production - 591 Mlbs (1974)

Annual US Consumption - 120 Mlbs (1975)

Atmospheric Release Rate - 366.8 Mlbs/yr

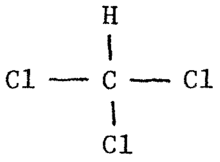
Chloroform(9)(10)(11)

Colorless liquid; heavy, ethereal odor

Synonyms: Trichloromethane, methanyl chloride

Molecular Formula: $CHCl_3$

Structure:



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ Cl & - & C & - & Cl \\ & & | & & \\ & & Cl & & \end{array}$$

Tetrahedral

Chemical Properties:

Molecular Weight: 119.39

Vapor Pressure: 200 mm at 25.9°C

Normal Boiling Point: 61.26°C

Liquid Density: 1.49845 g/ml at 15°C/4°C

Saturated Vapor Density: 4.12 g/l at NBP

Water Solubility: 8.0 g/l

Environmental Persistence:

$$BOD_5 = \frac{\text{4\% of theoretical at } 20^{\circ}C}{\text{Total theoretical } BOD_u} = 0.19$$

Atmospheric Reactivity: Activity towards OH

$t_{1/2} > 1$ year

Hazard Analysis:

Acute Local: Irritant 1

Acute Systemic: Inhalation 3

Chronic Local: U

Chronic Systemic: U

Fire Hazard: Slight when exposed to high heat; otherwise practically noninflammable.

Disaster Hazard: Dangerous; can revert to highly toxic phosgene gas when superheated.

Toxicology: Causes irritation of eyelid membranes. Upon inhalation, it causes dilation of the pupils with reduced reaction to light, as well as reduced intraocular pressure. The material is well known as an anesthetic. Prolonged inhalation induces paralysis accompanied by cardiac respiratory failure and finally death.

Prolonged administration as an anesthetic may lead to such serious effects as profound toxemia and damage to the liver, heart, and kidneys.

Toxicity:

Acute Toxicity	Dosage	Animal	Route
LD_{50}	800 mg/kg		
"	704 "		
LD_{Lo}	2500 "	mouse	oral
"	1000 "	dog	"
"	75 "	dog	I.V.
"	800 "	rabbit	S.C.
LC_{50}	28 ppm	mouse	INH.
"	100 "	dog	"
"	59 "	rabbit	"
LC_{Lo}	8000 " (4 hrs)	rat	"
	20,000 " (2 hrs)	guinea pig	"

Non-lethal Acute Effects:	Dosage	Animal	Route
Systemic	10 ppm (1 yr)	human	INH.

Motor Reflexes - rabbit

Kidney, liver, and vascular lesions

Chronic Toxicity: TWA - 50 ppm

NIOSH recommended TWA - 10 ppm

Carcinocenicity:	Dosage	Animal	Route
TD_{lo}	18 g/Kg (120 days)	mouse	oral

Other Chronic Effects:

CNS paralysis after prolonged exposure

Placental lesions

Alteration in neuroendocrine system

Production Data:

Annual US Production - 234.7 Mlbs

Annual US Consumption - All

Atmospheric Release Rate - 167.8 Mlbs/yr

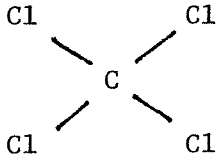
Carbon Tetrachloride(12)(13)(14)

Colorless liquid; heavy, ethereal odor

Synonyms: Tetrachloromethane; Perchloromethane; Methane tetrachloride

Molecular Formula: CCl_4

Structure:



Tetrahedral

Chemical Properties:

Molecular Weight: 153.82

Vapor Pressure: 115.2 mm @ 25°C

Normal Boiling Point: 76.54°C

Liquid Density: 1.5940 g/ml at 20°C/4°C

Saturated Vapor Density: 5.32 g/l at NBP

Water Solubility: Insoluble

Environmental Persistence: No BOD

Atmospheric Reactivity: Photodegradation

$$t_{1/2} = 10 \text{ to } 33 \text{ weeks}$$

Hazard Analysis:

Acute Local: 0

Acute Systemic: Ingestion 3; Inhalation 3; Skin Absorption 1

Chronic Local: Irritant 1

Chronic Systemic: Ingestion 3; Inhalation 3; Skin Absorption 3

Disaster Hazard: When heated to decomposition, it emits highly toxic fumes of phosgene.

Toxicology: CCl_4 has a narcotic action resembling chloroform, though not as strong. While narcosis is the immediate symptom, the after effects can include damage to the kidneys, liver, and lungs. Low concentrations, not potent enough to induce narcosis, usually result in severe gastro-intestinal upset, and may progress to serious kidney and hepatic damage. The kidney lesion is an acute nephrosis; the liver involvement consists of an acute degeneration of the central portions of the lobules. Prolonged exposure to small amounts of CCl_4 can also cause cirrhosis of the liver. In addition, prolonged contact with the skin can lead to dermatitis. Also, other effects include secondary anemia, visual disturbances, and slight jaundice.

Toxicity:

Acute Toxicity	Dosage	Animal	Route
LD_{50}	1770 mg/Kg	rat	oral
"	4620 "	mouse	I.P.
"	6380 "	rabbit	oral
LD_{lo}	3200 "	mouse	S.C.
"	1000 "	dog	oral
"	125 "	"	I.V.
"	4785 "	cat	S.C.

	Dosage	Animal	Route
LD_{lo}	3000 mg/Kg	rabbit	S.C.
LC_{50}	9526 ppm (8 hrs)	mouse	INH.
LC_{lo}	38,110 " (2 hrs)	cat	"
"	550 "	rabbit	"
"	20,000 " (2 hrs)	guinea pig	"
"	1000 "	human	"
"	4000 " (4 hrs)	rat	"

Chronic Toxicity: TWA - 10 ppm

Ceiling - 25 ppm

Peak Concentration - 200 ppm/5 min/4 hrs

Carcinogenicity:	Dosage	Animal	Route
Neoplastic Effects			
TD_{lo}	133 g/Kg (25 weeks, intermittent)	rat	S.C.
TD_{lo}	4800 mg/Kg (88 days, intermittent)	mouse	oral

Mutagenicity: positive

Teratogenicity: TLV = 10 ppm

Other Chronic Effects: Odor perception at 77 ppm

Production Data:

Annual US Production	- 1,047 Mlbs (1973)
Annual US Consumption	- 989.3 Mlbs (1973)
Atmospheric Release Rate	- 65 Mlbs/yr

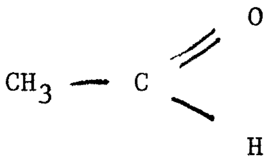
Acetaldehyde(15)(16)(17)

Colorless, fuming liquid; pungent, fruity odor

Synonyms: Acetic aldehyde; ethyl aldehyde

Molecular Formula: CH_3CHO

Structure:



Chemical Properties:

Molecular Weight: 44.05

Vapor Pressure: 923 mm at 25°C

Normal Boiling Point: 20.8°C

Liquid Density: 0.7834 g/ml at 18°C/4°C

Saturated Vapor Density: 1.52 g/l at NBP

Water Solubility: Infinite

Environmental Persistence: BOD_5 = 126 g/g at 20°C

LEL = 4%

UEL = 57%

Hazard Analysis:

Acute Local: Irritant 3; Ingestion 3; Inhalation 3

Acute Systemic: Ingestion 2; Inhalation 2

Chronic Local: Irritant 1

Chronic Systemic: Ingestion 2; Inhalation 2

Fire and Explosion Hazard: Severe when exposed to flame; can react vigorously with oxidizing materials; no spontaneous heating though.

Toxicology: A local irritant. CNS narcotic. A synthetic flavoring substance and adjuvant. A common air contaminant.

Toxicity:

Acute Toxicity	Dosage	Animal	Route
LD_{50}	1930 mg/Kg	rat	oral
"	640 "	rat	S.C.
"	1232 "	mouse	oral
"	560 "	mouse	S.C.
LD_{lo}	500	rat	I.P.
LC_{lo}	4000 ppm (4 hrs)	rat	INH.

Non-lethal Acute Effects:

TC_{lo}	134 ppm	human	INH.

Chronic Toxicity: TWA - 200 ppm

Carcinogenicity:

TC_{lo} = 60 mg/Kg (79 weeks) rat S.C.

Teratogenicity: TLV = 200 ppm

Other Chronic Effects:

Eye Irritation - 50 ppm

Production Rate:

Annual US Production - 1500 Mlbs (1976)

Annual US Consumption - 1300 Mlbs (1976)

Atmospheric Release Rate - 36.2 Mlbs/yr

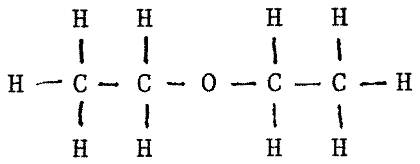
Diethyl Ether (18)(19)(20)

Colorless liquid; characteristic odor termed "ethereal"

Synonyms: Ethyl ether, ether, ethyl oxide

Molecular Formula: $C_4H_{10}O$

Structure:



$\mathrm{H-C-C-O-C-C-H}$

Chemical Properties:

Molecular Weight: 74.12

Vapor Pressure: 442 mm at 20°C

Normal Boiling Point: 34.5°C

Liquid Density: 0.7135 g/ml at 20°C/4°C

Saturated Vapor Density: 2.56 g/l at NBP

Water Solubility: Slight

Environmental Persistence:

1% of theoretical BOD_u

Atmospheric Reactivity: Reacts vigorously with oxidizing materials.

LEL = 1%

Fire and Explosion Hazard: Dangerous; easily ignited when heated or exposed to flame or sparks due to a low flash point. When allowed to stand, ether forms peroxides which are easily heat-detonated.

Toxicology: Powerful narcotic, previously used extensively in hospitals. Large doses can cause death. Also, it is a CNS depressant.

Toxicity:

Acute Toxicity	Dosage	Animal	Route
LD_{50}	1700 mg/Kg	rat	oral
LD_{50}	2000 "	"	I.P.

Chronic Toxicity: TWA = 400 ppm

Teratogenicity: TLV = 400 ppm

Production Data:

Annual US Production - 103.2 Mlbs (1969)

Annual US Consumption - 102 Mlbs (1969)

Atmospheric Release Rate - 35.7 Mlbs/yr

Note: The above three values have significantly decreased since the practice of using ether as an anesthetic has been stopped.

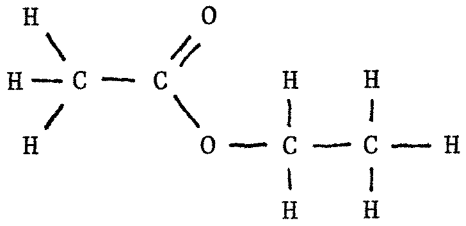
Ethyl Acetate (21)(22)(23)

Colorless liquid, fragrant odor

Synonyms: Acetic ester, ethylacetic ester, ethyl etharate, ethyl ethanoate

Molecular Formula: $CH_3COOC_2H_5$

Structure:



Chemical Properties:

Molecular Weight: 88.10

Vapor Pressure: 92.5 mm at 25°C

Normal Boiling Point: 77.06°C

Liquid Density: 0.8946 g/ml at 25°C/4°C

Saturated Vapor Density: 3.04 g/l at NBP

Water Solubility: Soluble - 89 g/l

Environmental Persistence:

Theoretic BOD_u = 1.82 g/g

69% of theoretical BOD after 20 days at 20°C

Hazard Analysis:

Acute Local: Irritant 1

Acute Systemic: Ingestion 2; Inhalation 2; Skin Absorption 2

Chronic Local: Irritant 1

Chronic Systemic: Ingestion 1; Inhalation 1; Skin Absorption 1

Fire and Disaster Hazard: Dangerous, when exposed to heat or flame. Can react vigorously with oxidizing materials. However, no spontaneous heating.

Explosion Hazard: Moderate, when exposed to flame.

LEL = 2.5%

UEL = 9%

Toxicology: Causes irritation to mucous surfaces, particularly the eyes, gums, and respiratory passages, and it is also mildly narcotic. On repeated or prolonged exposures, it causes conjunctional irritation and corneal clouding. It can cause dermatitis. High concentrations can cause congestion of the liver and kidneys. Other effects caused by large amounts are secondary anemia, fatty degeneration of the viscera and leucocytosis. Note that ethyl acetate is used as a synthetic flavoring agent and adjuvant.

Toxicity:

Acute Toxicity	Dosage	Animal	Route
LD_{50}	5000 mg/Kg	rat	S.C.
"	709 "	mouse	I.P.
"	3000 "	cat	S.C.
"	4930 "	rabbit	oral
"	3000 "	guinea pig	S.C.
LC_{50}	1600 "	rat	INH.
LC_{lo}	31 mg/m^3 (1 hr)	mouse	INH.

Chronic Toxicity: TWA = 400 ppm

Teratogenicity: TLV = 400 ppm

Production Data:

Annual US Production: - 212 Mlbs
Annual US Consumption: - All
Atmospheric Release Rate - 196.1 Mlbs/yr

Carcinogenesis

Note: Refer to Appendix B for medical terms.

As mentioned in the beginning of this chapter, all seven of the adsorbates are either proven or suspected carcinogens. Chemical carcinogens act on cellular material of target organisms by three principal mechanisms: the physical interaction of the carcinogen with cellular receptors, chemical reaction of the carcinogen with these receptors, or metabolite-receptor interaction following metabolism of the carcinogen within the target organ or elsewhere.(24)

In general, three major carcinogenic type chemicals exist: primary or ultimate carcinogens, secondary or procarcinogens, and co-carcinogens. Primary carcinogens are chemically and biologically reactive entities by virtue of their specific structure. They can interact specifically with certain elements of tissues, cells, and cellular component macromolecules to yield modified macromolecules causing tumors. Examples of such carcinogens are alkylating agents. Procarcinogens cover the majority of carcinogenic chemicals. Often, they are chemically, biochemically, and biologically inert. For procarcinogens there are specific spontaneous or biochemical (i.e., host-mediated and-controlled) activation reactions which convert them to primary carcinogens. Such compounds include many halocarbons. Co-carcinogens are not actually carcinogenic by themselves, but they serve to potentiate the effect of a carcinogen. Many of these compounds are found in tobacco smoke.(25)

The action of carcinogens is visualized best through alkylating agents. These compounds react directly with nucleophilic centers in various biological macromolecules, resulting in vesicant and other toxic actions, and in a considerable number of known cases, in mutagenic and carcinogenic activities.(26) Alkylating agents are readily adsorbed onto cell surfaces, where rapid uptake of the agent into whole cells occurs. The agents are rapidly sequested in a lipid or lipoprotein phase, and then slowly released by diffusion into the aqueous phase of the cell where alkylation takes place.(27)

Of the seven adsorbates used, each one is associated with carcinogenicity in a different manner. VCl, the raw material of a major part of the plastics industry, has come under intensive scrutiny as the cause of the normally very rare angiosarcoma of the liver in some exposed workmen. Though as an alkyl halide it bears a formal relationship to some alkylation carcinogens, VCl probably reacts via an entirely different biological action.(28) This is suspected because, while VCl shows a remarkable measure of carcinogenic potency in the rat and in man, it possesses negligible reactivity as an alkylating agent.(29) It has been suggested though that VCl is a primary carcinogen, reacting with the metabolite chloroethylene oxide.(30)

Chloroform and carbon tetrachloride have conclusively been proven to cause hepatocarcinogenesis. It has been suggested also that these compounds probably require activation to free radicals to perform this action. Methylene chloride, while proving non-carcinogenic via inhalation tests, did produce two cancerous skin tumors in 50 test mice when injected into the skin. Because of this, it has been hypothesized that methylene chloride, is effectively eliminated, either unchanged or by detoxification metabolism when inhaled.(31)

Of the three non-halogenated adsorbates studied, only acetaldehyde has been conclusively tied to carcinogenesis. Generated by both tobacco smoke and urban air pollution, acetaldehyde has been shown to inhibit mucous flow in the respiratory track, and thus, facilitate the uptake of carcinogens by the bronchial epithelium.(32) Also, more recently, as indicated in the toxicity data, a subcutaneous injection of acetaldehyde produced tumors in rats. Therefore, acetaldehyde is both a co-carcinogen and either a primary or secondary carcinogen. As for ethyl ether and ethyl acetate, while they both have been proven to be teratogenic, and are suspected carcinogens, no conclusive data to support this premise has yet been published.

FOOTNOTES - CHAPTER IV

1. Various collegiate and medical dictionaries were used as references.
2. N. Irving Sax, Dangerous Properties of Industrial Materials, Van Nostrand Reinhold Company, New York, 1975, pp. 289-90.
3. Dorigan, Fuller, and Duffy, Preliminary Scoring of Selected Organic Air Pollutants: Appendix I to IV, EPA-450/3-77-008, Appendix I, pp. AIV-288-289.
4. N. Irving Sax, p. 1235.
5. Robert C. Weast, Editor, Handbook of Chemistry and Physics, CRC Press, Cleveland, Ohio, 57 Ed., 1976-1977, p. C-298.
6. Dorigan, et. al., Appendix III, pp. A III - 186-187.
7. N. Irving Sax, pp. 921-922.
8. Robert C. Weast, p. C-373.
9. Dorigan, et. al., Appendix I, pp. AI-264-265.
10. N. Irving Sax, pp. 547.
11. Robert C. Weast, p. C-375.
12. Dorigan, et. al., Appendix I, pp. AI-222-223.
13. N. Irving Sax, p. 522.
14. Robert Weast, p. C-375.
15. Dorigan, et. al., Appendix I, pp. AI-6-7.
16. N. Irving Sax, p. 348.
17. Robert C. Weast, p. C-81.
18. Dorigan, et. al., Appendix II, pp. AII-306-307.
19. N. Irving Sax, p. 722.
20. Robert C. Weast, p. C-300.
21. Dorigan, et. al., Appendix II, pp. AII-234-235.

FOOTNOTES - CHAPTER IV (CONTINUED)

22. N. Irving Sax, p. 724.

23. Robert C. Weast, p. C-86.

24. Charles E. Searle, Editor, *Chemical Carcinogens*, American Chemical Society, Washington, D.C., 1976, p. 83.

25. *Ibid*. pp. 3-4.

26. *Ibid*. p. xvi.

27. *Ibid*. p. 83.

28. *Ibid*. pp. xvii, 327.

29. *Ibid*. p. 156.

30. *Ibid*. p. 95.

31. *Ibid*. p. 158.

32. *Ibid*. p. 339.

V. ADSORBENTS

Selection

The choice as to which adsorbents to test was based on a combination of previously known adsorption capacities and availability. Tenax was being used initially for trapping carcinogens in ambient air by the N.J.I.T. Air Pollution Laboratory. Since Tenax was suspected of not trapping VCl and other light organic species, it became the first test adsorbent. At this time, the use of stronger adsorbents was also being considered. Spherocarb, a carbonaceous molecular sieve, was readily obtained from an outside associate, and it became the second test adsorbent. Silica Gel was chosen next as it differed from the other two adsorbents, being amorphous and affected by humidity. Since the available Silica Gel was in the cut 28-200 mesh, a smaller mesh range of 120-170 was obtained by doing a sieve tray separation. A short time later, during a literature search, an article was found which showed that the adsorption capacity of Porapak-T was much greater than that of Tenax for some of the test adsorbates.(1) Thus, Porapak-T was purchased for testing. Lastly, use of the polymer XAD-2 was suggested by some EPA personnel at a conference at Research Triangle Park, NC. Since these people supplied the XAD-2 and because XAD-2 is commonly used as a water pollutant adsorbent, the decision was made to try it.

It should be noted that many other adsorbents were readily available or obtainable. However, these adsorbents were not chosen as they were either deemed incompatible with the adsorbates, or were similar to one of the five selected adsorbents. The five adsorbents chosen cover a range of properties in terms of shape, surface area, and polarity, and thus, this allows for adsorbent property comparisons. The following pages list available data on the five adsorbents.

Tenax (Tenax-G.C.)(2)(3)(4)

Manufacturer: Enka N.V, Netherlands

Mesh Size: 60/80

Diameter: .018 - .025 cm (.007 - .0098 inches)

Upper Temperature Limit: 400°C

Conditioning Temperature: 350°C

Desorption Temperature: 250°C

Pore Size: 720 Å

Surface Area: 18.6 m^2/g

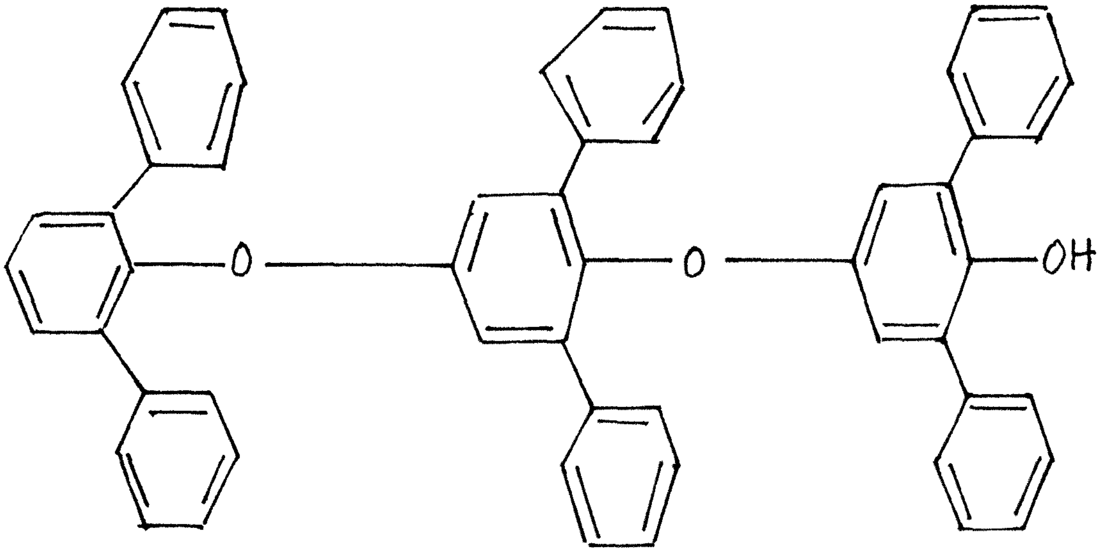
Composition: 2, 6-diphenyl - p - phenylene oxide polymer

Shape: Spherical

Weight of Adsorbent Used: .065 g

Experimental Bulk Packing: .127 g/ml

Structure:



XAD-2 (5)(6)(7)

Manufacturer: Rohm and Haas

Mesh Size: 20/50

Diameter: .035 - .084 cm (.0139 - .0331 inches)

Upper Temperature Limit: 210°C

Conditioning Temperature: 200°C

Desorption Temperature: 190°C

Average Pore Volume: .854 cc/g

Pore Size: 90 Å

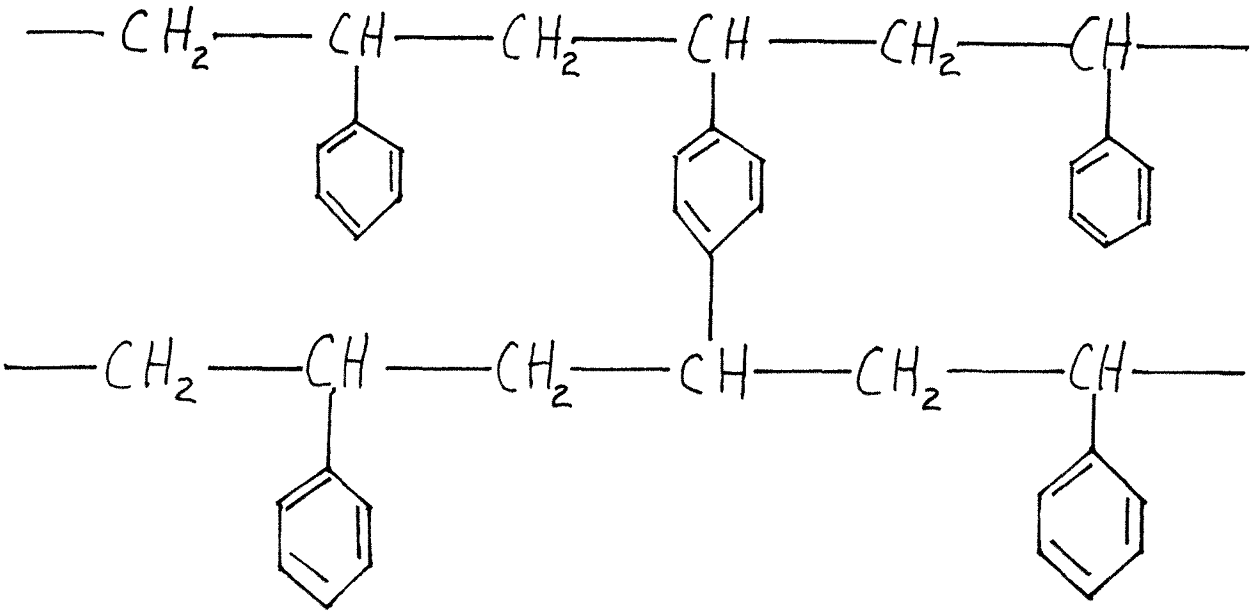
Surface Area: 300 m^2/g

Weight of Adsorbent Used: .164g

Experimental Bulk Packing: .320 g/cc

Composition: Cross-linked styrene-divinyl benzene polymer

Structure:



Porapak-T (8)(9)(10)

Manufacturer: Waters Assoc., Milford, Mass.

