AN ABSTRACT OF THE THESIS OF

ROBERT RAYMOND CLAEYS for the Ph. D.
(Name of student) (Degree)

in Chemistry (Analytical) presented on January 29, 1968
(Major) (Date)

Title: FLAME IONIZATION DETECTION OF HYDROCYANIC ACID. ANALYSIS OF TRACE AQUEOUS SOLUTIONS

Abstract approved: [redacted]
Professor Harry Freund

A gas chromatographic procedure was developed for the determination of nanogram quantities of hydrocyanic acid using a flame ionization detector. Excellent chromatograms were obtained on a porous polyaromatic polymer column (Porapak Q) at 60° C. The procedure was employed for the analysis of HCN in aqueous cyanide solutions. Solutions as low as 1 µg/liter (ppb) HCN were analysed in five minutes after a 30 minute concentration period in which air is swept through the solution and HCN collected in a cold trap for gas chromatographic analysis. When interferences are encountered on the Porapak Q column preliminary separation is achieved on a 1, 2, 3-tris(2-cyanoethoxy)-propane (TCEP) on Chromosorb W column. The HCN is trapped from the TCEP column effluent and reinjected on a Porapak Q column for analyses. The amount of chloroform in chlorinated water was also determined by this procedure.

Deactivated diatomaceous earth supports and the fluorocarbon supports were evaluated for the determination of trace quantities of HCN. These supports were either inefficient or adsorption on the solid support caused severe tailing.

Several stationary phases were investigated. Best results were obtained with Carbowax 1540 or 1, 2, 3-tris(2-cyanoethoxy)-propane when Chromosorb W was used as a solid support.

Flame Ionization Detection of Hydrocyanic Acid Analysis of Trace Aqueous Solutions

by

Robert Raymond Claeys

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of
Doctor of Philosophy

June 1968

APPROVED:

[redacted]

Professor of Chemistry
in charge of major

[redacted]

Head of Department of Chemistry

[redacted]

Dean of Graduate School

Date thesis is presented [redacted]

Typed by Ruth Baines for Robert Raymond Claeys

ACKNOWLEDGMENT

I wish to express my sincere gratitude to Dr. Harry Freund for his advice and consultation during the investigations described in this thesis. I also wish to thank the Department of Chemistry for support in this investigation.

TABLE OF CONTENTS

Table of Contents - Continued

Table of Contents - continued

LIST OF TABLES

LIST OF FIGURES

List of Figures - continued

FLAME IONIZATION DETECTION OF HYDROCYANIC ACID. ANALYSIS OF TRACE AQUEOUS SOLUTIONS

INTRODUCTION

Recent investigations of acute toxicity of fish to alkali cyanide salt solutions (72) and complex metal cyanide salt solutions (17) have found HCN to be the toxic factor, and not the free cyanide ion (CN^-) as originally believed. The heavy metal cations are highly toxic, but studies have shown the complex metallic cyanide ions of heavy metals are relatively nontoxic (48).

Doudoroff, Leduc, and Schneider (17) established a direct relationship between acute toxicity and HCN concentration in solutions containing metallocyanide complexes. Thus the need to determine undissociated HCN, rather than total cyanide ion concentration, is very important in toxicological evaluation of cyanide waste disposal in natural streams.

In conjunction with the work cited (17) Schneider and Freund (59) developed a gas chromatographic method for the analysis of hydrocyanic acid in dilute aqueous solutions. Air is passed through a cyanide solution, the HCN is removed from the effluent air by a cold trap, and the contents of the trap injected into a gas chromatograph equipped with a thermal conductivity detector. The lower limit of sensitivity of the method was just beyond the acute toxicity levels of

the fish studied.

To study the effects of sublethal exposures of hydrocyanic acid on fish and its aquatic environment, a more sensitive analytical method was needed. This research was undertaken to develop more sensitive detection methods for the analysis of aqueous hydrocyanic acid solutions.

Evaluation of Reported Analytical Methods for Cyanide Determination

Any determination of HCN in polluted water must be made without a significant change in the $HCN \rightleftharpoons H^+ + CN^-$ equilibrium in the solution. Removal of significant quantities of HCN from an alkali cyanide solution would produce additional HCN, giving rise to an erroneous analysis. Any addition of reagents also must not influence the $HCN\text{-}CN^-$ equilibrium.

Schneider (58, p 2) has calculated the distribution constant of HCN in equilibrium between air and water at low concentrations.

At 20° C $\frac{\text{mg of HCN per liter of gas}}{\text{mg of HCN per liter of solution}}$ = approximately 3×10^{-3}..(1).

Passing 1 liter of air through 10 liters of solution would remove 0.03 % of the hydrocyanic acid from the solution. Thus the method of Schneider and Freund (59) appeared to be a satisfactory and reasonable approach as an initial concentration step for any detection method.

Colorimetric Methods for Cyanide Ion Determination

Several sensitive colorimetric methods exist for the determination of cyanide ion concentrations. Hydrocyanic acid in the effluent air from a cyanide solution could be trapped in a weak solution of sodium hydroxide and the cyanide ion measured colorimetrically.

Snell and Snell (62, p 856-868) list seven principal colorimetric methods. The two most commonly used are the Aldridge (1) and the Epstein (18) methods. In the Epstein method CN^- is converted to CNCl by the addition of Chloramine T. The CNCl forms a blue dye on addition of pyridine containing 1-phenyl-3-methyl-5-pyrazolone and bispyrazolone. In the Aldridge method CN^- is converted to CNBr with bromine water. The CNBr forms a red color on addition of pyridine containing benzidine. The United States Food and Drug Administration has adopted the Aldridge method as an official procedure (70) while "Standard Methods for the Examination of Water and Waste Water", 1960, (3, p 350-358) elects to use the Epstein procedure. The latter reports 0.5 μg cyanide ion sensitivity in 25 ml of water with a 1 to 5 μg effective range and 1.7% coefficient of variation; and a 0.1 μg sensitivity with an effective range of 0.2 to 2 μg, and 3.9 % coefficient of variation when the colored cyanide complex is extracted from the 25 ml water solution with 10 ml of organic solvent. The minimum sensitivity was defined as amount of cyanide ion to

produce an absorbance of 0.05 with a precision of not more than twice the coefficient of variation given.

Grigorescu and Toba (24) have critically compared several colorimetric methods and report analysing 0.5 μg to 2.5 μg of cyanide ion in 1 cm^3 of 0.1 N NaOH by converting CN^- to CNBr with bromine water and measuring the CNBr colorimetrically by the addition of a pyridinic reagent and barbituric acid.

To study the physiological effects of prolonged exposure of fish to hydrocyanic acid or to test polluted water at sublethal levels a sensitivity of 1 μg of HCN/liter of solution was desirable. Using the distribution constant calculated by Schneider (equation 1) and assuming 0.2 μg maximum colorimetric sensitivity, approximately 67 liters of air would have to pass through the solution. Eleven hours would be required to concentrate 0.2 μg of HCN at the apparent maximum air flow of 100 ml/minute. Consequently, colorimetric methods appeared to be too time consuming.

Electrochemical Methods

Polarographic determination of cyanide ion at the dropping mercury electrode has been reported by Kolthoff and Miller (34), and Laitinen, Jenning and Parks (37) have published an amperometric titration procedure. Solutions as low as 4×10^{-5} M (1.08 μg/ml) HCN could be determined by the latter. Stange (65) has employed a

potentiometric procedure for the continuous monitoring of HCN in industrial air effluents. The detection range of the cell was 1×10^{-2} to 1×10^{-5} M HCN. All of the electrochemical methods reviewed were nearly equal or less sensitive than colorimetric procedures, and would be equally time consuming. Gas chromatographic analysis of molecular HCN offered still an additional approach.

Evaluation of Gas Chromatographic Ionization Detectors

The method of Schneider (59) employed a thermal conductivity thermistor bridge for the gas chromatographic detection of HCN. The output signal from the bridge was amplified by a d. c. chopper-stabilized operational amplifier with a gain of twenty. Greater sensitivity might be obtained by ionization detectors; consequently an evaluation of the existing ionization detectors was made.

Sternberg (63) has briefly reviewed detection devices for gas chromatography. The author has separated highly sensitive devices from normal sensitivity devices by distinguishing between those detectors which measure a bulk property of a mixture of carrier gas and sample and those which measure a specific property of the sample not possessed by the carrier gas. Bulk property detectors include thermal conductivity, gas density, dielectric constant, electron mobility and cross section detectors. With these detectors the response to the property measured is not in general more than ten fold

discrimination between pure carrier gas and pure sample vapors. Hence very fine measurement of the property is necessary for high sensitivity. For instance, with very fine design nearly 1 μg of propane can be detected by a thermal conductivity detector.

Some of the specific property detectors include hydrogen flame ionization, beta ionization, photoionization, far ultraviolet adsorption, and electron capture detectors. It is this group of detectors which appeared most promising for detecting trace amounts of HCN.

The same author also lists those detectors which are concentration sensing devices and those which are rate of introduction sensing devices. The concentration sensing devices include thermal conductivity, gas density, electron mobility, and electron capture detectors. The peak area (A) is proportional to the response factor (K) and the quantity of sample (Q), and inversely proportional to the flow rate (F).

$$A = \frac{KQ}{F} \qquad (2)$$

where F is in units of ml/min, Q in milligrams, K in mv/mg/ml, and A in mv-min. From equation 2 a decrease in the column flow will result in an increase in the peak area. This is particularly important in trace analysis where high sensitivities are needed.

The hydrogen flame and beta ionization detectors respond to the rate of introduction of sample into the detector.

$$R = \frac{K' dn}{dt} \qquad (3)$$

where t represents time in seconds, n is the number of moles of sample, K' is the response factor (coulombs/mole), and R is the response of the detector in ampheres. From equation 3 the response increases as the rate of sample entering the detector increases. Hence increasing the carrier gas flow will increase the response up to some maxima.

Beta Ionization Detectors

Lovelock (43) first introduced this detector in 1958 using argon carrier gas. The common term for this detector became the argon ionization detector. Further improvements by Lovelock involving a triode detector was later published (40). In this detector β radiation from a 10 mc Sr^{90} source in a 400 V potential field excites argon to its metastable state. The energy stored by the metastable atoms (11.7 ev) is then transferred to the column effluent vapors. Ionization occurs with all molecules whose ionization potential is equal to or less than 11.7 ev. The response is related to the mass of substance introduced, and is generally independent of the type of compound.

HCN has an ionization potential of 13.9 ev (49) and would not be detected by an argon ionization detector. In theory helium

and neon with a metastable excitation energy of 19.8 and 16.4 ev, respectively, could be used in place of argon to detect all molecules. Berry (8) has reported using helium with some success, but a very elaborate helium purifying procedure was required. Lovelock (42) in comparing ionization detectors notes little success has been achieved with helium carrier gas in beta ionization detectors. Consequently other ionization detectors were considered for HCN detection.[1]

Photoionization Detectors

With this detector the column effluent enters an ionization chamber where ionization of the sample vapor is achieved by ultraviolet light. The u. v. light is produced in the same chamber by a glow discharge within a hollow cathode. The vapor ions formed are collected at a cathode, and the current amplified by an electrometer. The discharge can be maintained in a helium atmosphere at atmospheric pressure if radiofrequency is supplied to the discharge (42).

[1]Since the completion of this work, Varian Aerograph (28) has reported using helium in a beta ionization detector. A molecular sieve trap at liquid nitrogen temperature is used to remove the impurities from the helium. The signal-to-noise ratio for methane was 55 times greater than a flame ionization detector. This promises to be an extremely sensitive detector for the detection of fixed gases and substances with high ionization potentials.

The detector has a low background current of 10^{-10} amperes, an ionization efficiency between a flame and an argon detector, and a wide range of linearity.

Lovelock (42) found most organic and inorganic gases could be detected. When commercial carrier gas is used the common contaminants absorb the more energetic photons; and the permanent gases, water vapor, and some molecules with high ionization potentials are not detected. Since HCN has a high ionization potential and gas purity might be a serious problem, further considerations of this detector were temporarily dropped.

Electron Capture Detectors

Lovelock and Lispsky (44) reported a sensitive and selective detector for the measurement of compounds having an affinity for free electrons. A low energy beta radiation source (^{3}H or ^{63}Ni) provides a source of electrons. The potential of the ion chamber is just sufficient for the collection of all of the free electrons. When an electron capturing compound enters the ion chamber the electron current drops as a result of the lower mobility of the negative molecular ion formed compared to that of a free electron. This detector may be potentially sensitive to the detection of HCN, and should be investigated.

Electron Mobility Detectors

This detector was developed for the analysis of permanent gases (41). Because of its high ionization potential, HCN might be detected as a permanent gas.

A collision between an electron and a noble gas atom in a low electric field is essentially elastic, while the collision between an electron and an organic molecule is inelastic. The direction of the electron following elastic collisions is completely randomized by the large number of collisions. Following inelastic collisions the energy and velocity of the electron is reduced and tends to drift in the direction of the electric field. Thus an increase in current would result when the sample vapor from the column effluent entered the ion chamber.

Willis (69) used an argon detector for an ion chamber and argon contaminated with an ionizable gas as a column carrier gas. As permanent gases from the column entered the detector a decrease in ion current would occur.

Lovelock (41) employed an argon detector containing a tritium source and pure monoatomic argon as a carrier gas. The tritium source served as a cathode, and a pulse generator was connected to the anode. The pulse duration was so adjusted that the electrons did not have sufficient time to migrate to the anode. The presence

of traces of more complex gases (N_2, CO, CH_4) from the column caused a lowering of the mean agitation velocity of the electrons, and this resulted in an increase in their bulk drift velocity toward the anode.

Smith and Fidiam (61) have described in detail a similar electron mobility detector for the detection of permanent gases. A specially built pulse generator with a pulse-width and amplitude constant to ±0.1 % or better was required for low noise and good baseline stability. The ultimate sensitivity of CO_2 was 4×10^{-10} gram/sec or 0.6 ppm in air. For a 30 second peak 12 nanograms of CO_2 could be detected. Hydrogen sulfide gave a negative peak indicating electron capture is dominant. Propane and the olefins gave anomolous responses.

Although this detector is very sensitive to permanent gases, it is uncertain what the response might be to HCN. The technical problems associated with building the detector and pulse generator and the anomalous response to olefins temporarily discouraged further investigation of this detector.

Flame Ionization Detector

Harley, Nel, and Pretorius (26) and McWilliam and Dewar (46) were the first to develop a hydrogen flame ionization detector. Very few ions are produced in a hydrogen-air or hydrogen-oxygen

flame; in the presence of organic carbon compounds a large increase of ions is produced, resulting in a large signal-to-noise ratio. Two different theories on the mechanism of ionization in a hydrogen flame has gained wide acceptance. One explanation, the carbon-aggregate hypothesis proposed by Stern and presented in several books on flames (22, p 206; 39, p 299), suggests that each detected species undergoes a series of reactions with the formation of carbon as one of the products. Stern calculated a species with an ionization potential of 5 ev was required to account for the high degree of ionization. Since CO, CO_2, OH, O, H_2O, CH, and C_2 all fall in the 11-16 range, solid graphite with a work function of 4 ev was credited as the principal source of ions.

Calote (10) suggested that chemi-ionization not thermal ionization must be responsible for the high ion concentration. The chemi-ionization theory holds that the energy released by strongly exothermic chemical reactions is retained in the product molecules and leads to ionization before thermal randonization of the enery occurs. Further support of both hypotheses is given by Perkins et al. (52) and Sternburg, Gallaway, and Jones (64).

Because of its high ionization potential and single carbon atom, HCN was thought to be insensitive to flame ionization detection. The flame ionization detector has been reported to be insensitive to carbon monoxide, formic acid, formaldehyde, carbon disulfide

and cyanogen (CN_2) (52). Sternburg, Gallaway, and Jones (64) found acetonitrile (CH_3-C≡N) to have an effective carbon number, Nc, of 1.35 based on the value of 7.00 for n-heptane:

$$Nc = 7.00 \times \frac{\text{Peak area acetonitrile/Moles of acetonitrile}}{\text{Peak area n-heptane/Moles of n-heptane}} = 1.35 \ldots (4).$$

If one gives a value of 0.35 for the -C≡N group HCN should be approximately 0.35 times as sensitive as methane.

Condon (11, p 35) has reported 3.3×10^{-12} grams per second or 0.002 ppm as the minimum detectable quantity of propane by flame ionization detection. Assuming the sensitivity of methane to be 1/3 that of propane and that HCN is 0.35 times as sensitive as methane, the minimum detectable quantity of HCN would be:

$$3 \times 10^{-12} \text{ g/sec} \times \frac{3}{0.35} = 2.6 \times 10^{-11} \text{ g/sec of HCN}$$

If a 30 second HCN peak is eluted from a chromatographic column, the minimum detectable quantity would be 7.8×10^{-10} g or 0.78 ng of HCN. For the analysis of 1 ug/liter solutions of HCN, collection of one liter of air would require the detection of three nanograms of HCN (equation 1). Thus the flame ionization detector appeared to meet the required sensitivity for this investigation.

A STUDY OF FLAME PARAMETERS

The electrode design, interelectrode distance, and the effects of air, hydrogen and carrier gas flow on detector response have been extensively studied by Desty, Geach and Goloup (14). They found the shape of the electrodes was not critical to response. Sternberg, Gallaway and Jones (64) have studied the mechanism of response of flame ionization detectors using a Beckman GC-2 hydrogen flame detector with a 0.016 inch ID jet, the same type of flame ionization detector used in our laboratory. A continuous-flow gas sample introduction system was employed to eliminate the need for a column in investigating flame response. The detector response showed a maximum at 30 ml/min hydrogen flow for heptane with a helium carrier gas flow of 60 ml/min. Keeping the hydrogen and helium flow constant the detector response increased with increasing air flow, reaching 90 % of maximum response at 200 ml/min air flow. The rate of mass input of heptane was also studied. The detector response increased with increasing mass input, reaching a maximum at 60 ml/min helium flow. Only a small decrease in response was evident above 60 ml/min helium flow.

The effect of the nature of carrier gas on response was also investigated. Helium, argon, and nitrogen were compared. The relative responses at maximum response parameters were I.00

for helium, 1.16 for argon, and 1.03 for nitrogen. Addition of oxygen to the carrier gas did not appreciably increase the detector sensitivity.

Enrichment of air with oxygen was also studied (64). A two-fold increase in sensitivity was obtained with a 50 % oxygen atmosphere using helium, argon, or nitrogen carrier gases. Instead of addition of oxygen to air, oxygen and nitrogen could be mixed, omitting the need for an air tank.

Enhancing Flame Ionization Detector Sensitivity

The placement of alkali salts in the upper combustion zone of the flame has greatly increased the detection of phosphorus compounds. Giuffrida (23) placed a spiral platinum wire coated with alkali sulfate salts just above the flame. Coahran[2] put sodium sulfate crystals in a ceramic cup which was placed on top of the jet tip. Hartmann (27) made a small cesium bromide disk with molding powder which sat on top of a quartz jet. The detection of phosphorus compounds was increased by more than 1000 times. Karman (31) increased the detection sensitivity of halide and phosphorus

---

[2]Coahran, D. R. Paper read at the Northwest Regional American Chemical Society Conference, Corvallis, Oregon. June 1965.

compounds by placing a platinum screen coated with sodium hydroxide above the flame and detecting the increase ion formation by a second flame ionization detector. Since both nitrogen and phosphorus are in Group V of the periodical table, it may be possible to selectively increase the sensitivity of the flame ionization detector to HCN and other nitrogen containing compounds.

Comparing the Sensitivity of HCN by Electron Capture and Flame Ionization Detection to Thermal Conductivity Detection

Experimental

Electron Capture Detection. An Aerograph 600-B gas chromatograph equipped with a 250 mc tritium foil electron capture detector and a Beckman GC-2 gas chromatograph equipped with a thermal conductivity detector were used to compare detector sensitivities. A 3.4 liter glass cylinder was vacuum filled with HCN and 3.0 cm^3 of the HCN-air mixture was injected into each instrument. The peak areas from each instrument were compared.

Flame Ionization Detection. Optimum response parameters were first established using a Beckman GC-gas chromatograph equipped with a flame ionization and thermal conductivity detector connected in series with the column. The signal from the flame detector was fed into a Beckman electrometer with a maximum current sensitivity of 5×10^{-13} amps/mv, i.e., an input signal of

5×10^{-13} amps will produce a one millivolt output signal. The electrometer output signal was recorded on a 1.05 mv, 1 second Brown recorder. Iron-constantan thermocouple measurements of the injection port column, and detector temperatures were also recorded by the use of 100/1500 ohm voltage dividers. The inlet heater tape was connected to a multitap transformer in the GC-2 circuitry by means of a single pole, four positioned switch. This permitted heating the inlet port at column temperatures below 100^{o} C.

A 3.4 liter glass cylinder filled with HCN and air served as a sample source. The variation in response to air, hydrogen, and nitrogen carrier gas flow rates was determined along with oxygen enrichment of the air feeding the flame.

In testing flame sensitivity enhancement the sensitivity of HCN was compared with and without the presence of inorganic salts in the flame. A small 2.6 mm OD x 1.6 mm ID x 3 mm long ceramic insulator was placed on the jet tip, and crystals larger than 1.6 mm were put into the ceramic cup. A small ball of platinum was also tested.

Results and Discussion

Preliminary results indicated the electron capture detector was not more than two to three times more sensitive to HCN than the thermal conductivity detector. The thermal conductivity detector

sensitivity at 20 ml/min helium flow and 250 ma current was 40 mv-ml/ul of benzene (16), and the standing current of the electron capture detector at 25 ml/min nitrogen flow was 6.6×10^{-12} amps or 2.20 millivolts. Both detectors are sensitive to water, which is a disadvantage in the analysis of aqueous solutions of HCN.

In determining the optimum flame parameters small variations in sample quantities were corrected by the thermal conductivity response where the carrier gas flow was held constant. Figure 1 shows the variation in detector response to changes in the hydrogen flow, keeping the air and carrier gas flow constant. Figure 2 shows the variation in detector response with increasing air flow. The air enters the detector chamber at the base of the detector and not through the jet tip. Very high air flows may cause physical turbulence and should be avoided.

A large increase in response was obtained with increasing carrier gas flow (Figure 3). Optimum conditions were obtained between 65-85 ml/min. The flame blew out when the carrier gas exceeded 125 ml/min. Figure 3 illustrates the effect of the rate of mass input on the response of a flame ionization detector as discussed previously.