Mesh Size: 80/100

Diameter: .015 - .018 cm (.0059 - .007 inches)

Upper Temperature Limit: 190°C

Conditioning Temperature: 180°C

Desorption Temperature: 170°C

Density: 0.43 g/ml

Surface Area: 250 - 350 m^2/g

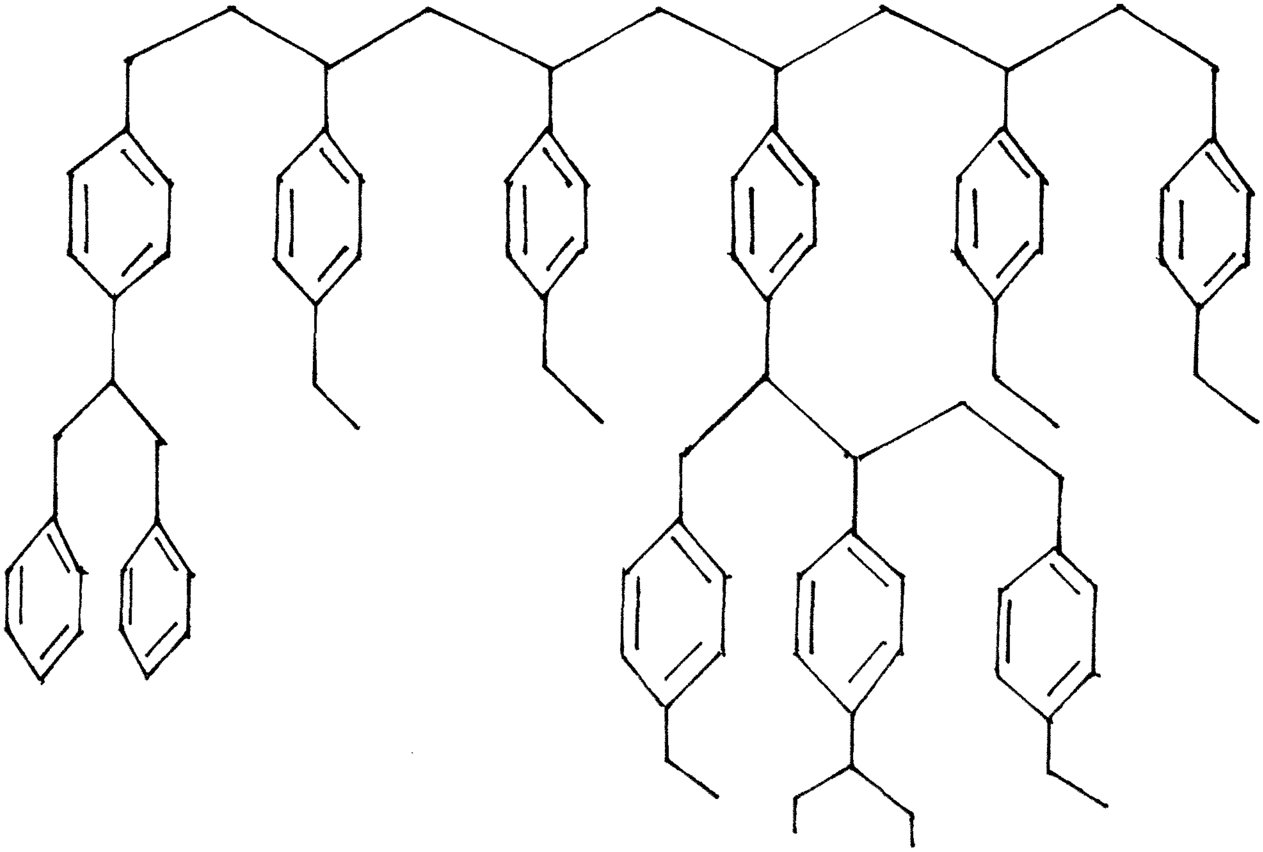
Weight of Adsorbent Used: .207 g

Experimental Bulk Packing: .404 g/ml

Shape: Spherical

Composition: ethyleneglycoldimethacrylate polymer

Structure: (Porapak; form not specified)



Silica Gel (11)(12)

Supplier: Matheson, Coleman and Bell

Mesh Size: 120/170 (sieved from 28/200)

Diameter: .0009 - .0124 cm (.0035 - .0049 inches)

Temperature Limit: non-friable ($>$ 500°C)

Weight of Adsorbent Used: .338 g

Experimental Bulk Packing: 0.66 g/ml

Formula: H_2SiO_3

Molecular Weight: 78.1

Surface Area: 500-600 m^2/g

Average Pore Diameter: approximately 80 Å

Structure: Amorphous

See Figure 7 (13)

Spherocarb[14]

Supplier: Analabs

Mesh Size: 80/100

Diameter: .015 - .018 cm (.0059 - .007 inches)

Upper Temperature Limit: Non-friable (> 300°C)

Packing Density: 0.5 ± 0.05 g/cc

Porosity: 0.75 ± 0.1 cc/g

Pore Size: 15 Å (average)

Surface Area: 1200 m^2/g

Composition: Carbon

Shape: Spherical

Weight of Adsorbent Used: .277 g

Experimental Bulk Packing: 0.54 g/cc

Structure: Carbon molecular sieve; 3-dimensional lattice

Preparation of the Adsorbents

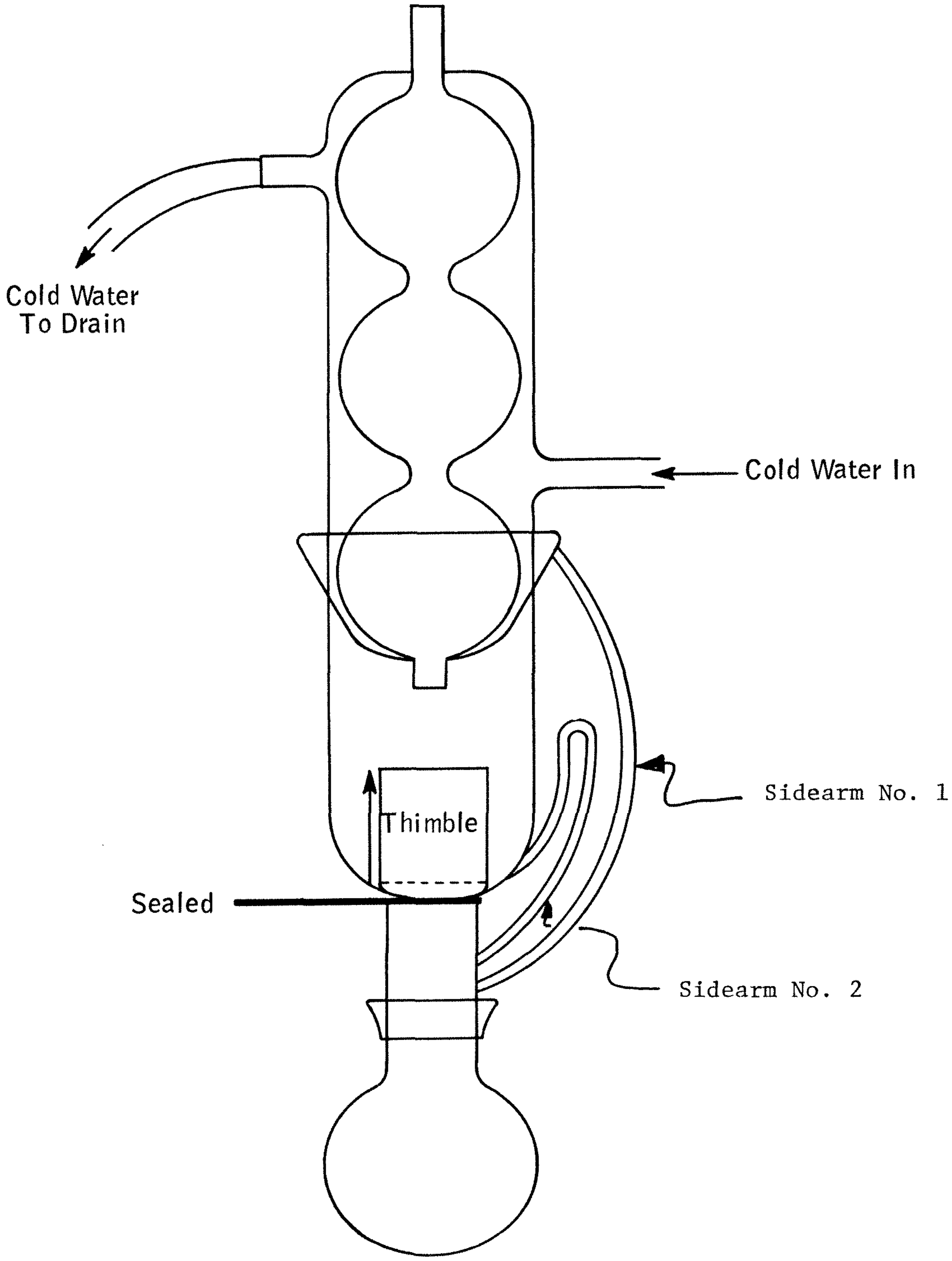
In the preparation of Tenax, a set of serial extractions is performed using the Soxhlet apparatus pictured in Figure 6.(15) The adsorbent is placed in a porous glass thimble which allows liquids, but not fine solids, to pass through it. The solvent is contained in the round bottom flask and heated. Vapors travel up through Sidearm No. 1 to the condenser. The condensed ultra-pure solvent then drains down through the adsorbent and begins to fill up the lower portion of the Soxhlet apparatus (see the arrow pictured). Once the liquid fills the thimble to the top, it will flow over the peak in Sidearm No. 2. This causes a siphoning action, whereby the solvent is returned to the flask. By using this method, adsorbent and solvent impurities are brought into the flask, and the adsorbent becomes purified.

The Soxhlet process is carried out by using in series a polar, a non-polar, and a low boiling solvent. For Tenax conditioning, acetone followed by cyclohexane followed by methanol was used. Each of these solvents was placed for 16 hours in the Soxhlet apparatus. After processing, the Tenax was vacuum dried, and readied for thermal conditioning. Note here that while XAD-2 and Porapak-T can also be decontaminated by the Soxhlet process, in this study they were instead subjected to extensive thermal conditioning under high purity gas purge for preparation as were Spherocarb and Silica Gel.(16)

Tenax was thermally conditioned by placing it in a low flow of helium, approximately 15 ml/min, and heating it to 350°C for more

Figure 6 (15)

SOXHLET APPARATUS



than an hour. Porapak-T and XAD-2 were conditioned by extensive heating for longer than 10 hours each at their respective conditioning temperatures of $180^{o}C$ and $200^{o}C$. Silica Gel was conditioned for four hours at $250^{o}C$ while Spherocarb was conditioned at $350^{o}C$ for 10 hours. For the above adsorbents, exclusive of Tenax, nitrogen was used as the clean-up gas.

A point should be brought out here that a capillary G.C. chromatogram later taken on the adsorbents revealed that thermal conditioning alone did not sufficiently clean the adsorbent materials while the Soxhlet process did. However, after using the Soxhlet process, the adsorbent gets progressively contaminated with each succeeding experimental run. In any respect, it was felt that the tenacious components sticking to the various adsorbents would require too much time and resources to be thoroughly stripped after each run and that the effect caused by these components was minimal because of their very low concentration and strong adsorption.

Adsorption Characteristics

To compare the five adsorbents used, analysis of some basic adsorbent characteristics is required. To begin with, several kinds of attractive adsorbate-adsorbent interactions (adsorption forces) can be distinguished: (1) dispersion forces, (2) induction forces, (3) electrostatic forces, (4) hydrogen bonding, (5) charge transfer, and (6) covalent bonding or ion exchange (chemisorption). These categories are usually separated into two main groups: the dispersion forces, and the specific interactions ("selectivity"). For non-polar adsorbents, dispersion forces contribute essentially all the adsorbate interaction, and selective adsorption of polar molecules does not occur. For polar adsorbates, both groups contribute considerably, with selectivity being high for polar and unsaturated molecules.(17)

The two parameters which are used to quantify polarity are dipole moment and polarizability, with the former applying to polar molecules and the latter more pertinent to non-polar ones. The dipole moment is measured as the product of the available charge times the distance separating unlike charges on a molecule.(18) Polarizability is the tendency for molecules to rotate when placed between two parallel plates; lower values indicate a greater polarity.(19) In terms of increasing overall polarity, the five adsorbents are ranked as follows: Tenax $<$ XAD-2 $\ll$ Porapak-T $\ll$ Silica Gel. The polarity of Spherocarb has not been determined.

Polarizability and dipole moment values for the adsorbates are listed in Table R2.

Adsorption dispersion forces exist between every nonbonded, adjacent pair of atoms and completely account for the van der Waals attraction between nonpolar molecules. Usually increasing with increasing molecular weight or increasing boiling point, these attractive forces are directly proportional to the polarizability squared (α^2) and are also inversely proportional to the distance between two molecules to the sixth power. Also, these dispersion forces become less prominent as the temperature is increased.(20)

Two important parameters which are often brought up in adsorption are adsorbent surface area and pore size. Internal pores generally contribute almost all the adsorbent surface area, and adsorption, therefore, occurs chiefly within these pores. For molecular sieves, pore adsorption is the main mechanism based on adsorbate entanglement within the lattice structure of the molecular sieve. It has been suggested that for an adsorbent, as pore diameter is reduced and the curvature within the pore (assumed cylindrical) is increased, a point will eventually be reached where the adsorption of a planar molecule becomes inhibited because the planes of adsorbate and adsorbent are no longer matched. This effect should be more pronounced for wider adsorbate molecules. However, for pores 20 Å or larger, this capture effect is negligible.(21)

There are other parameters associated with adsorbent structure that are also important in adsorption. For the adsorbent these parameters include active site spacings of functional groups, location of functional groups, pore and general particle shape, and location of localized charges. In addition, parameters which would be adsorbent-adsorbate related include intramolecular electronic and steric attractions, required adsorption area by the adsorbate, and the π electron properties of aromatic molecules.(22)

A point of interest when viewing polar adsorbents is that surface activity is intimately related to adsorbent water content. Almost all polar adsorbents lose water upon being heated, the water existing originally in the adsorbent as either bulk water unassociated with the surface, surface hydroxyl groups which are capable of condensing to liberate water and leave surface oxide groups, and molecular water which is more or less strongly adsorbed on the adsorbent surface. Heating an initially hydrated adsorbent to temperatures between 100° and 150°C serves to drive off adsorbed water. Thus, initially, activity is proportional to the degree of thermal heating. However, as the temperature is further raised, surface hydroxyls begin to leave the adsorbent. The activity of the adsorbent may either increase or decrease (i.e., silica gel) with increasing loss of surface hydroxyls, depending on their importance as adsorption sites.(23)

Outlining some of the characteristics of the five adsorbents can provide an understanding of their advantages and disadvantages.

To begin with, Tenax is a hydrophobic porous polymer, possessing low adsorption strength which allows for thermal elution of relatively high boiling compounds to take place.(24) Exhibiting good thermal stability to 320°C without showing any column bleed, Tenax does have a tendency to degrade at elevated temperatures.(25) This degradation, however, does not appear to affect the efficiency or capacity of adsorption.(26) Other advantages of Tenax are that it does not react with most organic pollutants, and it causes relatively small pressure drops across an adsorbent column. As for column efficiency, Tenax is largely influenced by particle size. Best results have been reported for 60/80 mesh size; also, column efficiency is largely dependent on carrier gas velocity. The suggested operating range is between 2.3 and 9.1 cm/sec, with rapidly decreasing efficiency outside these limits.(27)

XAD-2 can be compared to Tenax in terms of surface area, having about 15 times that of Tenax for similar mesh sizes. Nevertheless, the adsorption capabilities of the two adsorbents are very similar.(28) This is due to the fact that both adsorbents have localized negative charges available for adsorbate interactions. For XAD-2, the aromatic electrons are the negative charged portion. For Tenax, both aromatic π electrons and the ether oxygen lone-pair electrons are available for nonspecific and specific interactions with adsorbates.(29)

XAD-2 exhibits little change in adsorption capacity for different mesh sizes. Larger particles are, therefore, preferred as they are easier to handle, and they have a lower pump pressure requirement.(30) Furthermore, XAD-2 is thermally stable up to 210°C and does not begin to show a weight loss from thermal decomposition until 250°C.(31) However, experimentation has shown that XAD-2 darkens at temperatures above 150°C.(32)

Porapak-T is a moderately polar porous polymer adsorbent. It has been used primarily in the past for efficient separation of a wide variety of relatively low molecular weight compounds.(33) Porapak-T is limited to adsorption of light compounds as it only has an upper temperature limit of 190°C. Tests on the efficiency of desorption at 180°C of a compound is required before Porapak-T can be considered for use in the adsorbent cartridge concentration technique for ambient air sampling.

Spherocarb is a carbon molecular sieve, and as such, it has an extremely uniform lattice structure. This molecular sieve differs from amorphous activated carbon adsorbents in that the mechanism of adsorption is due largely to physical attraction. Here, adsorbates become entrapped in pore lattice chains, as opposed to activated carbon adsorption by specific interactions. Thus, compounds can be thermally desorbed more readily from Spherocarb than from activated carbon adsorbents.

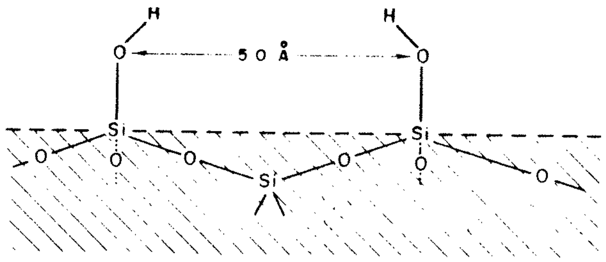
Silica Gel is the most complicated of all the adsorbents to categorize as its properties vary with production conditions and temperature. Silica Gel is produced by addition of acid to a concentrated solution of sodium silicate. When dried in air, the gel retains about 16% water. Other water/temperature ratios are as follows: 100°C/13% and 300°C/4%.(34) Variations of solution pH during the acid gelation of sodium silicate yields silica gels with surface areas varying from 200 m^3/g (pH ≐ 10) to 800 m^3/g (pH $\leq$ 4). Lower surface areas can be obtained by steam treatment of high surface area silicas.(35)

The surface of amorphous silica gel consists of a plane of exposed silicon atoms to which are attached covalent surface hydroxyl groups (see Figure 7). The surface hydroxyls are all equivalent and are so situated as to be incapable of hydrogen bonding with surrounding surface groups, including free hydroxyls. Upon heating the Silica Gel surface beyond the point where most adsorbed water is lost (150-200°C), the various surface hydroxyl reactions, seen in Figure 8, take place. At temperatures between 200 and 400°C, major amounts of reactive hydroxyls condense to liberate water and leave surface siloxane groups. Thus, adsorbent activity begins to decrease. This is shown in Figure 9. At even higher temperatures, free hydroxyls begin to migrate about the surface, form transient reactive groups, and then decompose to surface siloxane groups.(36)

The relative proportions of free and reactive hydroxyls on the silica gel surface are closely related to adsorbent pore diameter. Wide pore silica gels have a high proportion of free hydroxyls, while the surfaces of narrow pore silica gels are covered mainly by reactive hydroxyls. In either case, the sample selectivity based on pore size is not drastic.(37)

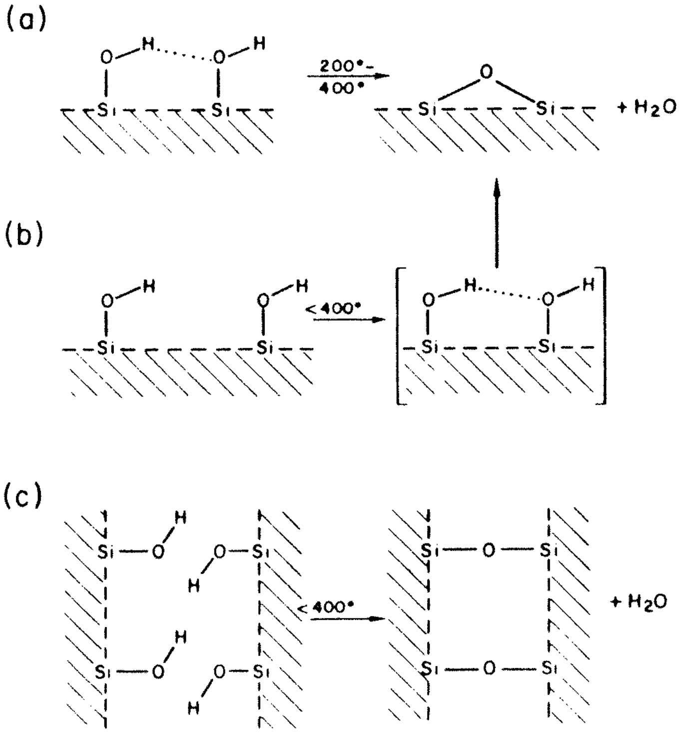
(36)
FIGURE 7

SURFACE STRUCTURE OF SILICA GEL



(36)
FIGURE 8

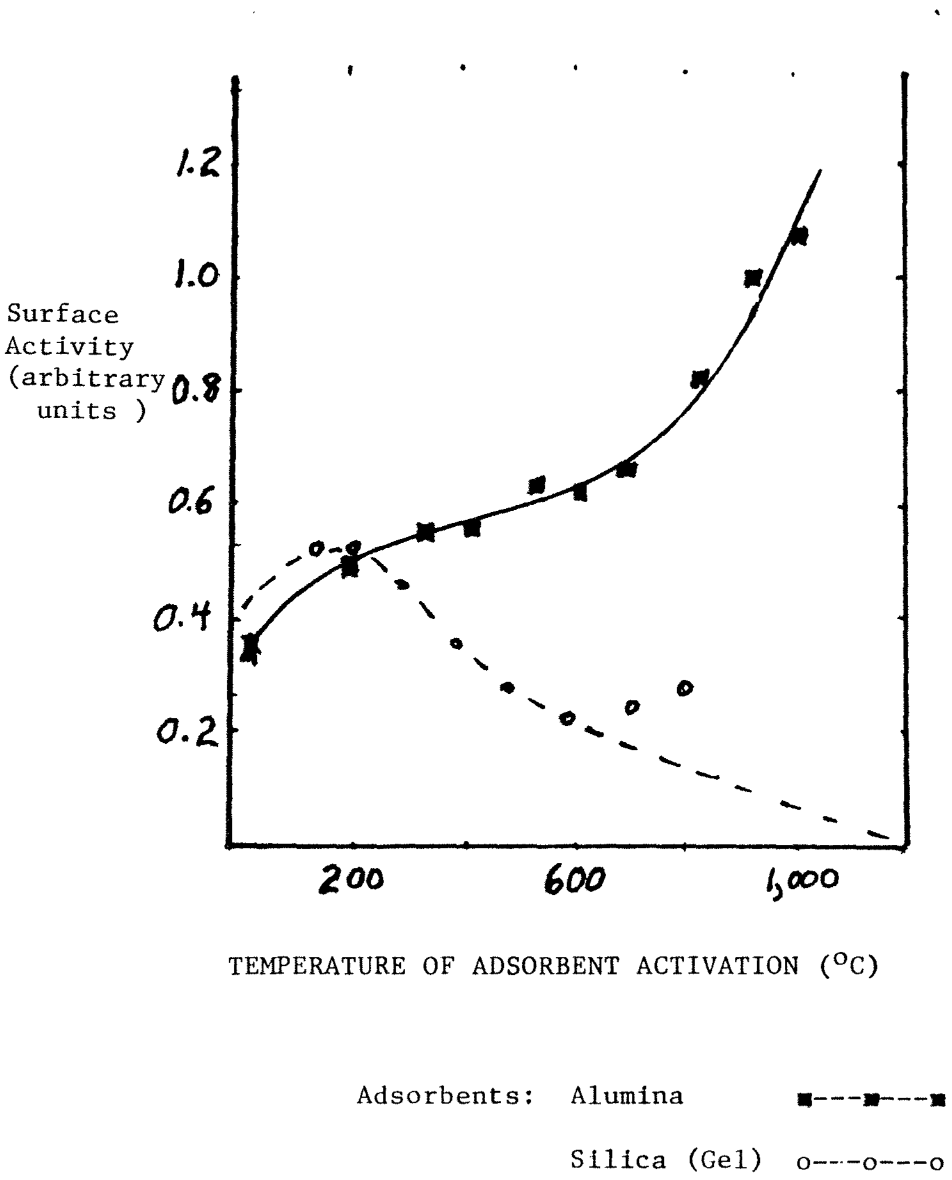
SURFACE HYDROXYL REACTIONS ON SILICA GEL



Reactions of hydroxyls on the silica surface at elevated temperatures. (a) Condensation of reactive hydroxyls; (b) condensation of free hydroxyls; (c) condensation of surfaces.

(36)
FIGURE 9

TYPICAL PLOT OF THE
VARIATION OF SURFACE ACTIVITY WITH TEMPERATURE



One additional fact about Silica Gel is that it is a polar adsorbent which readily shows selectivity in adsorbing polar molecules. This is another reason for Silica Gel's high retention of surface water. Only after prolonged heating at 900°C-1000°C is all the water lost from Silica Gel.(38)

Humidity Effects

The fact that water (humidity) is present in the air at concentrations which often change dramatically from day to day presents a major problem to sampling of air pollutants with the adsorbent concentration method. The problem stems from possible effects and interferences that the humidity may have on the adsorption-thermal desorption process. The fact that water is polar gives rise to three major types of adsorbate-humidity interactions. First, if the adsorbent is not very polar but the adsorbate is highly water soluble, then the humidity present will contribute to adsorbate elution. Second, if the adsorbent retains water but the adsorbate is insoluble in water, then humidity can displace some of the adsorbate; it can also interfere with adsorption by occupying and blocking adsorbent pores. Last, if the adsorbate is soluble in water and the adsorbent retains water, then humidity can aid in adsorption. Therefore, humidity can either aid or hinder adsorption.

FOOTNOTES - CHAPTER V

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2. Tenax product data sheet 4900-2, Altech Associates, Arlington Heights, Illinois.

3. R. F. Gallant, J. W. King, P. L. Levins, and J. F. Piecewicz, Characterization of Sorbent Resins for Use in Environmental Sampling, EPA-600/7-78-054, March, 1978.

4. J. Adams, K. Menzies, and P. L. Levins, Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds, EPA-600/7-77-044, April, 1977.

5. Ibid.

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7. Robert Sydor and Donald J. Pietrzyk, "Comparison of Porous Copolymers and Related Adsorbents for the Stripping of Low Molecular Weight Compounds from a Flowing Air Stream," Analytical Chemistry, Vol. 50, No. 13, November, 1978, p. 1843.

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12. Lloyd R. Snyder, Principles of Adsorption Chromatography, Marcel Dekker, Inc., New York, 1968, pp. 157-62.

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15. Figure drawn from apparatus used in the laboratory.

16. Many researchers have used thermal conditioning alone for the decontamination of sorbent resins, e.g., M. W. Dietrich, L. M. Chapman, and J. P. Mieure, "Sampling for Organic Chemicals in Workplace Atmospheres with Porous Polymer Beads," *American Industrial Hygiene Association Journal*, (39), May, 1978, p. 386.

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18. Robert C. Weast, Editor, *Handbook of Chemistry and Physics*, CRC Press, Cleveland, Ohio, 57 Ed., 1976-1977, p. F-100.

19. V. P. Frontasev and L. S. Shraiber, *Russian Journal of Phys. Chem.*, 43, 229 (1969).

20. Lloyd R. Snyder, p. 44.

21. *Ibid*. p. 61.

22. *Ibid*. p. 62.

23. *Ibid*. pp. 128-129.

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25. Robert Sydor and Donald J. Pietrzyk, p. 1846.

26. M. B. Neher and P. W. Jones, *Analytical Chemistry*, Vol. 49, No. 3, March, 1977, p. 514.

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28. R. F. Gallant, et al., p. 15.

29. *Ibid*.

30. Robert Sydor and Donald J. Pietrzyk, p. 1848.

31. J. Adams, et al., p. 7.

FOOTNOTES - CHAPTER V (CONTINUED)

32. *Ibid*. p. 15.

33. H. M. McNair and E. J. Bonelli, P. 59.

34. J. R. Partington, *General and Inorganic Chemistry*, 3rd Ed., MacMillan and Company, Ltd., London, 1961, pp. 501-2.

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36. *Ibid*.