An initial investigation of enriching the air with oxygen showed a 1.5 to 2.0 fold increase in HCN sensitivity, but the signal to noise ratio was not significantly larger. This may have been a gas

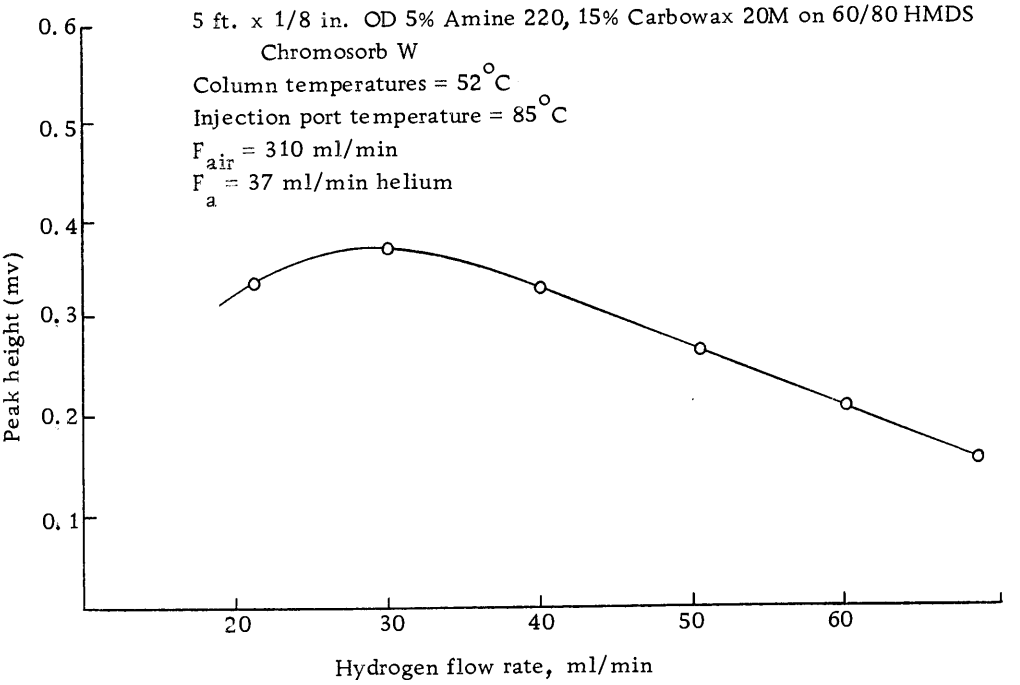


Figure 1. Effect of hydrogen flow rate on detector response to HCN.

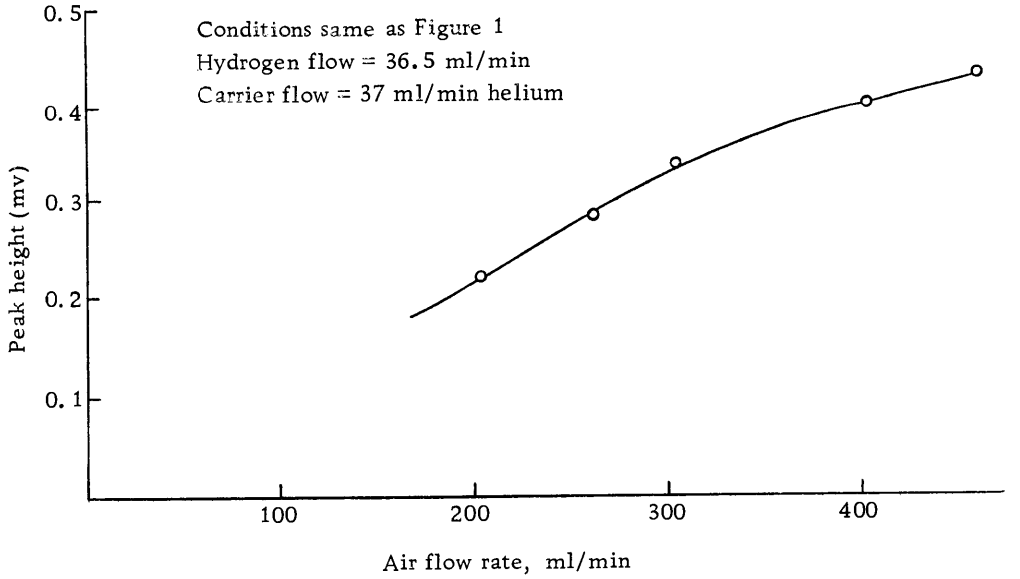


Figure 2. Effect of air flow rate on detector response to HCN.

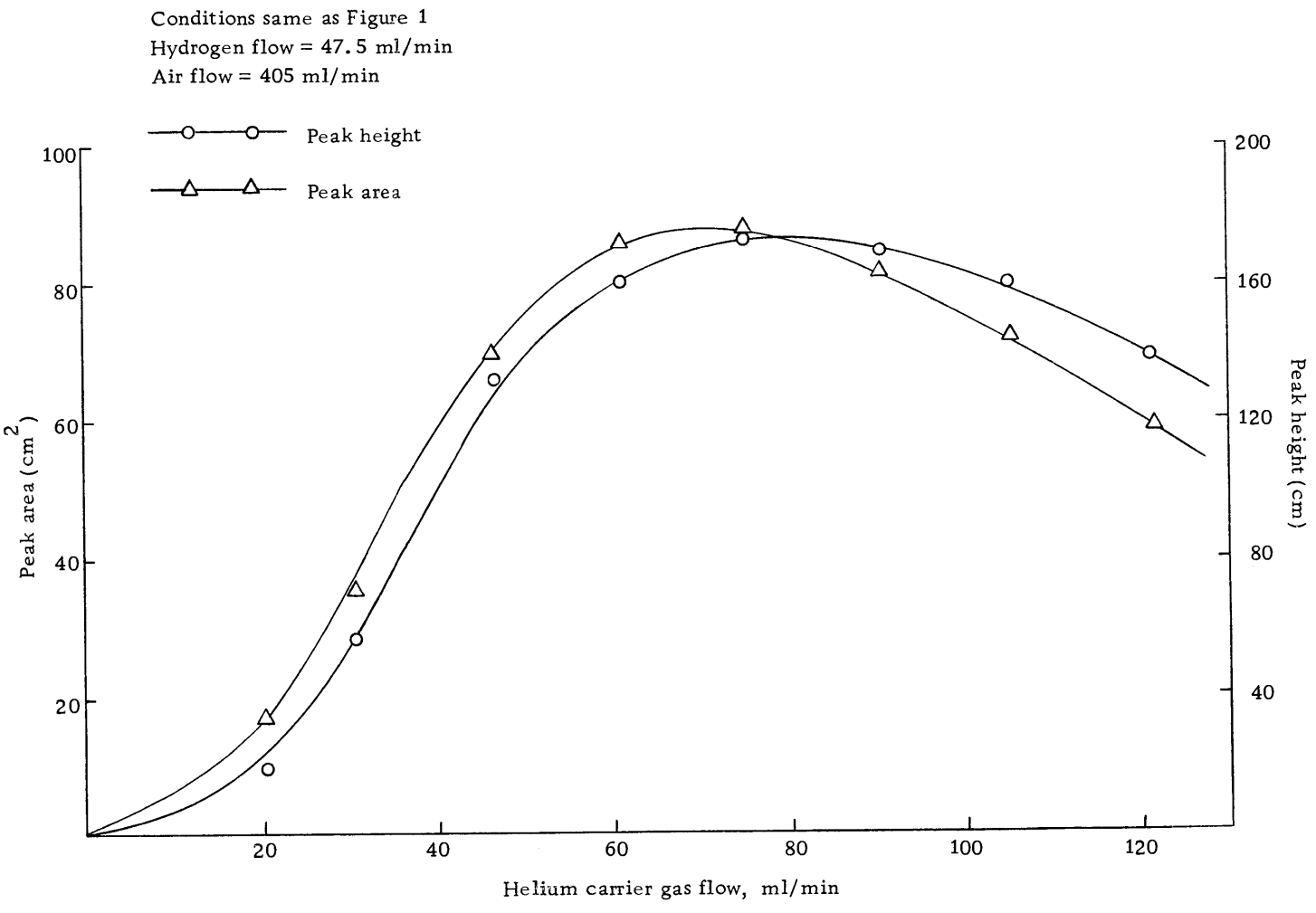


Figure 3. Effect of carrier gas flow on flame ionization response to HCN.

purity problem or a dirty detector problem. Further work may have been fruitful.

The placement of platinum gauze in the flame caused a small decrease in the sensitivity of HCN and a ten fold decrease in the sensitivity of hexane. The platinum gauze probably cooled the flame and reduced ion formation. The flame was easily extinguished by flow fluctuations. A 50 to 100 fold decrease in the peak area of HCN was observed when sodium hydroxide, sodium sulfate, calcium carbonate and ferrous sulfide were placed in the flame. Only a small decrease in peak area was observed with sodium cyanide. No improvement was found with any of the salts studied.

Operating the flame detector at the optimum response conditions described, the response to approximately 0.5 mg of HCN was 1300 times greater at an attenuation of 1.0×10^{-11} amps/mv than the thermal conductivity detector at full sensitivity. The flame ionization detector is also less sensitive to carrier gas flow fluctuations and temperature changes than a thermal conductivity detector.

INVESTIGATION OF SOLID SUPPORTS

Hydrocyanic acid is a polar molecule with a dipole moment of 2.93 debye units compared to 1.84 for water. Polar molecules tend to adsorb on the solid support and elute from the column with a tailing edge. Adsorption on the solid support is a particularly difficult problem with trace analysis. As the sample size becomes smaller a greater fraction of molecules are adsorbed, resulting in longer retention times and severe tailing. This effect is illustrated in Figure 4.

Adsorption may be caused by weak van de Waals forces or strong hydrogen-bonding forces. Hydrogen-bonding is the most influential in causing adsorption on the support. Tailing can also be caused by other factors such as non-plug injection of the sample on the column. However, if adsorption is occuring on the solid support in Figure 4, then the data should follow the Freundlich or Langmuir isotherm equation.

Freundlich Equation: $Y = K P^{1/n}$ .....(2).

Y is ratio of the weight of adsorbate per unit weight of adsorbent, K and N are constants, and P is the equilibrium pressure. If the equilibrium vapor pressure (P) of a solute is proportional to the sample size (λ) and the retention volume of a solute is proportional to the adsorption on the solid support, then we may substitute:

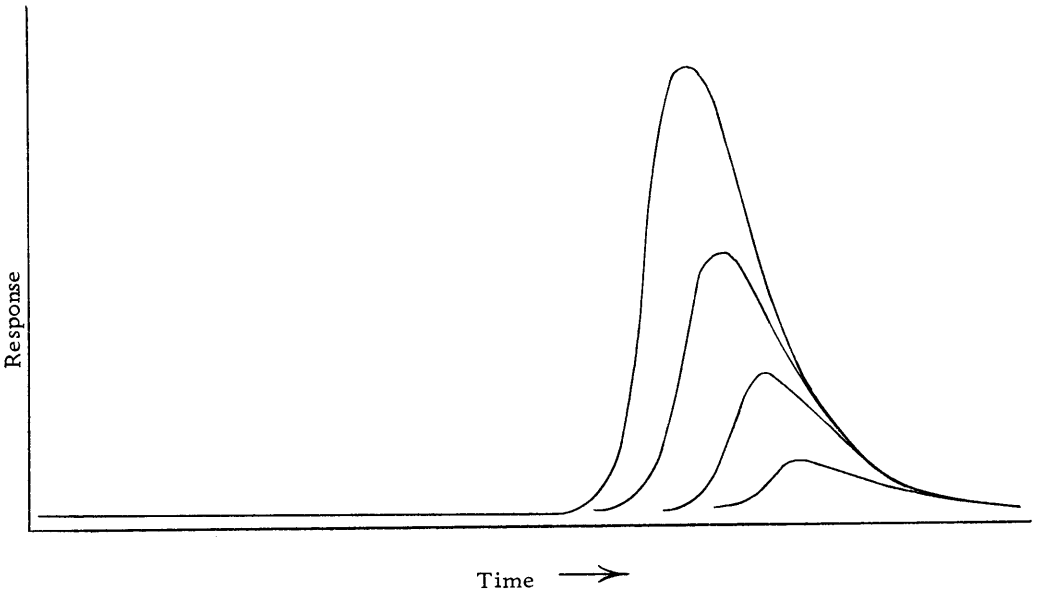


Figure 4. Chromatograms of decreasing sample size.

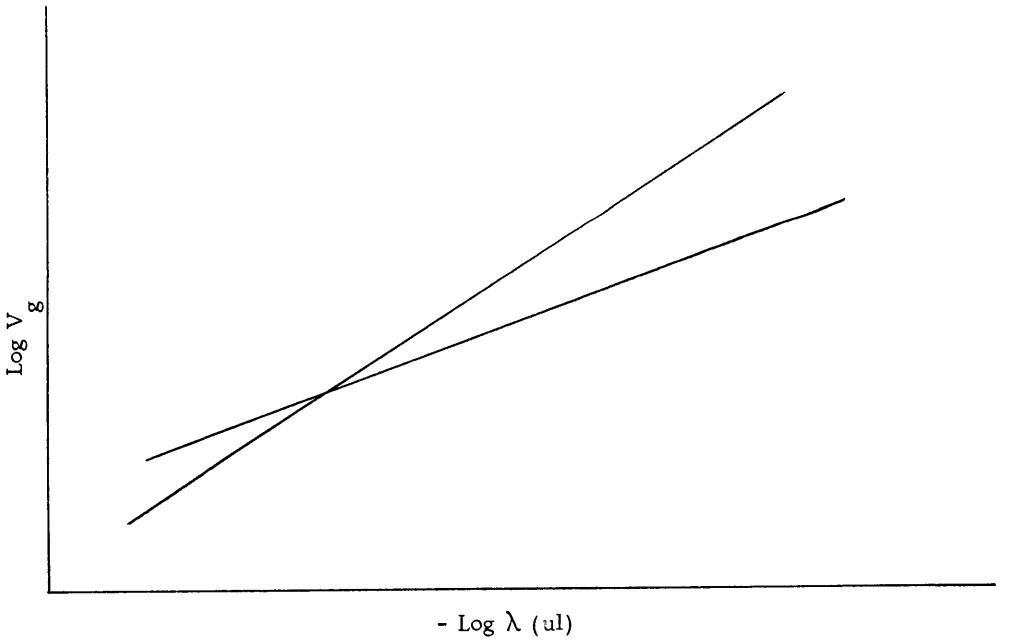


Figure 5. Effect of sample size on retention volume.

$$V_g = k\lambda^{1/n} \quad \ldots\ldots\ldots\ldots (3)$$

or

$$\text{Log } V_g = \text{Log } k + 1/n \log \lambda \quad \ldots\ldots\ldots (4)$$

In plotting the logarithm of the retention volume of methanol and ethanol against the logarithm of the sample size, Scholz and Brandt (60) obtained a straight line similar to Figure 5.

The amount of peak tailing is very dependent on the polarity of the stationary (liquid) phase and the solute being eluted through the column. Polar stationary phases tend to hydrogen bond with the hydroxyl groups on the surface of the support, thus deactivating the support. Nonpolar stationary phases do not deactivate the solid support and extreme tailing occurs with the polar solutes. For example, hexane is a nonpolar compound and does not adsorb on most solid supports. Hence a polar or nonpolar stationary phase may be used without peak tailing occuring. However, the polar ethanol molecule can readily hydrogen-bond with the solid support. Severe tailing may occur on a column containing a nonpolar stationary (SE-30). In substituting a polar stationary phase (Carbowax 20 M) the support is deactivated, and moderately good ethanol peaks are obtained. Consequently polar liquid phases must be used with active supports for trace HCN analysis; with inactive solid supports, such as Teflon, either polar or nonpolar liquid phases may be selected.

In selecting a suitable solid support for polar compound analyses the general function of the support should be kept in mind.

Besides the requirement of a high surface area, the support must (1) be inert to the compounds eluted, and (2) must have a strong affinity for the stationary (liquid) phase. These properties tend to be contradictory, and a compromise is sought. Highly active porous supports such as the diatomaceous supports, are easily wetted by the liquid phase and thin films result; the inert fluorocarbon supports are poorly wetted and an uneven distribution of the more polar liquid phases may occur.

Diatomaceous Earth Supports

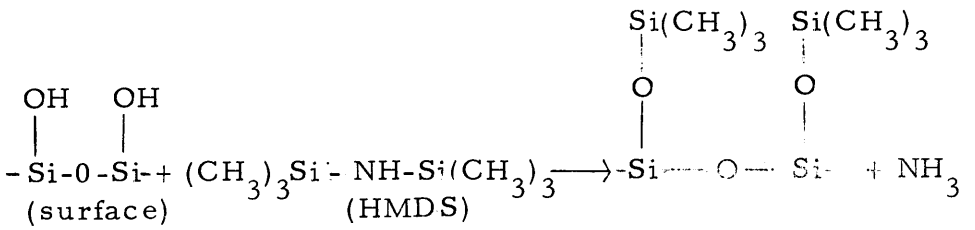
The first approach to the analysis of trace amounts of HCN was the use of diatomaceous earth supports deactivated for polar compound analysis. Ottenstein (50) has presented an excellent review of supports used in gas chromatography. Some of the physical properties of the supports are listed in Table 1. Note for a given column volume packed with Chromosorb P or W the surface area of the Chromosorb P column is eight times larger than the Chromosorb W column. Chromosorb P also is much less fragile than Chromosorb W, whose particles tend to break up during column packing. Martin (47) has measured the drop in surface areas as the concentration of liquid phase is increased. The difference in effective surface area between Chromosorb W and P becomes smaller as the liquid phase concentration increases. Ettre (19) found the specific surface areas

Table 1. Physical properties of some solid supports

Support	Mesh	Packed density g/cm^3	Surface area m^2/g	Surface area m^2/cm^3
Chromosorb P[b]	40/60	0.47	≈4.0	1.87
Chromosorb W[b]	40/60	0.24	≈1.0	0.24
Glass beads	80/120	1.46[a]	0.36[d]	0.5
Teflon-6	40/60	0.49[e] 0.95[a]	7-8[e]	3.4 6.7
Kel-F (3081)	Full range	1.35[a]	2.2[c]	3.0
Fluoropak 80	Full range	0.69[a]	1.3[c]	0.9
Porapak Q	50/80	0.30[a]	50	15

[a] Laboratory measurement
[b] Ottenstein (50)
[c] Kirkland (32)
[d] Sawyer & Barr (57)
[e] Johns-Manville Bulletin FF 124

of the solid support did not influence the efficiency of the column if the surface area was greater than 1 m^2/g. Thus adsorption properties may be more important to the gas chromatography of polar compounds than surface area when comparing supports. Perrett and Punnell (53) measured the surface concentration of hydroxyl groups by measuring the quantity of ammonia released by the reaction of hexamethyldisilizane (HMDS):



They report 4×10^{19} groups/m^2 for brick or Chromosorb P and 2.5×10^{19} groups/m^2 for celite or Chromosrob W. This data suggests that the major difference in adsorption of Chromosorb P or W is not fundamental, but lies in the greater surface area/unit volume of Chromosorb P.

The difference in density also results in a larger quantity of liquid phase with Chromosorb P when columns of equal percent liquid phase by weight are prepared. However, the film thickness will be comparable because of the larger surface area of Chromosorb P.

Several deactivation reagents have been used to react with the hydroxyl groups on the support and reduce the amount of

adsorption. Kirkland (33) has critically compared dimethyldichlorosilane (DMCS), hexamethyldisilazane (HMDS), and trimethylchlorosilane (TMCS) treatment of diatomaceous earth supports, and obtained best results with acid washed DMCS treated supports. With silanization a decrease in surface area from 1.5 m^2/gram to 0.8 m^2/gram was reported for Chromosorb W.

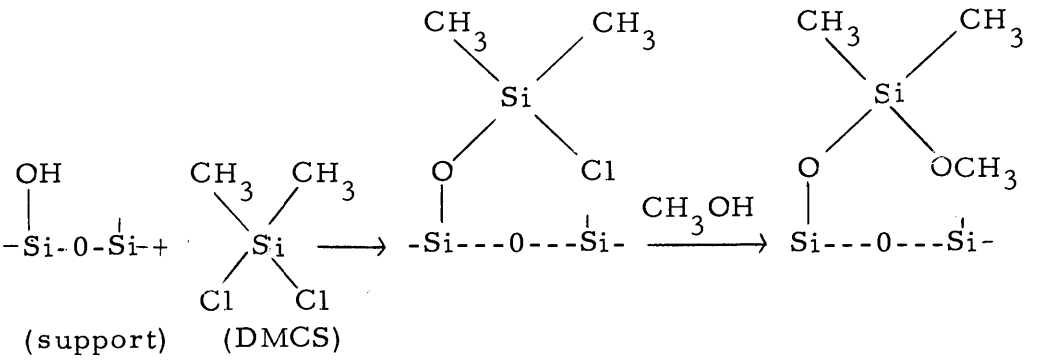
Column Preparation

Experimental. A detailed description of the column preparation is given here because of the wide variation in techniques which exist in the literature. Chromosrb W is comparatively more fragile than Chromosrb P, and should be handled with care.

In this work the support was size graded gently into small mesh cuts (40/60, 60/80), and poured into a verticle glass column. The material was then acetone washed and distilled water rinsed. Two column volumes of concentrated HCl were then added to remove iron on the surface of the support which could complex with HCN and any presence of sodium carbonate flux used in the preparation of Chromosorb W. Subsequently the support is washed with two column volumes of distilled water, and transferred to a large beaker. Distilled water is added under pressure to agitate the mixture. As the coarse particles settle out, the fine particles are decanted. This step is repeated until most of the fines are removed and the water

is neutral. The support is then vacuum dried in a petri dish overnight at 130° C.

To deactivate the solid support 20 ml of DMCS was dissolved in 200 ml of dry benzene, and 150 cm^3 of the dry acid washed support was then added. The mixture was reflux for four hours under dry conditions, 2 ml of isopropyl alcohol was then added, and the mixture refluxed for an additional two hours. Excess absolute methanol was added to destroy any unreactive DMCS and to react with any unreactive chloride groups:



The support was packed into a glass column and washed with two column volumes of absolute methanol, and then dried in a petri dish in an 130° C oven. This procedure is a modification of those reported by Perrett and Pernell (53) for HMDS silanization and that of Kirkland for DMCS treatment of the support (33).

Three methods of coating the support were investigated. Techniques in coating the solid support by rotary evaporation and by steam bath evaporation were first investigated using a red dye, 4-nitro-o-phenylene diamine. This compound is yellow when dissolved

in acetone; hence the removal of the solvent can be followed visually.

"In-place" coating of the support was also investigated as described by Averill (4). A 9 foot x 3/16 inch OD column (22.3 cm^3) was filled with Chromosorb W. Two column volumes of an 8 % w/v solution of Carbowax 1540 in chloroform (3.60 grams in 45 ml) was passed through the column at a rate of 0.3 ml/min or one drop per 10 seconds. The solution was collected at the end of the column, and the liquid phase weighed after evaporation of the solvent. The column was divided into two equal sections, and the HCN retention volume of each half was compared.

Evaporation of the solvent on a steam bath was used in most of our work. The stationary phase is first dissolved in a volume of solvent equal to the solid support volume. The solid support is added with stirring and allowed to stand for 10 to 30 minutes. The size of beaker is selected to give a support depth of not more than one inch. The beaker is rotated at a 45^{o} angle and the particles on the sides occasionally removed with a thin spatula. The support is poured into a petri dish just as it becomes free flowing, and dried under vacuum.

The aluminum tubing is first washed with concentrated nitric acid to remove nichel on the surface. After rinsing the tubing is washed with acetone and dried. The tubing is then filled with the coated support in a vertical position with light tapping and with soft vibration. After filling, the column is connected to a nitrogen

cylinder and 20 to 30 psig pressure is applied while gently vibrating the column. Additional packing is generally required. A small glasswool plug is installed, being careful not to crush the packing. Since glasswool is very adsorptive, fingers should always be washed just prior to installation. The ratio of the coil diameter to the column diameter should not be less than a factor of twenty.

Results and Discussion. In preparing gas chromatographic columns vertical packing resulted in a more tightly packed column than vacuum packing, especially with 1/8 inch OD columns over five feet in length. The front of the column should always be connected to a 20 to 30 psig gas cylinder for final packing.

With rotary evaporation of the solvent the solid support near the neck of the flask was not coated, and the bottom of the flask was colored when the support was coated with a red dye. The use of a large flask with respect to the solid support volume and very slow evaporation, 4 hours per 100 ml of solvent, is recommended. The roatary evaporation method has the advantage of slow solvent removal, and crushing of particles is avoided.

"In-place" coating of the support is time consuming and results in an uneven distribution of the liquid phase towards the front of the column. Nearly 3/4 of the liquid phase was contained in the first half and 1/4 in the second half of the column described. The concentration of the stationary phase on the column was calculated

to be 14.7 % w/w. Four column volumes of 4 % w/v solution may be necessary to distribute the liquid phase more evenly through the column.

Steam bath evaporation is fast, but the support can easily be crushed by mixing. Where an exact predetermined concentration of liquid phase is not critical the coating procedure of Parcher and Urone (51) appears to be the most satisfactory.

Chromatographic Column Comparisons

Experimental. In selecting the most suitable solid support for the analysis of HCN similar columns were prepared with 20% Carbowax 20M on Chromosorb P and W. Different column lengths and diameters were tested to determine optimum column parameters. Similar columns were also compared with and without DMCS treatment of Chromosrb W.

Results and Discussion. When equal length columns of Chromosorb P and W were compared, HCN tailing was reduced slightly with Chromosorb W, but the resolution of the two columns appeared to be comparable. Thus Chromosorb W was used in many of the studies in this investigation.

In comparing the effect of silanization of the support on HCN tailing, little improvement could be observed with a polar liquid phase on acid washed Chromosorb W by DMCS treatment. The upper

chromatogram in Figure 6 shows the results obtained on the untreated Chromosorb W column.

The lower chromatogram in Figure 6 shows the combined effect of a longer column with courser support and a larger column diameter. Shorter columns with smaller diameters and a finer particle size packing are particularly desirable in trace analysis of polar compounds. Adsorption is reduced owing to a smaller quantity of support with smaller column diameters, and peak broadening is diminished. Best results were obtained with a 60/80 mesh cut support (250 to 177 microns) using 1/8 inch OD columns under 8 feet in length. With longer columns 3/16 inch OD tubing was required since inlet pressures were limited to 25 psig to avoid leaks in a gas sampling valve used to introduce HCN samples.

Although suitable chromatograms could be obtained with microgram quantities of HCN on a column as shown in the upper chromatogram of Figure 6, smaller quantities eluted similar to the broken curve in the same figure. Therefore other supports were investigated.

Glass Bead Solid Support

Glass beads are similar to the diatomaceous earth supports in their molecular constituents. Frederick, Miranda and Cooke (21) found glass beads much less adsorptive than Chromosorb P coated

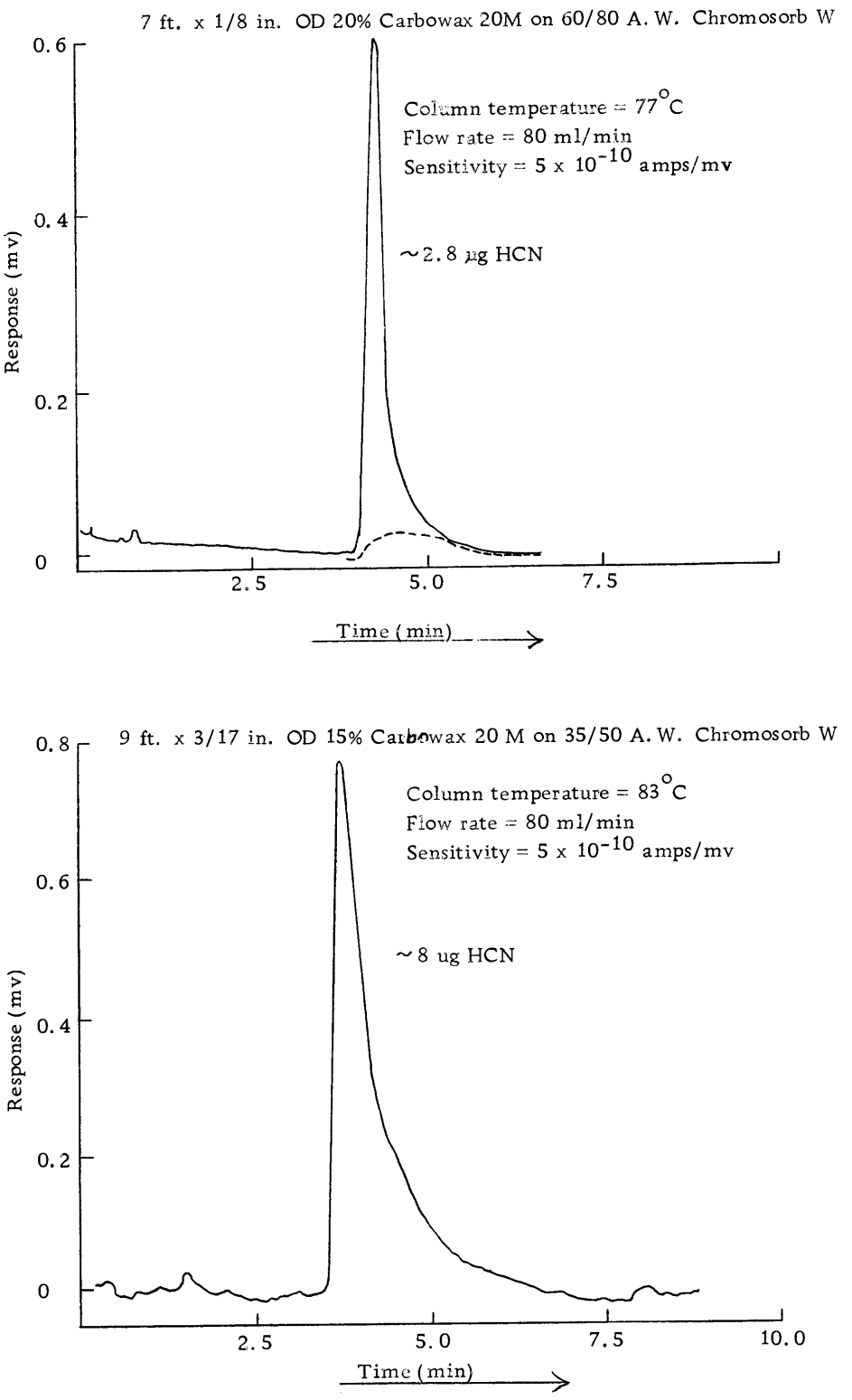


Figure 6. Effect of column diameter and particle size on HCN tailing.

with low concentrations of nonpolar stationary phases. Optimum conditions for 70/80 mesh glass beads were reported to be 0.16 % liquid phase and 70 ml/min helium flow for 1/4 inch OD columns. In investigating glass bead columns Dewar and Mairer (15) found glass beads to be inefficient because of adsorption and nonuniformity of the stationary phase layer. Addition of 1.25 % w/w Super-floss prevented pockets of the liquid phase from forming between two glass beads in contact with each other. They were able to obtain HETP values of 1 mm, which is comparable to efficient diatomaceous earth columns.

Experimental. In our investigation a 14 foot x 3/16 inch OD aluminum column was filled with 0.2 % Carbowax 1540 on 80/120 mesh glass beads. The column preparation described for diatomaceous earth supports was also used for glass beads. A chromatogram obtained with this column is shown in Figure 7 for 7 ug of HCN.

Results and Discussion. The HCN peak in Figure 7 shows severe tailing. A chromatogram of chloroform and methylene chloride shows the poor resolution obtained on this column. The particles were tacky and did not pack well. A 0.1 % Carbowax 1540 on 80/120 mesh glass bead packing was nearly free flowing, but the column efficiency remained poor. Silanization may have reduced HCN adsorption, but poor column efficiencies discouraged further research with this support.

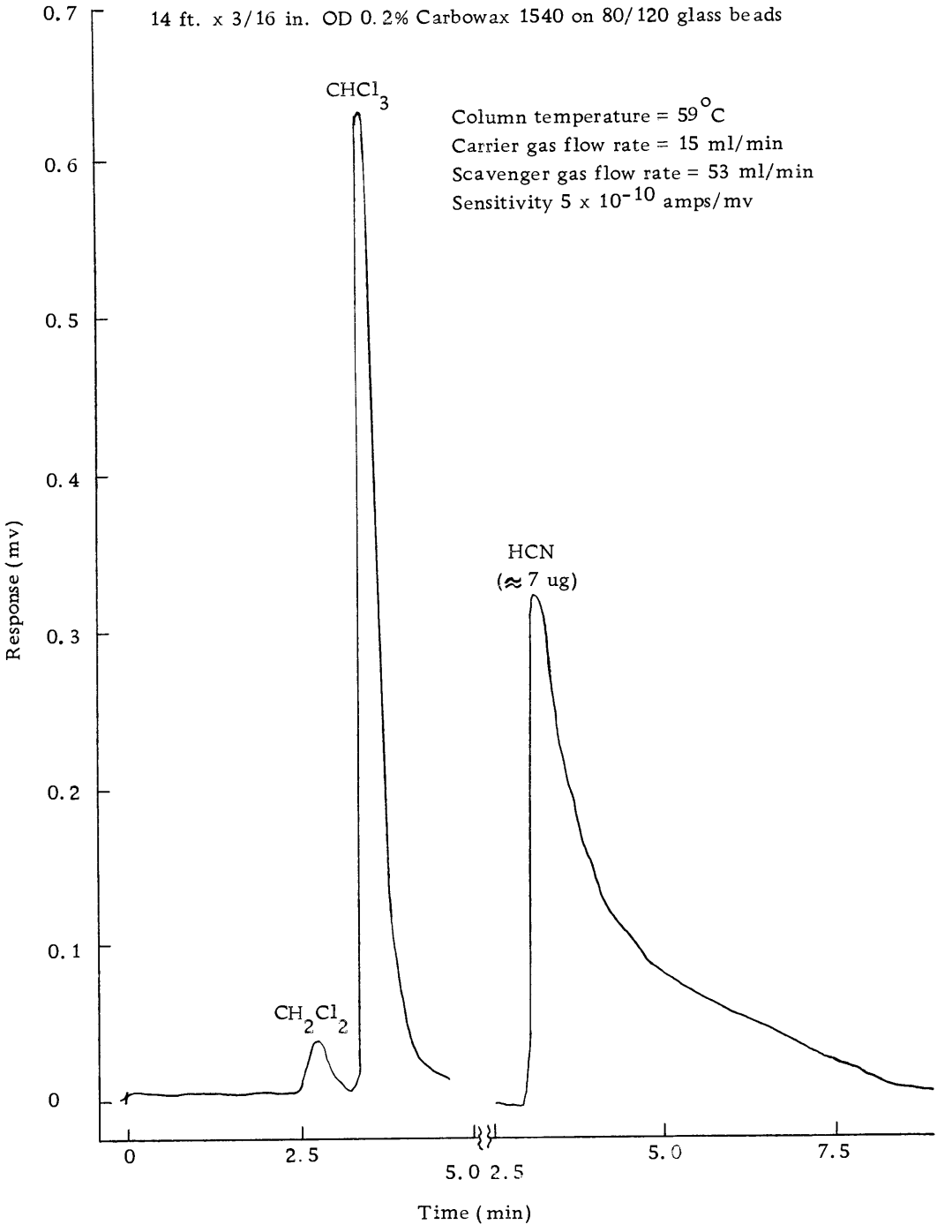


Figure 7. Glass bead chromatographic column.

Investigation of Fluorcarbon Polymers as Solid Supports

In contrast to active silicate supports the fluorocarbon polymers are inert and are poorly wetted by most stationary phases. Being inert, nonpolar stationary phases can be used for the separation of polar compounds without peak tailing occurring. For example, Runge (56) used 5 % Aroclor 1232 and Kel-F Grade 1 oil on Haloport F to separate HCl, $(CN)_2$, HCN, and other reactive gases.

Kirkland (32, 33) has extensively compared Teflon 6, Kel-F, and Fluoropak 80. The lowest HETP values were obtained with Teflon-6; however the surface energy of Kel-F is 31 dynes per square cm compared to 19 dynes per square cm for Teflon (33). Thinner films should be obtained on Kel-F, especially with polar liquid phases which do not wet the inert fluorocarbon polymers as well as nonpolar liquid phases. In addition, Kel-F is much harder than Teflon and easier to pack into a column.

The optimum stationary phase concentration reported in the literature varies from 2 % to 20 %. Kirkland (32) found 15-20 % optimum for Teflon-6 and Kel-F and 2-5 % for Fluoropak 80. Bennett analysed water in organic solvents with a 5 % Carbowax 20M on Teflon column (7), while Kuwada used a 20 % Ucon oil 550X on Fluoropak 80 for analysis of water in hydrazine (36). Hamlin et al. (25) separated inorganic fluorine gases on a 50 % Kel-F oil

on Kel-F column. Landault and Guiochon found the optimum polyglycol 1500 concentration on teflon to be 20 % w/w (38). The latter coated the Teflon support by adding the powder to a 5 % solution in dichloromethane and evaporating the solvent at room temperature with continuous mixing. The support was dried at 40° C and packed grain by grain into horizontal 40 cm column sections, employing vacuum and vibration. The total column length studied was 200 cm. The authors selected 500 to 400 u (35-42 mesh), aqua regia washed, Haloport F (F & M Scientic Corp) for their support material. HETP values of 2.3 mm were obtained for 0.4 ul of methanol at 70° C. Other studies (50) on the efficiences of Teflon supports show an optimum liquid phase concentration of 2 % with the number of plates decreasing as the percent of liquid phase increased. Thus considerable differences in the optimum liquid phase concentration can be found in the literature.

Experimental

A 15 % w/w Carbowax 400 on 40/50 mesh Teflon-6 (Analabs Inc., Hamden, Connecticut) chromatographic support was prepared as suggested by Kirkland (32). The Teflon powder was cooled to 0° C in a copper beaker, and shaken vigorously to put the powder in a free flowing state. The Teflon powder was then added to a dichloromethane solution containing the stationary phase in an evaporation

dish. The solution volume was twice the volume of the support (60 ml of solution). A stream of nitrogen was passed over the solution while the Teflon powder was continuously turned over. Approximately one hour was required to evaporate the solvent. The resulting packing was not free flowing, but more of a paste.

A 15 % w/w Carbowax 400 on 50/80 Kel-F powder (#6051 Applied Science Lab., State College, Pa.) chromatographic support was prepared by the usual steam bath evaporation technique. Upon complete removal of the solvent the packing was also a paste. The procedure was repeated with 1, 2, 3-tris (2-cyanoethoxy)-propane, and a paste was obtained again.

Attempts to coat the fluorocarbon supports were again repeated at lower concentrations. Three similar columns containing Teflon-6, Fluoropak 80, and Chromosorb P were prepared. The latter two supports were coated on a stream bath, while Teflon-6 was coated as described above. The results are shown in Figure 8. Short one meter columns were also prepared, and the chromatograms of a test mixture described by Kirkland (32) is shown in Figure 9. Both the Kel-F and Chromosorb P supports were coated by evaporation on a steam bath.

Results and Discussion

Teflon-6, Kel-F, and Fluoropak 80 all became tacky when the

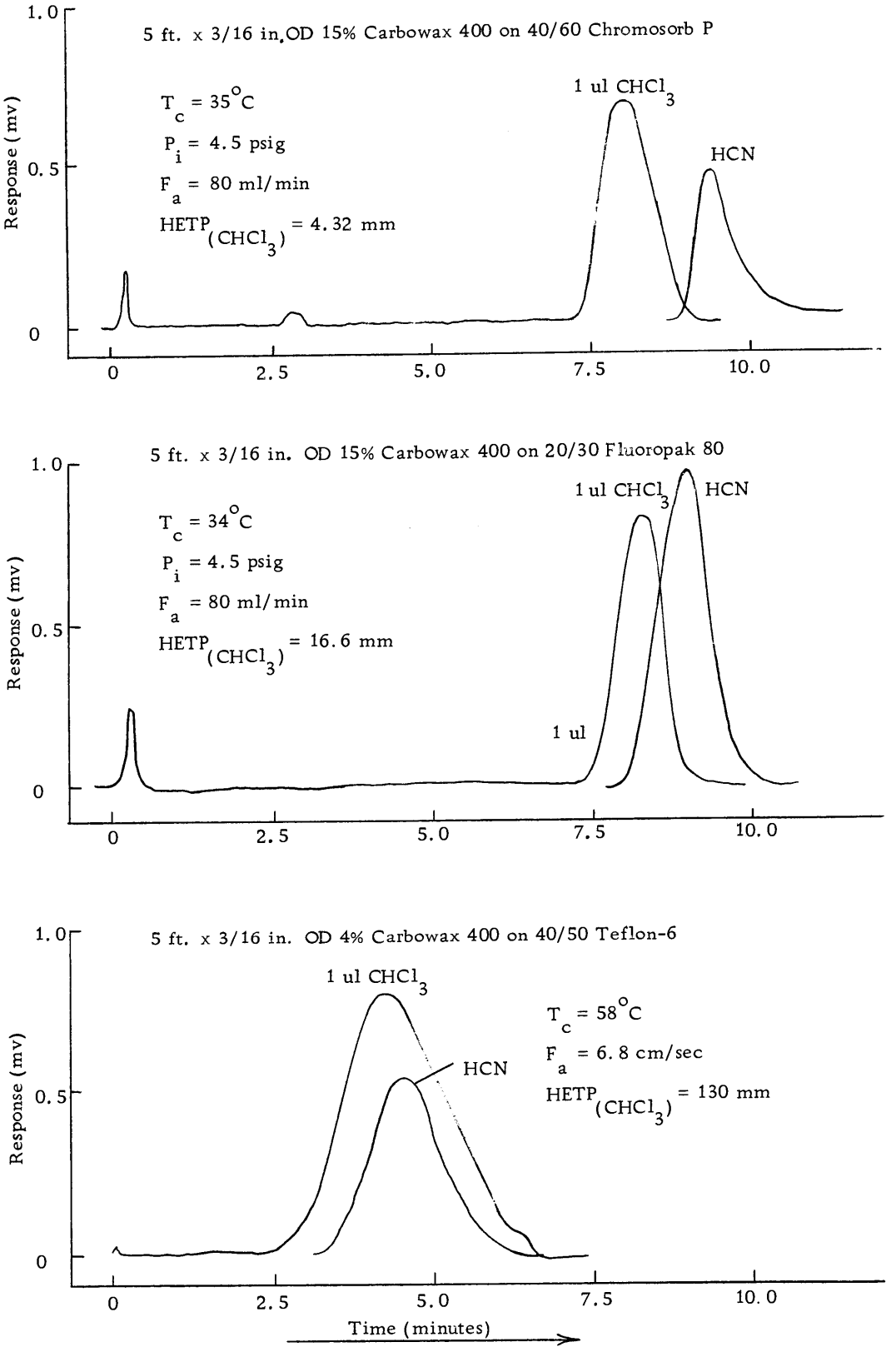


Figure 8. A comparison of Chromosorb P, Fluoropak 80, and Teflon-6 solid supports.

liquid phase concentration exceeded 5 % w/w. HETP values for chloroform were measured for each column. A smaller sample size would have probably greatly improved column efficiency.

Because of the very poor results obtained with Teflon-6, a shorter column containing Kel-F support was investigated, Figure 9. Owing to the very poor column efficiencies obtained on Kel-F, an identical column was packed in a 0^{o} C room, adding the Kel-F support nearly grain by grain. No improvement in column efficiency was obtained.

With 4 % stationary phase concentrations on Kel-F and Fluoropak 80 nearly symmetrical HCN peaks were observed, but the column efficiencies of these columns were much poorer than a similar column containing Chromosorb W. Clearly the advantage of inertness of the fluorocarbon polymers was offset by a reduction in column efficiency; hence other supports were investigated.

Other Chromatographic Supports

Baum has investigated microporous polyethylene as a low temperature support (6). Liquid phase concentrations up to 20 % were employed without evidence of being tacky. Symmetrical peaks with low molecular weight alcohols were obtained with satisfactory column efficiency. However, the material was no longer commercially available.