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VI. EXPERIMENTAL METHODOLOGY

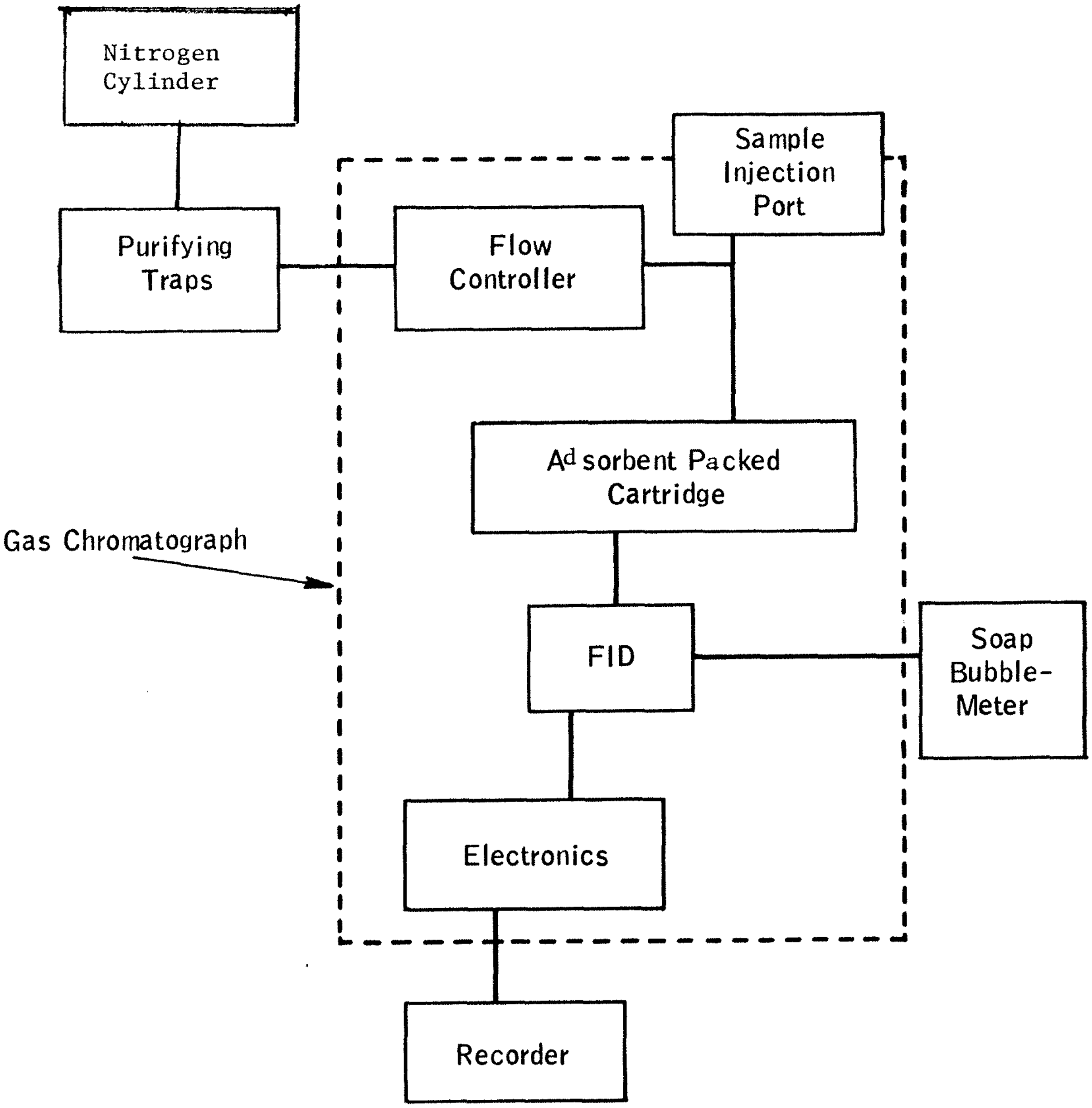
A schematic diagram of the experimental operation is shown in Figure 10. The gas chromatograph (G.C.) used was a Varian Model 3700 equipped with a flame ionization detector (FID) and a temperature programming module. The recorder was a Honeywell Brown Model 15307850 operated at 0.25 inches per minute. The carrier gas was 99.999% pure nitrogen purchased from Matheson Gas Company, East Rutherford, New Jersey. This gas was further purified by means of an activated charcoal trap. The carrier gas flow rate was set at 50 ml/min and checked frequently at the FID outlet using a soap bubble-meter and a stopwatch. Test runs below ambient temperature were performed using low grade liquefied carbon dioxide purchased from Liquid Carbonic Corp., Harrison, New Jersey.

The six liquid adsorbates tested were either reagent or technical grade, and as such were at least 99.5% pure. Vinyl chloride, the only test vapor, was obtained from Matheson Gas Company in a lecture bottle at a concentration of 50 ppm in nitrogen and a pressure of 2000 psig. Purity was approximately ± 2%.

Adsorbent cartridges were made from 6-inch long by 1/8 inch o.d. (.216 cm. i.d.) stainless steel tubing and were packed tightly with a 5-1/2 inch length of "prepared" adsorbent. The ends were plugged with 1/4 inch length glass wool plugs, and the cartridge was placed in the G.C. Using a Swagelok connection, the cartridge was

Figure 10

SCHEMATIC OF EXPERIMENTAL OPERATION



attached to either the vapor or liquid sample inlet line, depending on the adsorbate being tested. The cartridge was then set for thermal conditioning.

Prior to conditioning, the desired carrier gas flow rate for conditioning was set using the G.C. flow controller while measuring the flow rate using a soap bubble-meter and a stopwatch at the FID outlet. The cartridge was then disconnected from the FID and thermally conditioned at the desired temperature listed in the Adsorbent section. The reason the cartridge was disconnected was that the initially high concentration of contaminants eluting from the unconditioned cartridge packing could build up and affect operation of the FID. Cartridge conditioning time was set at anywhere from 4 to 26 hours.

A few hours before the end of thermal conditioning, the FID was connected to monitor the relative cartridge elution level. If a flat baseline was obtained at $30^{o}C$, the temperature was then raised to about $10^{o}C$ below the adsorbent conditioning temperature, as this was the maximum temperature where any elution test could be performed. Here, if a low level constant bleed relative to the $30^{o}C$ baseline was achieved, a test was started; it was felt that a low-level column bleed would not interfere with results since it was constant. If a constant, low-level bleed was not yet obtained, however, further conditioning was performed before testing was begun.

Prior to each G.C. run, the cartridge temperature was allowed to equilibrate for 5 minutes. The sample was then introduced to the carrier gas stream as the chart drive was started simultaneously. The experimental run was carried out past the desired incipient elution point until the original pre-injection baseline was re-established. Once the incipient elution point had been determined, if it appeared that a baseline return would be time consuming because of a large degree of tailing or a small, slow column bleed, the column temperature was raised by as much as 100°C to facilitate cartridge cleaning. Following each run, a check was performed on the carrier gas flow rate.

Sample Introduction

Two separate methods of sample induction into the carrier gas stream were used, dependent on the state of the sample. For the six adsorbate liquids, .05 μl of sample contained in either a 0.5 μl S.G.E. syringe or a 1.0 μl Hamilton syringe was injected through a teflon septum into a heated sample inlet compartment set at least 30°C above the boiling point of the liquid. For vapor injection of vinyl chloride, the sample lecture bottle was connected to a gas sampling valve loop. The loop, at atmospheric pressure, was flushed out several times with sample using a pressure head of about 10 psig. The vapor sample was then injected by means of the gas sampling valve. Note that the temperature for both injection ports was always maintained at 90°C or greater.

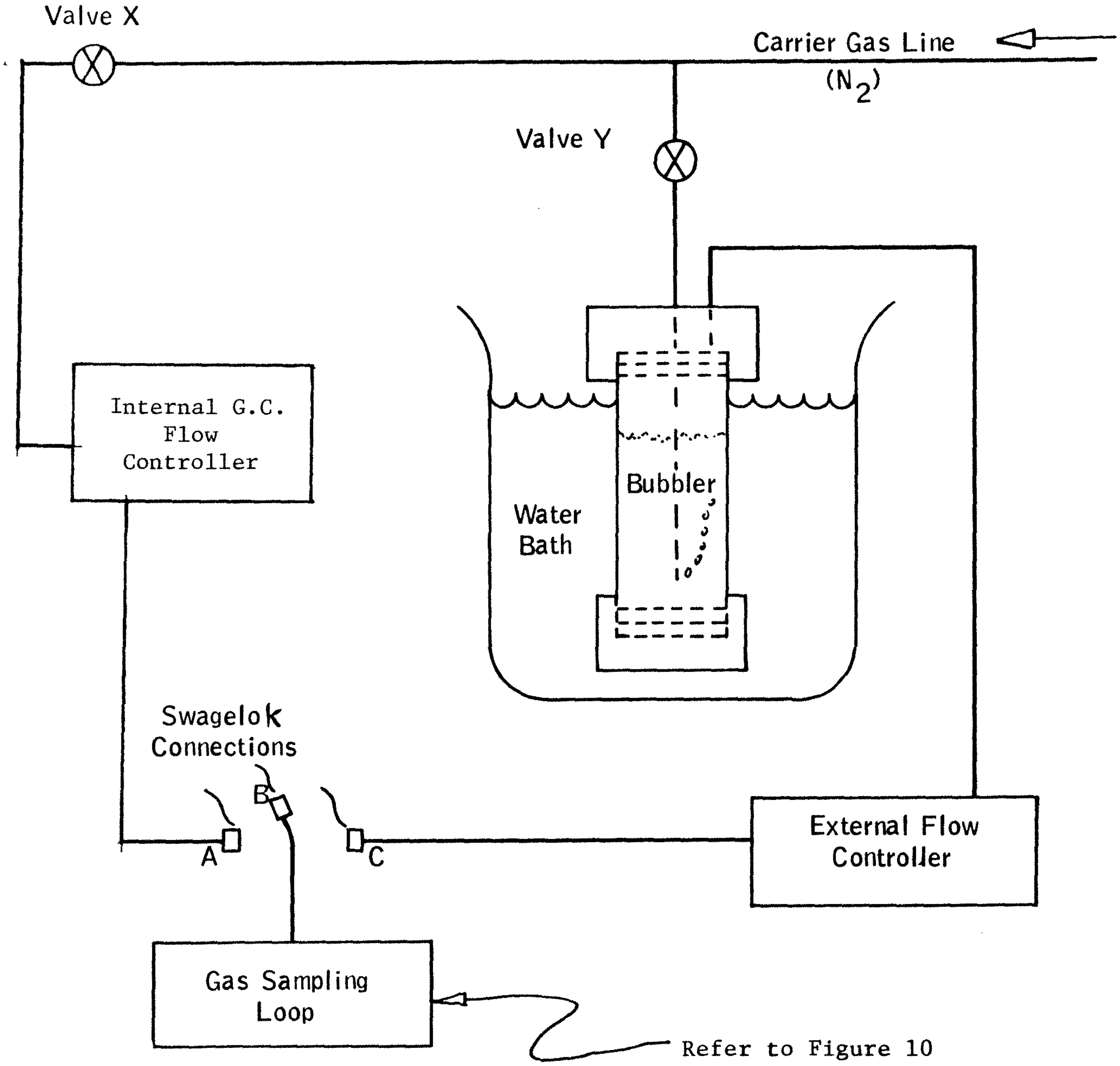
In the tests conducted on the affect of sample size on incipient elution for small injection volumes, vinyl chloride was used as the test adsorbate. Tests were performed by changing the injection loop coil of the gas sampling valve before each run. Injection loop coils of 0.25, 1.0, and 2.0 mls were used, while adsorbents chosen were Silica Gel and Porapak-T.

Humidity Study

The apparatus used in the humidity studies is shown in Figure 11. This apparatus was set up between the carrier gas line and the gas sampling valve. The bubbler, constructed from 5-1/2 long by 3/4-inch diameter (nominal) stainless steel tubing was filled with distilled water, and submerged in a water bath at between 5 and 15°C. Valve X was closed and Connection A separated from B. Opening Valve Y, the flow rate through the bubbler was adjusted to 50 ml/min by using the external flow controller and measuring the flow at Connection C. The humidity induction line was then connected to the gas sampling loop with Connections B and C. The system was allowed to equilibrate for 5 minutes before performing a run. Vinyl chloride was injected as the test sorbate following the same procedure for the "dry" test. Runs were performed on XAD-2, Silica Gel, and Porapak-T.

Figure 11

HUMIDITY APPARATUS



Detector Sensitivity

Since the response of a FID can vary markedly for different compounds and since varying amounts (weights) of sample were used for each adsorbate, various detector sensitivity settings were used. For vinyl chloride, the sensitivity was set anywhere from 4 to 6 x 10^{-12} amps/millivolt while the range of the liquid samples covered from 4 to 32 x 10^{-11} amps/millivolt.

VII. RESULTS AND DISCUSSION

Parameter Analysis

Normalized incipient elution volume values (V_N in ml/ml) are listed in Appendix C. These values are the product of the time to incipient elution taken from the chromatogram times the carrier gas flow rate, divided by the bulk adsorbent packing volume in the cartridge. Values were obtained using the displacement analysis technique where the sample is injected into the cartridge as a plug. Gallant et al. has indicated that these values would be the same if the frontal method were used instead.(1) This is important in that the frontal method, where a set sample concentration is continuously fed to the adsorbent, closely models the actual air sampling conditions.

In ambient air sampling, adsorbent cartridges of the same dimensions are usually used to negate any possible adsorption effects due to differences in cartridge geometries. It is, therefore, logical to employ the "bulk cartridge volume occupied by the adsorbent" as the parameter for normalization. In this way, sampling system adsorption capabilities can be directly compared, as evidenced in the work performed by Vidal-Madjar et al.(2) When using the more conventional normalization parameter of adsorbent mass, to compare adsorption potentials of adsorbents for a certain system where a specific size sampling cartridge is used, application of an additional factor "adsorbent bulk packing density" is required.

In this study, incipient elution volume was used as the main adsorption criterion. Arguments against using incipient elution volume as a parameter are that it is dependent on the dispersion of the chromatographic peak in the sorbent bed, and thus, it varies with flow rate and the randomness of packing.(3) Also, it is said to be difficult to precisely locate the point of incipient elution. These faults can be greatly minimized by tight packing of the adsorbent, by adjusting the G.C. electrometer readout sensitivity to an optimum level and by defining what sensitivity increment will be considered incipience on the chromatogram. In these experiments the so-called faults were well controlled, as evidenced by the good linearity of the data plots which will be discussed.

In most adsorption presentations, breakthrough volume data are taken at the peak height in the displacement method or at the challenge concentration in the frontal method (see Figure 1).(4) The breakthrough volume (Vg^T) from the displacement method is supposed to indicate that 50% of the amount of sample on the adsorbent has already eluted. This is based on the peak being located at the center of a symmetrical elution profile. Unless the shape of the isotherm is known, the actual amount to have broken through the cartridge at Vg^T cannot be accurately determined. This discrepancy occurs when there are strong specific adsorbate-adsorbent attraction forces present and when there is a large degree of adsorbate peak tailing. In the frontal method, V_F values are supposed to indicate that the same amount of adsorbate retained on the adsorbent has already eluted through the cartridge. This analysis has the same purported "failing" that incipient elution analysis has in that the actual location of the challenge concentration plateau is often difficult to pinpoint. A major problem with both of the above methods is that unless the exact isotherm shape is known, the amount of material eluted cannot be accurately determined.

In this study, the seven test adsorbates have been classified into two groups: Group 1, halocarbons, includes the following compounds, listed in order of increasing boiling point:

Vinyl Chloride (VCl)
Methylene Chloride
Chloroform
Carbon Tetrachloride (CCl_4)

Group 2, the oxy-hydrocarbons, are also listed below in order of increasing boiling point:

Acetaldehyde
Ethyl Ether
Ethyl Acetate

Figures R1 through R7 show plots of the natural logarithm (ln) for the normalized incipient elution volume (V_N) versus $10^3/T(^oK)$. These plots have been developed from the chromatographic data listed in Appendix C. Plots R1 through R7 are grouped for each adsorbate, and plots R8 through R17 are categorized according to each adsorbent. Of the 35 possible adsorbate-adsorbent combinations, data was obtained for 31. Those combinations not successfully obtained were

CCl_4 on Tenax, and Spherocarb, and ethyl acetate on Silica Gel and Spherocarb. From the plots of $\ln V_N$ versus $10^3/T(^{\circ}K)$, linear regression lines were determined in the form of $\ln V_N = \ln V_{io} + m\,(10^3/T)$. Termed the "characteristic elution equation," values from the equation are listed in Table R1.(5) As a check on linearity, values were calculated for the correlation coefficient(6) and the standard error of estimate.(7) Also listed in Table R1, the calculations for these two parameters are shown in Appendix E, based on the data compiled in Appendix H. For the correlation coefficient, the closer the value is to unity, the less deviation there is. In the standard error of estimate, for lines constructed parallel to the linear regression line at respective vertical distances Sy, 2Sy, and 3Sy, 68%, 95%, and 99.7% of sample points will fall between these lines. Analysis of the correlation coefficient and the standard error of estimate values for the 31 successful adsorbate-adsorbent combinations shows that all the plots exhibit good linearity without significant deviation, therefore allowing a certain degree of temperature extrapolation.

TABLE R1

Values from the Characteristic Equation

$$\ln V_N = \ln V_{io} + m \frac{10^3}{T}$$

$$V_N = V_{io} e^{\left[m\left(\frac{10^3}{T}\right)\right]}$$

Adsorbent	Adsorbate	Data Points	ln V_{io} (intercept)	(m) Slope (°K)	Correlation Coefficient	Standard Error of Estimate
Tenax	Vinyl Chloride	5	-15.572	5.724	.9973	.005
	Chloroform	5	-18.117	7.371	.9996	.026
	Methylene Chloride	4	-16.407	6.508	.9997	.021
	Ethyl Acetate	5	-21.003	8.549	.9994	.045
	Ethyl Ether	5	-21.645	8.159	.9992	.041
	Acetaldehyde	5	-19.664	6.964	.9994	.036
XAD-2	Methylene Chloride	5	-24.348	8.901	.9869	.205
	Chloroform	4	-29.468	10.960	.9984	.080
	Carbon Tetrachloride	4	-24.420	9.784	.9998	.018
	Acetaldehyde	4	-16.981	6.171	.9999	.015
	Ethyl Ether	5	-25.599	9.511	.9926	.185
	Ethyl Acetate	4	-25.653	10.196	.9988	.060
	Vinyl Chloride	5	-16.016	6.130	.9986	.039
Porapak-T	Carbon Tetrachloride	5	-17.675	8.316	.9996	.032
	Methylene Chloride	5	-16.452	7.493	.9997	.026
	Chloroform	5	-16.268	7.932	.9986	.048
	Acetaldehyde	5	-12.900	5.798	.9644	.051
	Ethyl Ether	5	-18.802	8.229	.9998	.015
	Ethyl Acetate	5	-18.880	8.963	.9979	.018
	Vinyl Chloride	5	-17.090	6.892	.9992	.025
Silica Gel	Vinyl Chloride	15	-14.181	6.672	.9961	.076
	Methylene Chloride	6	-11.157	6.091	.9986	.040
	Chloroform	4	- 9.945	5.785	.8470	.454
	Carbon Tetrachloride	4	-11.200	6.316	.9984	.035
	Acetaldehyde	5	-17.654	9.778	.9920	.094
	Ethyl Ether	7	- 9.760	5.190	.9780	.179
Spherocarb	Vinyl Chloride	7	- 8.987	6.088	.9987	.041
	Methylene Chloride	4	-10.754	7.282	.9985	.034
	Acetaldehyde	5	-10.243	6.548	.9971	.066
	Ethyl Ether	5	-11.396	8.622	.9996	.020
	Chloroform	5	-10.101	7.906	.9986	.030

FIGURE R1

Effect Of Temperature On Normalized Incipient Elution Volume (V_N) For Vinyl Chloride

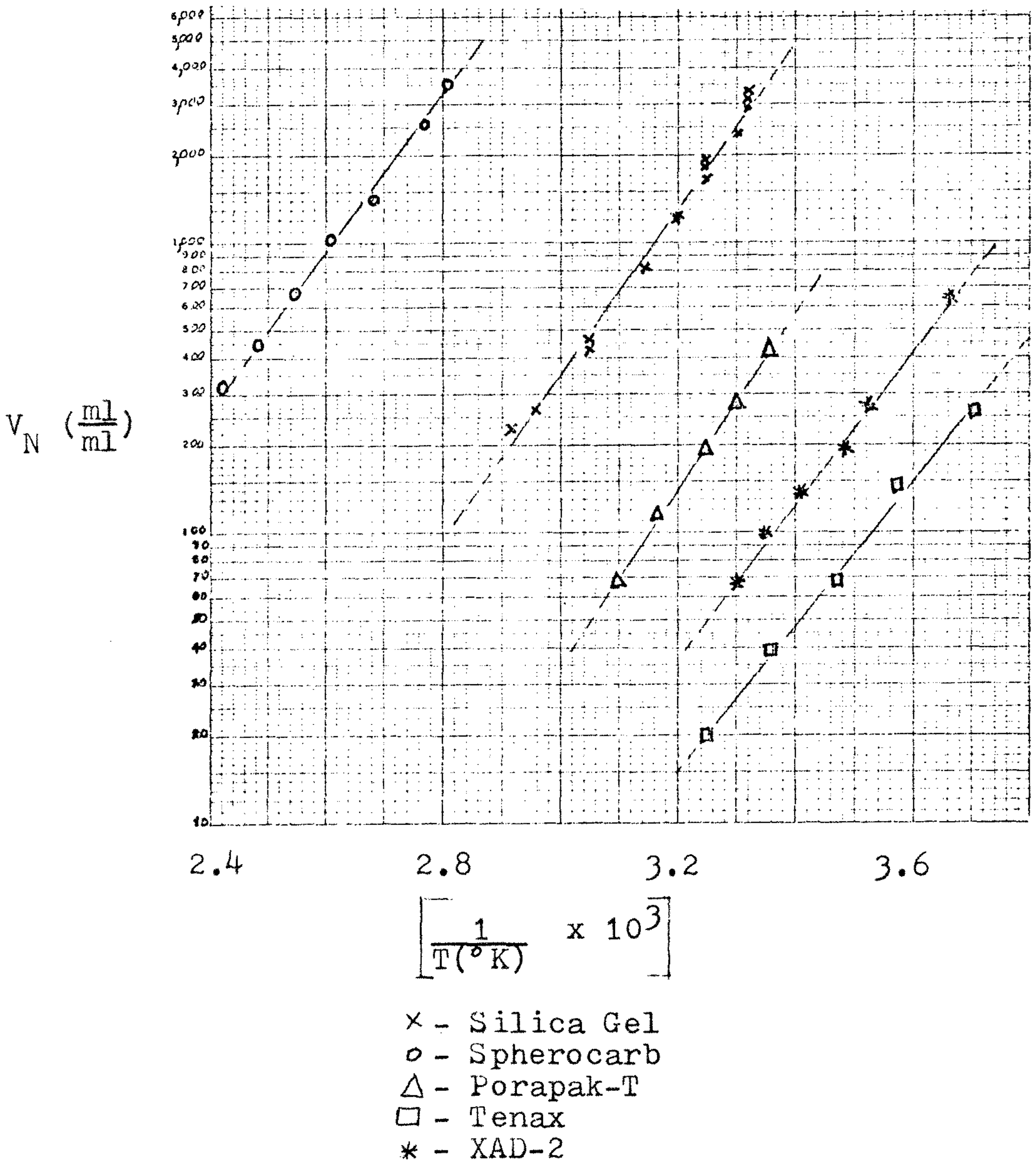


FIGURE R2

Effect Of Temperature On Normalized Incipient Elution Volume (V_N) For Methylene Chloride

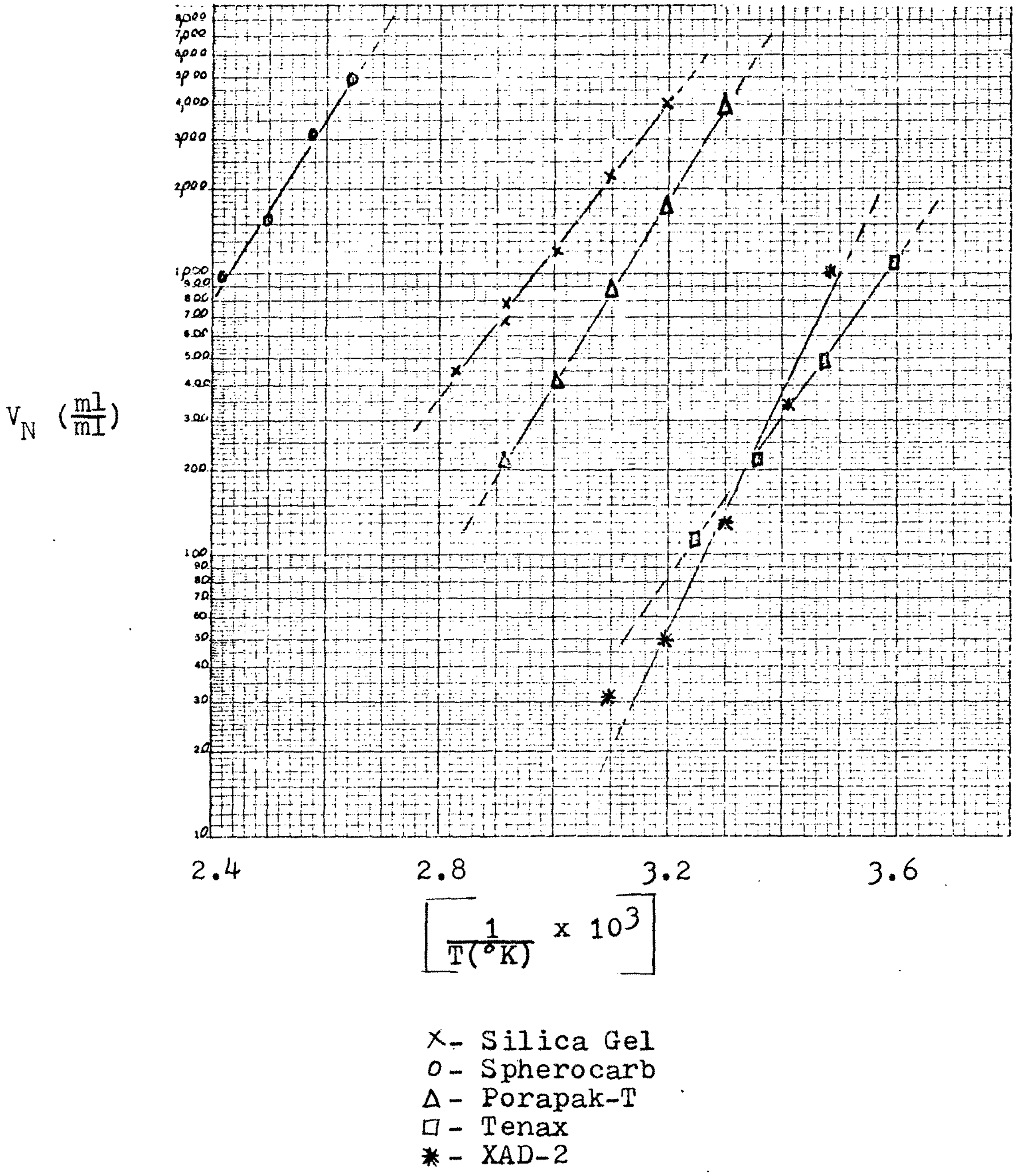


FIGURE R3

Effect Of Temperature On Normalized

Incipient Elution Volume (V_N)

For

Chloroform

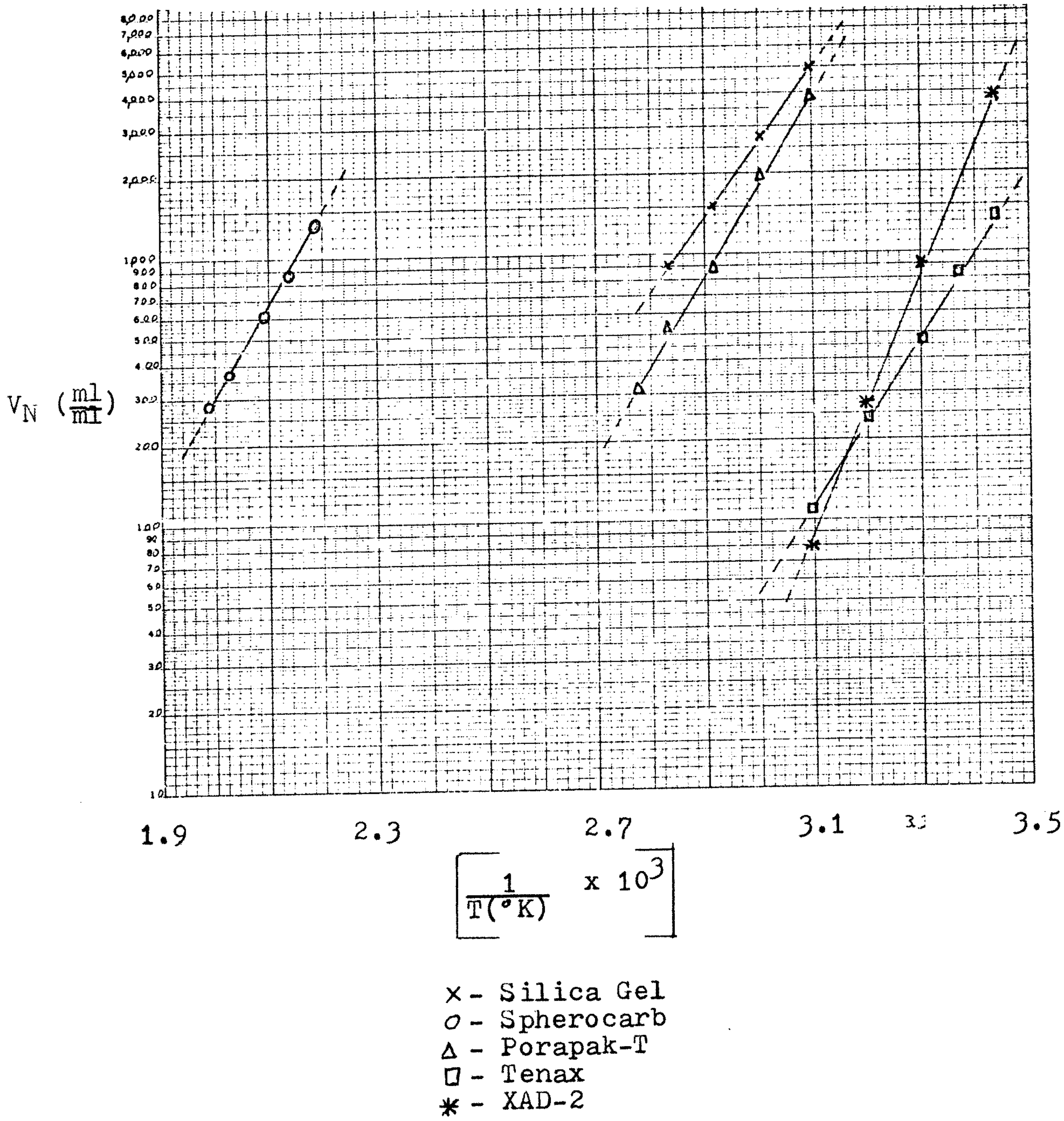


FIGURE R4

Effect Of Temperature On Normalized Incipient Elution Volume (V_N) For Carbon Tetrachloride