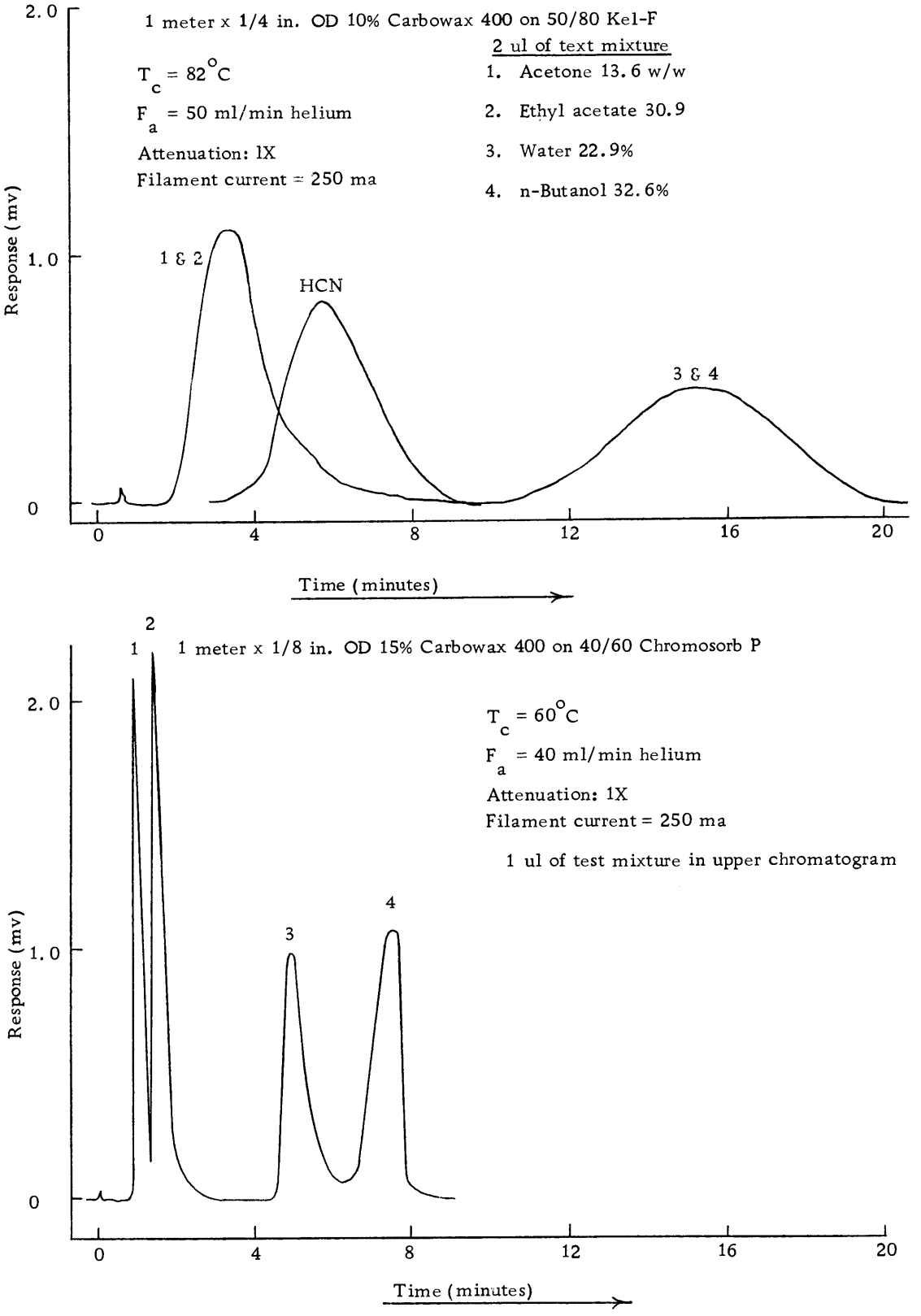


Figure 9. A comparison of Kel-F and Chromosorb P solid supports.

Tide has been used for the separation of alcohols and nitrogen compounds. Porcaro and Johnson (54) separated primary amyl alcohols with Tide as the column packing, the approximately 20 % alkyl aryl sulfonate serving as the liquid phase. HCN, being acidic, would probably react with the sulfonate ions forming a sulfonic acid. In addition, the carrier consists of sodium sulfate, chloride, phosphate, and silicate (50). Some adsorption would probably occur on the silicate material.

NaCl has the advantage of being free of silicate material which is responsible for much of the adsorption of polar compounds. In this work the maximum liquid phase concentration for 60/80 mesh sodium chloride appeared to be approximately 0.5 % w/w. Very poor column efficiencies were obtained with NaCl. For trace analysis sharp peaks are desirable for high sensitivity; consequently additional experimentation with NaCl was discontinued.

In comparing the results obtained with the different solid support materials investigated, only the diatomaceous earth supports gave satisfactory column efficiencies to separate HCN from interfering compounds and sharp peaks for the high sensitivity needed for trace analysis. Peak tailing was minimized by DMCS deactivation of the support and the use of polar stationary phases.

TESTING HCN CONCENTRATION PROCEDURE FOR INTERFERING COMPOUNDS

Instrumental Modifications

A 15 % Carbowax 1540 on Chromosorb W column was prepared and installed in a Beckman GC-2 gas chromatograph equipped with a flame ionization detector. Gas samples were injected onto the column by a gas syringe to test the chromatographic system. Favorable noise levels were obtained at a sensitivity setting of 1.0×10^{-11} amps/mv after 32 hours of column conditioning at 130° C (maximum temperature, 150° C) with the flame detector disconnected from the column.

In order to analyse the contents of the concentration columns used to trap HCN from the effluent air of aqueous solutions (59), a Perkin Elmer gas sampling valve was mounted initially on an independent stand and connected to the Beckman GC-2 instrument with a minimum of 1/8 inch OD aluminum tubing. This produced severe tailing owing to a lack of plug injection. The gas sampling valve was then mounted in back of the instrument and the chromatographic column connected directly to the gas sampling valve. The portion of the column outside of the oven was wrapped with wet asbestos and a thermocouple installed. After drying, nichrome wire was wrapped around the asbestos covered column and the exposed wire covered with wet asbestos. A Variac was connected to the nichrome wire to heat

the exposed portion of the column to the same temperature as the oven. Considerable improvement in the column efficiency and the peak profile of HCN was observed, pointing to the need to keep the dead volume between the gas sampling valve and the front of the column to a few cubic centimeters.

Purifying the Air Sweep Gas

The purity of the air sweep gas was determined by passing 5 liters of air through a concentration column at -78° C. The contents of the concentration column was analysed and found to contain many impurities. With the increased sensitivity of flame ionization detection a very clean air supply is required. High purity grade air is recommended.

Addition of a molecular sieve trap to the air stream did not remove the low molecular weight hydrocrabons. A 65° C chromic acid gas scrubber followed by a base scrubber was also ineffective. An Arthur H. Thomas type 5680 microcombustion furnace filled with platinum gauze, copper oxide, 1:1 copper oxide-lead chromate, and silver wire was installed in the air stream in place of the gas scrubbers. The platinum gauze and copper oxide were heated to 850° C, and the 1:1 copper oxide-lead chromate and silver wire to 650° C. Some impurities were still present. Best results were obtained with a Hoskins Type FD-3034 combustion furnace with a

30 mm OD x 61 cm quart combustion tube filled with copper oxide and platinized asbestos and heated to a bright red temperature. The large diameter combustion tube permits longer contact time.

Testing Water Blanks

Several different natural water sources were analysed for interfering compounds. First well water and then river water was tested by trapping 10 liters of effluent air. Only traces of rapidly eluting compounds were detected at a sensitivity of 5×10^{-10} amps/mv. However chromatograms from the analyses of laboratory tap and distilled water contained a large peak at nearly the same retention volume as HCN.

The retention volumes of many of the common contaminates found in river water (59) were compared with the retention volume of HCN. Acrylonitrile and chloroform are the only compounds which interfere with HCN on a 7 ft x 1/8 OD, 15 % Carbowax 20 M on 40/60 Chromosorb W chromatographic column at 71° C and 40 ml/min carrier flow. Most of the compounds elute before HCN. Water and H_2S are eluted after HCN. The interfering peak found in the tap water was trapped from the gas chromatographic effluent for positive identification by mass spectrometry.

Mass Spectrographic Identification

Since the interfering compound represented only a very small quantity of material, mass spectrometry offered the most convenient and precise method of identification. Sufficient quantities would have to be acquired by repeated collection of the effluent air from the tap water and repeated collection of the interfering compound as it eluted from a gas chromatographic column. A Kerns Excelo four way valve (Kern Lab. Supply Comp., Los Angeles, Calif.) was mounted on the floor of the Beckman GC-2 chromatographic oven. The valve was installed to switch the column effluent either to the flame detector or a cold trap. The cold trap, shown in Figure 10, was connected to the Excelo valve with a two foot x 1/8 inch OD aluminum tubing leading to the outside of the instrument. All glass to metal connections were made with Swagelok fittings. Small sections of 6 mm tubing were added to the ends of the Excelo valve so that 1/4 inch OD ferrules would properly fit the glass. At the glass connection the back ferrule was reversed and a Viton o-ring replaced the front ferrule.

Approximately 20 liters of air were passed through 20 liters of tap water, and the effluent air trapped at -78° C. The cold trap was then connected to the gas sampling valve, warmed to 70° C, and the contents injected onto the chromatographic column. When

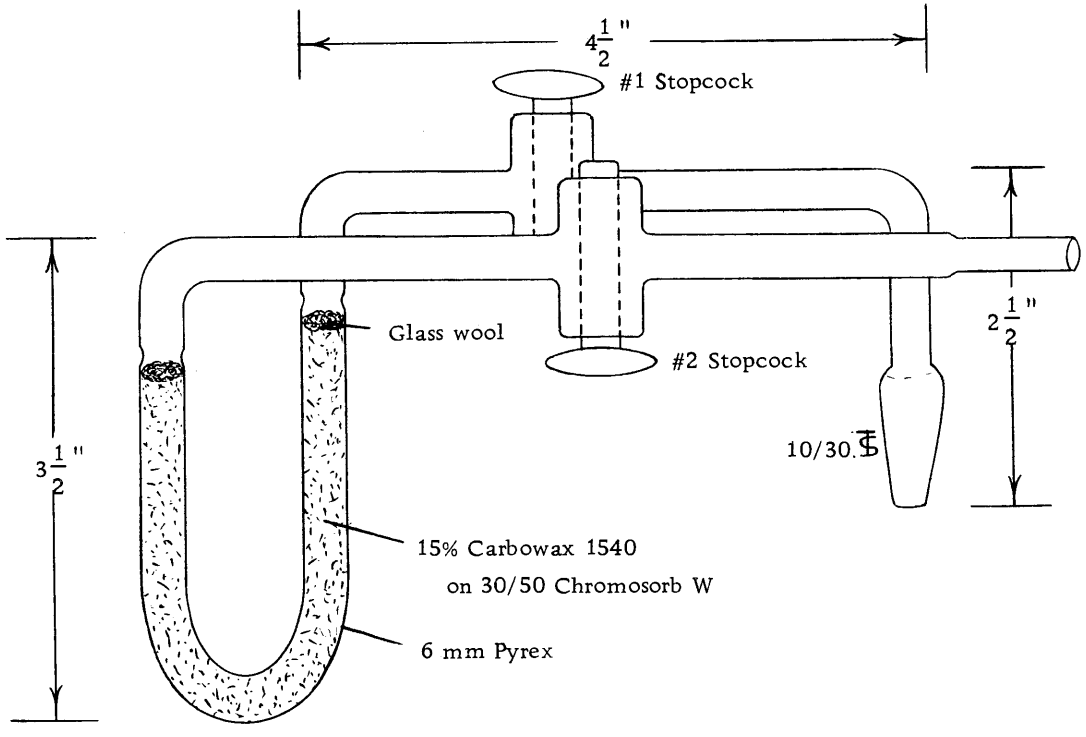


Figure 10. Cold trap for mass spectrographic determination.

the interfering compound was first detected by the flame detector the Excelo valve was turned, and the column effluent trapped at -78° C using a pint Dewar flask filled with dry ice and acetone. A total of 140 liters of air was collected.

Keeping the trap at -78° C stopcock #1 (Figure 10) was closed, and the trap evacuated to 1 mm by a vacuum pump to remove most of the carrier gas. Stopcock #2 was then closed and the trap connected to a Consolidated Engineering Corp. Model 21-401 mass spectrometer. Stopcock #1 of the cold trap was then opened and the inlet system of the mass spectrometer evacuated by the forepump. Closing the forepump valve, the Dry Ice-acetone bath was removed and the trap warmed to 70° C. A 5 mm sample was taken and expanded to 50 microns. The sample was scanned from a m/e of 1 to 95. Table 2 shows a comparison of the principal peaks to data published by the Dow Chemical Company for chloroform.

Table 2. Mass spectrographic data of chloroform

m/e	Relative Intensity	Dow R. I.	Ion
83	100	100	$HCCl^{35}Cl^{35+}$
85	65.7	65.7	$HCCl^{35}Cl^{37+}$
47	21.4	21.5	CCl^{35+}
87	10.6	10.5	$HCCl^{37}Cl^{37+}$
48	10.2	9.8	$HCCl^{35+}$

Chloroform is a known impurity in chlorine production, and chlorinated water should contain some chloroform.

Determination of the Chloroform Concentration in Chlorinated Water

Experimental

A 10 mg/l stock solution of chloroform was prepared by adding 13.43 ul reagent grade chloroform to 2.00 liters of well water. Twenty liter standard solutions of 10, 20, 30 and 40 ug/liter were prepared by adding 20, 40, 50 and 80 ml aliquots, respectively, of the 10 mg/liter stock solution to 18 liters of well water, and diluting up to 20.00 liters at 20.0° C. Two liters of air were trapped (59) and injected onto a Carbowax 1540 column. The calibration curve is shown in Figure 11. Twenty liters of laboratory tap and distilled water were analysed in a similar manner.

Results

Both the tap and distilled water was found to contain 28 + 1 ug/liter of chloroform based on duplicate analyses. Duplicate analyses of each standard solution illustrates the accuracy of this technique for the measurement of trace quantities of certain organic compounds in water.

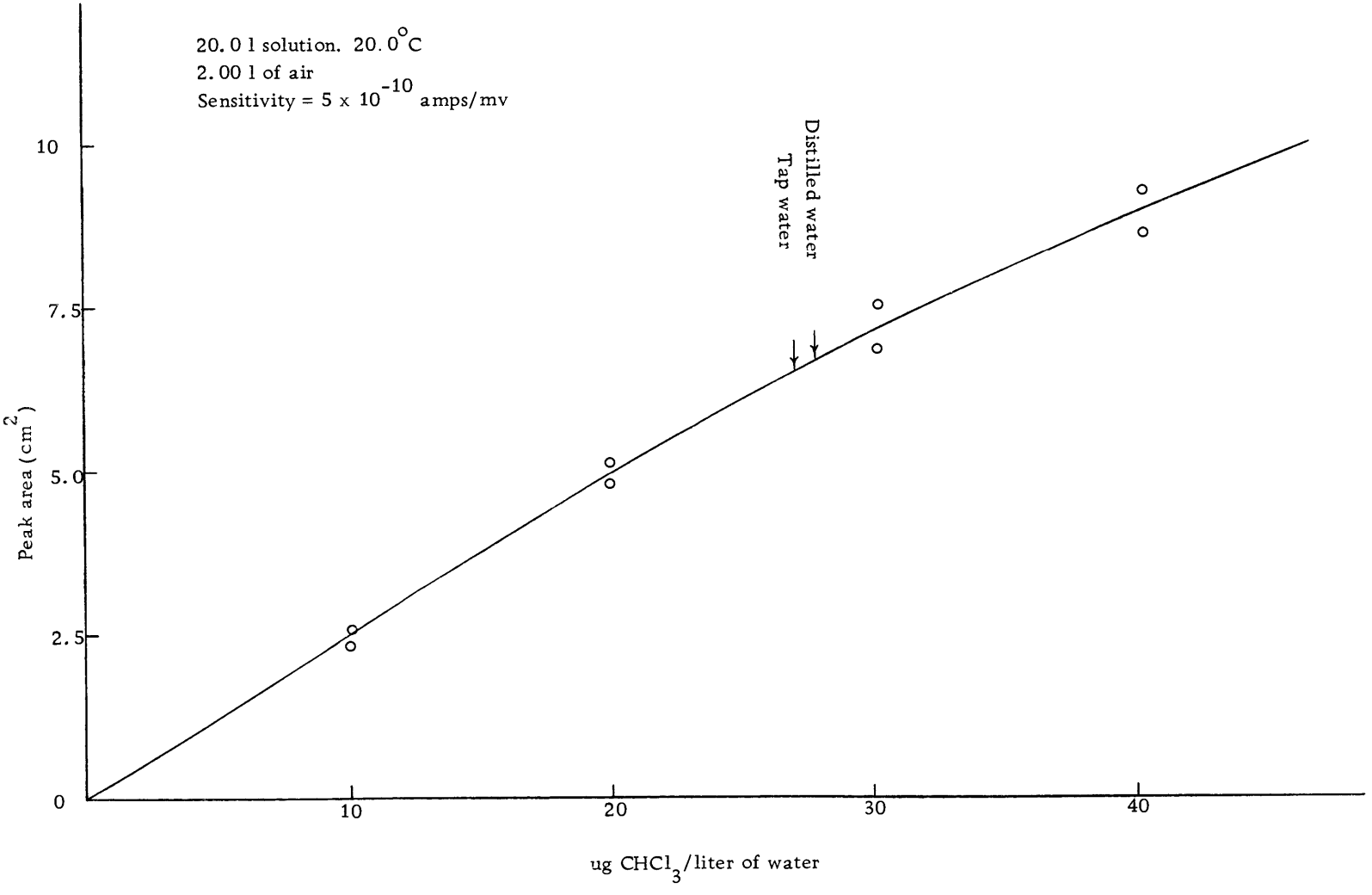


Figure 11. Standardization curve for the determination of $CHCl_3$ in water.

Investigation of Stationary Phases for the Separation of HCN and $CHCl_3$

Hydrocyanic acid and chloroform are not separated by Carbowax 1540 or 20M. This prompted a search for a different polar stationary phase. A literature search revealed polyethylene glycol polymers (Carbowaxes) were predominately used in the analysis of HCN (9, 71). Isbell found either glyceryl triacetate or tributyrate would separate HCN and cyanogen (30), while Schneider and Freund used dinonylphthalate to separate HCN and water (59).
HCN and $CHCl_3$ are readily separated by the ester stationary phases, but HCN adsorption on the solid support is much greater compared to the more polar stationary phases. Hence a moderately polar stationary phase was desired which prevented adsorption of HCN on the solid support and separated HCN from $CHCl_3$.

Experimental

Two attempts were made to use a modified Carbowax stationary phase. In the first investigation 5 % Amine 220 was added to a 10 % Carbowax 20M packing. The second modification was the addition of 5 % phosphoric acid (85 %) to a 15 % Carbowax 20M packing. In addition, several other stationary phases were examined by the polarity mixture introduced by Averill (4). Table 3 lists some of the stationary phases examined along with the relative

Table 3. Polarity of stationary phases

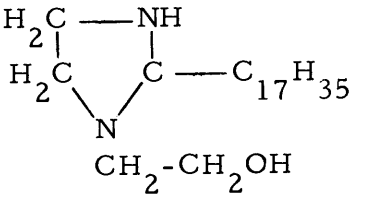
Stationary Phase	1st 2nd 3rd 4th Elution Order	Classification (Polarity)	Relative Retention Time of $CHCl_3$ (HCN 1.00)
1. Carbowax 400	C M (B E)	strong	0.82 at 35° C
2. Carbowax 1540	C M (B E)	strong	0.97 at 71° C
3. 1, 2, 3-Tris (2-cyanoethoxy)-propane	C (B E) M	moderate	1.12 at 37° C
4. β, β'-Oxydipropionitrile	C (B M) E	strong	1.17 at 24° C
5. Dimer Acid	C M (B E)	strong	1.0 at 55° C
6. Tricresylphosphate	C E (M B)	mild	2.54 at 35° C
7. Tributyrin	(E C) (M B)	weak	4.09 at 35° C
8. Didecylphthate	E (C M) B	weak	3.43 at 40° C

C - Cyclohexane
B - Benzene
M - Methyl Ethyl Keytone
E - Ethanol

retention times of $CHCl_3$ to HCN.

Results

Amine 220 is a common name for 1-hydroxyethyl-2-heptadecenylglyoxalidine:



The basic nature of this compound should retain HCN on the column, allowing $CHCl_3$ to elute ahead of HCN. The addition of Amine 220 caused a small increase in tailing, and appeared to react with HCN. Upon comparing equal quantities of HCN from Carbowax 20M columns with and without the addition of 5 % Amine 220, a 14 % loss in the peak area of HCN resulted on the column containing Amine 220.

The addition of phosphoric acid reduced the retention volumes of both HCN and $CHCl_3$ more than 50 %, with chloroform having a relative retention volume of 0.74 compared to 1.00 for HCN. Although chloroform and HCN were separated by this column, water was not eluted. Since water is collected along with HCN in the concentration procedure, the continual injection of water vapor should damage this column.

The addition of phosphoric acid also reduced the retention volumes of acids, alcohols and mercaptans. Aldehydes were not detected possibly owing to an acid catalyzed condensation reaction. All basic compounds were not eluted from this column.

Unable to modify the Carbowax 20M stationary phase other compounds were examined, as shown in Table 3. 1, 2, 3-Tris(2-cyanoethoxy)-propane (45) was selected because of the excellent separation of alcohols and polar compounds obtained by this stationary phase. β, β'-Oxydiproprionitrile is a strong polarity stationary phase (12, p 110), whereas tricresylphosphate has been used as a general purpose stationary phase (68). Dimer acid is a 36 carbon dibasic acid (Empol 1022, Emery Industries, Los Angeles, California). An acidic liquid phase is desirable in that potentially interfacing amines are not eluted.

The polarity of each of the above stationary phases was examined using the polarity mixture introduced by Averill (4), and discussed by Ettre (20). The mixture is made up of cyclohexane (b. p. 81.4° C), benzene (v. p. 80.1° C) methyl ethyl keytone (b. p. 79.6° C) and ethanol (b. p. 78.5°C). All components have nearly the same boiling point, but differ widely in polarity. Nonpolar stationary phases have an ethanol, methyl ethyl keytone (MEK), benzene, cyclohexane elution order, while polar stationary phases tend to have the reverse elution order. Cyclohexane elutes before

benzene with slightly polar staionary phases. The order of elution, the resolution between components, and the degree of tailing provide a practical test of column performance. The elution order and the separation is given in Table 3 for each of the stationary phases.

In comparing the relative retention times of HCN and $CHCl_3$ in Table 3 relatively long columns would be required to separate HCN and $CHCl_3$ by the polar liquid phases. Carbowax 400 will separate these two compounds (Figure 9), but a rather long column would be required if chloroform was present in much larger quantities than HCN. 1, 2, 3-Tris(2-cyanoethoxy)-propane gave superior chromatograms of HCN, but did not resolve HCN from $CHCl_3$. The mildly polar tricresylphosphate appeared to be the best compromise between good separation of HCN and $CHCl_3$ and the least amount of HCN tailing. The slightly polar esters readily separate HCN and $CHCl_3$, but HCN adsorption was much greater.

Testing a Tricresylphosphate Column

Several solutions of varying concentrations of HCN were analysed (59) using a 6 ft x 3/16 inch OD, 15 % tricresylphosphate column. At concentrations below 0.1 mg of HCN per liter of solution and electrometer sensitivities of 5×10^{-10} amp/mv many contaminates were detected that were not observable at the lower sensitivity settings. Some of the contaminates were traced to the

drying agent and the water. The drying agent was heated to 200° C for 24 hours to remove residual organic compounds. Although most of the impurities were removed by preheating the drying agent, periodic contamination resulted in interfering peaks. Complete separation of HCN on a single column appeared very difficult.

TWO COLUMN CHROMATOGRAPHIC SYSTEM

Two Columns in Series

Separation of HCN from a wide range of contaminants might be better achieved by connectiong two columns in series instead of using a single column. Merely placing two columns in series would give a separation similar to a single mixed liquid phase column. If a valve were installed in series between the two columns some of the compounds could be vented into the atmosphere. Figure 12 shows two columns connected in series with a 4-way valve. A HCN sample is injected onto column 1 by turning the gas sampling valve. As soon as HCN has eluted from column 1 onto column 2, the Excelo valve is turned; thus many compounds remaining on the first column are eluted into the atmosphere. The HCN solute is eluted from column 2 by the alternate gas flow route. The function of column 3 is to match the resistance to flow of column 1, preventing a large change in the carrier gas flow in column 2 after turning the Excelo valve.

Two stationary phases of different polarity were selected for columns 1 and 2. A mild polarity stationary phase was employed in the first column. Phthalic acid was combined with didecylphthalate. Addition of phthalic acid reduces HCN tailing and provides an acidic stationary phase. The more popular terephthalic acid was not immediately available. HCN is eluted rapidly on this column along

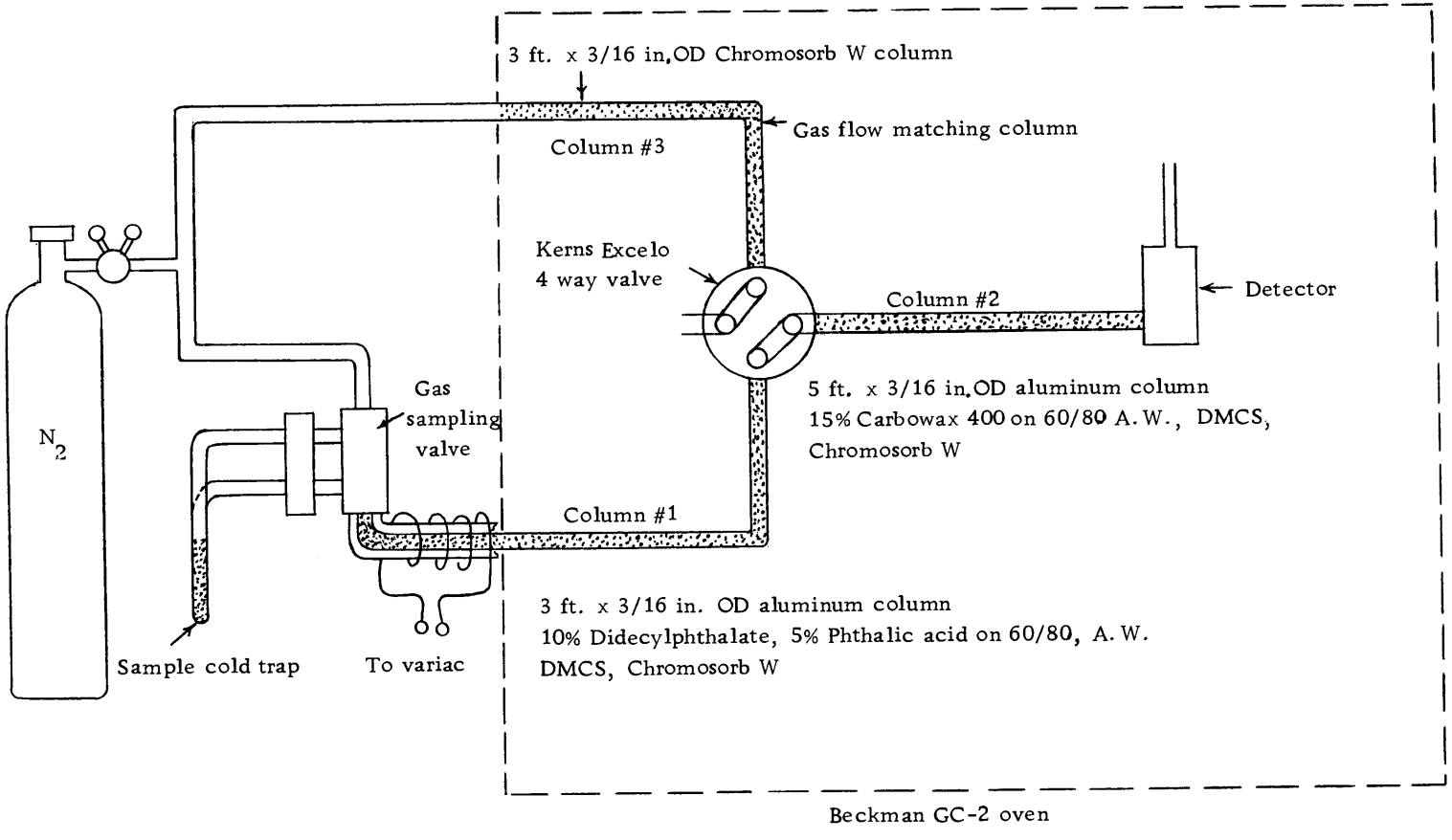


Figure 12. Two column switching apparatus.

with the low molecular weight gases, since compounds tend to elute in the order of increasing vapor pressure with nonpolar stationary phases. The higher molecular weight contaminates are eluted into the atmosphere upon turning the Excelo valve. A strong polarity stationary phase (Carbowax 400) retains the polar HCN solute on the second column, separating it from the low molecular weight contaminants.

The first column was connected directly to a gas sampling valve as previously described (p 44). The Excelo valve was mounted on an aluminum plate which was attached to the chromatographic oven floor. Glass to metal connections were made with Swagelok fittings and Viton o-rings. The Excelo valve had a tendency to leak at temperatures above 50° C; thus the column temperature was adjusted to 30° C, and 3/16 inch OD columns replaced 1/8 inch columns to reduce the resistance to flow.

An O to 100 μg/l calibration curve was prepared by analysing standard solutions. The curve intersected the concentration axis at -10 μg/l, indicating the presence of an impurity or an error in the preparation of the standard solutions. No interferences were ever observed by this technique, and the technique seemed very reliable.

The principal difficulty with this system was that the HCN solute was not injected as a plug on to the second column, and a broad eluting peak was obtained (Figure 13). Therefore, the length

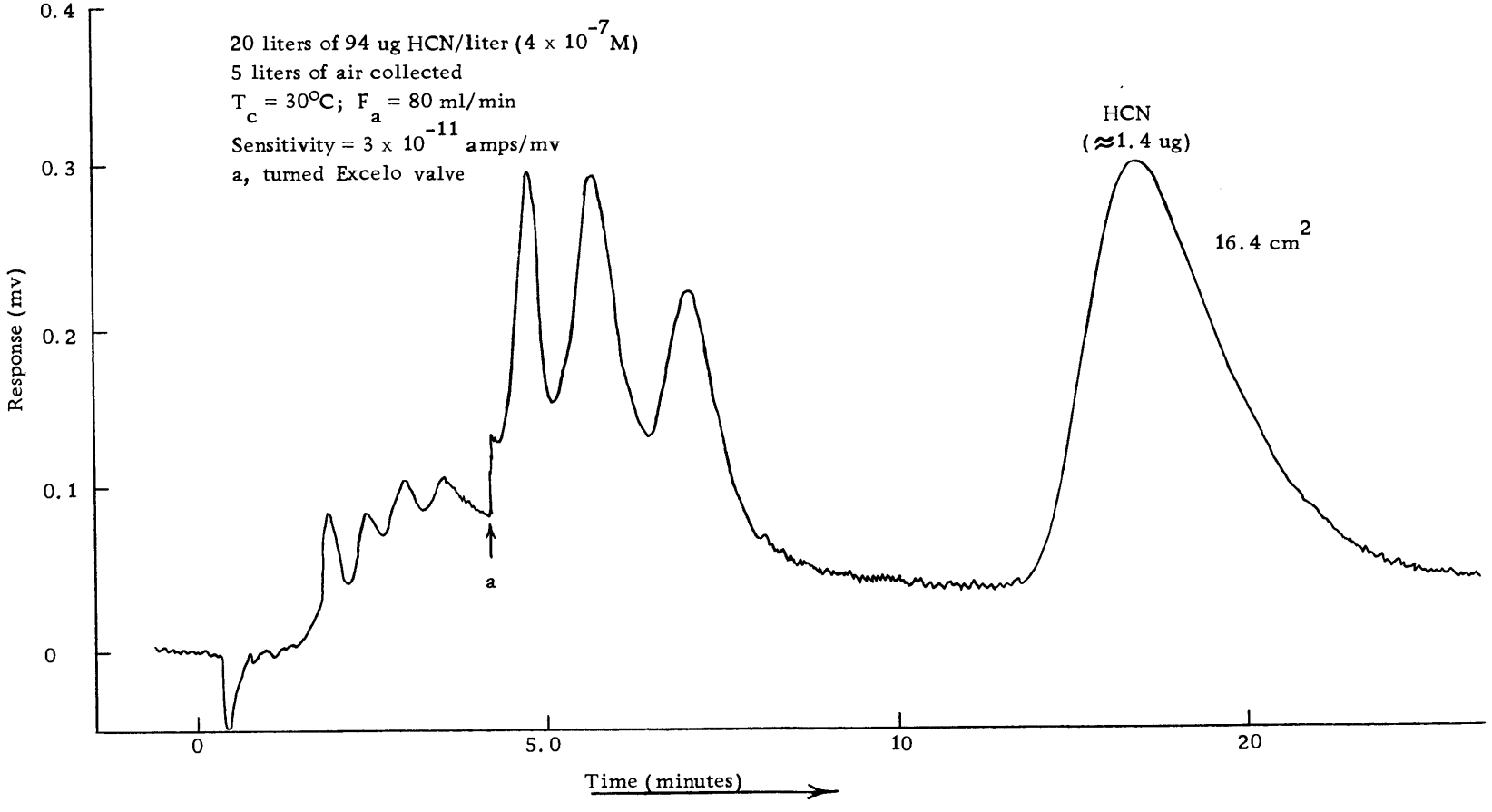


Figure 13. HCN chromatogram employing two column switching technique.

of the first column was kept at a minimum. Because of the rather broad HCN peak, the analytical precision of this technique was not as good as expected. Favorable column efficiencies were obtained with solutes which did not absorb on the solid support, indicating HCN tailing was not caused by poor chromatographic conditions. Owing to such a broad HCN peak the lowest measurable concentration with the collection of 5 liters of air was 10 μg HCN/liter of solution.

Two Column Dual Oven Chromatographic System

Connecting two columns in series resulted in a broad chromatographic peak with HCN because of the lack of plug injection onto the second column. If two individual columns contained in separate chromatographic ovens were used for analyses, the HCN solute would be trapped from the column effluent of one column and injected onto the second column as a plug. In this investigation two similar gas chromatographic ovens were built, and a much improved HCN chromatogram was obtained.

Apparatus

A flow diagram is shown in Figure 14. A cold trap containing a sample of HCN is attached to the gas sampling valve of the first oven. After warming the cold trap, the contents are injected onto column 1. A second cold trap is connected to the exit of

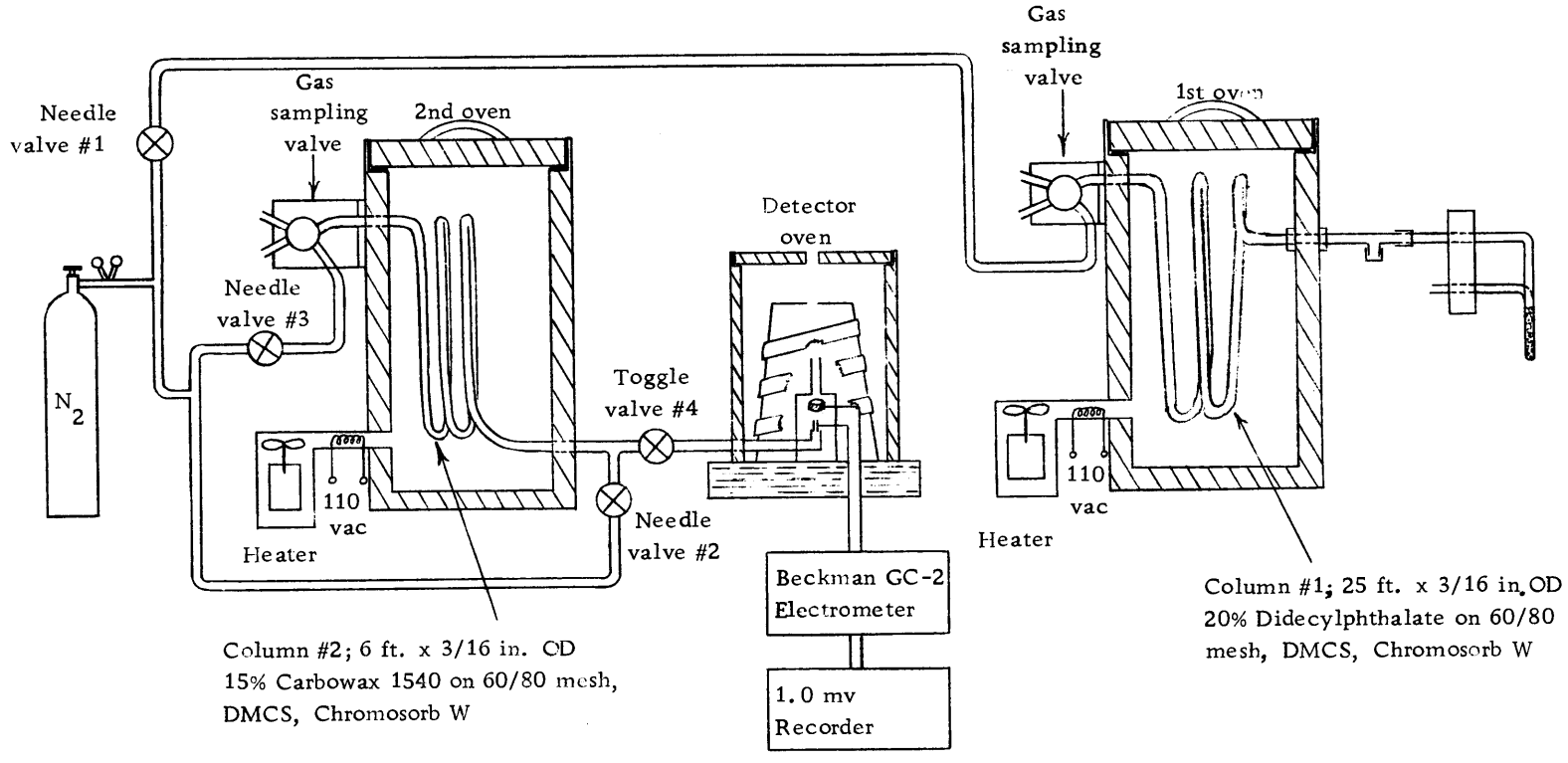


Figure 14. Two column dual oven.

column 1, to trap HCN just as it elutes from the column. The contents of the second cold trap are injected onto column 2 in like manner. The effluent of column 2 is analysed by a flame ionization detector. Compounds which elute before and after HCN from column 1 are eluted into the atmosphere.

The columns used for the two column dual oven technique and the two column switching technique were similar. The first column was lengthened to a 25 foot x 3/16 inch OD column filled with 20 % didecylphthalate on 60/80 mesh, acid washed, DMCS treated Chromosorb W.. The second column was a 6 foot x 3/16 inch OD column containing 15 % Carbowax 1540 on 60/80 mesh, acid washed, DMCS treated Chromsorb W.

A common nitrogen source was used for convenience. The flow rates were adjusted with Nupro 2M needle valves (Nuclear Products Co., Cleveland, Ohio). A Perkin Elmer gas sampling valve was mounted on the side of each oven. Each air bath oven was constructed with 3/8 inch aluminum plate. The interior walls and upper lid were insulated with 0.5 inches of A. P. Green high temperature insulating cement (A. P. Green Fire Brick Company, Missouri) and lined with an asbestos sheet. The outside dimensions were $9\frac{1}{2}$ inches long x $9\frac{1}{2}$ inches high x $6\frac{1}{2}$ inches wide. To heat each oven a hair dryer (Standard Products Corp., Whitman, Mass.) was rewired to control the voltage to the 80 ohm heating elements

by a Variac. The hair driers were made to blow warm air into one side of the oven. A thermocouple was wrapped around the column to indicate column temperature. An asbestos sheet was used to deflect the air off the column. The maximum oven temperature was 90° C. All connections were made with Swagelok fittings (Crawford Fitting Company, Solon, Ohio).

Provisions were made to backflush the second column. In backflushing valves numbers 3 and 4 are closed, while the gas sampling valve and valve number 2 are opened (Figure 14).

The exit end of the column 1 is attached to the oven wall by a bulkhead union. A union tee with 1/8 inch fittings is connected to the outside bulkhead fitting. An 1/8 inch Swagelok cap is connected to one fitting of the tee and serves as a valve by tightening and loosening the cap. A cold trap is connected to the other tee fitting.

A flame ionization detector was housed in a $5\frac{1}{2}$ inch OD x 5 inch long aluminum tube. Inside a 600 ml copper beaker was inverted over a Beckman Flame Detector (Model 104000). A $\frac{1}{4}$ inch hole was drilled through the lid and top of the beaker to allow the gases to escape. A 32 ohm, 110 V heating tape was wrapped around the copper beaker. Glass wool provided insulation between the copper beaker and the aluminum pipe. The copper beaker, electrometer, and recorder were grounded to a common earth ground. The input cable

was silver soldered to the detector anode, and contact between the jet tip and the 300 V source wire was periodically polished with silver polish. The detector temperature inside the flame detector was 110° C at 110 VAC without a flame; hence water condensation and a possible loss of sensitivity was reduced.

Procedure

The temperature and flow rate of column 1 is adjusted to 35° C and 80.0 ml/min. The retention time of HCN is determined by connecting the exit of column 1 to the flame detector with 0.020 inch ID stainless steel capillary tubing. A sample of HCN is injected onto the column from a cold trap connected to the gas sampling valve. The cold trap will decrease the column flow; thus the trap is kept in series with the carrier gas stream for only 40 seconds. The effluent of column 1 was trapped from $6\frac{1}{2}$ minutes to $11\frac{1}{2}$ minutes for the analysis of HCN. The temperature and flow rate of column 2 is adjusted to 60° C and 80.0 ml/min.

Experimental Results

Chromatograms of the two column dual oven technique showed many additional peaks, attributed to impurities in the nitrogen carrier gas. These compounds were trapped out of the carrier gas along with HCN. A pre-purified grade of nitrogen is required. A 850° C

microcombustion furnace (Type 5680, Arthur H. Thomas Co., Philadelphia, Pa.) filled with copper oxide was placed in the nitrogen carrier gas stream at the cylinder to insure gas purity. Figure 15 shows a chromtogram of 0.6 μg of HCN. The column efficiency and the reproducibility of analysis was greatly improved over the two columns in series switching technique. In comparing Figures 13 and 15 note approximately the same peak height was obtained with less than half the amount of HCN at a factor of five difference in sensitivity.

A 0 to 1 μg/l calibration curve intersected the concentration axis at 0.07 μg/l, indicating a small loss of HCN by adsorption on the solid support or in trapping. The trapping period was supposedly more than sufficient for complete collection.

Although column 1 was lengthened to a 25 foot x 3/16 inch OD column to separate HCN from interfering compounds, HCN was not completely separated from all compounds as seen in Figure 15. Occasional contamination was also observed. Thus the purity of the HCN solute eluting from the second column was determined by mass spectrographic analysis.

Determining HCN Purity by Mass Spectrometry Using Two Column Dual Oven Chromatographic System

Three liters of air were trapped from a 50 μg/liter HCN solution, and the contents of the trap analysed by the two column dual

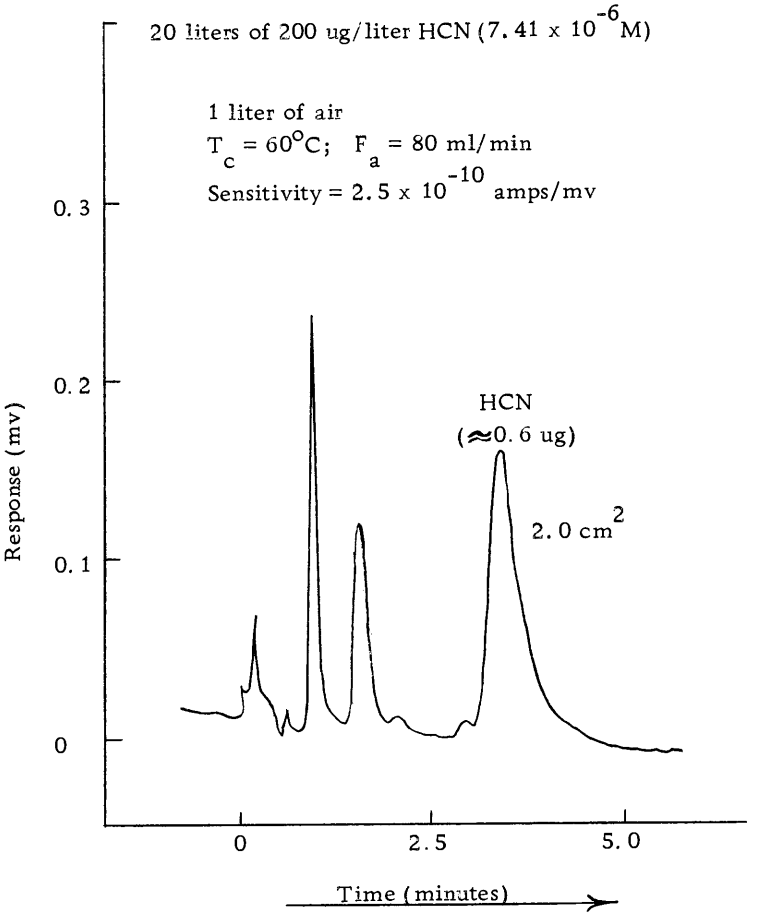


Figure 15. HCN chromatogram employing two column, dual oven technique.

oven chromatographic system. The backflush system was disconnected, and a two foot x 1/8 inch OD aluminum tube was used to connect the end of the second column to the cold trap described in Figure 10. About 80 % of the column effluent passed through the trap and 20 % through the flame detector. The same procedure as described on page 49 was followed for removing the carrier gas from the trap.

Table 4 lists the chart units for each of the mass units obtained above background. First the background chart divisions were subtracted from the results obtained from the HCN sample. The chart divisions contributed by HCN were subtracted from the sample assuming the chart divisions at the m/e of 27 was solely contributed by HCN. The relative m/e intensities were taken from the American Petroleium Institute Spectra, Series 233. The chart divisions contributed by the presence of air were subtracted assuming the chart divisions at m/e of 32 were contributed by molecular oxygen. Finally the chart divisions contributed by water were subtracted from the remaining net divisions using the chart divisions at m/e of 18 as the base peak for water. The remaining chart divisions at 2, 29, 30, 31 and 52 were not accounted for by the above procedure. The m/e peak at 52 may indicate the presence of a trace of cyanogon $(CN)_2$. Cyanogen is not detectable by flame ionization detection (34), and does not interfere. Small impurities appear to be present, but their concentration is assumed to be small when comparing the chart divisions of m/e of 27 to 29 or 30.