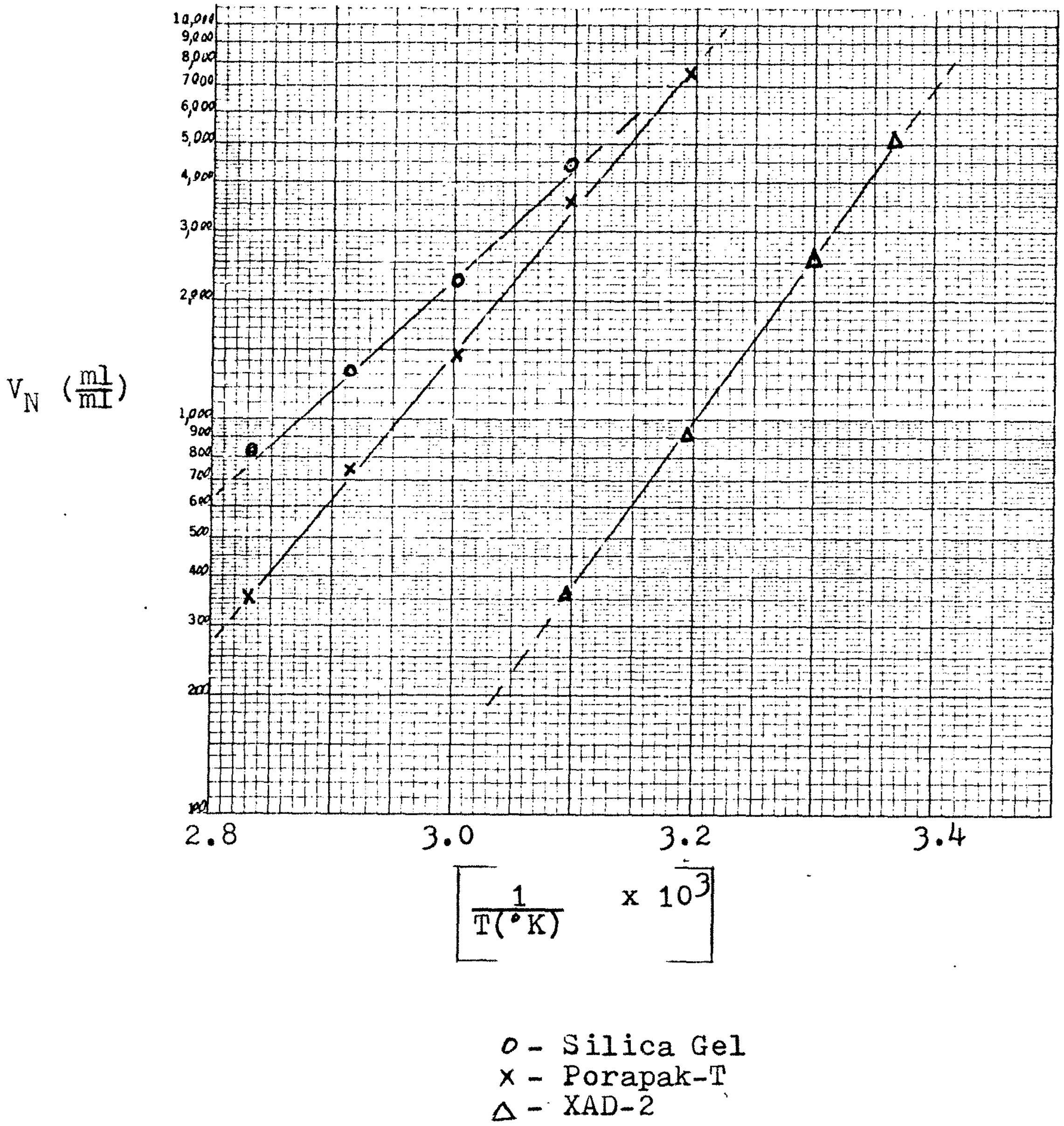


FIGURE R5

Effect Of Temperature On Normalized Incipient Elution Volume (V_N) For Acetaldehyde

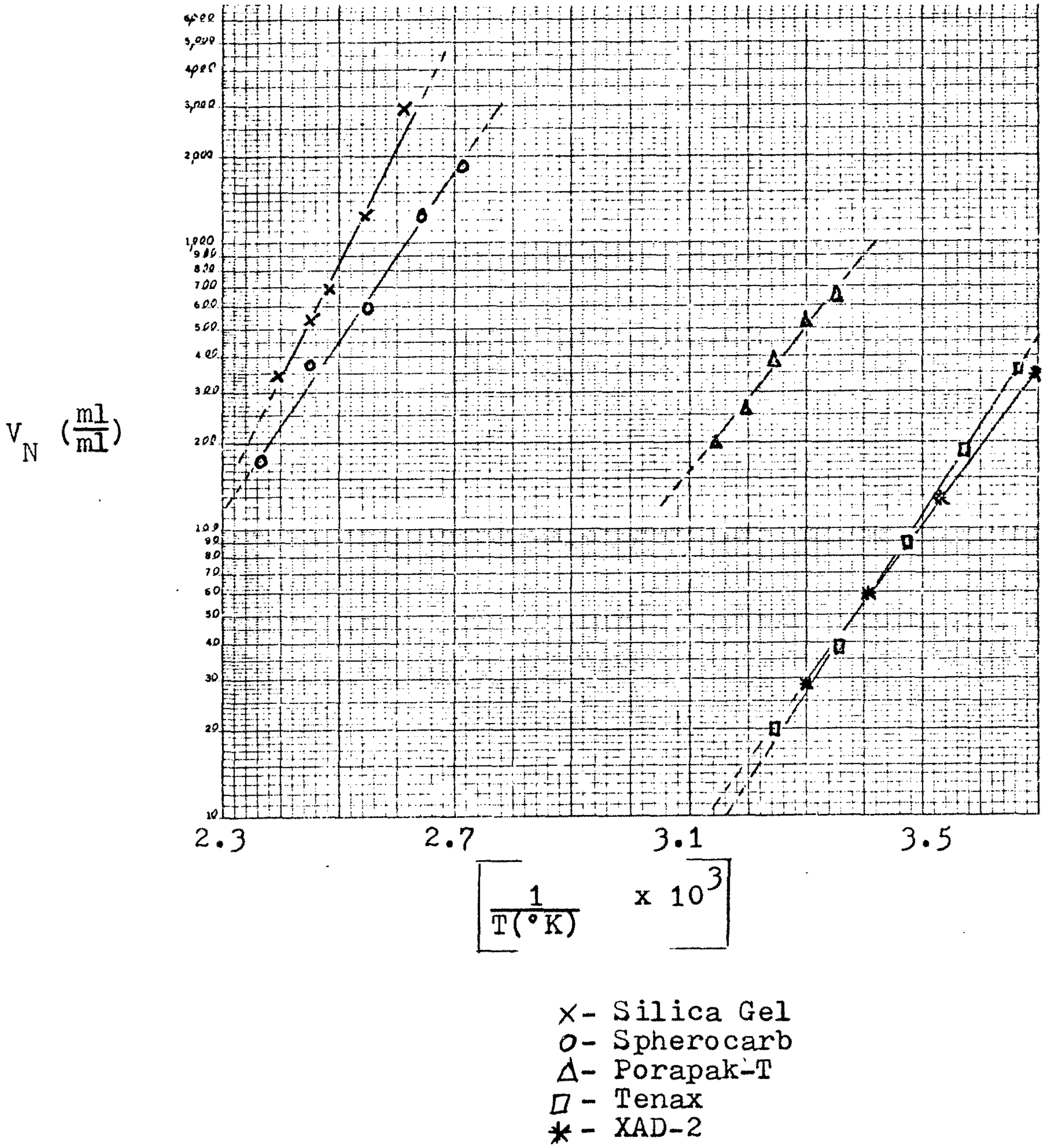


FIGURE R6

Effect Of Temperature On Normalized Incipient Elution Volume (V_N) For Ethyl Ether

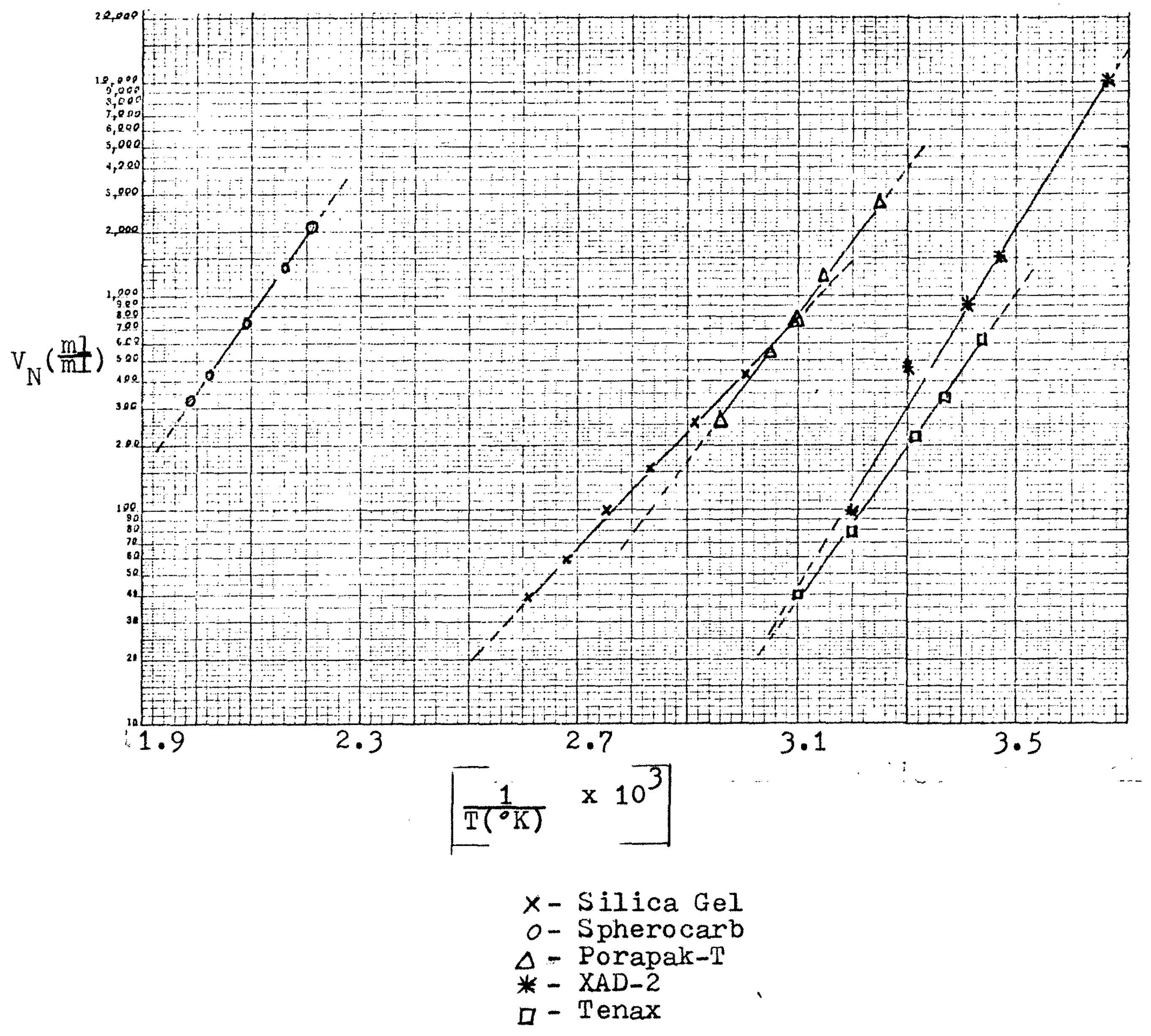


Figure R7

Effect Of Temperature On Normalized Incipient Elution Volume (V_N) For Ethyl Acetate

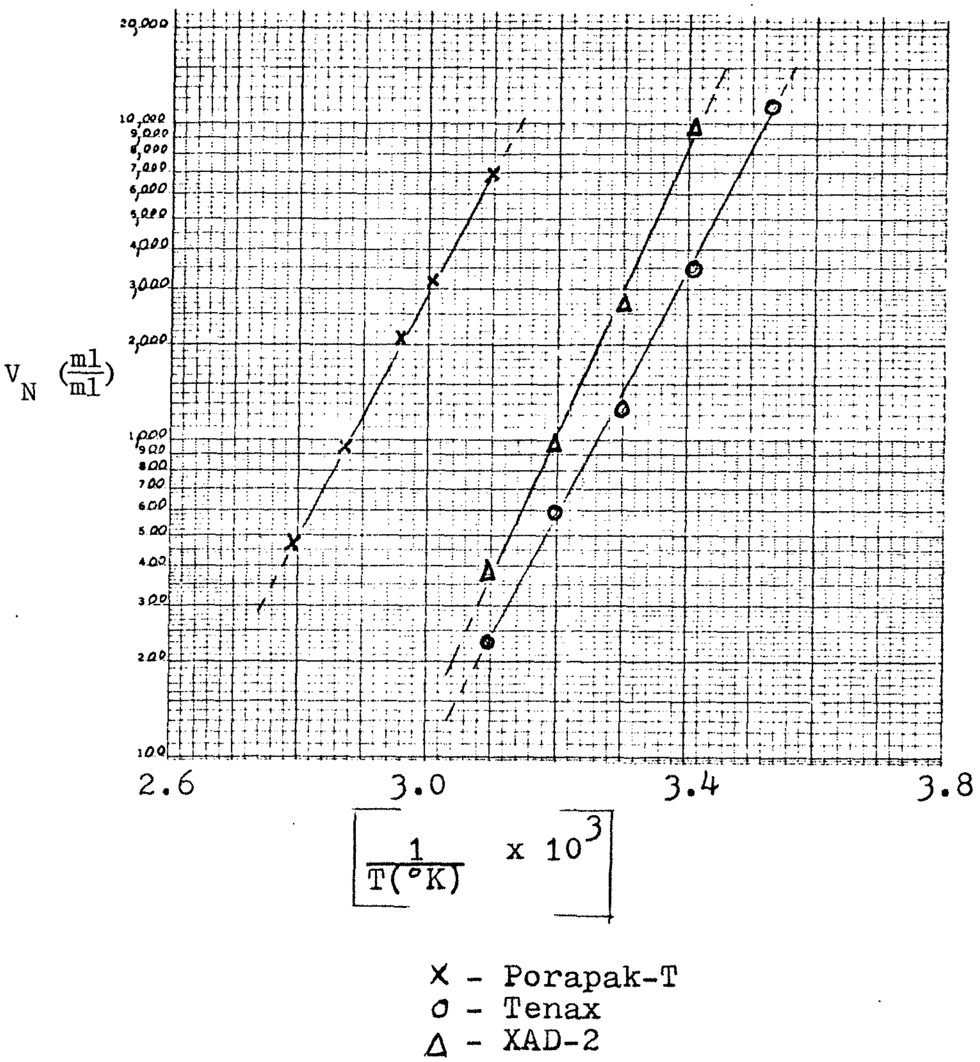


FIGURE R8

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Oxy-hydrocarbons on TENAX

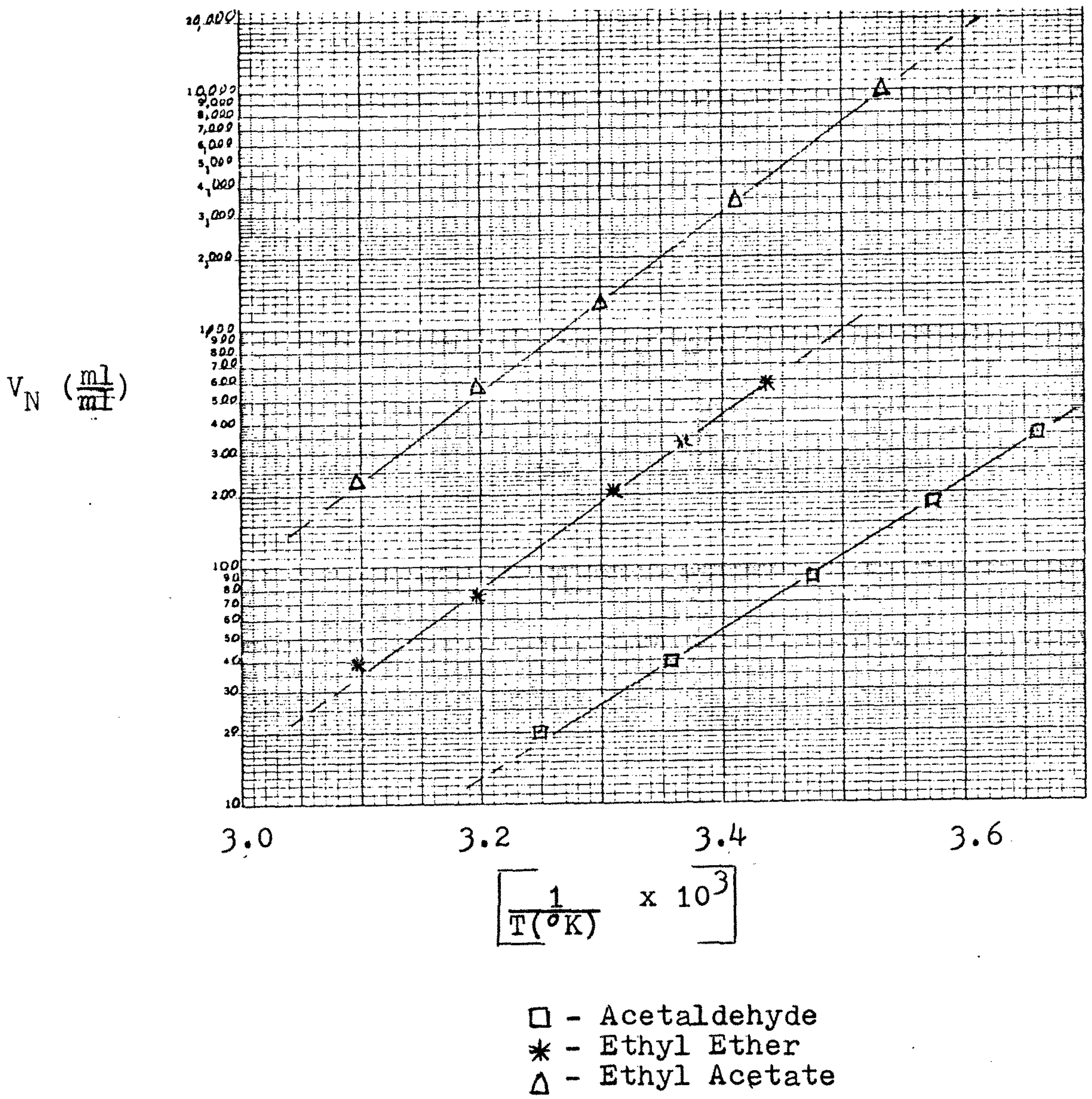


FIGURE R9

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Halocarbons on TENAX

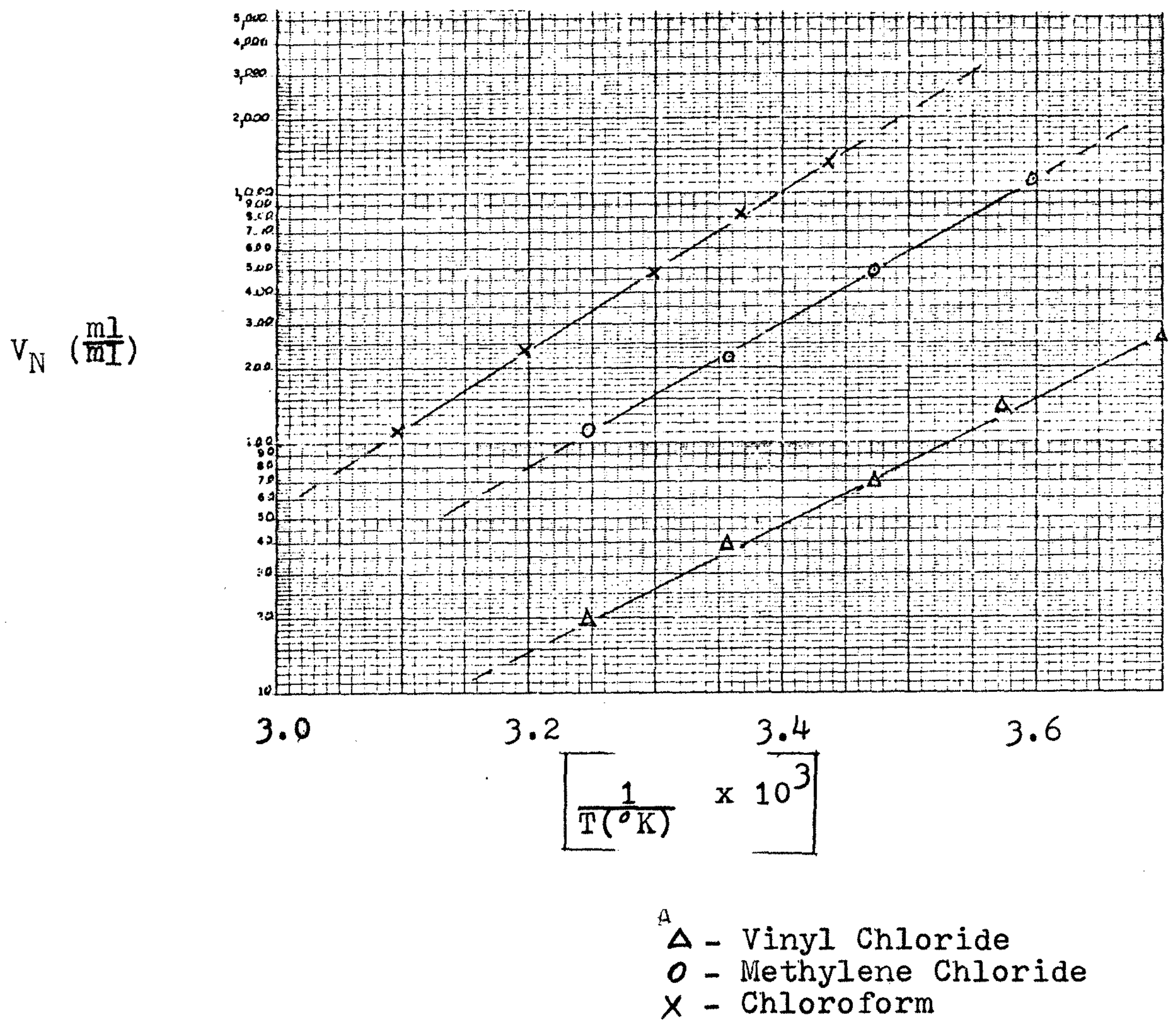


FIGURE R10

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Oxy-hydrocarbons on XAD-2

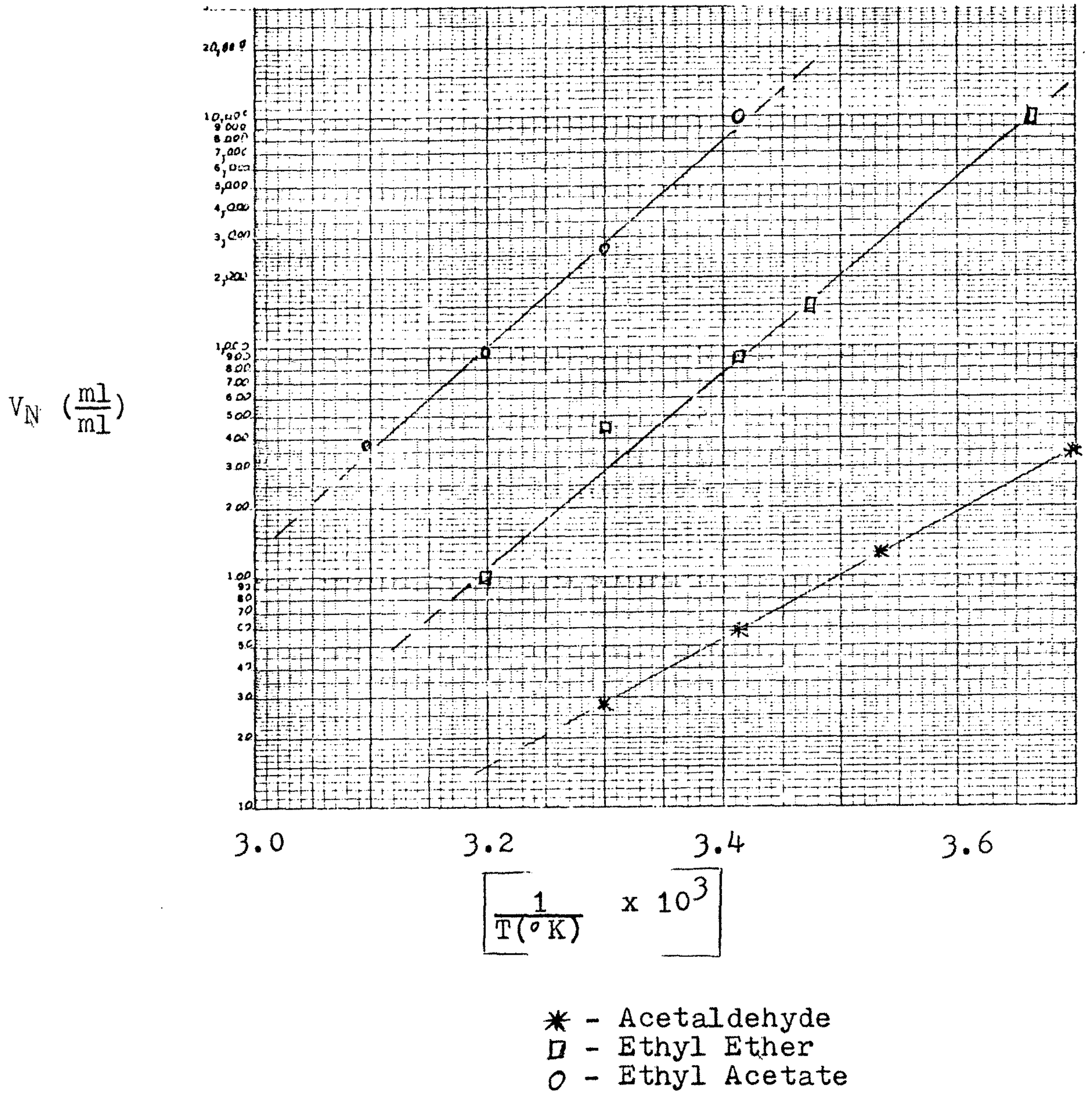


FIGURE R11

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Halocarbons on XAD-2

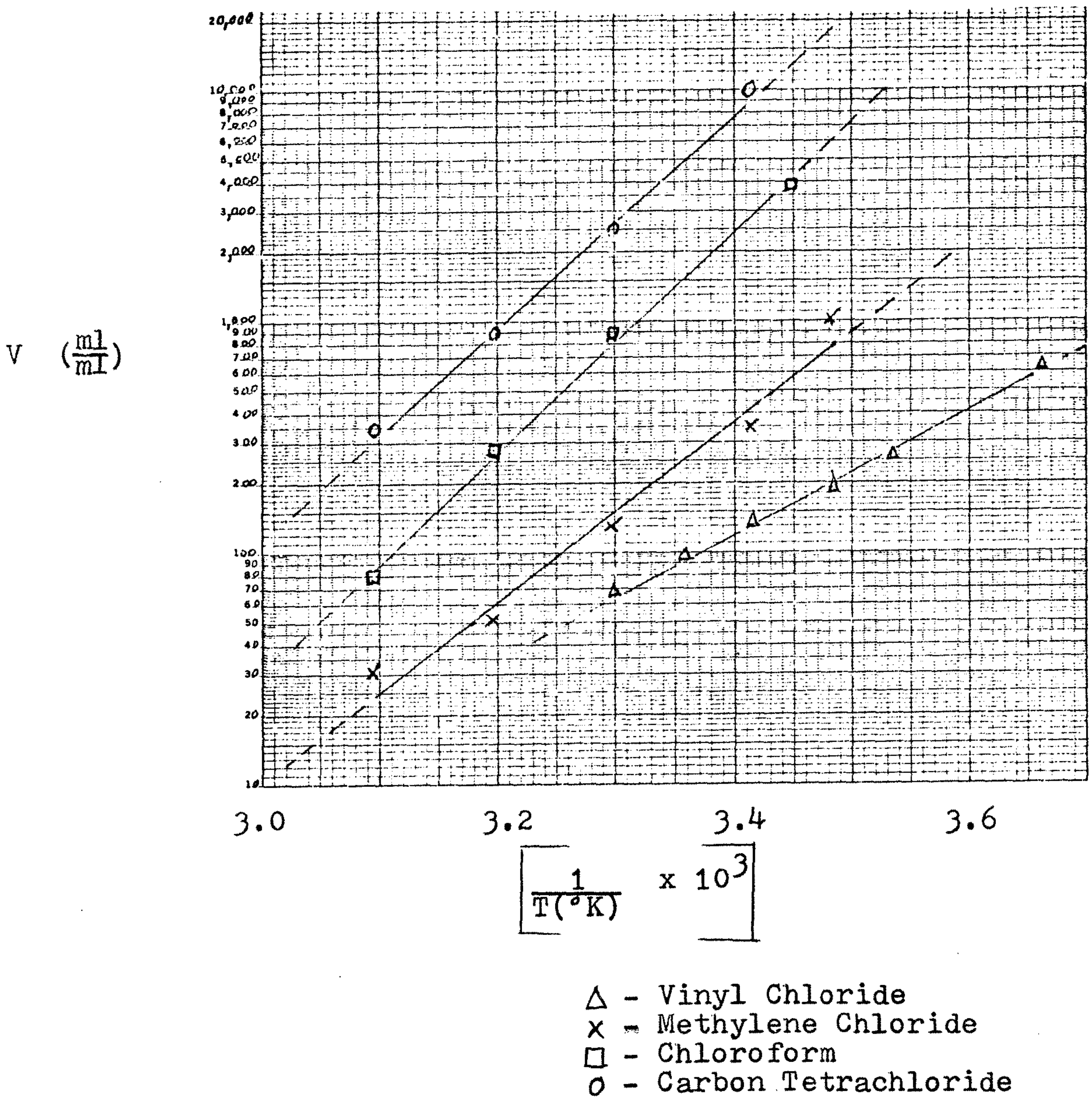


FIGURE R12

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Oxy-hydrocarbons on Porapak-T

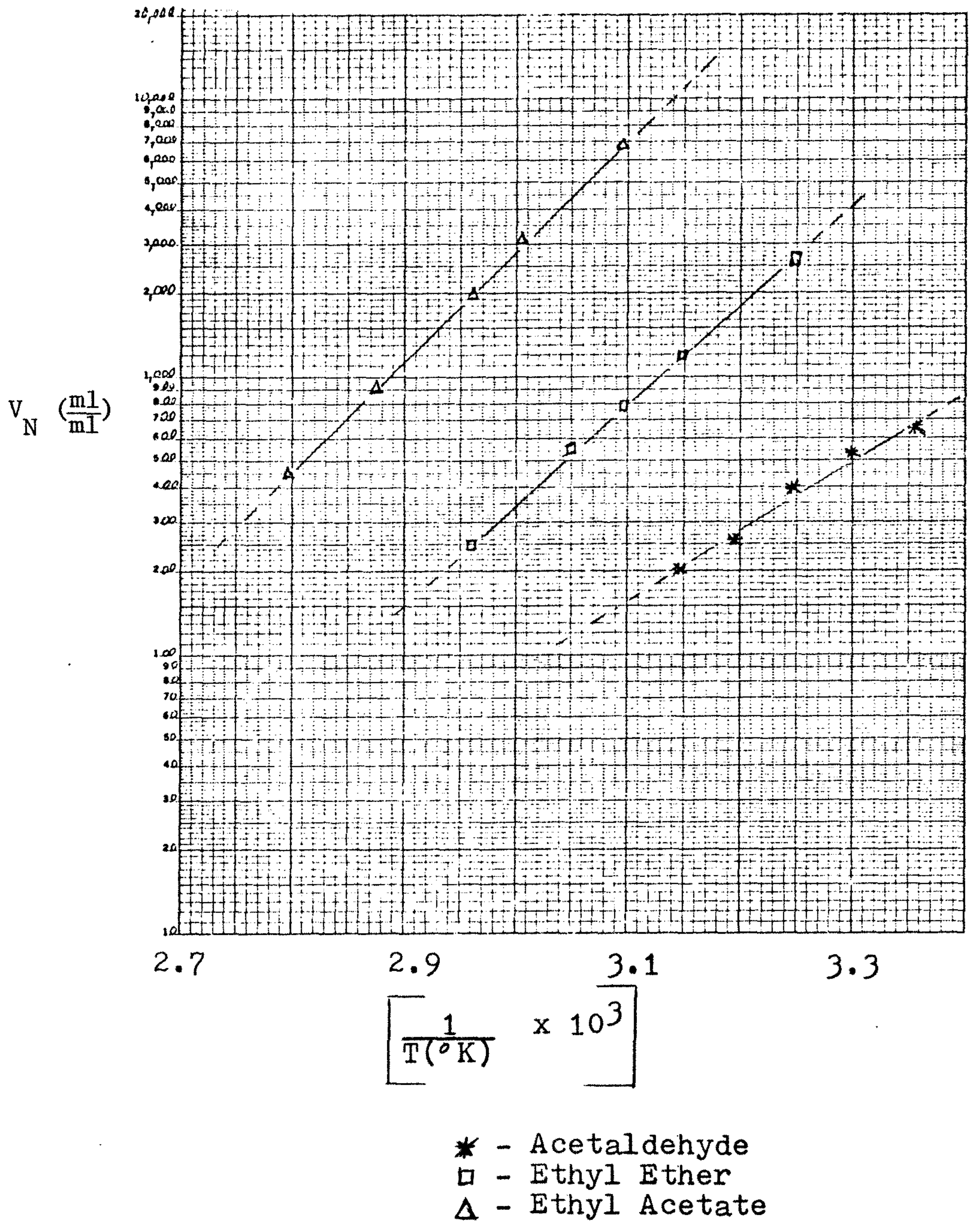


FIGURE R13

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Halocarbons on Porapak-T

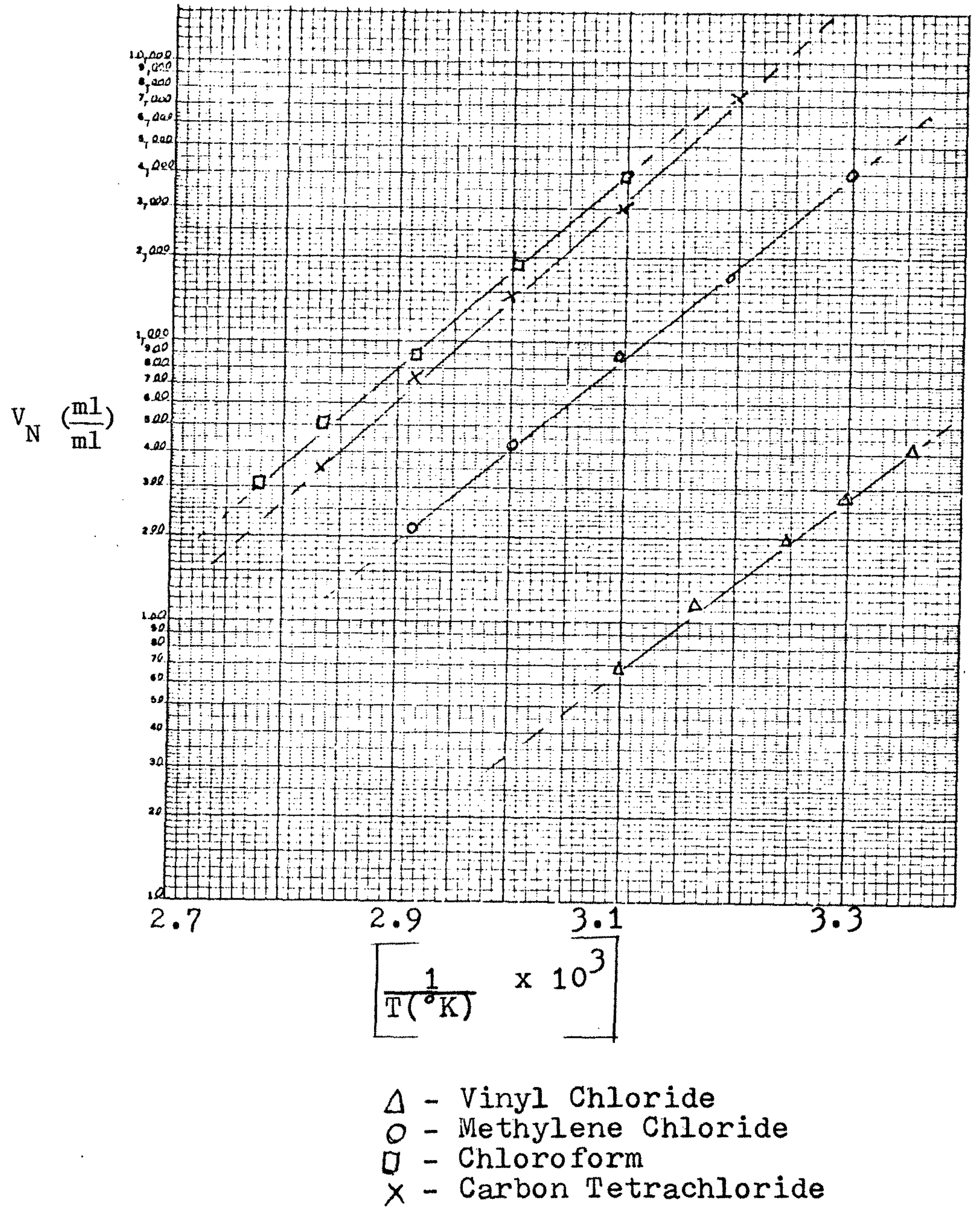


FIGURE R14

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Halocarbons on Silica Gel

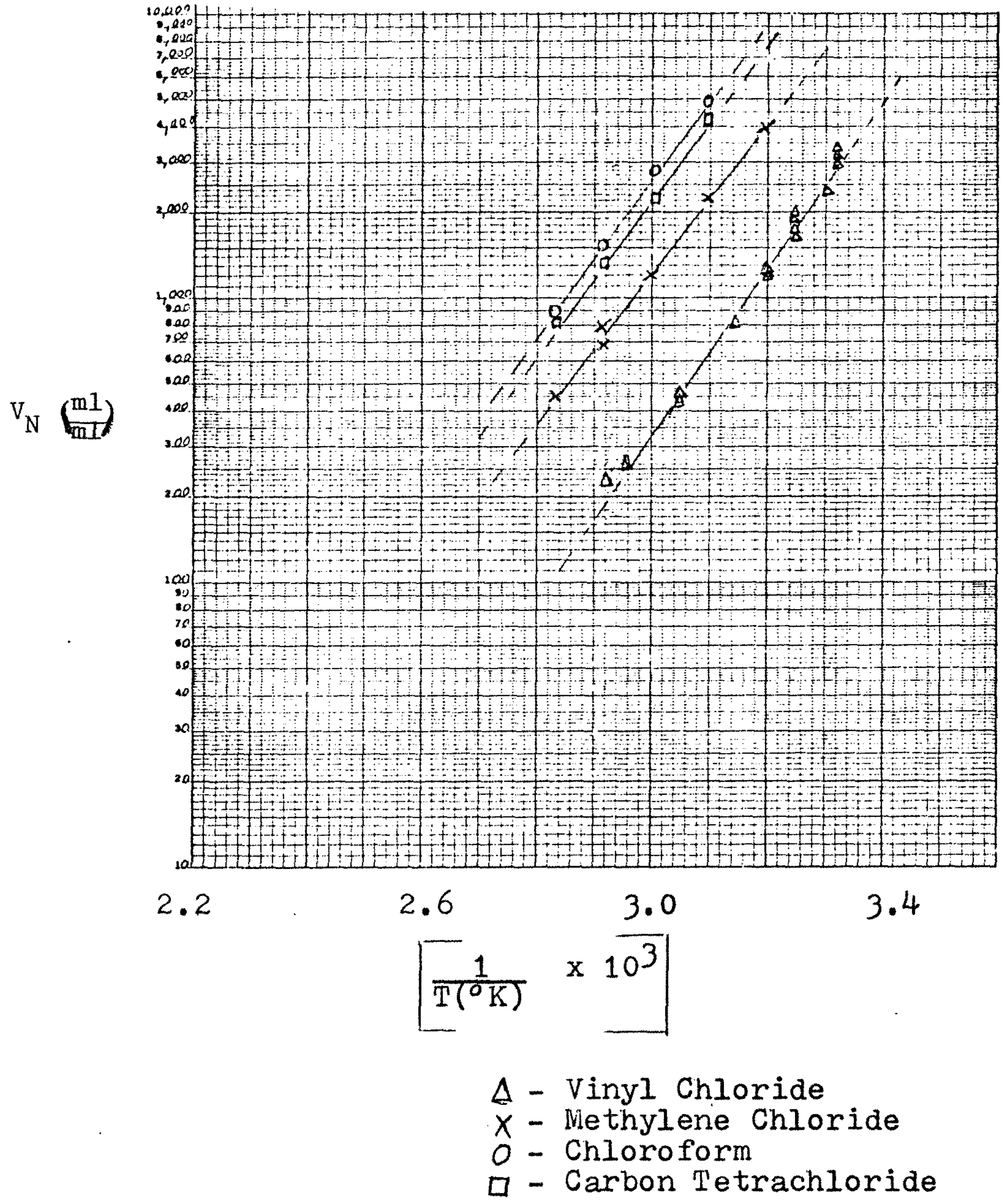


FIGURE R15

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Oxy-hydrocarbons On Silica Gel

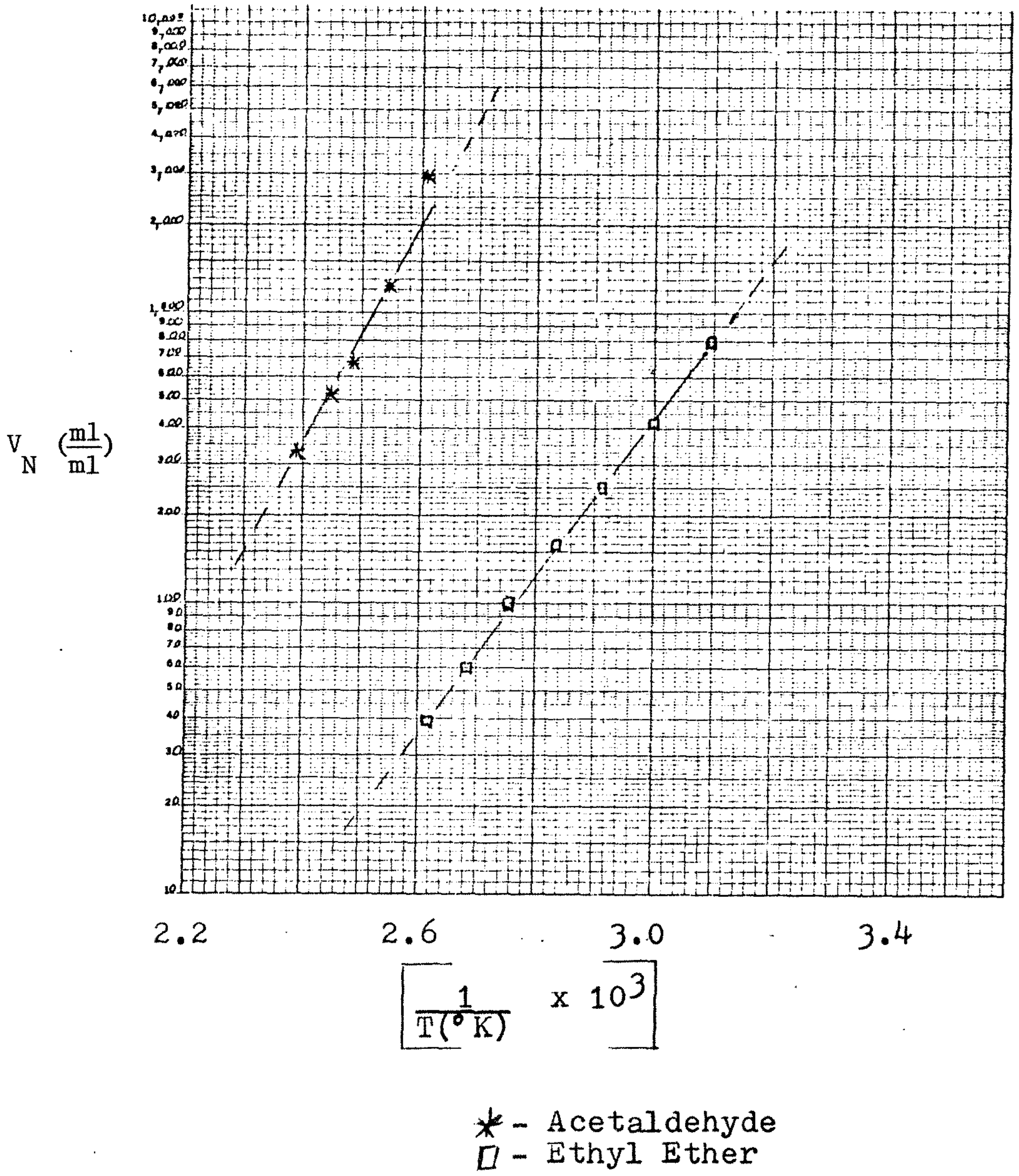


FIGURE R16

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Oxy-hydrocarbons on Spherocarb

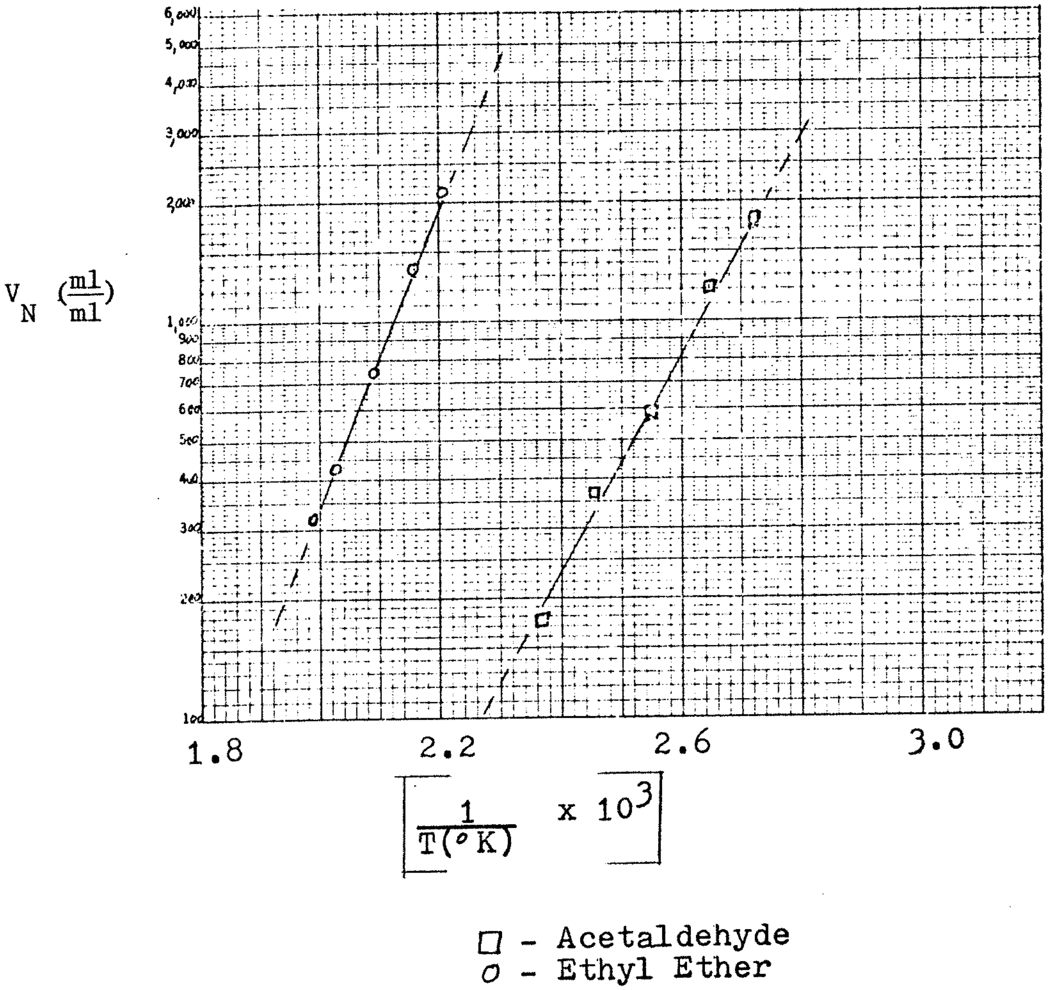
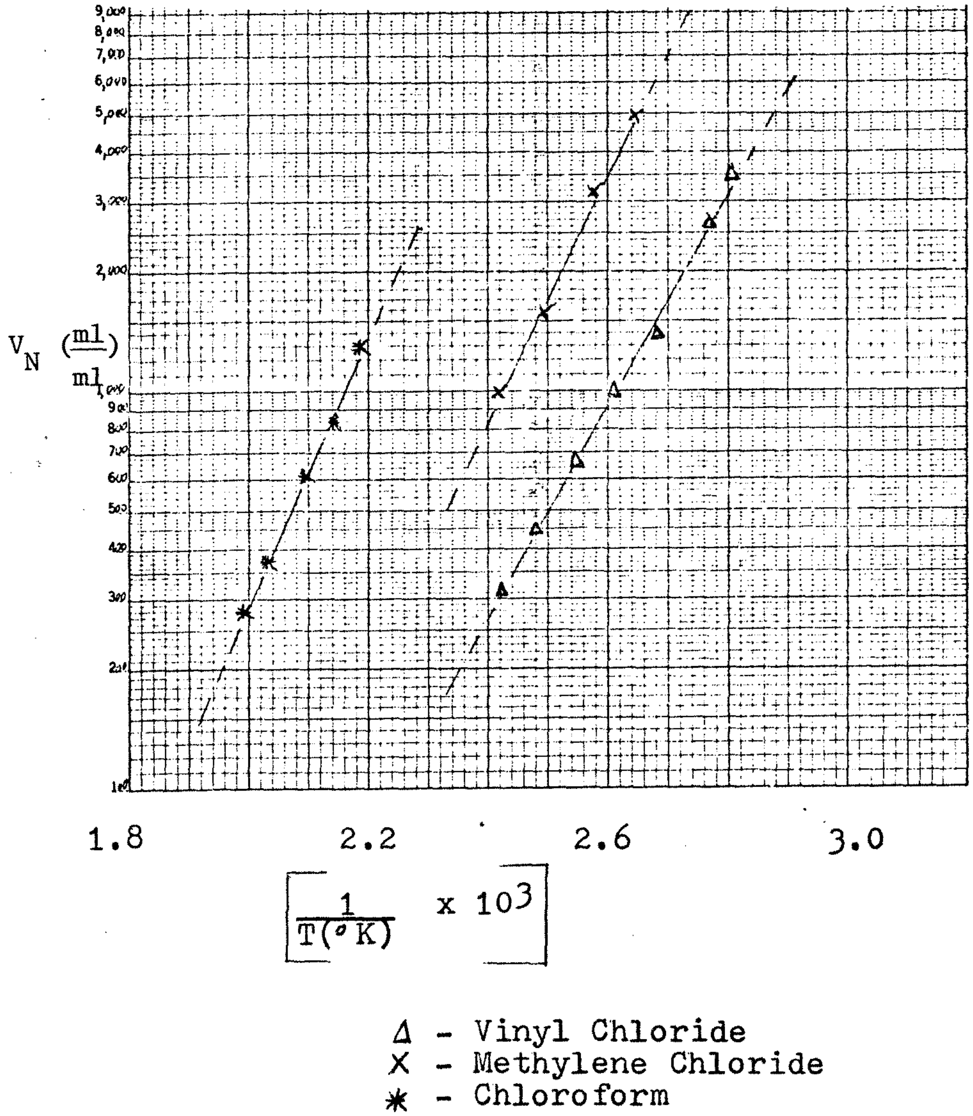


FIGURE R17

Effect Of Temperature On Normalized Incipient Elution Volume (V_N)

Halocarbons on Spherocarb



Adsorbates

Halocarbons: The experimentally determined plot for vinyl chloride (VCl) on each of the selected adsorbents is shown in Figure R1. Of the four tested halocarbons, VCl is the most volatile, and it has the lowest polarizability value (α); see Table R2. The order of increasing VCl retention at a given temperature on the five adsorbents is Tenax $<$ XAD-2 $\ll$ Porapak-T $\ll$ Silica Gel $<$ Spherocarb. Table R3 lists normalized incipient elution volumes (V_N) at 39.5°C and 21°C as derived from the characteristic elution equation. The magnitude of these values gives an indication of the strengths of the various adsorbents. Note that extrapolation to 21°C for Spherocarb is very extensive while extrapolation for XAD-2 and Tenax is minimal. In Figure R1 all the adsorbent lines have approximately the same slope. This result appears to be coincidental, but it is probably tied to the temperature dependence of elution, being similar for different adsorbents with very small amounts of adsorbate.