Table 4. Mass spectrographic analysis of the HCN chromatographic peak

m/e	Sample Divisions	Background Divisions	Net Divisions	Net Divisions after HCN correction	Net Divisions after Air correction	Net Divisions after Water correction
2	40.5	3	37.5	36.5	36.5	34.5
12	44	0	44			
13	23	0	23			
13.5	14.5	0	14.5			
14	12	0	12			
15	4	0	4			
16	19	1	18	18	18	
17	400	14.5	385	385	385	
18	1815	69	1746	1746	1746	
19	2	0	2	2	2	
20	3	0	3	3		
26	470	2	468			
27	3140	2	3138			
28	117	22	95	41		
29	26	2	24	22	22	22
30	16	0	16	16	16	16
31	11	0	11	11	11	11
32	15	3	12	12		
44	20.5	4	16.5	16.5	16.5	16.5*
52	17	1	16	16	16	16

* CO_2

INVESTIGATION OF PORAPAK Q

Introduction

O. H. Hollis has reported the use of porous polyaromatic polymer beads for the gas chromatography of polar compounds (29). Ethylvinylbenzene is crosslinked with divinylbenzene to give a porous polymer of high surface area. See Table 1. Being free of silicates, polar compounds should not adsorb on this material. Evaluation of one of the polymers, Porapak Q, yielded excellent column efficiencies with HCN and no tailing.

Porapak Q can be coated with at least 20 % liquid phase or can be used without a liquid phase. It is stable up to 230° C. Its two disadvantages are its limited column capacity, 0.1 µl of benzene for 3/16 inch OD columns, and its high retention of nonpolar compounds. For trace analysis the limited column load characteristic does not present a problem, and its high retention of nonpolar compounds is an advantage in HCN analysis.

Averill's polarity mixture (4) was again used to characterize the polarity of Porapak Q. A nonpolar elution order was obtained with ethanol eluting rapidly, followed by methyl ethyl keytone, and later cyclohexane and benzene eluting together. The retention volumes on a similar column containing 10 % w/w Carbowax 400 on Porapak Q were considerably reduced with cyclohexane eluting just behind

methyl ethyl keytone. Thus coating Porapak Q with a stationary phase appeared to only modify the column characteristics. The effects of liquid films on Porapak Q were studied more comprehensively in order to develop a satisfactory two column dual oven system.

Three 6 foot x 3/16 inch OD columns were prepared. Table 5 gives the contents of each. The column temperature was adjusted to 100° C and column flow rate to 40 ml/min. Relatively large columns were selected so that small differences in retention volumes could be measured. The retention volumes of the "polarity mixture" (4) were exceedingly large at 100° C; consquently low boiling solutes differing in polarity were selected. Table 6 gives the net retention volume for each solute studied.

The net retention volumes, Vn (p119), of Column B were corrected to 0.259 g of liquid phase by multiplying the net retention volumes by 0.259/0.803. With very polar compounds like methanol and HCN addition of a polar liquid film to Porapak Q (Column C) gives an additive effect, i.e. the net retention volume is the sum of the retention of Porapak Q (Column A) plus the retention of the liquid phase (Column B). Pentane is not soluble in Carbowax 1540 and this polar liquid film appears to prohibit the solute from diffusing into the Porapak support. Hence a large drop in the net retention volume occurs on Column C. On the other hand, dichloromethane is soluble in Carbowax 1540; and only a small change occurs in the net retention

Table 5. Experimental data of the columns investigated

Column	Support	Liquid Phase	Wt. of Support (grams)	Wt. of Liquid Phase, w_L (grams)
A	50/80 Porapak Q		5.340	0
B	60/80 Chromosorb W	15% Carbowax 1540	4.54	0.803
C	50/80 Porapak Q	5% Carbowax 1540	4.93	0.259

Table 6. Net retention volume data (V_N)

Column	CH_3OH	HCN	CH_2Cl_2	$n\text{-}C_5H_{12}$
A	82	58	542	870
B*	17	25.5	11	0.65
C	93	108	434	391

*corrected to $w_L = 0.259$ g

volume. Addition of nonpolar liquid films generally reduce retention volumes owing to the probable large decrease in surface area.

Two Column Chromatographic System with Porapak Q

Preliminary analyses of HCN solutions yielded chromatograms similar to those shown in Figure 18 by direct injection on a Porapak Q column. Attempts were made to eliminate some of the contaminates by first injecting the HCN sample on a Chromosorb W column coated with a mild polarity stationary phase (didecylphthalate or tributyrin), trapping the HCN, and reinjecting on a Porapak Q column. Similar chromatograms to those obtained by direct injection on Porapak Q were obtained. However, many of the impurities were eliminated when HCN was first separated from similar polar compounds on a 9-foot x 3/16 inch OD 15 % 1, 2, 3-tris(2-cyanoethoxy)-propane on Chromosorb W column. The 1, 2, 3-tris(2-cyanoethoxy)-propane column is moderately polar in nature, whereas Porapak Q is non-polar. Better separations were obtained with contrasting columns.

No interfering compounds were present when analyses of river water was made directly on a Porapak Q column; however many peaks were present. Table 7 gives the relative retention times of many of the possible interferences found in polluted water (59). Most of the amines are eluted with differing degrees of tailing. No interferences were found in this class of compounds. Propane was

Table 7. Relative retention data of some possible water pollutants

Compound	Boiling Point	Relative Retention Data*
Ethane	-88.6	0.3 e
Water	100.0	0.51 d
Hydrogen sulfide	-61.8	0.54 d
Trimethylamine	3.5	0.57
Methylamine	-6.5	0.58
Diethylamine	55	0.58
Propane	-42.1	0.97 c, e
Hydrocyanic acid	27	1.00
Methanol	64.7	1.35 b
Methanethiol	7.6	3.4
Ethanol	78.5	3.5 a
Acetone	56.5	5.9 a
Carbon disulfide	46.3	6.0
Acrylonitrile	79.0	7.2 a
Ethanethiol	34.7	10.6
Cyanogen bromide	61.6	$\gg$10 d

* 1 M x 1/8 inch OD 80/100 Porapak Q column at a column temperature of 60° C and nitrogen carrier flow of 15 ml/min.

a - Hollis (29) at 100° C
b - Partial separation
c - Interference
d - Not detectable by flame ionization detection
e - Not a common water pollutant

the only hydrocarbon tested which interferes with HCN, and methanol is the only alcohol. Cyanogen chloride may be found in chlorinated water containing cyanide ions, but this compound appears to be insensitive to flame ionization detection. Acetaldehyde and acetic acid are expected to have a relative retention volume to HCN of two or greater. Formaldehyde and formic acid are also not detectable.

Compound A in Figure 19 has a relative retention time of 0.46 and tails similar to the amines; hence the compound may be methyl amine. No compounds similar to compound B with a relative retention of 1.9 have been tested.

Analysis of Aqueous Solutions

Concentration Column

Schneider (58, p 25) has compiled the vapor pressure of solid HCN (m. p. 260° K) between 140 and 260° K. At Dry Ice-acetone temperature, 195° K, solid HCN has a vapor pressure of 0.6 mm mercury or 1.3 mg of HCN/liter of air. Hence HCN could not be removed from a stream of air by a simple glass bead trap at 195° K. However, the above author obtained excellent results in trapping HCN with a short U-tube concentration column filled with di-n-butylphthalate on 40/60 mesh firebrick at Dry Ice-acetone temperatures.

In this work the concentration column was reduced in size, and

60/80 mesh Chromosorb W coated with 20 % didecylphthalate, Carbowax 1540, or 1, 2, 3-tris(2-cyanoethoxy)-propane were substituted for di-n-butylphthalate. Many liquid films could be used for trapping HCN; however the material should be a liquid at 195° K, have a low vapor pressure at 100° C when the trap is warmed, and be moderately polar to retain HCN and deactivate the support material. 1, 2, 3-Tris(2-cyanoethoxy)-propane meets all three of these qualities, but with the advent of Porapak Q this material replaced previously used materials. Porapak Q has a high surface area and the retention of solutes is very temperature dependent. It is very retentive at low temperatures and nonabsorptive at high temperatures.

The efficiency of all packing materials were tested by connecting the trap of interest in front of and in series with the larger di-n-butylphthalate trap described by Schneider (7, p 38). Even Carbowax 1540 which is a solid at 195° K was 100 % efficient in trapping HCN.

Investigation of Drying Agents

The sweep air becomes saturated with water upon passing through an aqueous solution of HCN. The water vapor must be removed from the air stream prior to trapping out HCN since the ice formed will block passage of air through the cold trap. The water vapor may be removed by a drying agent, but HCN tends to adsorb

on many of the commonly used drying materials. Adsorption can be reduced by heating the drying agent, sacrificing drying efficiency. Water condensed in the cold trap will flood the chromatographic column; consequently an efficient drying agent is required.

The adsorption of HCN on drying agents was studied by gas-solid chromatography. Two foot x $\frac{1}{4}$ inch OD columns were filled with 20/35 mesh drying materials ($\approx$10 cc), and a fixed quantity of HCN gas was injected onto each column at 62° C and 100 ml/min nitrogen carrier flow. The results for each material investigated are given in Table 8. Only the four absorbents listed were chemically compatible and had sufficient capacity and efficiency for this investigation, and only calcium chloride and magnesium perchlorate proved to be potentially useful. The more than 50 % loss of peak area and excessive tailing indicates magnesium perchlorate adsorbs HCN at this temperature.

The effect of water vapor is not taken into account with the gas-solid chromatography study. Water should deactivate the adsorbent, permitting better recovery of HCN. In comparing $CaCl_2$ and $Mg(ClO_4)_2$ as drying agents, analysis of aqueous solutions of HCN gave identical results with either material after equilibrium was established.

The volume of air passing through an aqueous solution of HCN required to establish equilibrium with the drying agent depends on

Table 8. Adsorption of HCN on drying agents

Adsorbent	Retention Time (Minutes)	Peak Area (cm^2)	Remarks
NaCl	0.15	Spike	No adsorption
$CaCl_2$	0.70	7.2	No tailing
$Mg(ClO_4)_2$	2.5	3.0	Large tailing peak, loss of HCN
$CaSO_4$*	25.0	6.1	Broad symmetrical peak
Silica Gel	-	-	No elution

*Drierite, Nonindicating

the concentration of HCN in the air and the temperature of the drying agent. To determine equilibrium conditions successive one liter air samples from a 1.8 mg/liter HCN solution were analysed. Table 9 shows the results for 2 grams of calcium chloride at 70° C and 95° C, and 2 and 5 grams of magnesium perchlorate at 95° C. Two liters of air were required to establish equilibrium using 2 grams of $CaCl_2$ and 4 liters of air for 2 grams of $Mg(ClO_4)_2$. With 5 grams of magnesium perchlorate a slightly lower peak area was obtained for HCN, and a larger volume of air was necessary to establish equilibrium.

At concentrations of 0.12 and 0.01 mg of HCN/liter of solution equilibrium was obtained with 5 and 9 liters of air, respectively, for 2 grams of $Mg(ClO_4)_2$ at 95° C. Approximately 10 liters of air can be dried by 3 grams of calcium chloride at 70° C, and 20 liters of air by 3 grams of magnesium perchlorate at 95° C before drying efficiencies become unfavorable.

The equilibration volume for calcium chloride was much larger than predicted from the gas-solid chromatography data. This may be the result of adsorption on the glass walls of the concentration apparatus. Reducing the size of the apparatus or substituting Teflon tubing for glass may reduce the equilibrating volume.

Reproducible results can be obtained with either $CaCl_2$ or $Mg(ClO_4)_2$ if collection is begun after 2 liters of air is passed through the apparatus and new drying agent is used with each analysis. If

Table 9. Determining equilibration volumes

Volume of Air (liters)	Peak Area (cm^2) at 2.5×10^{-10} amps/mv			
	$CaCl_2$, 70° C (2 grams)	$CaCl_2$, 95° C (2 grams)	$Mg(ClO_4)_2$, 95° C (2 grams)	$Mg(ClO_4)_2$, 95° C (5 grams)
0.5 - 1.5	3.8	4.0		
1.5 - 2.5	4.2	4.4	4.3	3.25
2.5 - 3.5	4.9	4.8	4.3	3.5
3.5 - 4.5	4.7	4.8	4.8	4.0
4.5 - 5.5			4.7	4.3
5.5 - 6.5			4.9	4.6
6.5 - 7.5				4.5
7.5 - 8.5				4.5

time permits collection may begin after equilibrium has been established.

Effect of Air Flow Rate and Solution Temperature

Equilibrium conditions must be established between the air and water before quantitative measurement is possible. Schneider (58, p 19) found equilibrium established between flow rates of 25 to 125 ml/min. A similar study was made with a medium porosity glass frit bubbler (58, p 35). The air volume was measured by water displacement instead of flow rate. Equilibrium conditions were found to exist at all flowrates (25-85 ml/min), confirming previous results. The effect of temperature is shown in Figure 16. A 2 % error would occur from a one degree error in solution temperature.

Stability of HCN Solutions

The strongest stock solution, 0.1 M KCN, was found to decay at a rate of 0.0005 M per day at 20° C (35, p 546). No loss of HCN from a 2.0 mg/liter (7.4×10^{-5} M) solution buffered at a pH of 6.5 was observed after seven days. A 20% loss of HCN was measured after 14 days from a 1.2 mg/liter standard solution; however the solution was then stable to at least 23 days. Standard solutions as low as 5.0 μg/liter (2×10^{-7} M) were found to be stable at least seven days. Normally standard solutions were analysed as they were

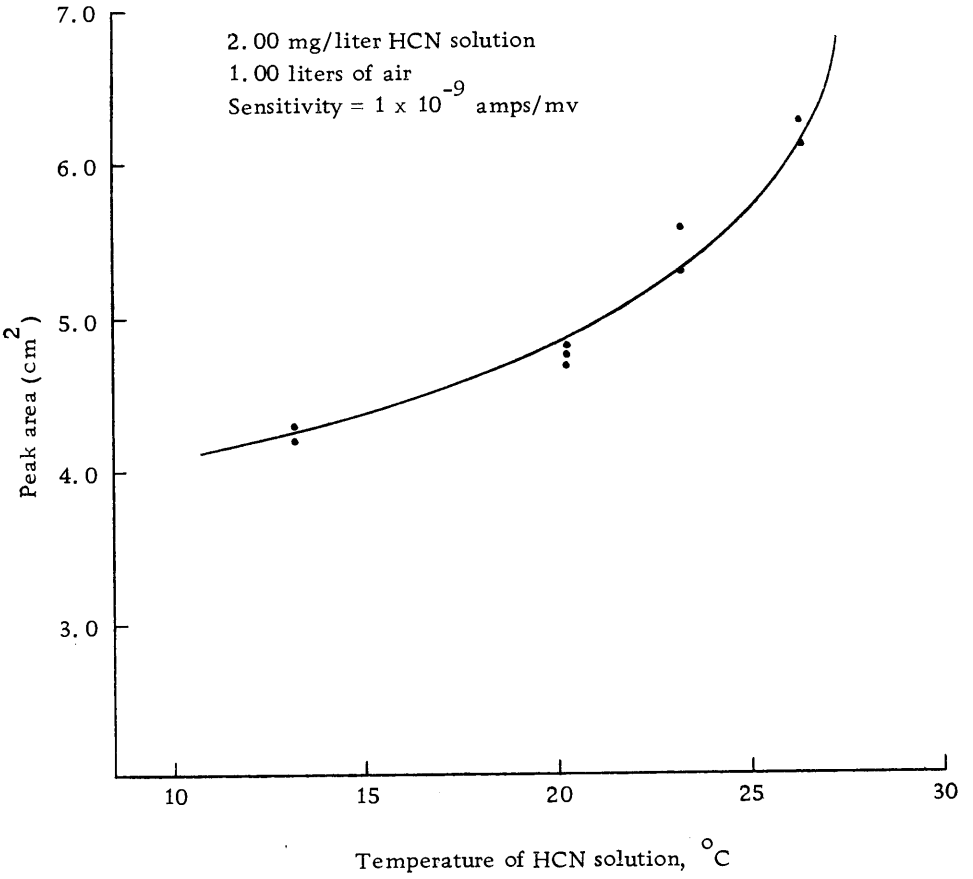


Figure 16. Effect of temperature on the distribution of HCN between air and water.

prepared.

Purification of Water

Water used in the preparation of standards must be free of metal ions which could complex with CN^- ions, and chlorine which could form cyanogen chloride (ClCN). Standard solutions were compared using base-permanganate distilled water and boiled ion-exchanged water. The distilled water was prepared by a continuous tap water fed five liter still (800 watts) to which a 100 ml aliquot of a base - permanganate solution was added. This solution was prepared by adding 6.3 g of potassium permanganate and 18.8 g of sodium hydroxide to 300 ml of water, and diluting up to 500 ml. Chlorine is completely removed, but only 50 % of the chloroform is removed. The ion-exchanged water was prepared by boiling distilled water in 4 liter Erlenmeyer flasks to 3/4 volume while sweeping the water with nitrogen gas using medium porosity glass frits. The cooled water was then passed through a Dowex 50W-X4 cation exchange resin in the sodium form. No chlorine was detected colorimetrically (67). Analysis of 5 μg/liter standard HCN solutions with water prepared from the two methods described gave comparable results. The boiling procedure was much faster and was principally used in the prepration of the standard solutions.

Preparation of Standard Solutions

All stock solutions were prepared at 20.0° C following a dilution scheme which avoided pipetting small quantities of stock solution to prevent volitility losses. Once cleaned with ethanolic-base and rinsed with 0.1 N HCl and distilled water, all pipettes and volumetric flasks were used only for its original purpose. Chromic acid should not be used. The following dilution scheme was followed:

a. $0.1\ M \xrightarrow[1000\ ml]{100\ ml} 0.01\ M \xrightarrow[20,000\ ml]{30,\ 60,\ 90,\ 120,\ 150\ ml} 0$ to $2000\ \mu g/l$

b. $0.01\ M \xrightarrow[1000\ ml]{100\ ml} 0.001\ M \xrightarrow[20,000\ ml]{30\text{-}150\ ml} 0$ to $200\ \mu g$/liter HCN range

c. $0.1\ M \xrightarrow[2000\ ml]{100\ ml} 0.005\ M \xrightarrow[2000\ ml]{50\ ml} 1.25 \times 10^{-4}\ M \xrightarrow[20,000\ ml]{6\text{-}150\ ml}$

0-20 μg/liter HCN Range

The 0.1 M KCN stock solution was standardized with a 0.05 M $AgNO_3$ solution (35, p 546, 547) using two 10 ml long stem burettes to measure the KCN and $AgNO_3$ solutions. The silver nitrate solution was standardized with sodium chloride by a standard gravimetric procedure using scintered glass crucibles. Volumetric procedures gave consistantly slightly lower results for the molarity of the silver nitrate solution.

Drying Agent

The drying agent was size graded to 20-35 mesh and dried at 200° C for 48 hours. About 1.5 grams of drying agent was weighed out and placed in the drying tube. Calcium chloride was heated to 70° C and magnesium perchlorate to 95° C.

Operating Procedures

The apparatus described by Schneider (59) was used to concentrate HCN with the addition of a Hoskins combustion furnace described on page 45. To prepare standard solutions an appropriate aliquot of KCN stock solution plus 100 ml of buffer solution (59) is added to approximately 18 liters of water. The solution is diluted to 20.00 liters at 20.0° C and stirred for one hour with a glass propeller. At the same time 1.5 g of drying agent is added to the drying tube and air passed through the apparatus, bypassing the standard solution.

After suitable stirring, the concentration column is connected to the apparatus and cooled to -78° C with Dry Ice-acetone. A medium porosity bubbler (59) is placed in the standard solution and connected in series with the air stream. After the air flow is adjusted to 50 ml/min, the concentration column is then switched into the air stream and the volume of air measured by water displacement using a 1 or 2

liter volumetric flask. The first sample of HCN, collected before equilibrium is established, is used to test the gas chromatographic operating conditions.

The gas chromatographic apparatus is shown in Figure 14 with the first oven disconnected. A 5-foot x 3/16 inch OD aluminum column is filled with 50/80 Porapak Q and conditioned at 90° C. The column temperature is adjusted to 51° C, the nitrogen flow to 80 ml/min, the detector hydrogen flow to 35 ml/min (8 psig), and the detector air flow to 400 ml/min (13 psig).

After collecting two liters of air, the cold trap is removed from the concentration board and connected to the gas sampling valve. A dewar flask filled with 95° C water is used to warm the trap. The recorder should be turned on while the trap is warming to observe baseline stability. The content of the trap is then injected on the column, and the gas sampling valve returned to its original position after 40 seconds. The trap is then removed and a vacuum applied for five minutes at 95° C to remove any remaining compounds. After HCN has eluted from the column (t_R = 5.3 min), valves #3 and 4 are closed and valve #2 and the gas sampling valve are opened to backflush the column (Figure 14).

Calibration curves were prepared for three concentration ranges; 0-20 μg/liter, 0-200 μg/liter, and 0-2000 μg/liter HCN. Two liters of air were trapped for the lowest concentration range

and one liter for the upper two concentration ranges. The results of plotting peak area of HCN against the concentration of the standard solution is shown in Figure 17. The two upper concentrations do not intersect zero, indicating a small loss of HCN. The data for the construction of the calibration curves is given in Tables 10 and 11.

A typical chromatogram at two different concentrations is shown in Figure 18. No tailing of HCN was evident, even at the lowest concentration. It is important that the contents of the cold trap are injected on the column no longer than 40 seconds since Compound A (Figure 18) is not injected as a plug and will tail into the HCN elution area. Compounds A and B have not been identified, but compound A may be methyl amine (p 64).

The minimum detectable quantity at a sensitivity of 5×10^{-12} amps/mv was 6 ng of HCN, while 15 ng of HCN or 6.7 ng of carbon was required to produce a 1 cm^2 peak at the practical operating range of 1.0×10^{-11} amps/mv. This compares to roughly 4.4 ng of benzene (4.1 ng of carbon) to produce a 1 cm^2 peak. The values for HCN and benzene are only approximate, but it appears the sensitivity of flame ionization detection of HCN is within the expected value for a single carbon molecule.