Elution plots for methylene chloride are shown in Figure R2. Of the four halocarbons, methylene chloride ranks second in both boiling point and polarizability. Adsorption is similar to that of VCl in that methylene chloride is greatly retained by Spherocarb, moderately retained by Silica Gel and Porapak-T, and retained to a much lesser degree by XAD-2 and Tenax G.C. The difference from VCl retention is that the slopes of the elution lines for methylene chloride are not nearly equal. The lines for Silica Gel and Porapak-T

TABLE R2

Adsorbate Values

Adsorbate	Vapor Pressure (torrs at 25°C)	Water Solubility (g/l)	Dipole Moment (Debye units)	Polarizability (Å^3)	Molecular Weight	Boiling Point (°C)
Vinyl Chloride	2660	1.1	1.45	6.15	62.5	-13.4
Methylene Chloride	436	slight	1.60	6.48	84.93	40
Chloroform	200	8.0	1.01	8.51	119.39	61.3
Carbon Tetrachloride	115	Insoluble	0	10.48	153.82	76.5
Acetaldehyde	923	Infinite	2.69	4.57	44.05	20.8
Ethyl Ether	442	slight	1.15	8.92	74.12	34.5
Ethyl Acetate	93	89	1.78	8.82	88.10	77.1

Note: Both a higher dipole moment and a lower polarizability value are indicative of a higher adsorbate polarity.

TABLE R3

V_N Values* at 39.5°C and 21°C

Adsorbent	Adsorbate	V_N (ml/ml) 21°C	 39.5°C
Tenax	Vinyl Chloride	49	16
	Chloroform	1,048	238
	Methylene Chloride	308	83
	Ethyl Acetate	3,214	575
	Ethyl Ether	449	87
	Acetaldehyde	56	14
XAD-2	Methylene Chloride	375	63
	Chloroform	2,467	272
	Carbon Tetrachloride	7,037	981
	Acetaldehyde	55	16
	Ethyl Ether	855	126
	Ethyl Acetate	8,327	1,069
	Vinyl Chloride	126	37
Porapak-T	Carbon Tetrachloride	4.06×10^4	7,600
	Methylene Chloride	8,390	1,860
	Chloroform	4.49×10^4	9,090
	Acetaldehyde	917	285
	Ethyl Ether	9,780	1,870
	Ethyl Acetate	1.10×10^5	1.81×10^4
	Vinyl Chloride	574	143
Silica Gel	Vinyl Chloride	4,980	1,300
	Methylene Chloride	1.42×10^4	4,160
	Chloroform	1.69×10^4	5,260
	Carbon Tetrachloride	2.93×10^4	8,200
	Acetaldehyde	5.98×10^6	8.35×10^5
	Ethyl Ether	2,680	942
Spherocarb	Vinyl Chloride	1.23×10^5	3.61×10^4
	Methylene Chloride	1.22×10^6	2.82×10^5
	Acetaldehyde	1.68×10^5	4.48×10^4
	Ethyl Ether	6.13×10^7	1.08×10^6
	Chloroform	1.96×10^7	3.99×10^6

* V_N values were derived using the values found in Table R1 for the characteristic elution equation.

begin to converge at high $10^3/T$ values, while those for XAD-2 and Tenax intersect. This occurs with chloroform also, as shown in Figure R3. Ranked third among the halocarbons in boiling point and polarizability, chloroform follows an adsorption pattern very similar to that for methylene chloride. Table R2 lists V_N values for chloroform and methylene chloride at 39.5°C and 21°C as a comparison of relative adsorbate-adsorbent strengths. Here, there is some extrapolation for Porapak-T and Silica Gel and a large degree of extrapolation for Spherocarb.

Figure R4 shows the elution plots obtained for CCl_4. Of the five adsorbents tested, CCl_4 results were only obtained for three. An elution plot was not obtained for CCl_4 or Tenax as elution occurred immediately upon injection, even at temperatures as low as 0°C. Since CCl_4 has the greatest boiling point in Group 1, this lack of adsorption suggests that the effect of other forces in addition to dispersion forces must be present to a certain degree to promote adsorption, even when dealing with high boiling compounds. This effect (termed "specificity") is a mutual adsorbate-adsorbent attraction based upon chemical, ionic, or polar interactions. CCl_4 is a very non-reactive, stable, symmetrical molecule with a dipole moment of zero and a high polarizability value ($\alpha = 10.48$). Its low polarity, coupled with the presence of very strong electron withdrawing chlorine atoms, probably limit the interaction of CCl_4 with the low polarity Tenax.

An elution plot of CCl_4 on Spherocarb was not obtained because CCl_4 did not readily or reproducibly elute, even at temperatures as high as 190°C. This is because of the high trapping ability of carbon molecular sieves for high boiling compounds. The CCl_4 probably becomes so strongly solvated in the lattice cage of Spherocarb that desorption becomes difficult and non-uniform. Carbon molecular sieves operate most effectively on a certain range of adsorbate molecule sizes, based on the sieve pore size. CCl_4 was evidently within the range required by Spherocarb for efficient adsorption.

The three illustrated elution plots for CCl_4, seen in Figure R4, follow the basic trends that methylene chloride and chloroform follow. Porapak-T and Silica Gel have moderate adsorption capabilities compared to Spherocarb. They have much greater adsorption capacities than XAD-2, which is shown in the V_N values for these three adsorbents, listed in Table R3.

Oxy-Hydrocarbons: The experimentally determined plots for the three oxy-hydrocarbon adsorbates are shown in Figures R5, R6, and R7. Acetaldehyde, shown in Figure R5, is highly adsorbed by Silica Gel and Spherocarb, moderately adsorbed by Porapak-T, and only slightly adsorbed by XAD-2 and Tenax. This trend is very similar to that for methylene chloride, chloroform, and CCl_4, except that here Silica Gel retains acetaldehyde to a greater extent, even more than Spherocarb. As discussed in the Adsorbents section, Silica Gel is polar and shows facile adsorption with polar molecules. Moreover, the structure of Silica Gel causes it to retain a large degree of water even at high temperatures. Since acetaldehyde is extremely polar ($\alpha = 4.57$), and since it has an infinite solubility in water, acetaldehyde is tenaceously held by the Silica Gel. The V_N values listed in Table R3 verify this. It should be noted here that the values listed for Silica Gel and Spherocarb at 21°C and 39.5°C incorporate a large degree of extrapolation due to tenacity of the adsorbent.

Figure R6 shows the elution plot for ethyl ether. The adsorption trends and the slopes of the plot lines for ethyl ether are similar to those for methylene chloride and chloroform. Silica Gel, however, does not change the trend as it does for acetaldehyde. This is probably due to the low polarity of ethyl ether and its slight solubility in water. V_N values are listed in Table R3. Again, Spherocarb values were derived using extrapolation while a lesser degree of extrapolation was used for Silica Gel and Porapak-T values.

The plot for the third oxy-hydrocarbon tested, ethyl acetate, is shown in Figure R7. Again, results for only three adsorbents were obtained. The two adsorbents which did not yield results were Spherocarb and Silica Gel. As mentioned previously for CCl_4, Spherocarb is very retentive towards high boiling compounds. Ethyl acetate also has the highest boiling point of all seven adsorbates tested. Its lack of elution from Silica Gel can be attributed to dispersion forces (based on boiling point), specificity due to high adsorbent polarity, and attraction based on ethyl acetate's polarity and high water solubility(8) (89 g/l). The adsorption capacities of the three remaining adsorbents show that XAD-2 and Tenax have similar, low capacities whereas Porapak-T has a greater capacity. Here, the plots for XAD-2 and Tenax do not intersect, although they converge at very low V_N values. V_N values for the three adsorbate-adsorbent combinations are listed in Table R3, where some extrapolation for Porapak-T was required.

In Figures R1 through R7 the trapping capacities of Tenax and XAD-2 are very similar, with XAD-2 being slightly higher. This concurs with Gallant et al.,(9) who noted that both resins are approximately equivalent in their capacity to trap sorbent vapors at a given challenge concentration. This interaction is due predominantly to non-specific dispersion forces between adsorbent and adsorbate yielding Type I, Langmuir isotherms. This is of interest because both Tenax and XAD-2 have the potential for specific interactions.

Holzer et al.(10) performed tests on Tenax and found the following breakthrough volumes at $25^{\circ}C$: 5.1 l/g for chloroform, 25.1 l/g for CCl_4 and 30.1 l/g for ethyl acetate. Since it was not indicated in the article, it is assumed that these values are for peak elution (Vg^T), and thus, values for incipient elution would be somewhat less. The values obtained in this study from the experimental plots, converted to the proper units are: 5.8 l/g for chloroform, 0 l/g for CCl_4, and 16.5 l/g for ethyl acetate. The chloroform values for the two analyses concur very well. The discrepancy in ethyl acetate values, off by close to a factor of 2, can probably be attributed to somewhat different testing systems and the peak height elution point determination. Holzer used a 152.4 cm (5 feet) x 1/8 inch (no i.d. given) stainless steel cartridge packed with 0.95 g of Tenax. No indication was given of the sampling flow rate. The system used in this study consisted of a 14 cm x .216 cm i.d. stainless steel cartridge packed with .065 g of Tenax, and operated at a flow rate of 50 ml/min. The values obtained in this study were interpolated directly from the experimental data. Holzer's values were extrapolations from tests performed at between 100°C and 200°C. Since Holzer's data was presented on semi-logarithmic plots, interpretation errors were magnified. It is reasonable to conclude that Holzer's extrapolated values incorporate this margin of error. More significantly though, the major discrepancy between the two analyses lies in the values for CCl_4 retention. Herein, it was found that CCl_4 was not retained by Tenax, eluting immediately upon injection. This major discrepancy must be explained by the combination of larger adsorbent volume, i.e., longer column length in Holzer's work, and the very low adsorbent retention ability of Tenax for CCl_4. Evidently, CCl_4 retention on Tenax is more dependent upon diffusion into the pores of the Tenax rather than adsorption onto its surface. This would require a certain amount of adsorbent-adsorbate contact time. While Holzer did not indicate a linear velocity through his column, assuming a 30 ml/min flow rate conventionally used with a F1D and an 1/8 inch column of the same i.d. as used in this study (.216 cm), a linear velocity of 18.2 cm/sec would be achieved. This would yield an 8.4 second adsorbate-adsorbent contact time in the 152.4 cm (5 feet) long column.

In comparison, a 30.3 cm/sec linear velocity used in this study yielded a contact time of 0.46 seconds. This significantly demonstrates the value in the type of measurements taken in this study using adsorbent cartridges and flow rates which much more closely resemble actual sampling conditions, where this data is meant to be utilized. The discrepancy also dramatizes the effects of adsorption rates. Obviously, low flow (linear) velocities allow more time for adsorbent-adsorbate interaction permitting a larger degree of retention.

Tests on the trapping capacities of Tenax and Porapak-T for methylene chloride, chloroform, and CCl_4 have been reported by Vidal-Madjar et al.(11) Elution values obtained at 20°C on Tenax were: 170 ml for methylene chloride, 660 ml for chloroform, and 1100 ml for CCl_4. These values were based on a total cartridge adsorbent packing volume of 1.2 ml. Equivalent values obtained herein from experimentation, converted to a cartridge volume of 1.2 ml are 384 ml for methylene chloride, 1320 ml for chloroform, and 0 ml for CCl_4. Differences in values for methylene chloride and chloroform can be attributed to different testing systems. Vidal-Madjar reported using a 10 cm x 4 mm i.d. cartridge packed with Tenax (60/80 mesh) with a packing density of .207 g/ml. Again, no indication of system flow rate was given. The Tenax (60/80 mesh) cartridge used in this study had a packing density of 0.127 g/ml. A note of concern is that Adams et al.(12) reported the density of Tenax (35/60 mesh) to be .128 g/ml. As the bulk density of an adsorbate should be greater for larger mesh numbers, a comparison with the packing density value given by Adams indicates that the cartridge used in this study was packed relatively tight, while the cartridge used by Vidal-Madjar was packed extremely tight. It is possible that the greater packing density might have lead to channelling of the adsorbent when gas was forced through the tightly packed Tenax particles. This channelling would have then effected lower adsorption capacities. The values reported by Vidal-Madjar found a significant retention for CCl_4 whereas CCl_4 eluted immediately upon injection in this study. Again, this is probably attributed to the dependence of pore diffusion for adsorbent retention on adsorbate-adsorbent contact time.

Vidal-Madjar also reported the following elution values for Porapak-T at 60°C: 530 ml for methylene chloride, 1100 ml for chloroform, and 800 ml for CCl_4. This compares to 516 ml for methylene chloride, 2368 ml for chloroform, and 1781 ml for CCl_4 found in this study. The values for methylene chloride closely agree, while those for chloroform and CCl_4 again differ by about a factor of two. More significant, both analyses show that chloroform has a greater retention on Porapak-T than does CCl_4, owing to the fact of Porapak-T specificity. The 100/200 mesh Porapak-T used by Vidal-Madjar had a packing density of .493 g/ml as opposed to a .404 g/ml packing density for the 100/120 mesh Porapak-T used here. While the difference in packing densities could partly be due to differing mesh sizes, it is still probable that the Vidal-Madjar cartridge was more tightly packed than the cartridge used in this study. As such, this could account for lower adsorption values due to channelling of the adsorbate. An interesting fact to note is that exclusive of CCl_4 on Tenax, four of the five values reported by the two analyses differed by about a factor of 2.(13)

Adsorbents

Adsorption plots drawn up for each of the five adsorbents are shown in Figures R8 through R17. The trend for increasing adsorption usually follows the adsorbate boiling point, as based on dispersion forces. Deviations from this progression readily show up in these plots. In Figure R8, the relative adsorption of the oxy-hydrocarbons on Tenax follows the trend based on boiling point. In Figure R9, however, the halocarbons do not follow this progression as CCl_4 is not retained by Tenax. As previously mentioned, this lack of adsorption is based on the fact that the lowly polar Tenax will not interact with the CCl_4 as CCl_4 is compact, minimally polar, and contains the highly electron withdrawing chlorine atoms. Therefore, CCl_4 does not have surface charges readily available to promote adsorption.

The adsorption plots for XAD-2, pictured in Figures R10 and R11 for Group 1 and Group 2 adsorbates, both follow the trend based on boiling point. This is also the case for oxy-hydrocarbon retention on Porapak-T, shown in Figure R12. Halocarbon retention, however, does not follow this order. Seen in Figure R13, chloroform exhibits a greater degree of adsorption than CCl_4. This is in concurrence with the progression shown by Vidal-Madjar,(14) et al. where chloroform was better retained than CCl_4, which was better retained than methylene chloride. This can be attributed to a stronger adsorbent-adsorbate attraction (specificity) for chloroform than for CCl_4. Porapak-T is a moderately polar adsorbent, as indicated by McNair and Bonelli,(15) and as such, selectively adsorbs polar molecules to a much greater extent than non-polar ones. As shown in Table R2 values, chloroform has a certain degree of polarity (α= 8.51), whereas CCl_4 is minimally polar (α= 10.48). Again, CCl_4 has electron withdrawing chlorine atoms which limit polar attraction with an adsorbent. Chloroform's significant degree of specific adsorbate-adsorbent attraction, when coupled with adsorption based on dispersion forces, gives chloroform a higher retention on Porapak-T than CCl_4 which does not exhibit strong specific adsorbate-adsorbent attractive forces.

As indicated earlier, Silica Gel is a very polar adsorbent which chemically retains a certain degree of water, even at high temperatures. Therefore, adsorption on Silica Gel, in addition to depending on dispersion forces, also depends on adsorbate polarity and solubility. In Figure R14, the halocarbons were retained according to the same progression as shown for Porapak-T, with chloroform retention slightly greater than that for CCl_4. As mentioned for Porapak-T, this can be attributed to a combination of dispersive forces and specific adsorbate-adsorbent interaction forces prompted by the polarity of chloroform. Here, this is more prevalent as Silica Gel is more polar than Porapak-T. In addition, chloroform shows an average degree of water solubility (8 g/l)(16) as opposed to the non-solubility of CCl_4 in water; chloroform is also better retained by Silica Gel due to solubility effects.

For oxy-hydrocarbon adsorption on Silica Gel shown in Figure R15 the effects of polarity and water solubility are clearly indicated. Ethyl ether, which has a slight degree of water solubility and a moderate boiling point, is retained to a fair degree. Acetaldehyde, which has a low boiling point, an infinite solubility in water, and which is only slightly retained by non-polar adsorbents, shows a large degree of adsorption here. Ethyl acetate, which normally is retained to a large extent on non-polar adsorbents due to high dispersion forces, was retained so strongly that it did not even elute from the Silica Gel. The above results can be tied to a combination of dispersion forces, specific adsorbate-adsorbent attraction forces based on adsorbate polarity, and solubility effects based on adsorbate water solubility.

Of the five adsorbents tested, Spherocarb is the most retentive. Being only minimally polar, Spherocarb adsorbs molecules according to the mechanisms of entrapment within its lattice structure and dispersion forces. Figure R16 for the oxy-hydrocarbons shows acetaldehyde was slightly retained, ethyl ether was more strongly retained, and ethyl acetate was so tenaceously retained that it did not readily elute. By comparison to Silica Gel, this clearly indicates that Spherocarb adsorption is not affected to any significant degree by adsorbate polarity or water solubility, and that adsorption occurs based almost entirely on dispersion forces. This is verified by Figure R17 for the halocarbons. Here, the halocarbon adsorption progression follows boiling point, with CCl_4 not readily eluting. The fact that CCl_4 did not elute from Spherocarb while it did not adsorb on Tenax indicates that adsorbate entrapment is totally responsible for adsorption. Since the polarities of Tenax and Spherocarb probably do not vary much, similar desorption trends would be expected if adsorption were based on polarity.

A note must be interjected here to explain what is meant by a compound not readily eluting. For CCl_4 on Spherocarb, and ethyl acetate on Silica Gel and Spherocarb, temperatures were raised to anywhere from 190°C to 240°C trying to recover the adsorbates. However, the results yielded non-reproducable broad "humps." Attempts to repeat these experiments consistently failed, even after performing adsorbent cleanings at 350°C before each test. This adsorbent cleaning process was extremely slow, sometimes taking several hours, even at 350°C, due to a continual low level adsorbate bleed. All these factors indicated a very large tenacity of adsorption which made desorption difficult.

Humidity

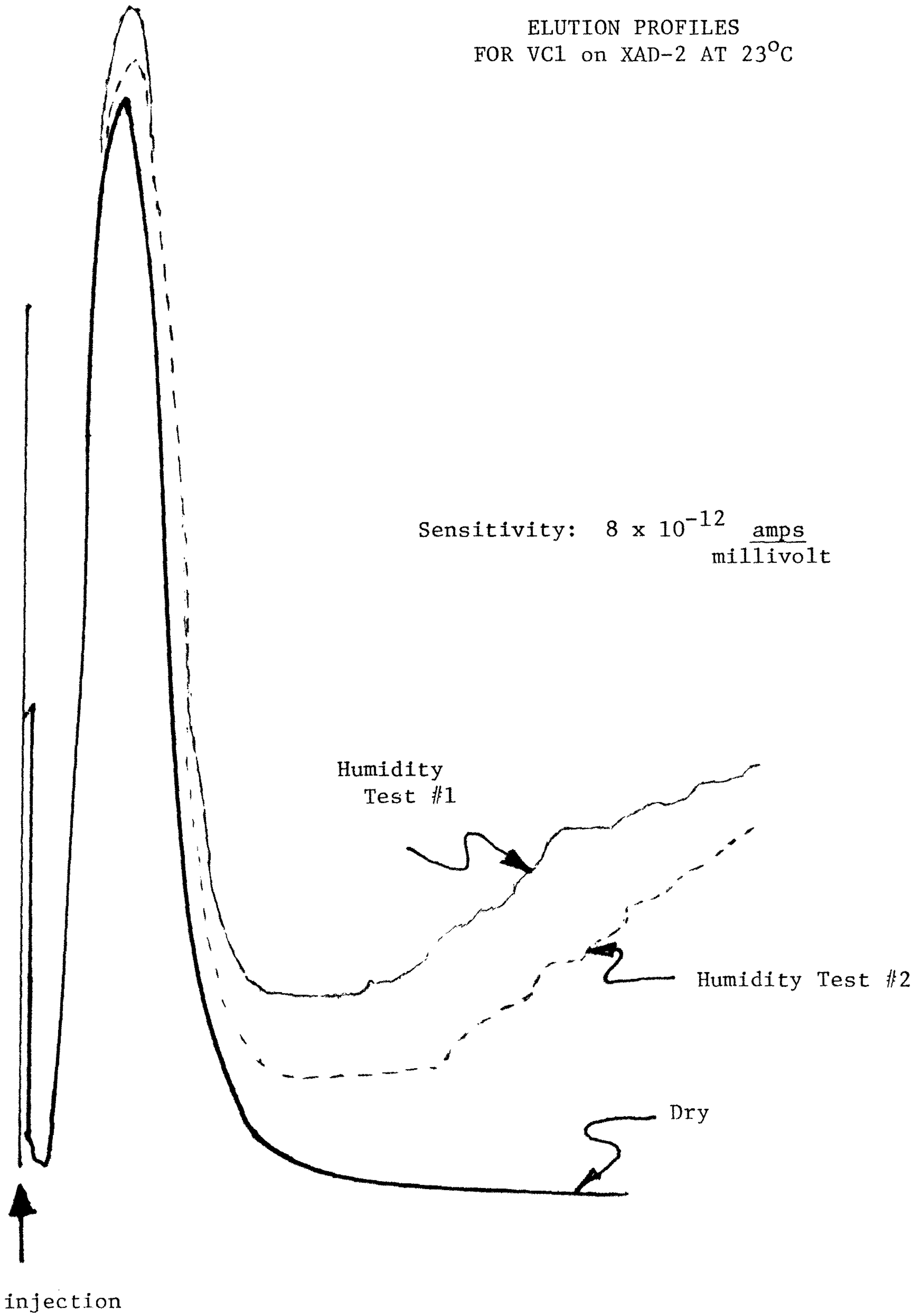
An analysis was performed on the effect of humidity on incipient elution and on the shape of the elution profile. Runs were performed using VCl on Porapak-T at temperatures of 22°C and 35°C, on XAD-2 at 23°C, and on Silica Gel at 30°C. Tests were not performed on Tenax as it has been classified as hydrophobic. Janak et al.,(17) and Pellizzari et al.(18) found that the ability of Tenax to collect and retain vapors from ambient air was apparently not affected by humidity conditions. Humidity test runs were also not performed on Spherocarb.

Results on Porapak-T indicate that humidity had little or no effect on incipient elution or the elution profile for vinyl chloride. Humidity did not appear to alter incipient elution times for XAD-2 either. The shape of the elution profile, however, did change. The "dry" profile for XAD-2 is projected as a somewhat symmetrical peak, with a minimal degree of tailing. In the humidity tests, the eluent peak would occur with the FID signal returning to near baseline and then a gradual increase in G.C. signal would occur, as shown in Figure R18. The fact that the humidity did not affect the retention time indicates that it is: one, probably a small effect, and two, either a chemical or physical effect that causes additional retention of a fraction of the VCl or breakdown of the adsorbent. The low temperatures utilized suggest it may be the former here.

On Silica Gel, the elution profile took the form of a broad peak with a large degree of tailing. When the column temperature was raised to 130°C to clean the cartridge, a slow, continual bleed began and

FIGURE R18

ELUTION PROFILES
FOR VCl on XAD-2 AT 23°C



continued until the temperature was reduced back to 30°C. This is explained by the known strong interaction between Silica Gel and water and its high heat of hydration. This concurs with the chapter on Adsorbents where it states that Silica Gel retains water, even when heated to very high temperatures (at 300°C, 4% water is retained)(19). Thus, in essence, "dry" Silica Gel actually retains water to a certain degree. As for the incipient elution volume, the V_N value obtained from the "wet" case (898 ml/ml) varies markedly from the dry case value (2537 ml/ml) using identical size injection loops of 1 ml. In a further "dry" test performed on Silica Gel, the retention volume V_N for a 2 ml loop was closer (1660 ml/ml) to the elution volume obtained for the wet case with a 1 ml injection volume. Since studies on sample injection size showed little effect (see the next section, this chapter) on incipient elution values, these two sets of results seem somewhat ambiguous, and it appears that further tests on the humidity effects on Silica Gel are warranted to resolve this problem.

Sample Injection Size

It was first realized in this study that since six of the seven organic adsorbates tested would be injected as liquids, and since control of the .05 ml liquid injection amount was not accurate, the effect of sample injection size had to be evaluated. Snyder has indicated that for a very small quantity of sample, incipient elution time is not a function of sample size (see Figure 4). Therefore, tests were performed on Silica Gel and Porapak-T using vinyl chloride (VCl) to verify this.

Since VCl is a gas, constant temperature and accurately known sample injection loops can be utilized to control the amount of sample injected. Gas sample loops of 0.25, 1.0, and 2.0 ml volumes were used. Table lists the various injection amounts and the V_N values obtained from the Equation $\ln V_N = \ln V_{ni} + m\left(\frac{1}{T}\right)$, as derived from the plots listed in Figure 18. From this data, it can be seen that for injection amounts varied by factors of up to 8, there was no marked increase in V_N. Viewing Porapak-T in Figure 18, the three plot lines show nearly identical data for all injection sizes. Small differences here in V_N values can be attributed to slight fluctuations in operating conditions and parameters. Therefore, it is concluded that sample injection size does not have any effect on incipient elution for small adsorbate injection amounts in this study. The amounts injected for VCl were 4.20×10^{-10}, 1.68×10^{-9}, and 3.36×10^{-9} g moles, respectively, for the 0.25, 1.0, and 2.0 ml injection loops. Unfortunately, these values are from about 1/300 to

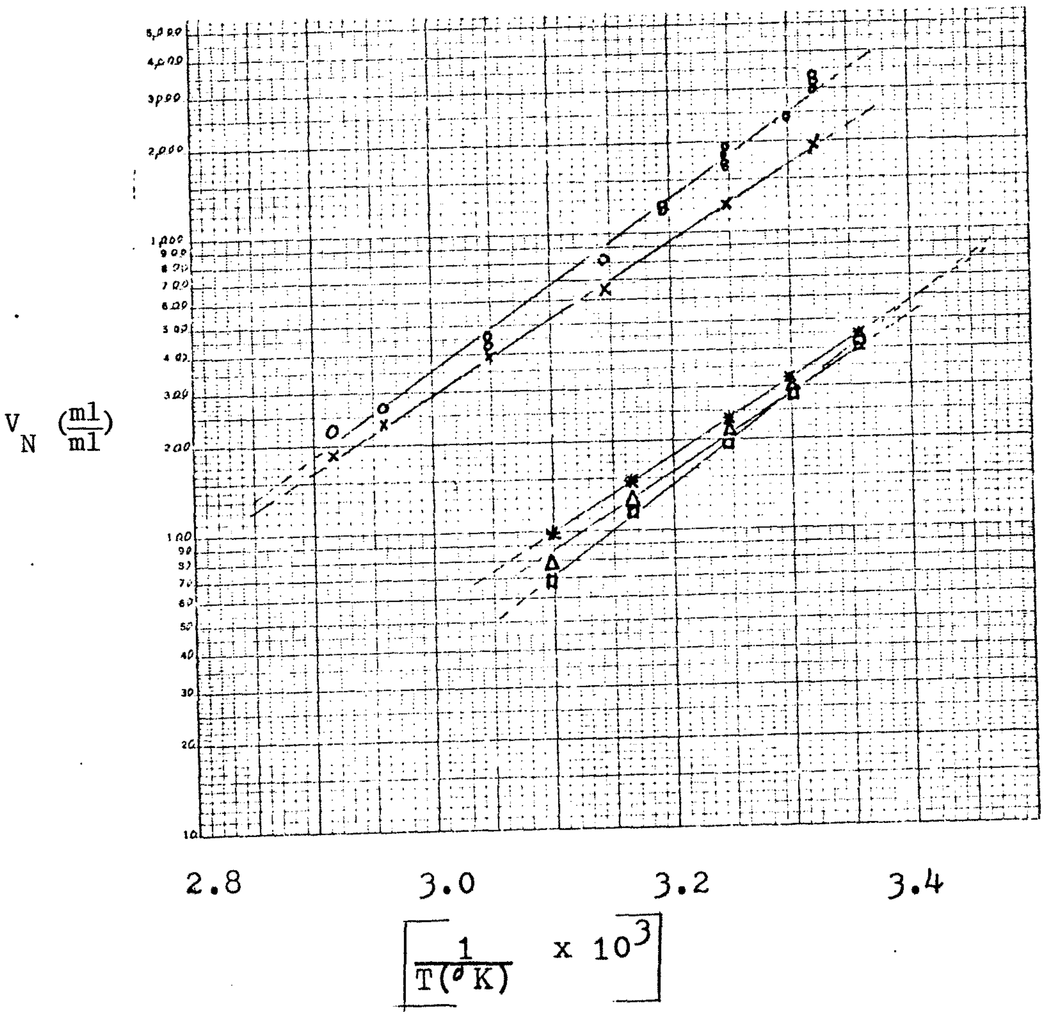
FIGURE R19

Effect Of Sample Size On Incipient Elution Volume (V_N)

Adsorbate: Vinyl Chloride

Adsorbents: Silica Gel

Porapak-T



o - 1 ml loop : Silica Gel
x - 2 ml loop : Silica Gel

✳ - 0.25 ml loop : Porapak-T
□ - 1.0 ml loop : Porapak-T
△ - 2.0 ml loop : Porapak-T

1/2400 the size of the amounts injected for the six liquids tested (see Appendix D). Thus, the fact that sample injection size does not affect incipient elution for small injection amounts cannot be extrapolated to include the liquids injected here until further tests are performed.

FOOTNOTES - CHAPTER VII

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14. Ibid.

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VIII. CONCLUSIONS AND RECOMMENDATIONS

In ambient air sampling, if a certain compound is targeted, a specific adsorbent should be chosen, using scientific literature as a basis. If, however, a wide range of compounds is to be analyzed, a series of adsorbents may be required. These adsorption studies indicate that the preferred case would be to use Porapak-T backed by Spherocarb. However, until further analysis is performed on the quantitative efficiency of thermal desorption on Porapak-T at (near its upper temperature limit) 180°C, it is not recommended for use. Thus, instead, Tenax should be placed in front of Spherocarb. In this way, there will be minimal humidity effects, the heavier compounds will deposit on the Tenax with the lighter ones eluting to the Spherocarb cartridge, and thermal desorption will be efficient. However, if CCl_4 is to be analyzed, Tenax should be replaced by XAD-2. As for Silica Gel, it can be used with caution for adsorption of water soluble compounds in either dry atmospheres or for short duration sampling.

Possible follow-up research studies should be conducted on adsorbent desorption efficiencies, ease of adsorbent purification including Soxhlet extraction and thermal conditioning, and the effect of humidity on adsorption. Elution studies should, in addition, be carried out to determine optimum flow rates for ambient air sampling.

APPENDIX A

Langmuir Isotherm Derivation$^{(1)}$

μ = number of molecules striking cm^2 of surface per second.

α = fraction of molecules which adhere to the surface.

$\alpha\mu$ = number of molecules adhering to surface /cm^2· second

θ = fraction of total surface covered.

$1-\theta$ = fraction of total surface that is bare.

$(1-\theta)\alpha\mu$ = rate of adsorption

ν = number of molecules vacating surface/cm^2 - second.

$\nu\theta$ = desorption rate.

At equilibrium, the rate of adsorption is equal to the rate of desorption.

$$(1-\theta)\alpha\mu = \nu\theta$$

$$\theta = \frac{\alpha\mu}{\nu + \alpha\mu} \qquad (1)$$

Assuming a unimolecular layer, θ is proportional to the amount of gas adsorbed by a mass of adsorbent.

X = mass of gas adsorbed

* m = mass of catalyst

K = constant

$$\theta = K\left(\frac{X}{m}\right) \qquad (2)$$

* Note that for a specific sized adsorbent, m could be expressed as an equivalent volume occupied by the adsorbent.

The number of molecules striking the surface is proportional to the pressure.

K' = constant

p_x = partial pressure of unadsorbed component

$$\mu = K'p_x \quad (3)$$

Substituting for Equation (1) using Equations (2) and (3) yields:

$$\theta = K\left(\frac{X}{m}\right) = \frac{\alpha(K'p_x)}{\gamma + \alpha(K'p_x)} = \frac{\left(\frac{\alpha}{\nu}\right)K'p_x}{1 + \left(\frac{\alpha}{\nu}\right)K'p_x}$$

Note: This is in the same form for m as

$$\theta = \frac{K_{th}p_x}{1 + K_{th}p_x} \qquad \text{Here, } K_{th} = \frac{\alpha}{\nu}K'$$

$$\frac{X}{m} = \frac{\left(\frac{\alpha}{\nu}\right)\left(\frac{K'}{K}\right)p_x}{1 + \left(\frac{\alpha}{\nu}\right)K'p_x}$$

Let $\left(\frac{\alpha}{\nu}\right)K' = K_1$ and $\frac{1}{K_1} = K_2$

$$\frac{X}{m} = \frac{K_1K_2p_x}{1 + K_1p_x}$$

which rearranges to

$$\frac{p_x}{\left(\frac{X}{m}\right)} = \frac{1}{K_1K_2} + \frac{1}{K_2}p_x$$

which is in the form of the slope-intercept equation.

Footnote:

(1) From college notes given by Dr. Deran Hanesian, N.J.I.T., 1977.

APPENDIX B

Dictionary

Adjuvant - chemical that heightens the action of a drug.

Alkylating agent - compound that reacts with smaller molecules to form more branched and more complex molecules. Such species include nitrogens or sulfur mustards, sulfonic esters and sultones, lactones, Be, Cd, Mn, Ni, etc.

Angiosarcoma - tumor of the blood vessels.

Cancer - abnormal cellular growth and malignancy.

Carcinogenic - cancer causing.

Dermatitis - inflammation of the skin.

Epithelium - membrane tissue.

Gastric - pertaining to the stomach.

Hepato - pertaining to the liver.

Jaundice - liver disease due to presence of bile pigments in the blood.

Leucocytosis - increase in the number of white blood corpuscles.

Lipid - water insoluble substance which is greasy and includes fats, waxes, and sterols.

Lobules - small lobes.

Metabolite - product of metabolism.

Mutagenesis - change in organism by changing genes.

Necrosis - tissue death.

Neoplasm - a tumor

Nephrosis - kidney disease characterized by degenerative lesions of the renal tubules

Oncogenesis - causing of tumors.

Renal - pertaining to the kidney.

Teratogenic - affects offspring and unborn.

Tubules - minute tubes.

Tumor - local swelling from some abnormal growth of tissue.

Vesicant - attacks skin and produces blisters.

Viscera - internal organs.

APPENDIX C

Incipient Elution Values

(Raw data taken from the chromatograms)

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• w = .338 g Tout = 260° 1.

VCl on Silica Gel 120/170 Carrier = 50 ml/min

T °C	$10^3/T$ °K	$t_{MIN.}$	V_B	V_B/g	$V_g/.512$	SAMPLE SIZE	S	SLOPE	INTERCEPT
						2 ml			
28	3.322	20.0	1000	2959	1953		✓	5.754	−11.572
35	3.247	12.5	625	1849	1221		✓		
45	3.145	6.6	330	976	645		✓		
55	3.049	4.0	200	592	391		✓		
65	2.959	2.4	120	355	234		✓		
70	2.915	1.9	95	281	186		✓		

VCl on Silica Gel 120/170

T °C	$10^3/T$ °K	$t_{MIN.}$	V_B	V_B/g	$V_g/.512$	SAMPLE SIZE	S	SLOPE	INTERCEPT
						1 ml			
28	3.322	32.4	1620	4793	3164	✓		6.672	−14.181
28	"	34.2	1710	5059	3340	✓			
28	"	30.4	1520	4497	2969	✓	✓		
30	3.300	24.5	1225	3624	2393	✓	✓		
35	3.247	19.6	980	2899	1914	✓	✓		
35	"	18.7	935	2766	1826	✓	✓		
35	"	17.2	860	2544	1680	✓	✓		
35	"	17.0	850	2515	1660	✓	✓		
40	3.195	12.3	615	1820	1201	✓	✓		
40	"	12.4	620	1834	1211	✓	✓		
45	3.145	8.3	415	1228	811	✓	✓		
55	3.049	4.7	235	695	459		✓		
55	"	4.4	220	651	430		✓		
65	2.959	2.7	135	399	264		✓		
70	2.915	2.3	115	340	225		✓		

Note: ~~All~~ Data points were taken on 3 different days.

Do over, esp. for 1 ml dose to verify whether breakthrough or XS breakthrough

Silica Gel 120/170

2.

w = .338

T°C	$10^3/T°K$	t_{MIN}	V_B	V_B/g	$V_B/.512$	SAMPLE SIZE	S	SLOPE	INTERCEP
	Methylene	Chloride	on	Silica	Gel				
40	3.195	41.2	2060	6195	4023	.05 µL			
50	3.096	23.0	1150	3402	2246			6.091	−11.15
60	3.003	12.6	630	1864	1230				
70	2.915	7.0	350	1036	684				
70	"	8.0	400	1183	781			✓	
80	2.833	4.6	230	680	449				
	Chloroform	on	Silica	Gel					
50	3.096	50.8	2540 ~~[illegible]~~	7515 ~~[illegible]~~	4961 ~~[illegible]~~	.05 µL			
60	3.003	28.0	1400	4142	2734			5.785	−9.94
70	2.915	15.5	775	2293	1514				
80	2.833	9.2	460	1361	898 ~~[illegible]~~			✓	
	Carbon	Tetrachloride	on	Silica	Gel				
50	3.096	45.2	2260	6686	4414				
60	3.003	23.0	1150	3402	2246	.05 µL		6.316	−11.199
70	2.915	13.7	685	2027	1338				
80	2.833	8.5	425	1257	830			✓	
	1,1,1	Trichloroethane							
40	3.195	26.4	1320	3905	2578				
50	3.096	16.3	815	2411	1592	.05 µL		6.245	−12.00
60	3.003	9.2	460	1361	898				
70	2.915	4.7	235	695	459				
80	2.833	2.9	145	429	283				

Silica Gel 120/170

2

w = ,338.

T °C	$10^3/T$ °K	t min.	V_B	V_B/g	$V_i/,512$	Sample Size	S	Slope	Intercept
		Acetaldehyde.							
110	2.611	30.4	1520		2969	.05 μL			
120	2.545	12.6	630		1230			9,778	-17.654
130	2.481	7.0	350		684				
135	2.451	5.5	275		537			✓	
145	2.392	3.5	175		342				
		Ether							
110	2.611	0.4	20		39	.05 μL			
100	2.681	0.6	30		59				
90	2.755	1.0	50		98			5,190	-9.760
80	2.833	1.6	80		156				
70	2.915	2.6	130		254			✓	
60	3.003	4.3	215		420				
50	3.096	7.9	395		771				
~~40~~									

Spherocarb

w = .277

T^0C	$10^3/T^0K$	$t_{MIN.}$	V_B	V_B/g	$V_i/.51$	Sample Size	S	Slope	Intercep
	VCl					1μl			
83	2.809	36.2	1810	6534	3535				
88	2.770	26.7	1335	4819	2607				
100	2.681	16.8	720	2599	1406			6,088	−8.987
110	2.611	10.5	525	1895	1025		✓		
120	2.545	6.9	345	1245	674				
130	2.481	4.6	230	830	449				
140	2.421	3.3	165	596	322				
	Methylene Chloride					.05μL			
105	2.646	50.3	2515	9079	4912				
115	2.577	32.2	1610	5812	3144			7.282	−10.75
128	2.494	16.1	805	2906	1572		✓		
140	2.421	10.3	505	1823	986				
	Acetaldehyde.								
95	2.717	18.8	940	3394	1836	.05μL			
105	2.646	12.7	635	2292	1240			6.548	−10.24
120	2.545	6.0	300	1083	586		✓		
135	2.451	3.8	190	686	371				
150	2.364	1.8	90	325	176				

Spherocarb

W = .277 g.

T °C		$10^3/T$ °K		t min.	V_B	V_o/g	$V_i/.512$	Sample Size	S	Slope	Intercep
			Ether								
180		2.20[illegible]		21.6	1080	3,899.	2109				
190		2.160		14.1	705	2,545	1377	✓		8.622	-11.396
205		2.092		7.7	385	1,390	752				
220		2.028		4.4	220	794	430				
230		1.988		3.3	165	596	322				
			Chloroform								
185		2.183		13.7	685	2,473	1338				
195		2.137		8.8	440	1,588	859	✓		7.406	-10.10
205		2.092		6.3	315	1,137	615				
220		2.028		3.8	190	586	371				
230		1.988		2.9	145	523	283				

Poropak T. w= .207 g

T°C	$10^3/T°K$		t min,	V_B	V_0/g	$V_i/.512$	Sample Size	S	Slope	Intercept
			Carbon Tetrachloride							
40	3.195		76.5	3825	18,478	7471				
50	3.096		31.3	1565	7,560	3057			8.316	-17.67
60	3.003		15.2	760	3,671	1484		✓		
70	2.915		7.7	380	1836	742				
80	2.833		3.6	180	870	352				
			Methylene Chloride							
30	3.300		40.5	2025	9,783	3955				
40	3.195		17.6	880	4,251	1719		✓	7.493	-16.452
50	3.096		9.0	450	2,174	879				
60	3.003		4.4	220	1063	430				
70	2.915		2.2	110	531	215				
			Chloroform							
50	3.096		40.6	2030	9,807	3965				
60	3.003		20.2	1010	4,879	1973			7.932	-16.26
70	2.915		9.0	450	2,174	879		✓		
80	2.833		5.4	270	1,304	527				
87	2.778		3.2	160	773	313				
			Acetaldehyde							
25	3.356		6.8	340	1643	664	✓			
30	3.300		5.5	275	1329	537			5.798	-12.900
35	3.247		4.1	205	990	400				
40	3.195		2.7	135	652	264				
45	3.145		2.1	105	507	205				

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Poropak T

$T_{Det} = 260°$

w = .207g

T°C	$10^3/T°K$	$t_{MIN.}$	V_B	V_B/g	$V_i/.512$	Sample Size	S	Slope	Intercept
		Ether							
35	3.247	27.8	1390	6715	2715	.05 μL			
45	3.145	12.4	620	2995	1211				
50	3.096	8.0	400	1932	781		✓	8.229	-18.80
55	3.049	5.6	280	1353	547				
65	2.959	2.6	130	628	254				
		Ethyl Acetate							
85	2.793	4.8	240	1,159	469	.05 μl.	✓		
75	2.874	9.8	490	2,367	957				
65	2.959	21.4	1078	5,169	2090			8.963	-18.88
60	3.003	32.6	1630	7,874	3184				
50	3.096	71.2	3560	17,198	6953				

Poropak T. w = .207

VCl

T °C	$10^3/T$ °K	$t_{min.}$	V_B	V_B/g	$V_x/.512$	Sample Size	S	Slope	Intercept.
50	3.096	0.7	35	169	68	1 ml			
43	3.164	1.2	60	290	117				
35	3.247	2.0	100	483	195		✓	6.892	-17.090
30	3.300	2.9	145	700	283				
25	3.356	4.3	215	1039	420				
50	3.096	1.0	50	242	98	0.25 ml.			
43	3.164	1.5	75	362	146			5.841	-13.502
35	3.247	2.4	120	580	234				
30	3.300	3.3	165	797	322				
25	3.356	4.6	230	1111	449				
50	3.096	0.8	40	193	78	2 ml.			
43	3.164	1.3	65	314	127			6.330	-15.206
35	3.247	2.2	110	531	215				
30	3.300	3.1	155	749	303				
25	3.356	4.1	205	990	400				

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Tenax

W = .065g

8

T°C	$10^3/T°K$	$t_{min.}$	V_B	V_a/g	$V_i/.512$	Sample Size	S	Slope	Interc
	Vinyl Chloride					1ml			
35	3.247	.2	10	154	20				
25	3.356	.4	20	308	39		✓		
15	3.472	.7	35	538	68			5.724	-15.57
7	3.571	1.5	75	1154	146				
0	3.704	2.7	135	2077	264				
0°		2.9	145		283	.25ml			
8°		1.6	80		156				
	Chloroform.								
50	3.096	1.1	56	862	109	.05μL			
40	3.195	2.4	122	1,877	238				
30	3.3	4.8	244	3,754	477		✓	7.371	-18.11
24	3.367	8.3	422	6,492	824				
18	3.436	13.7	696	10,708	1359				
	Carbon Tetrachloride — not held, even @ 10°C								
	Methylene Chloride								
35	3.247	1.2	59	908	115		✓		
25	3.356	2.3	113	1738	221			6.508	-16.407
15	3.472	5.1	251	3862	490				
5	3.597	11.5	566	8708	1105				

Tenax W= .065g

T °C		$10^3/T$ °K	$t_{MIN.}$	V_B	V_0/g	$V_i/.51$	Sampl Size	S	Slope	Intercep
			Ethyl Acetate				.05 µL			
50		3,096	2,5	118		230				
40		3,195	6.4	304		594				
30		3,3	13,3	654		1077	✓		8,549	-21.003
20		3,413	36.6	1800		3516				
10		3,534	105.6	5193		10,143				

~~V_B~~= See pg 30 for V_B

T °C		$10^3/T$ °K	$t_{MIN.}$	V_B	V_0/g	$V_i/.51$	Sampl Size	S	Slope	Intercep
			Ether							
50		3,096	.4	20		39	.05 µL			
40		3,195	.8	40		78				✓
29		3,311	2.2	110		215	✓		8.159	-21.645
24		3,367	3.4	170		332				
18		3,436	6.3	315		615				
			Acetaldehyde – ~~Not [illegible]~~							
35°	12/28	3.247	0.2	10		20	.05 µL			
25	12/28	3.356	0,4	20		39			6.964	-19.664
15°	12/28	3.472	0,9	45		88	✓			
7°	1/16	3,571	1,9	95		186				
0°	1/16	3.663	3,6	180		352				

6.5
6

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XAD - 2

W = .164

T°C	$10^3/T°K$	t_{min}	V_B	V_g/g $V_i/.517$	Sample Size		S Slope	Interc
		Methylene Chloride						
50	3.096	0.3	16	31	.05 μL			
40	3.195	0.5	26	51				
30	3.3	1.3	67	131		✓	8.901	-24.34
20	3.413	3.4	176	344				
14	3.484	10.2	528	1631				
	Flow = 51.7 ml/min							
		Chloroform.						
50	3.096	0.8	41	80		✓	10.960	-29.4
40	3.195	2.7	140	273				
30	3.3	8.9	460	898				
17	3.448	37.9	1960	3828				
		Flow = 51.7						
		Carbon Tetrachloride						
50	3.096	3.7	185	361	.05 μL			
40	3.195	9.4	470	918		✓	~~23.685~~	~~-70.4~~
30	3.3	21.3	1315	2568			9.784	-24.4
24	3.367	52.6	2630	5137				
		Acetaldehyde						
30	3.3	.3	15	29		✓	6.171	-16.9
20	3.413	.6	30	60				
10	3.534	1.3	65	127				
0	3.704	3.6	180	352				

1

XAD-2 W=.164

T°C	$10^3/T_{°K}$	t_{MIN}	V_B	V_B/g	V_i/1.51	Sample Size	S	Slope	Intercep
		Ether							
0	3.663	105.7	5285		10,322	.05μL			
15	3,472	15.4	770		1504				
20	3,413	9.5	475		928		✓	9.511	-25.59
30	3,3	4.7	235		457				
40	3,195	1,0	50		98				
		Ethyl Acetate							
20	3,413	102.2	5110		9980	.05μL			
30	3,3	28,1	1405		2744		✓	10.196	-25.65
40	3,195	10,0	500		977				
50	3,096	4,0	200		391				
		VCl				1ml			
0	3.663	6.7	335		654				
10	3.534	2.6	140		273			6.130	
14	3.484	2.0	100		195	✓		~~6.130~~	-16,01
20	3.413	1.4	70		137				
25	3.356	1.0	50		98				
30	3.3	0.7	35		68				

APPENDIX D

Injection Amounts

VCl $n = \frac{PV}{RT}$

Sample loop: given in ml

Standard Cylinder: 50 ppm

$$\frac{50 \text{ ml}}{10^6 \text{ ml}} \times V \text{ ml} = 5 \times 10^{-5} V \text{ l}$$

$$P = 1 \text{ ATM}$$

$T_{INJ} = 90^\circ C \equiv 363^\circ K$ $R = .08205 \frac{\text{l atm}}{\text{g mole}^\circ K}$

$$n = \frac{(1)\ 5 \times 10^{-5}\ V}{(.08205)(363)}$$

$$n = 1.6787 \times 10^{-6}\ V \text{ g moles}$$

where V is in liters (sample loop)

2.0 ml loop = 2×10^{-3} l $n = 3.3575 \times 10^{-9}$ g moles

1.0 ml loop = 1×10^{-3} l $n = 1.6787 \times 10^{-9}$ g moles

0.25 ml loop = 2.5×10^{-4} l $n = 4.1968 \times 10^{-10}$ g moles

Liquids:

$n = \frac{V}{M}$ $V = .05\,\mu L \equiv 5 \times 10^{-5}$ ml

Adsorbate	Density (g/ml)	Mol. Wt.	n (g-moles)
CCl_4 (1)	1.5940	153.82	5.1814×10^{-7}
$CHCl_3$ (2)	1.4832	119.38	6.212×10^{-7}
CH_2Cl_2 (3)	1.3266	84.93	7.81×10^{-7}
Acetaldehyde (4)	0.7834	44.05	8.892×10^{-7}
Ether (5)	0.71378	74.12	4.815×10^{-7}
Ethyl Acetate (6)	0.9003	88.12	5.108×10^{-7}

Footnotes:

[1] Robert C. Weast, Editor, Handbook of Chemistry and Physics, CRC Press, Cleveland, Ohio, 57 Ed., 1976-1977, p. C-375.

[2] *Ibid*.

[3] *Ibid*. p. C-373.

[4] *Ibid*. p. C-81

[5] *Ibid*. p. C-300.

[6] *Ibid*. p. C-86

APPENDIX E

Determination of the Standard Error of Estimate (S_{y},) and the Correlation Coefficient (C_c)(1)

For a data point ($10^3/T(^oK)$), there is a Y value (ln V_n). For this same $\left[10^3/T(^oK)\right]$ value, there is also an estimated Y value (Yest), found from the linear regression line equestion. In addition, there is an average Y value ($\bar{Y}$), which is the average of all the (ln V_N) data point values. For n data points, the standard error of estimate can be found from the equation:

$$S_y = \sqrt{\frac{\sum (Y - Yest)^2}{n}}$$

and the correlation coefficient can be found from the following equation:

$$C_c = \pm \sqrt{\frac{\sum (Yest - \bar{Y})^2}{\sum (Y - Yest)^2 + \sum (Yest - \bar{Y})^2}}$$

Footnote:

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[1] Murray R. Spiegel, Schaum's Outline of Theory and Problems of Statistics, Schaum Publishing Co., New York, 1961, p. 243.

APPENDIX F

Calculation of Polarizability Values from Index of Refraction Values(1)

Adsorbate	n_4^{20} (normal chain refractive index)	ρ density (g/ml)	Mol. Wt. (Mw) (g/mole)	Polarizability ($\mathring{A}^3$)
CCl_4	1.4601	1.5940	153.82	10.48
Chloroform	1.4459	1.4832	119.38	8.51
Methylene Chloride	1.4242	1.3266	84.93	6.48
Vinyl Chloride	1.3700	0.9106	62.50	6.15
Acetaldehyde	1.3316	0.7834	44.05	4.57
Diethyl Ether	1.3526	0.7138	74.12	8.92
Ethyl Acetate	1.3723	0.9003	88.12	8.82

$$\alpha = .3964 \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right) \frac{M_w}{\rho} \quad (2)$$

Footnotes:

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[1] Robert C. Weast, Editor, Handbook of Chemistry and Physics, CRC Press, Cleveland, Ohio, 57 Ed., 1976-1977, pp. C-81, C-86, C-298, C-300, C-373, C-375.

[2] V. P. Frontasev and L. S. Shraiber, Russian Journal of Phys. Chem., 43, 229 (1969), p. 209.

APPENDIX G

Cartridge Volume Occupied by the Adsorbent

6-inch long cartridge packed to 5-1/2 inches (13.97 cm) with adsorbent.

1/8-inch nominal O.D.; i.d. is 0.216 cm.

$$\text{Volume} = \frac{\pi D^2}{4} \quad L$$

$$\text{Volume} = \frac{(0.216)^2}{4} \; (13.97) = 0.512 \text{ ml}$$

APPENDIX H

Values for the Correlation Coefficient and the Standard Error of Estimate

$10^3/T$ °K	V_i	Y $\ln V_i$	Y_{EST} $\ln V_i$ est from slope equation	$(Y - Y_{EST})$	$(Y - Y_{EST})^2$	$(Y_{est} - \overline{Y})$	$(Y_{est} - \overline{Y})^2$
2.611	2969	7.996	7.876	0.120	.0143	1.124	1.263
2.545	1230	7.115	7.231	− 0.116	.0135	0.479	0.229
2.481	684	6.528	6.605	− 0.077	.0059	−0.147	0.022
2.451	537	6.286	6.312	− 0.026	.0007	− 0.440	0.194
2.392	342	5.835	5.735	0.1	.0100	−1.017	1.034
N=5		$\overline{Y} = 6.752$ ③			$\Sigma = .0444$		$\Sigma = 2.742$

① $m = 9.778$

② $\ln V_{10} = -17.654$

Acetaldehyde on Silica Gel

Standard Error of Estimate

$$S_{Y,X} = \sqrt{\frac{.0444}{5}} = .094$$

On a Ward Plot

Example

$$\text{Correlation Coefficient} = \pm\sqrt{\frac{2.742}{2.742 + .0444}} = .992$$

See pg 243.