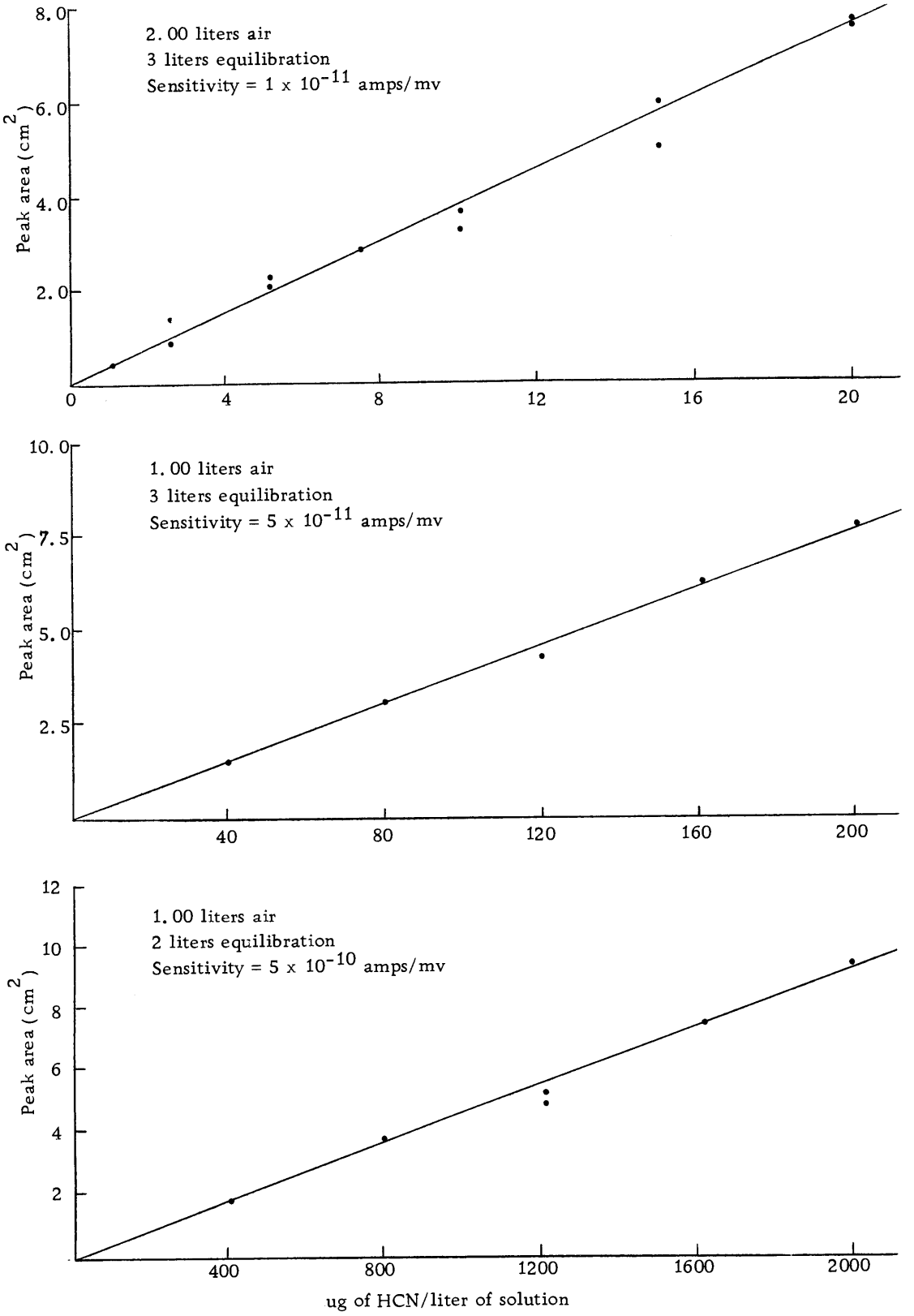


Figure 17. Calibration curves.

Table 10. Data for the construction of calibration curves for 0-20 μg/l HCN solutions

Run No.	HCN Concentration (μg/l)	Peak area (cm^2) at 1 x 10^{-11} amps/mv for the increments of air trapped (liters) *				
		1.0-3.0	3.0-5.0	5.0-7.0	7.0-9.0	9.0-11.0
1	0.99	0.65	0.40			
2	0.99		0.45			
3	2.47	0.95	1.15			
4	2.47		0.80			
5	4.94	2.3	2.3			
6	4.94	2.5	2.0			
7	7.41	3.0				
8	7.41	2.7	2.8			
9	9.87		3.25	3.70	3.90	4.15
10	14.8	6.0	5.0			
11	14.8	4.2	6.0			
12	19.8	7.7	7.7			
13	19.8	7.4	7.6			

* 1.5 g of $Mg(ClO_4)_2$ drying agent at 95° C.

Table 11. Data for the construction of calibration curves for 20-2000 μg/l HCN solutions

Run No.	HCN concentration (μg/l)	Peak area (cm^2) at 5 x 10^{-11} amps/mv for the increments of air tapped* (liters)							
		1.0-2.0	2.0-3.0	3.0-4.0	4.0-5.0	5.0-6.0	6.0-7.0	7.0-8.0	9.0-10
14	39.4	1.25	0.8	1.4, 1.7	1.5				
15	79.1		3.1	2.4	3.3	3.2			
16	118.5	3.7	4.2		4.95	5.3		5.1	4.3
17	158.0			7.0	6.5		6.9	7.5	
18	197.4	8.4	8.0	8.6	9.2				
19	394	17	19	19	12				
20	790		38	39	39	40			
21	1185		52	59	64	64	69		
22	1185		47	59	66	69	66		
23	1580		76	76	88	76	88		
24	1974		96	95	106	104	110		

* 1.5 g of $Mg(ClO_4)_2$ drying agent at 95° C.

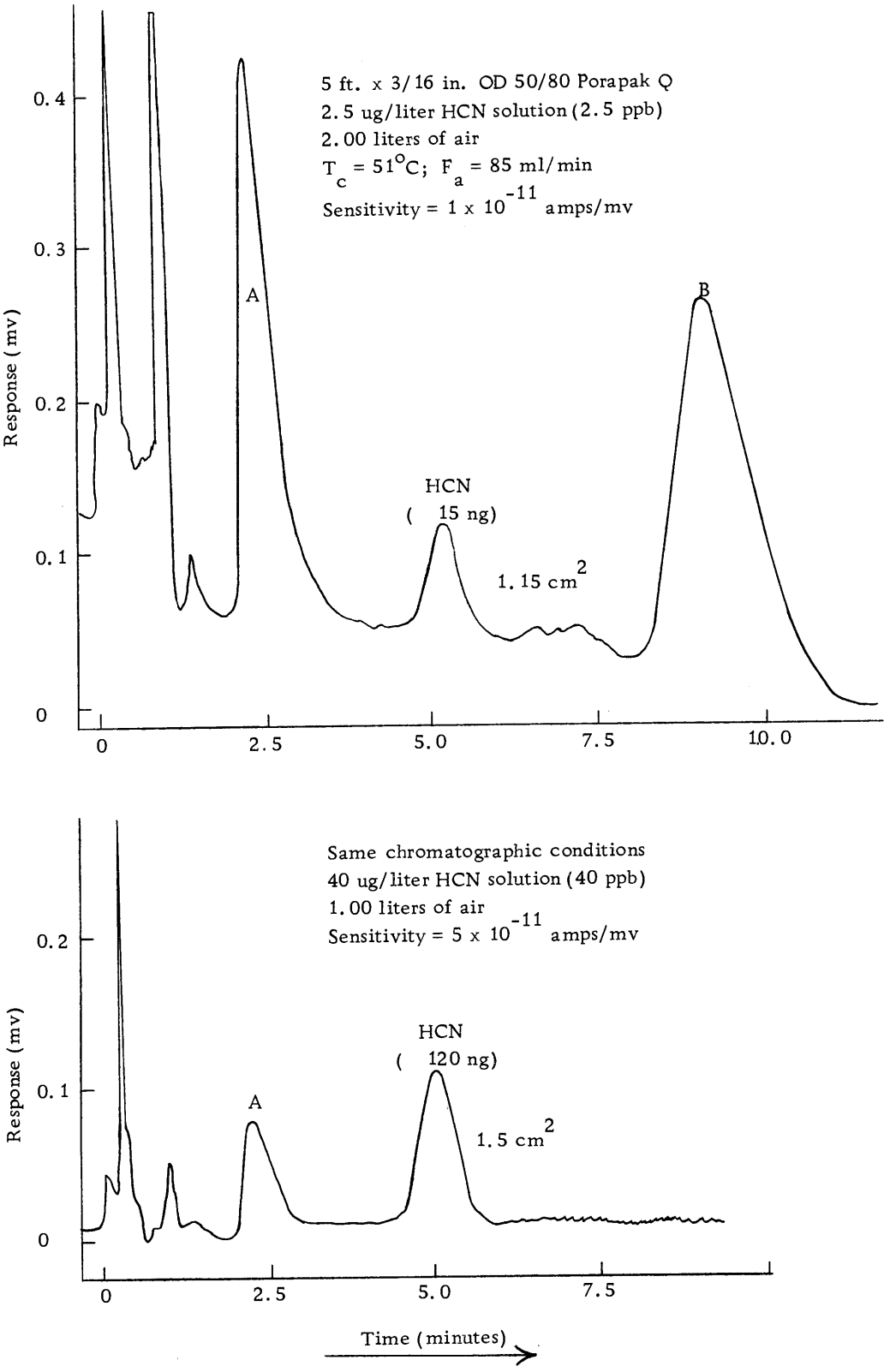


Figure 18. Chromatograms of HCN on Porapak Q.

CONCLUSION

The high sensitivity of the flame ionization detector has permitted detection of nanogram quantities of HCN. Flame ionization detection is approximately 100 times more sensitive than existing colorimetric methods and thermal conductivity detectors. Solutions as low as 1 μg of HCN/liter of solution (1 ppb) may be analyzed in five minutes after a 30 minute collection period. This should permit detection of sublethal HCN concentrations in industrial waste water or make possible physiological studies of prolonged exposures of HCN to aquatic inhabitants.

The flame ionization detector is relatively insensitive to small fluctuations in temperature and column flow rate, and is rugged and dependable. Its insensitivity to water is a particular advantage in the analysis of aqueous hydrocyanic acid solutions. A large linear response range also adds to its versatility.

The high sensitivity of the flame detector imposes additional contamination problems. The air, nitrogen, and hydrogen gases must be free of organic compounds, as well as the drying agent and glassware employed in the concentration of HCN. With the flame ionization detector response being proportional to the number of carbon atoms in a molecule, it may be several times more sensitive to the impurities present than to the single carbon HCN molecule.

The high sensitivity of the flame detector increases the demands on column separation. More efficient columns are necessary to completely separate HCN from minor detectable contaminates. Determination of nanograms quantities of polar compounds also requires a column packing that is nearly completely inert. Excellent results were obtained with Porapak Q. Other porous aromatic polymers may be equally satisfactory.

The ultimate sensitivity of this method is limited by the capacity of the drying agent and the concentration of interfering substances. Generally five liters of air can be collected without excessive contamination occuring. No attempts were made to determine concentrations below 1 μg of HCN/liter of solution.

The presence of HCN in industrial air may be more easily determined by potentiometric methods similar to the one developed by Strange (16) or by one of the many colorimetric methods. Although these methods are less sensitive, large volumes of air may be rapidly collected. The analysis of polluted water for mercaptans, amines, and other volatile carbon compounds may be carried out by the method described for HCN analysis in aqueous solutions. Detection of possible chlorine-containing compounds in chlorinated water may also be possible.

BIBLIOGRAPHY

1. Aldridge, W. N. The estimation of micro quantities of cyanide and thiocyanate. Analyst 70:474-475. 1945.

2. Amell, A. R., D. S. Lamprey and R. C. Schiek. Gas chromatographic separation of simple aliphatic amines. Analytical Chemistry 33:1805-1806. 1961.

3. American Public Health Association, American Water Works Association and Water Pollution Control Federation. Standard methods for the examination of water and wastes, including bottom sediments and sludges. 11th ed. New York, 1960. 626p.

4. Averill, Warren. Columns with minimum liquid phase concentration for use in gas-liquid chromatography. In: Gas chromatography: Third International Symposium held under the auspices of the Instrument Society of America, June 13-16, 1961. New York, Academic, 1962. P. 1-6.

5. Averill Warren. In-place coating of the solid support for gas chromatography. Journal of Gas Chromatography 1:34-35. 1963.

6. Baum E. H. Evaluation of microporous polyethylene as a low temperature gas chromatographic support. Journal of Gas Chromatography 1:13-15. 1963.

7. Bennett, O. F. Water determination by gas chromatography. Analytical Chemistry 36:684. 1964.

8. Berry, R. An ultra-sensitive ionization detector for permanent gas analysis. Nature 188:578-579. 1960.

9. Borodulina, R. I., P. Ya. Vertebnyi and I. A. Revel'skii. Chromatographic analysis of an aqueous solution of technical acrylonitrile and of a condensate containing acrylonitrile, acetonitrile, hydrocyanic acid and acrolein. Gazovaya Khromatografiya Akademiya Nauk SSSR, Trudy Vtoroi Vesesoyuznoi Konfenentsee. Moscow, 1962, p. 317-321. 1964. (Abstracted in Chemical Abstracts 62:3894h. 1965)

10. Calcote, H. F. Mechanisms for the formation of ions in flames. Combustion and Flame 1:385-403. 1957.

11. Condon, R. D., P. R. Scholly and W. Averill. Comparative data on two ionization detectors. In: Gas chromatography; Proceedings of the Third Symposium organized by the Institute of Petroleum, Edinburgh, June 8-10, 1960. Washington, D. C., Butterworths, 1960. p 30-45.

12. Dal Nogare, Stephen and Richard S. Juvet, Jr. Gas-liquid chromatography. New York, Wiley, 1962. 450 p.

13. Dennison, J. E. and Harry Freund. Separation and determination of arsenic trichloride and stannic chloride by gas chromatography. Analytical Chemistry 37:1766-1768. 1965.

14. Destry, D. H., C. J. Geach and A. Goldup. An examination of the flame ionization detector using a diffusion dilution apparatus. In: Gas chromatography; Proceedings of the Third Symposium organized by the Institute of Petroleum, Edinburgh, June 8-10, 1960. Washington, D. C., Butterworths, 1960. p 46-64.

15. Dewar, R. A. and V. E. Mairer. High efficiency glass columns for gas chromatography. Journal of Chromatography 11:295-300. 1963.

16. Dimbat Martin, P. E. Porter and F. H. Stross. Gas chromatography. Apparatus requirements for quantitative application of gas-liquid partition chromatography. Analytical Chemistry 28:290-297. 1956.

17. Doudoroff, Peter, Gerard Leduc and Carl R. Schneider. Acute toxicity to fish of solutions containing complex metal cyanides in relation to concentrations of molecular hydrocyanic acid. Transactions of the American Fisheries Society 95:6-22. 1966.

18. Epstein, Joseph. Estimation of microquantities of cyanide. Analytical Chemistry 19:272-275. 1947.

19. Ettre, L. S. The effect of the surface area on the separation in gas-liquid partition chromatography. Journal of Chromatography 4:166-169. 1960.

20. Ettre, L. S. Possibility of investigating and expressing collumn efficiencies. Journal of Gas Chromatography 1:36-47. 1963.

21. Frederick, D. H., et al. The use of lightly loaded columns in gas chromatography. Analytical Chemistry 34:1521-1526. 1962.

22. Gaydon, A. G. and H. G. Wolfhard. Flames, their structure, radiation, and temperature. London, Chapman and Hall, 1953. 383 p.

23. Giuffrida, L. A flame ionization detector highly selective and sensitive to phosphorus - a sodium thermionic detector. Journal of the Association of Official Analytical Chemists 47: 293-300. 1964.

24. Grigorescu, I. and Gh. Toba. Determination of hydrocyanic acid in an industrial atmosphere. Revue de Chimie, Bucharest 15:572-574. 1964. (Abstracted in Chemical Abstracts 63:18927h. 1965).

25. Hamlin, A. G., G. Iveson and T. R. Phillips. Analysis of volatile inorganic fluorides by gas-liquid chromatography. Analytical Chemistry 35:2037-2044. 1963.

26. Harley, J., W. Nel and V. Pretorius. Flame ionization detector for gas chromatography. Nature 181:177. 1958.

27. Hartmann C. H. Aerograph phorphorus detector. Varian Aerograph Research Notes, Spring 1966, p 1-8.

28. Hartmann, C. H. and K. Thompson. Helium detector for ppb analysis of fixed gases. Varian Aerograph Research Notes, Spring 1967, p 1-8.

29. Hollis, O. L. Separation of gaseous mixtures using porous polyaromatic polymer beads. Analytical Chemistry 38:309 - 316. 1966.

30. Isbell, R. E. Determination of hydrogen cyanide and cyanogen by gas chromatography. Analytical Chemistry 35:255-256. 1963.

31. Karmen A. Specific detection of halogens and phosphorus. Analytical Chemistry 36:1416-1421. 1964.

32. Kirkland, J. J. Fluorine-containing polymers as solid supports in gas chromatography. Analytical Chemistry 35:2003-2009. 1963.

33. Kirkland, J. J. Some recent developments in column technology. In: Gas chromatography, Fourth International Symposium held under the auspices of the Instrument Society of America, June 17-21, 1963. New York Academic, 1963. p 77-103.

34. Kolthoff, I. M. and C. S. Miller. Anodic waves involving electrooxidation of mercury at the dropping mercury electrode. Journal of the American Chemical Society 63:1405-1411. 1941.

35. Kolthoff, I. M. and E. B. Sandell. Textbook of quantitative inorganic analysis. 3d ed. New York, Macmillan, 1952. 759 p.

36. Kuwada, D. M. Determination of water in hydrazine by gas chromatography. Journal of Gas Chromatography 1:11-13. 1963.

37. Laitinen, H. A., W. P. Jennings and T. D. Parks. Amperometric titration of cyanide with silver nitrate, using the rotating platinum electrode. Industrial Engineering Chemistry, Analytical ed., 18:574-575. 1946.

38. Landault, C. and G. Guiochon. The use of teflon as a support in gas-liquid chromatography. Application to the separation of strongly polar substances. Journal of Chromatography 9:133-146. 1962.

39. Lewis, B. and G. von Elbe. Combustion, flames and explosions of gases. New York, Academic, 1951. 795p.

40. Lovelock J. E. Argon detectors. In: Gas chromatography; Proceedings of the Third Symposium organized by the Institute of Petroleum, Edinburgh, June 8-10, 1960. Washington, D. C., Butterworths, 1960. p 16-29.

41. Lovelock, J. E. An ionization detector for permanent gases. Nature 187:49-50. 1960.

42. Lovelock, J. E. Ionization methods for the analysis of gases and vapors. Analytical Chemistry 33:162-178. 1961.

43. Lovelock, J. E. A sensitive detector for gas chromatography. Journal of Chromatography 1:35-46. 1958.

44. Lovelock, J. E. and S. R. Lipsky. Electron affinity spectroscopy - a new method for the identification of functional groups in chemical compounds separated by gas chromatography. Journal of the American Chemical Society 82:431-433. 1960.

45. McNair, H. M. and T. DeVries. 1, 2, 3-Tris(2-cyanoethoxy)-propane as a stationary liquid for gas chromatography columns. Analytical Chemistry 33:806. 1961.

46. McWilliam, G. and R. A. Dewar. Flame ionization detector for gas chromatography. Nature 181:760. 1958.

47. Martin, R. L. Adsorption on the liquid phase in gas chromatography. Analytical Chemistry 33:347-352. 1961.

48. Milne, D. Disposal of cyanides by complexation. Sewage and Industrial Wastes 22:1192-1199. 1950.

49. Morrison, J. D. and A. J. C. Nicholson. Studies of ionization efficiency. Part 11. The ionization potentials of some organic molecules. The Journal of Chemical Physics 20: 1021-1023. 1952.

50. Ottenstein, D. M. Column support material for use in gas chromatography. Journal of Gas Chromatography 1:11-23. 1963.

51. Parcher, J. F. and Paul Urone. An improved solution coating technique for gas chromatographic support. Journal of Gas Chromatography 2:184-185. 1964.

52. Perkins G. et al. Response of the gas chromatographic flame ionization detector to different functional groups. In: Gas chromatography: Third International Symposium held under the auspices of the Instrument Society of America, June 13-16, 1961. New York, Academic, 1962. p 269-285.

53. Perrett, R. H. and J. H. Purnell. A study of the reaction of hexamethyldisilazane with some common gas-liquid chromatographic solid supports and its effect on their adsorptive properties. Journal of Chromatography 7:455-466. 1962.

54. Porcaro, P. J., and V. D. Johnson. Primary amyl alcohols determined by gas chromatography. Analytical Chemistry 33:361-362. 1960.

55. Recommendations on nomenclature and presentation of data in gas chromatography. Pure and Applied Chemistry 8:553-562. 1964.

56. Runge, Henner. Gas chromatographische analyse anorganischer case. Zeitschrift fur Analytische Chemie 189:111-124. 1962.

57. Sawyer, D. T. and J. K. Barr. Evaluation of support materials for use in gas chromatography. Analytical Chemistry 34:1518-1520. 1962.

58. Schneider, C. R. Determination of low level hydrocyanic acid in solution using gas-liquid chromatography. Ph. D. thesis. Corvallis, Oregon State University, 1962. 121 numb. leaves.

59. Schneider, C. R. and Harry Freund. Determination of low level hydrocyanic acid in solution using gas-liquid chromatography. Analytical Chemistry 34:69-74. 1962.

60. Scholz, R. G. and W. W. Brandt. The effect of solid supports on retention volumes. In: Gas chromatography; Third International Symposium held under the auspices of the Instrument Society of America, June 13-16, 1961. New York, Academic, 1962. p 7-26.

61. Smith, V. N. and J. F. Fidiam. Electron drift-velocity detector for gas chromatography. Analytical Chemistry 36:1739-1744. 1964.

62. Snell, F. D. and C. T. Snell. Colorimetric methods of analysis; including some turbidimetric and neophelometric methods. Vol. 2. New York, Van Nostrand, 1948. 950 p.

63. Sternburg James C. Detection devices for gas chromatography. In: Gas chromatography: Fourth International Symposium held under the auspices of the Instrument Society of America June 17-21, 1963. New York Academic, 1963. p 161-191.

64. Sternberg, J. C., W. S. Gallaway and D. T. Jones. The mechanism of response of flame ionization detectors. In: Gas chromatography: Third International Symposium held under the auspices of the Instrument Society of America, June 13-16, 1961. New York, Academic, 1962. p 231-267.

65. Strange, John P. Potentiometric recorder for hydrogen sulfide and hydrogen cyanide. Analytical Chemistry 29: 1878-1881. 1957.

66. Table 54: Values of the correction factor j of James and Martin used in gas chromatography. Journal of Chromatography 2:D33-D45. 1959.