⑤

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y-Y_{est})$	$(Y-Y_{est})^2$	$(Y_{est}-\bar{Y})$	$(Y_{est}-\bar{Y})^2$
3,322	3164	8,060	7,983	.076616	.005870	.920945	.848
"	3340	8,114	7,983	-.130616	.017061	"	.848
"	2969	7,996	7,483	.012616	.000159	"	.848
3,300	2393	7,780	7,837	-.0566	.003204	.774945	.601
3,247	1914	7,557	7,483	.0740	.005478	.420945	.177
"	1826	7,510	"	.027	.000729	"	.177
"	1680	7,427	"	-.056	.003136	"	.177
"	1660	7,415	"	-.068	.004624	"	.177
3,195	1201	7,091	7,136	-.04504	.002029	.074	.005
"	1211	7,099	"	-.037	.001369	.075	.005
3,145	811	6,698	6,802	-.1044	.010908	-0,26	.068
3,049	459	6,129	6,162	-.03293	.001084	-0,9	0.810
"	430	6,064	6,162	-.098	.009604	0.9	.810
2,959	264	5,576	5,561	.01455	.000212	-1.501	2.253
2.915	225	5,416	5,268	.14812	.021940	-1,794	3.218

$\bar{Y} = 7.062$

$\Sigma = .08741$

Σ 11.022

m = 6.672

$\ln V_i$ =

−14.181

<u>VCl on</u>
<u>Si gel</u>

<u>1 ml loop</u>

$$S_{Y,X} = \sqrt{\frac{.08741}{15}} = .0763$$

$$\text{Cc Cor Coef} = \pm\sqrt{\frac{11.022}{11.022 + .08741}} = .9961$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_i$ est	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.322	1953	7.577	7.543	.0342	.001170	1.242	1.544
3.247	1221	7.107	7.111	-.00424	.0000 18	.8104	.657
3.145	645	6.469	6.524	-.05533	.003061	.2234	.050
3.049	391	5.969	5.972	-.00295	.000009	-.3286	.108
2.959	234	5.455	5.454	.000914	.000001	-.8466	.717
2.915	186	5.226	5.201	.02509	.000630	-1.10	1.209
		$\bar{Y} = 6.301$			$\Sigma = .00489$		$\Sigma = 4.285$

$m = 5.754$

$\ln V_i = -11.572$

VCl on Silel

2 ml loop

$$S_{Y,X} = \sqrt{\frac{.00489}{6}} = .0285$$

$$\text{Cor Coef} = \pm\sqrt{\frac{4.285}{4.285 + .00489}} = .9994$$

Cor Coef $= \sqrt{\dfrac{1.31}{1.374 +}}$ .9999

$10^3/T$	V_i	$\overset{Y}{\ln V_i}$	$\overset{Y_{est}}{\ln V_{i\,est}}$	$(Y-Y_{est})$	$(Y-Y_{est})^2$	$(Y_{est}-\bar{Y})$	$(Y_{est}-\bar{Y})^2$
2.809	3535	8.170	8.114	.0558	.0031	1.169	1.368
2.77	2607	7.866	7.877	−.0108	.0001	0.932	0.869
2.681	1406	7.249	7.335	−.0859	.0074	0.086	.007
2.611	1025	6.932	6.909	.0232	.0005	−.036	.001
2.545	674	6.513	6.507	.0060	.00004	−.438	0.191
2.481	449	6.107	6.117	−.0103	.0001	−.838	.685
2.421	322	5.775	5.752	.0230	.0005	−1.193	1.422
	$\bar{Y} =$	6.945			$\Sigma =$ .0117		$\Sigma =$ 4.543
N=7					7		7

$m = 6.088$

$\ln V_{\infty 0} = -8.987$

VCl on Spherocarb

$$S_{Y,X} = \sqrt{\frac{.0117}{7}} = .0409$$

$$\text{Cor Coef} = \pm\sqrt{\frac{4.543}{4.543 + .0117}} = .9987$$

$10^3/T$	V_i	$\overset{Y}{\ln V_i}$	$\overset{Y_{est}}{\ln V_{i\,est}}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \overline{Y})$	$(Y_{est} - \overline{Y})^2$
3.096	98	4.585	4.582	.003264	.000011	−.79909	.639
3.164	146	4.984	4.979	.005076	.000026	−.40209	.162
3.247	234	5.455	5.464	−.008727	.000076	.082906	.007
3.3	322	5.774	5.773	.0007	0 —	.341906	.154
3.356	449	6.107	6.100	.0066	.000044	.7189	.517

$\overline{Y} = 5.381$ $\Sigma = .000157$ $\Sigma = 1.379$

$m = 5.841$

$\ln V_{oi} = -13.502$

VCl on

Porapak-T

.25 ml loop

$$S_{Y,X} = \sqrt{\frac{.000157}{5}} = .0056$$

$$\text{Cor Coef} = \pm\sqrt{\frac{1.379}{1.379 + .000157}} = .9999$$

		Y	Y_{est}				
$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.096	68	4.220	4.248	−.02763	.000764	−.94008	.884
3.164	117	4.762	4.716	.0457	.00209	−.47208	.223
3.247	195	5.273	5.288	−.0153	.00023	.09992	.010
3.300	283	5.645	5.6536	−.0086	.00007	.46552	.217
3.356	420	6.040	6.0396	.00045	.0000002	.85152	.725
					03		

$m = 6.892$

$\overline{\ln V_{oi}} = 17.09$

$N = 5$

VCl on Porapak

1 ml Sample

$\bar{Y} = 5.188$

$\Sigma = .00315$

$\Sigma = 2.059$

$$S_{Y,X} = \sqrt{\frac{.00315}{5}} = .0251$$

$$\text{Cor. Coef.} = \pm\sqrt{\frac{2.059}{2.059 + .00315}} = .9992$$

$10^3/T$	V_i	$\overset{Y}{\ln V_i}$	$\overset{Y_{est}}{\ln V_{i\,est}}$	$(Y-Y_{est})$	$(Y-Y_{est})^2$	$(Y_{est}-\bar{Y})$	$(Y_{est}-\bar{Y})^2$
3.096	78	4.357	4.392	−.03468	.001203	−.8633	.745
3.164	127	4.844	4.822	.02188	.000479	−.4333	.188
3.247	215	5.371	5.348	.02349	.000552	.09265	.009
3.3	303	5.714	5.683	.031	.000961	.42765	.183
3.356	400	5.991	6.037	−.04648	.002160	.781654	.611

$\bar{Y} = 5.255$

$\Sigma = .005355$

$\Sigma = 1.736$

$m = 6.33$

$\ln V_{10} =$
-15.206

VCl on

Porapak

2 ml loop

$$S_{Y,X} = \sqrt{\frac{.005355}{5}} = .0327$$

$$\text{Cor. Coef} = \pm\sqrt{\frac{1.736}{1.736 + .005355}} = .9985$$

		Y	Y_{est}				
$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y-Y_{est})$	$(Y-Y_{est})^2$	$(Y_{est}-\bar{Y})$	$(Y_{est}-\bar{Y})^2$
3,247	20	2.496	3,012	−.01563	.000251	−1,27567	1,6277
3,356	39	3.664	3.636	.02826	.000798	−.6517	.425
3.472	68	4.220	4.300	−.07973	.006357	.0123	.00015
3,571	146	4,984	4,866	.117596	.013829	.6963	.485
3,704	264	5.576	5.628	−.05160	.002672	1,3403	1.796

$m = 5,724$

$\ln V_{i\,i} = 75.574$

VCl m

~~Temp~~

$\bar{Y} = 4.288$

$\Sigma = .0239$

$\Sigma = 4.333$

$$S_{Y,X} = \sqrt{\frac{.0239}{5}} = .0048$$

$$\text{Cor. Coef} = \pm\sqrt{\frac{4,333}{4,333 + .0239}} = .9973.$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \overline{Y})$	$(Y_{est} - \overline{Y})^2$
3.663	654	6.483	6.438	.04481	.002008	1.2563	1.578
3.534	273	5.609	5.647	−.03842	.001476	.4273	.183
3.484	195	5.273	5.341	−.06792	.004613	.1593	.025
3.413	137	4.920	4.906	.01431	.000205	−.27567	.076
3.356	98	4.585	4.556	.02872	.000825	−.6257	.391
3.3	68	4.220	4.213	.007	.000049	−.46867	.938

$m = 6.13$

$\ln V_{oi} = -16.016$

VCl on XAD-2

$\overline{Y} = 5.182$

$\Sigma = .00918$

$\Sigma = 3.191$

$$S_{Y,X} = \sqrt{\frac{.00918}{6}} = .0391$$

$$\text{Cor Coef} = \pm\sqrt{\frac{3.191}{3.191 + .00918}} = .9986$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.195	4023	8.300	8.304	−.004	.000016	1.233	1.520
3.096	2246	7.717	7.701	.016	.00026	.630	.397
3.003	1230	7.115	7.134	−.019	.00037	.063	.004
2.915	684	6.528	6.598	−.070	.0049	−.473	.224
2.915	781	6.6606	6.598	.062	.0039	−.473	.224
2.833	449	6.107	6.099	.008	.00007	−.472	.945
		$\bar{Y} = 7.071$			$\Sigma = .0095$		$\Sigma = 3.314$

N = 6

m = 6.091

$\ln V_{10} = -11.157$

Methylene Chloride in Si Gel

$$S_{y,x} = \sqrt{\frac{.0095}{6}} = .0398$$

$$\text{Cr Coeff.} = \pm\sqrt{\frac{3.314}{3.314 + .0095}} = .9986$$

$10^3/T\,°K$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y-Y_{est})$	$(Y-Y_{est})^2$	$(Y_{est}-\overline{Y})$	$(Y_{est}-\overline{Y})^2$
2.646	4912	8,499	8,514	-.01517	.00023	.8123	.660
2.577	3144	8.053	8,012	.04129	.00170	.3104	.096
2,494	1572	7,360	7,407	-.04731	.00224	-.2946	.087
2,421	986	6,894	6,876	.01828	.00033	-.8256	.682

$m = 7,282$

$\ln V_{\infty} = -10,754$

$N=4$

$\overline{Y} = 7.702$

$\Sigma = .0045$

$\Sigma = 1,525$

Methylene Cl
in
[illegible]

$$S_{Y,X} = \sqrt{\frac{.0045}{4}} =$$

$$\text{Cor Coef} = \pm\sqrt{\frac{1.525}{1.525+.0045}} = .9985$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3,300	3955	8,283	8.275	.0081	.00007	1.4859	2.208
3.195	1719	7,449	7,488	-.03914	.00153	0.6989	0.488
3,096	879	6,779	6,746	.03267	.00107	-0.0431	0.019
3,003	430	6,064	6,049	.01452	.00021	-0.7401	0.548
2.915	215	5,371	5,390	-.01910	.00036	-1.399	1.957

$m = 7,493$

$\ln V_{oi} = -16.452$

$N = 5$

Methylene Chloride on Porapak

$\bar{Y} = 6,789$

$\Sigma = .00324$

$\Sigma = 5.22$

$$S_{Y,X} = \sqrt{\frac{.00324}{5}} = .0255$$

$$\text{Cor Coef} = \pm\sqrt{\frac{5.22}{5.22 + .00324}} = .9997$$

		Y	Y_{est}				
$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.247	115	4.745	4.724	.020524	.000421	-1.1123	1.237
3.356	221	5.398	5.434	-.03585	.001285	-.4023	.162
3.472	490	6.194	6.189	.00522	.000027	.3527	.124
3.597	1105	7.068	7.002	.005724	.000033	1.166	1.359

$m = 6.508$

$\ln V_{oi} = 16.407$

Methylene Cl
on Tenax

$\bar{Y} = 5.836$

$\Sigma = .00177$

$\Sigma = 2.882$

$$S_{Y,X} = \sqrt{\frac{.00177}{4}} = .0210$$

$$\text{Cor Coef} = \pm\sqrt{\frac{2.882}{2.882 + .00177}} = .9997$$

		Y	Y_{est}				
$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.096	31	3.434	3.209	.2245	.050402	-1.7950	3.222
3.195	51	3.932	4.091	-.158695	.025184	-.91299	.834
3.3	131	4.875	5.025	-.1503	.022590	.02101	.00044
3.413	344	5.841	6.031	-.1901	.036143	1.02701	1.055
3.484	1031	6.938	6.663	0.27492	.075579	1.6590	2.752

$m = 8.901$

$\ln V_o =$

-24.348

Methylene Cl on XAD-2

$\bar{Y} = 5.004$

$\Sigma = .20990$

$\Sigma = 7.863$

$$S_{Y,x} = \sqrt{\frac{.2099}{5}} = .2049$$

$$\text{Cor Coef.} = \pm\sqrt{\frac{7.863}{7.863 + .2099}} = .9869$$

$10^3/T\,°K$	V_i	Y $\ln V_i$	Y_{est} $\ln V_i$ est from Eq.	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.096	4961	8.509	7.965	0.544	0.296	0.329	0.108
3.003	2734	7.914	7.427	0.487	0.237	−0.210	0.044
2.915	1514	7.323	6.918	0.405	0.164	−0.719	0.516
2.833	898	6.800	6.444	0.356	0.127	−0.193	1.422
$N = 4$		$\bar{Y} = 7.637$			$\Sigma = 0.824$		$\Sigma = 2.090$

Chloroform on Silica.

$m = 5.785$

$\ln V_{i0} = -9.945$

$$S_{XY} = \sqrt{\frac{.824}{4}} = .454$$

$$\text{Cor Coef} = \pm\sqrt{\frac{2.09}{2.09 + .824}} = .847$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
2.183	1338	7.199	7.158	.04120	.00170	0.7704	.594
2.137	859	6.756	6.794	−.03812	.00145	0.4064	.165
2.092	615	6.422	6.438	−.01635	.00027	.0504	.003
2.028	371	5.916	5.932	−.01637	.00027	−.4556	.208
1.988	283	5.645	5.616	.02887	.00083	−.7716	.595

$N=5$

Chloroform on Spherocarb.

$m = 7.906$

$\ln V_a = -10.101$

$\bar{Y} = 6.388$

$\Sigma = .00452$

$\Sigma = 1.565$

$$S_{Y,X} = \sqrt{\frac{.00452}{5}} = .0301$$

$$\text{Cor Coef} = \pm\sqrt{\frac{1.565}{1.565 + .00452}} = .9986$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \overline{Y})$	$(Y_{est} - \overline{Y})^2$
3.096	3965	8.285	8.289	-.00447	.00002	1.356	1.839
3.003	1973	7.587	7.552	.0352	.00124	.619	.383
2.915	879	6.779	6.854	-.0748[illegible]	.00559	-.079	.006
2.833	527	6.267	6.203	.06364	.00405	-.730	.533
2.778	313	5.746	5.767	-.02110	.00045	-1.166	1.359

$m = 7.932$

$\ln V_i =$ ~~[illegible]~~ -16.268

$N = 5$

Chloroform on Porapak

$\overline{Y} = 6.933$

$\Sigma = .0114$

$\Sigma = 4.12$

$$S_{Y,X} = \sqrt{\frac{.0114}{5}} = .0477$$

$$\text{Cr Cof} = \pm\sqrt{\frac{4.12}{4.12 + .0114}} = .9986$$

		Y	Y_{est}				
$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y-Y_{est})$	$(Y-Y_{est})^2$	$(Y_{est}-\overline{Y})$	$(Y_{est}-\overline{Y})^2$
3,096	109	4,691	4,704	–.01262	.000159	–1,348	1,817
3,195	238	5,472	5.433	.03866	.001494	–.6190	.383
3,3	477	6,168	6,207	– .0393	.001544	.1550	.024
3,367	824	6,714	6,701	.01284	.000165	.649	.421
3.436	1359	7.215	7,210	.00524	.000027	1,158	1,341

$m = 7,371$

$\ln V_{dr} = 18.117$

Chloroform on Temp

$\overline{Y} = 6.052$

$\Sigma = .00339$

$\Sigma = 3,986$

$$S_{Y,X} = \sqrt{\frac{.00339}{5}} = .0260$$

$$\text{Cor. Coef.} = \pm\sqrt{\frac{3,986}{3,986 + .00339}} = .9996$$

		Y	Yest				
$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y-Y_{est})$	$(Y-Y_{est})^2$	$(Y_{est}-\bar{Y})$	$(Y_{est}-\bar{Y})^2$
3.096	80	4.382	4.464	-.08216	.006750	-1.7964	3.227
3.195	273	5.609	5.549	.0598	.003576	-.7114	.506
3.3	898	6.800	6.7	.1	.010000	.4396	.193
3.448	3828	8.250	8.322	-.07208	.005196	2.0616	4.250

$m = 10.966$

$\ln V_{i_i} =$

-29.468

Chloroform on XAD

$\bar{Y} = 6.260$

$\Sigma = .02552$

$\Sigma = 8.176$

$$S_{Y,X} = \sqrt{\frac{.02552}{4}} = .0799$$

$$\text{Cor Coef} = \pm\sqrt{\frac{8.176}{8.176 + .02552}} = .9984$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})'$	$(Y_{est} - \bar{Y})^2$
3.096	4414	8.393	8.354	.0387	.00149	.8466	0.717
3.003	2246	7.717	7.767	−.0499	.00249	.2596	.067
2.915	1338	7.149	7.211	−.0121	.00015	−.2964	.088
2.833	830	6.721	6.693	.0278	.00077	−.8144	.663
$N = 4$		$\bar{Y} = 7.507$			$\Sigma = .0049$		$\Sigma = 1.535$

Carbon Tet on Sibel

$m = 6.316$

$\ln V_0 = -11.20$

$$S_{Y,X} = \sqrt{\frac{.0049}{4}} = .035$$

$$\text{Cor Cof} = \pm\sqrt{\frac{1.535}{1.535 + .0049}} = .9984$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \overline{Y})$	$(Y_{est} - \overline{Y})^2$
3.195	7471	8.919	8.895	.02438	.000594	1.551	2.406
3.096	3057	8.025	8.071	−.04634	.00215	.7271	.529
3.003	1454	7.302	7.298	.00405	.000016	−.0459	.002
2.915	742	6.609	6.566	.04286	.001836	−.77789	.605
2.833	352	5.864	5.884	−.02023	.00041	−1.460	2.131

Carbon Tet in Porapak

$m = 8.316$

$\ln V_i = -17.675$

$\overline{Y} = 7.344$

$\Sigma = .00501$

$\Sigma = 5.673$

$$S_{Y,X} = \sqrt{\frac{.00501}{5}} = .0316$$

$$\text{Cr Coef} = \pm\sqrt{\frac{5.673}{5.673 + .00501}} = .9996$$

		Y	Y_{est}				
$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \overline{Y})$	$(Y_{est} - \overline{Y})^2$
3.096	361	5.889	5.871	.017736	.000315	−1.4055	1.976
3.195	918	6.822	6.840	−.01788	.000320	−6.4365	.191
3.3	2568	7.851	7.867	−.0162	.000262	0.59045	.349
3.367	5137	8.544	8.523	.02127	.000452	1.2465	1.554

$m = 9.784$

$\ln V_{oi} = -24.420$

<u>Carbon Tet. on XAD-2</u>

$\overline{Y} = 7.277$

$\Sigma = .00135$

$\Sigma = 4.070$

$$S_{Y,X} = \sqrt{\frac{.00135}{4}} = .01836$$

$$\text{Cor Coef} = \pm\sqrt{\frac{4.07}{4.07 + .00135}} = .9998$$

$10^3/T\,°K$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
2.717	1836	7.515	7.548	−.0329	.00108	1.128	1.273
2.646	1240	7.123	7.083	.0400	.00160	.663	.440
2.545	586	6.373	6.422	−.0487	.00237	.002	.00005
2.451	371	5.916	5.806	.1099	.01207	−.614	.377
2.364	176	5.170	5.236	−.0665	.00442	−1.184	1.401
N=5		$\bar{Y} = 6.420$			$\Sigma = .02154$		$\Sigma = 3.491$

$m = 6.548$

$\ln V_{\infty} = -10.243$

Acetaldehyde on Spherocarb

$$S_{y \cdot y} = \sqrt{\frac{.02154}{5}} = .0656$$

$$\text{Cor Coef} = \pm\sqrt{\frac{3.491}{3.49 + .02154}} = .9971$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \overline{Y})$	$(Y_{est} - \overline{Y})^2$
3.356	664	6.498	6.558	−.06009	.003611	.62306	.388
3.300	537	6.286	6.233	.0526	.002767	.29806	.089
3.247	400	5.991	5.926	.0649	.00421	−.00894	.0000
3.195	264	5.576	5.625	−.0486	.00236	−.30994	.096
3.145	205	5.323	5.335	−.01171	.00014	−.5999	.360

$m = 5.798$

$\ln V_{0i} = -12.9$

$\overline{Y} = 5.935$

$\Sigma = .01309$

$\Sigma = .933$

<u>Acetaldehyde on Propat</u>

$S_{Y,X} = \sqrt{\frac{.01309}{5}} = .0512$

$\text{Cor Coef} = \pm\sqrt{\frac{.933}{.933 + .01309}} = .9644$

		Y	Y_{est}				
$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.247	20	2.996	2.948	.04789	.002293	−1.497	2.242
3.356	39	3.664	3.707	−.04318	.001864	−.7382	.545
3.472	88	4.477	4.515	−.03801	.001445	.0698	.005
3.571	186	5.226	5.204	.022	.000484	.7588	.576
3.663	352	5.864	5.845	.019	.000356	1.3998	1.959

$m = 6.964$

$\ln V_{0i} = -19.664$

Acetaldehyde on Temp.

$\bar{Y} = 4.445$

$\Sigma = .00644$

$\Sigma = 5.327$

$$S_{Y,X} = \sqrt{\frac{.00644}{5}} = .0359$$

$$\text{Cor Coef} = \pm\sqrt{\frac{5.327}{5.327 + .00644}} = .9994$$

$10^3/T$	V_i	$\ln V_i$ Y	$\ln V_{i\,est}$ Y_{est}	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.3	29	3.367	3.383	−.0163	.000266	−1.1594	1.344
3.413	60	4.094	4.081	.01338	.000179	−.46136	.213
3.534	127	4.844	4.827	.01669	.000278	.28464	.081
3.704	352	5.864	5.876	−.01238	.000153	1.3336	1.779

m = 6.171
$\ln V_{0i} =$
−16.981

Acetaldehyde
on

$\bar{Y} = 4.542$

$\Sigma = .000876$

$\Sigma = 3.417$

$$S_{y,x} = \sqrt{\frac{.000876}{4}} = .01480$$

$$\text{Cor. Coef} = \pm\sqrt{\frac{3.417}{3.417 + .000876}} = .9999$$

$10^3/T\,°K$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y-Y_{est})$	$(Y-Y_{est})^2$	$(Y_{est}-\overline{Y})$	$(Y_{est}-\overline{Y})^2$
2.611	39	3.664	3.791	−0.127	.0162	−1.295	1.677
2.681	59	4.078	4.154	−0.076	.0058	−0.932	0.869
2.755	98	4.585	4.538	0.047	.0022	−0.548	0.300
2.833	156	5.050	4.943	0.107	.0114	−0.143	0.020
2.915	254	5.537	5.369	0.168	.0283	0.283	0.080
3.003	420	6.040	5.826	0.214	.0460	0.740	0.548
3.096	771	6.648	6.308	0.340	.1154	1.222	1.493
		$\overline{Y} = 5.086$			$\Sigma = .2253$		$\Sigma = 4.987$

$N = 7$

Ether on Si Gel.

$m = 5.19$

$\ln V_{10} = -9.76$

$$S_{Y,X} = \sqrt{\frac{.2253}{7}} = .179$$

$$\text{Cor Coef} = \pm\sqrt{\frac{4.987}{4.987 + .2253}} = .978$$

$10^3/T\,°K$	V_i	$\overset{Y}{\ln V_i}$	$\ln V_{i\,est}$ (Y_{est}) from Eq.	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \overline{Y})$	$(Y_{est} - \overline{Y})^2$
2.208	2109	7.654	7.641	.01262	.00016	.97246	.946
2.160	1377	7.228	7.2275	.00048	.0000002	.5590	.312
2.092	752	6.623	6.641	−.01822	.00033	−.02754	.001
2.028	430	6.064	6.089	−.0254	.00065	−.5795	.336
1.988	322	5.775	5.745	.03046	.00093	−.9235	.853

$m = 8.622$

$\ln V_{i_0} = -11.396$

Elton A
[illegible]

$N = 5$

$\overline{Y} = 6.669$

$\Sigma = .00207$

$\Sigma = 2.448$

$$S_{y,x} = \sqrt{\frac{.00207}{5}} = .020346$$

$$\text{Cor Coef} = \pm\sqrt{\frac{2.448}{2.448 + .00207}} = .9996$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.247	2715	7.907	7.918	−.01056	.000112	1.2164	1.480
3.145	1211	7.099	7.078	.02080	.000432	.37638	.142
3.096	781	6.661	6.675	−.01398	.000196	−.02662	.001
3.049	547	6.304	6.288	.01578	.000249	−.4136	.171
2.959	254	5.537	5.548	−.01061	.000113	−1.1536	1.331

$m = 8.229$

$\ln V_a = -18.802$

Ether on Porapak

$\bar{Y} = 6.702$

$\Sigma = .00110$

$\Sigma = 3.125$

$$S_{Y,X} = \sqrt{\frac{.0011}{5}} = .0148$$

$$\text{Cor Coef} = \pm\sqrt{\frac{3.125}{3.125 + .0011}} = .9998$$

		Y	Y_{est}				
$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.096	39	3.664	3.615	.04874	.002375	−1.5085	2.276
3.195	78	4.357	4.423	−.06601	.004357	−.70053	.491
3.311	215	5.371	5.369	.001551	.000002	.24547	.060
3.367	332	5.805	5.826	−.02135	.000456	.70247	.493
3.436	615	6.422	6.389	.03268	.001068	1.26547	1.601

$m = 8.159$

$\ln V_{0i} = -21.645$

Ether in Temp

$\bar{Y} = 5.124$

$\Sigma = .00826$

$\Sigma = 4.921$

$$S_{Y,X} = \sqrt{\frac{.00826}{5}} = .0406$$

$$\text{Cor Coef} = \pm\sqrt{\frac{4.921}{.00826 + 4.921}} = .9992$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y-Y_{est})$	$(Y-Y_{est})^2$	$(Y_{est}-\bar{Y})$	$(Y_{est}-\bar{Y})^2$
3.663	10,332	9.242	9.240	.002207	.000005	2.421	5.861
3.472	1504	7.316	7.423	−.107192	.011490	.602	.362
3.413	928	6.833	6.862	−.029043	.000843	.041	.002
3.3	459	6.129	5.787	.3417	.116759	−1.0340	1.069
3.195	98	4.585	4.789	−.203645	.041471	−2.0320	4.129

$m = 9.511$

$\ln V_i = -25.599$

<u>Ether on XAD.</u>

$\bar{Y} = 6.821$

$\Sigma = .17057$

$\Sigma = 11.423$

$$S_{Y,X} = \sqrt{\frac{.17057}{5}} = .1847$$

$$\text{Cor. Coef} = \pm\sqrt{\frac{11.423}{.17057 + 11.423}} = .9926$$

$10^3/T$	V_i	Y $\ln V_i$	Y est $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
2,793	469	6,151	6,154	−.00266	.000007	−1,3604	1,851
2,874	957	6.864	6,880	−.01566	.000245	−.6344	.403
2.959	2090	7,645	7.642	.00348	.000012	.1276	.016
3,003	3184	8.066	8,036	.03011	.000907	.52157	.272
3,096	6953	8.847	8.869	−.02245	.000504	1,3546	1.835

$m = 8{,}963$

$\ln V_o' = -18{,}880$

Ethyl Acetate on Porapak

$\bar{Y} = 7.514$

$\Sigma = .00168$

$\Sigma = 4{,}377$

$$S_{\cancel{y},x} = \sqrt{\frac{.00168}{5}} = .0183$$

$$\text{Cor Coef} = \pm\sqrt{\frac{4{,}377}{4{,}377 + .00168}} = .9979$$

$10^3/T$	V_i	Y $\ln V_i$	Y_{est} $\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.096	230	5.438	5.465	−.02670	.000713	−1.8084	3.270
3.195	544	6.387	6.311	.07595	.005768	−.9623	.926
3.3	1277	7.152	7.209	−.0567	.003215	−.0644	.004
3.413	3516	8.165	8.175	−.00974	.000095	.9016	.813
3.534	10,143	9.225	9.209	.01583	.000251	1.9356	3.747

$m = 8.549$

$\ln V_{0i} = 21.08$

Ethyl Acetate
on temp

$\bar{Y} = 7.273$

$\Sigma = .0100$

$\Sigma = 7.834$

$$S_{y,x} = \sqrt{\frac{.0100}{5}} = .0448$$

$$\text{Cor Coef} = +\sqrt{\frac{7.834}{7.834 + .0100}} = .9994$$

$10^3/T$	V_i	$\ln V_i$	$\ln V_{i\,est}$	$(Y - Y_{est})$	$(Y - Y_{est})^2$	$(Y_{est} - \bar{Y})$	$(Y_{est} - \bar{Y})^2$
3.413	9980	9,208	9,146	.06205	.003850	1,6513	2,727
3,3	2744	7,917	7,994	-.0768	.005898	.4993	.249
3,195	977	6,884	6,923	-.03422	.001538	-.57168	.327
3,096	391	5,969	5.914	.05518	.003045	-1,58068	2,499

$\bar{Y} = 7,495$

$\Sigma = .01433$

$\Sigma = 5,802$

m = 10,196

$\ln V_{0i}$ = -25,153

Ethyl Acetate
on XAD.

$$S_{Y,X} = \sqrt{\frac{.01433}{4}} = .0599$$

$$\text{Cor Coef} = \pm\sqrt{\frac{5,802}{5,802 + ,01433}} = .9988$$

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