67. Webber, H. M. and Elizabeth A. Wheller. The adsorptiometric determination of chlorine in water. Analyst 90: 372-373. 1965.

68. Williams, Ian H. Gas chromatographic techniques for the identification of low concentrations of atmospheric pollutants. Analytical Chemistry 37:1723-1732. 1965.

69. Willis, V. Analysis by gas chromatography of a 'pure' sample with an 'impure' carrier. Nature 183:1754. 1959.

70. Winkler, W. O. Report on cyanide residues in food. Journal of the Association of Official Analytical Chemists 42: 552-553. 1959.

71. Woolmington, K. G. Determination of hydrogen cyanide by gas chromatography. Journal of Applied Chemistry (London) 11:114. 1961.

72. Wuhrmann, K. and H. Woker. Experimentelle untersuchungen über die ammoniak-and blausaurevergiftung. Schweizerische Zeirschrift für Hydrologie 11:210-244. 1948.

73. Urone, Paul, John Elvans Smith and Richard J. Katnik. Gas chromatography study of some chlorinated hydrocarbons. Analytical Chemistry 34:456-480. 1962.

APPENDIX

CHROMATOGRAPHIC BEHAVIOR OF THE STATIONARY PHASE NEAR ITS FREEZING POINT

In an attempt to separate HCN and $CHCl_3$ on a Carbowax 20 M column the relative retention times of the two compounds were determined at column temperatures between ambient and 100° C. Only small changes in the relative retention times were observed, but the absolute retention volume decreased 50 % as the column temperature dropped below the freezing point of the stationary phase. This was also observed by Urone (73). However no sharp decrease was found in the retention volumes near the freezing point of Carbowax 1540. Since additional information could not be found in the literature, the effect of temperature on the specific retention volume above and below the freezing point of five different stationary phases was investigated further.

The first two stationary phases investigated were Carbowax 1540 and 20 M. Carbowax 1540 is a polyethylene glycol polymer with an average molecular weight of 1300 to 1600. Carbowax 20 M is synthesized by joining glycol 6000 with a diepoxide. Both polymers have a crystalline appearence, rather sharp melting points, and give a polar elution order (Table 3).

Ethylene glycol succinate was also selected as a polar crystalline polymer. Halocarbon 6-00 is a chlorotrifluoropolyethylene polymer. It has a broad melting point, and is very viscous. Dennison

and Freund(13) have found this polymer useful as a stationary phase in separating some metal halides. Cetyl alcohol (1-hexadecanol) was selected as a crystalline compound in contrast to polymeric stationary phases. This compound has been used in the separation of aliphatic amines (2).

The polarity of the stationary phase above and below its freezing point was investigated using the "polarity mixture" previously described(page 55). Changes in the column efficiencies were observed as the column temperature passed through the melting point zone. Since some columns gave very skewed peaks, peak profiles were compared instead of calculating theoretical plates.

Experimental

The gas chromatograph was a modified Beckman GC-2 described on page 16. Flow rates were measured by soap films in a modified 50 ml buret. Table 11 lists the columns investigated in this study. Acid washed 40/60 mesh Chromosorb W was used in columns 1 through 5, and 60/80 mesh in column 6. In coating the solid support for the first five columns the solvent was removed on a steam bath, while a rotary evaporator was employed in the preparation of column 6. After filling the columns by verticle packing, the columns were conditioned for 12 hours at the temperatures listed in Table 11.

All flow rates were corrected for the vapor pressure of the water in the buret (12, p 77). Using the symbolism recommended by the IUPAC (55), the column flow was adjusted to give a F_c^o flow rate of 30± 2 ml/min at each column temperature, where $F_c^o = jF_c$. This was done to avoid any effects of changing carrier gas flow rates. The j values were taken from a prepared table (66). The resulting linear flow rate was approximately 6.3 cm/sec. Ten microliters of each component of the polarity mixture was analysed separately to guarantee resolution.

The specific retention volumes, V_g, defined as the net retention volume at 0°C per gram of liquid phase were calculated from isothermal chromatograms over a range of column temperatures. An example is provided on the last page. The column temperatures were selected to place the freezing point of the stationary phase in the center of the temperature range.

Results and Discussion

Graphs of the logarithm of the specific retention volume against the reciprocal of the absolute column temperature were constructed for each component of the polarity mixture. From the graphs the order of elution of each solute can be observed. Changes in the peak profiles with temperature were also followed. The results of each column are summarized below.

Column 1, Carbowax 20M

The plot of the log Vg vs 1/T is shown in Figure 19. The specific retention volumes of both the nonpolar and polar sources decrease abruptly as the column temperature approaches the freezing point. Below the freezing point of Carbowax 20M the order of elution of ethanol and benzene are reversed.

The column efficiency also decreases sharply as the column temperature approaches the freezing point. Below the freezing point the column efficiency improves again. The peak profile for ethanol is given in Figure 25.

Column 2 Carbowax 1540

Figure 20 shows the results of plotting log Vg vs 1/T for a Carbowax 1540 column. There is no discontinuity in the slope of the plot at the freezing point. There is also no sudden loss in column efficiency near the freezing zone, but rather a gradual asymmetric peak is obtained with a leading edge common to low column temperatures (Figure 25). The order of elution and the degree of separation between cyclohexane and ethanol is typical of a polar stationary phase.

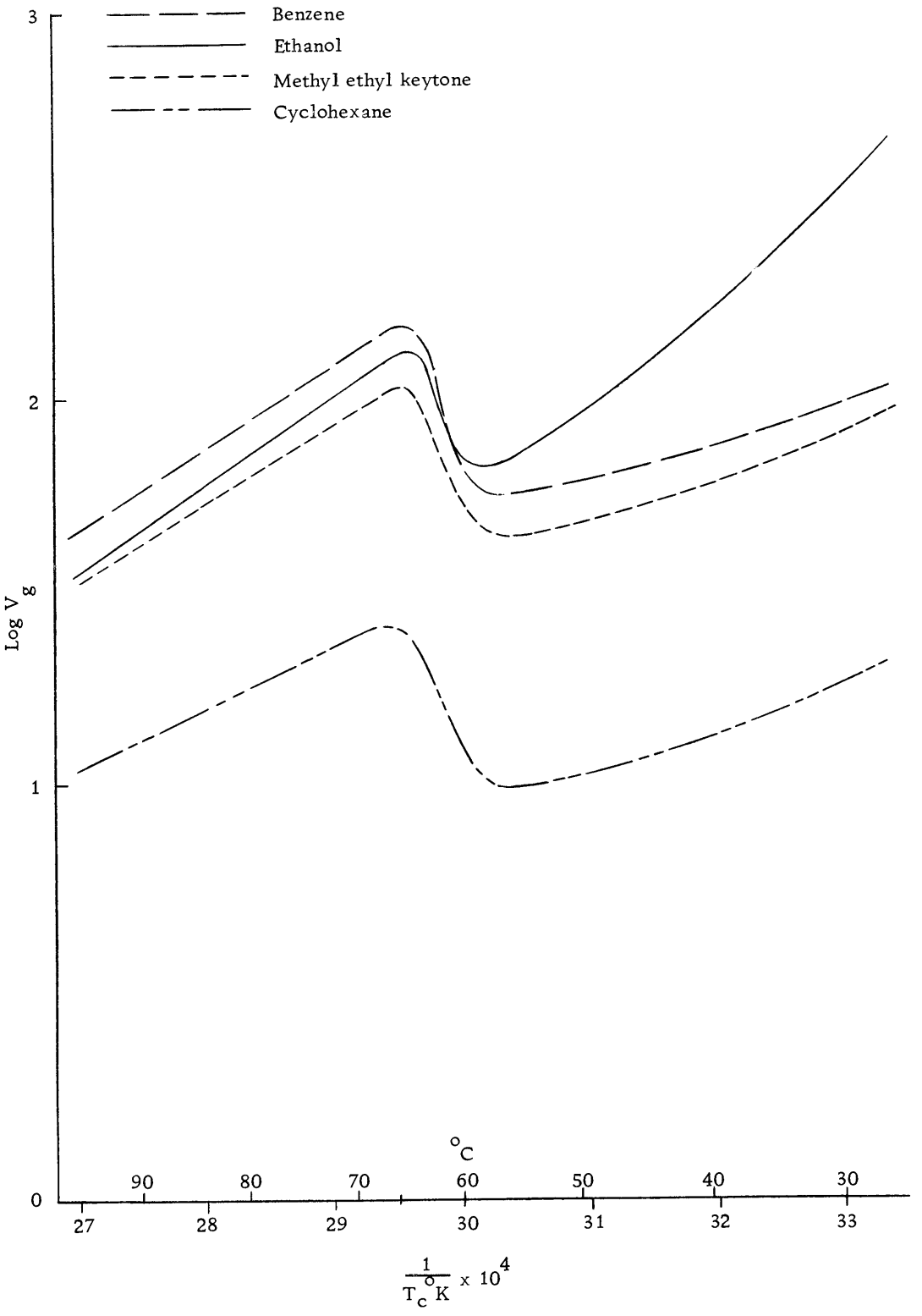


Figure 19. Specific retention volumes on column 1, Carbowax 20M.

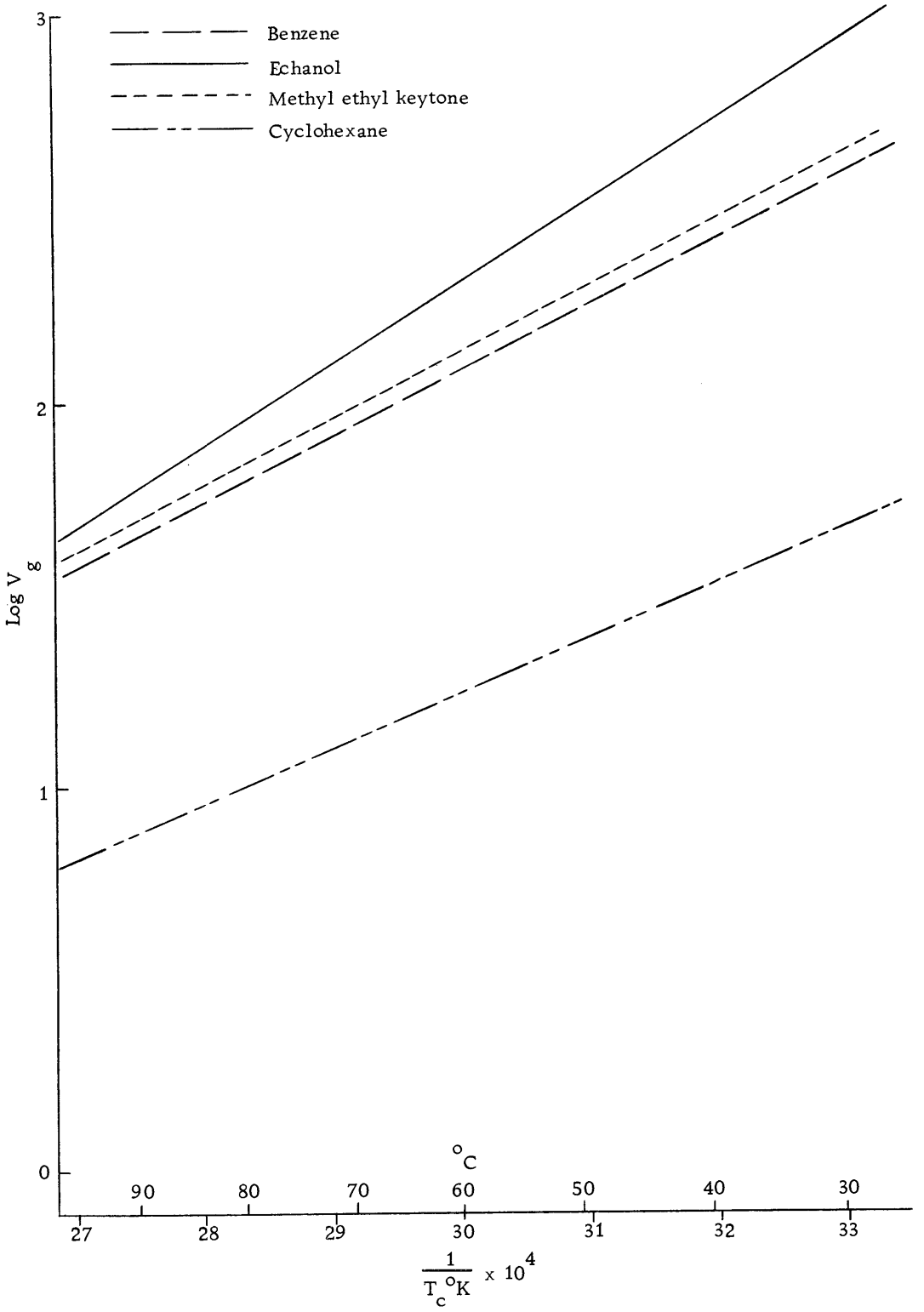


Figure 20. Specific retention volumes on column 2, Carbowax 1540.

Column 3 Halocarbon 6-00

There is no sharp discontinuity in the log Vg vs 1/T plot for the Halocarbon 6-00 column as shown in Figure 21. In the liquid state a slightly polar elution order is obtained. As the column temperature approaches the freezing zone the elution order of cyclohexane and MEK are reversed. Note cyclohexane now elutes between ethanol and MEK.

Halocarbon 6-00 is very viscous near its freezing zone. Being very viscous poor mass transfer effects result in broad peaks. The number of theoretical plates (55) for benzene for each column at the specified temperature is listed in Table 12. Halocarbon 6-00 is considerably less efficient than the other stationary phases.

Before this column was conditioned ethanol and MEK eluted as severe tailing peaks. After column conditioning only a small amount to tailing was present. Figure 25 shows the peak asymmetry for ethanol after column conditioning. The ethanol peak remains skewed well below the measured melting range.

Column 4 Cetyl Alcohol

Cetyl alcohol shows a large discontinuity at its freezing point (Figure 22). Ethanol is the last solute to elute below the freezing point and the first to elute at higher temperatures while the other

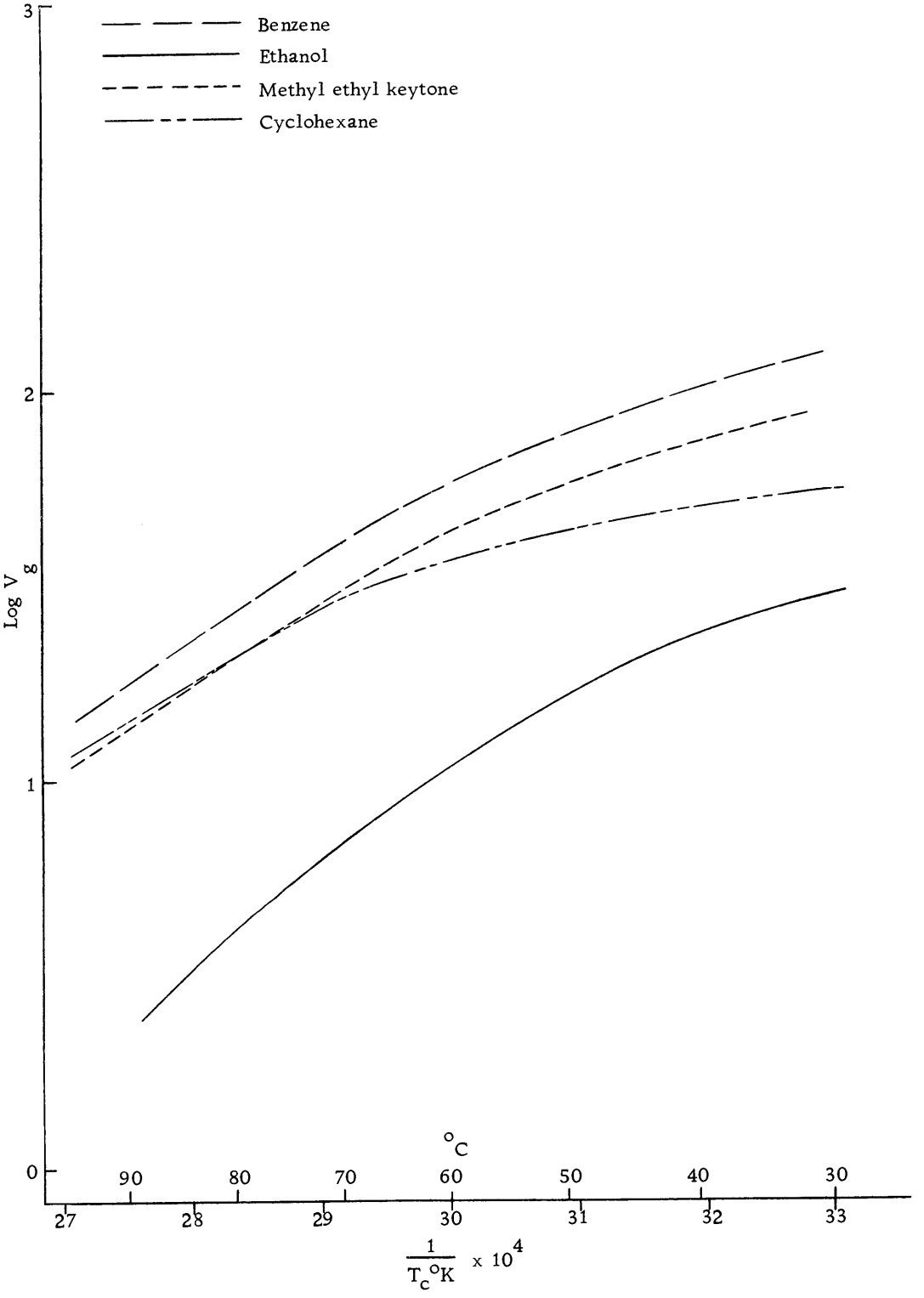


Figure 21. Specific retention volumes on column 3, Halocarbon 6-00.

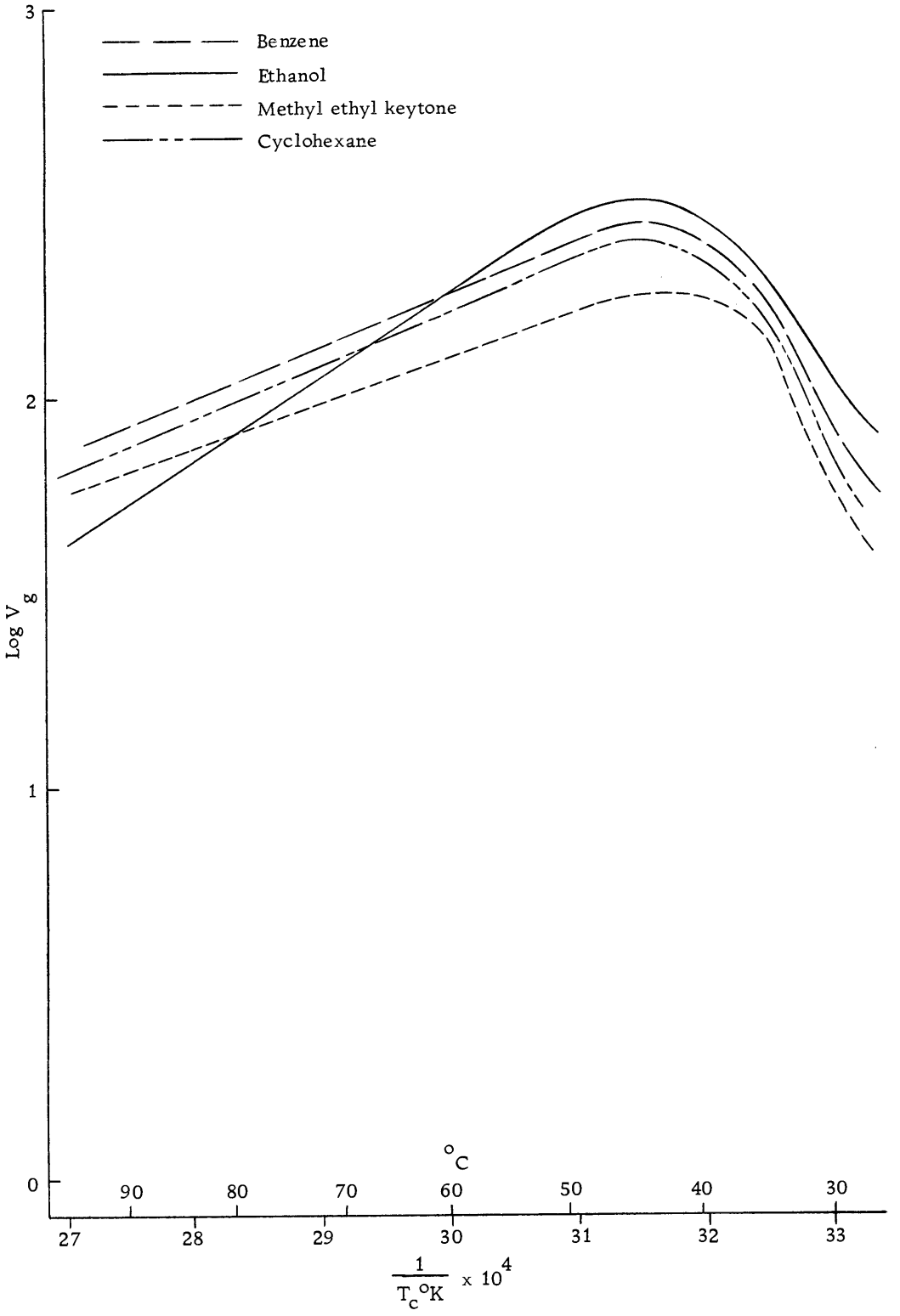


Figure 22. Specific retention volumes of column 4, cetyl alcohol.

components of the polarity mixture keep their respective elution order. Hydrogen bonding probably accounts for the change in the ethanol elution order. As a liquid the hydroxyl group of cetyl alcohol may hydrogen bond with the solid support leaving a less polar stationary phase than in the solid state.

As with Carbowax 20M the column efficiency improves as the temperature drops further below the freezing point (Figure 25). No tailing peaks due to adsorption are present with this slightly polar stationary phase.

Column 5, Ethylene Glycol Succinate

Ethylene glycol succinate (EGS) is a polyester polymer. The retention times for the polarity mixture were too short for measurement at 50° C; thus toluene (b. p. 110.6° C), methyl isobutyl keytone (b. p. 119° C), and n-butanol (b. p. 117.7° C) were substituted in investigating this stationary phase. The log Vg vs 1/T plot is given in Figure 23. Accompaning the discontinuity is a small change in the peak shapes of each solute at the freezing point, but the peaks do not become highly skewed below the freezing point as in the case of columns 1, 3, and 4. The order of elution and the degree of separation of n-butanol and methyl isobutyl keytone classifies EGS as a polar stationary phase useful in separating alcohols and keytones.

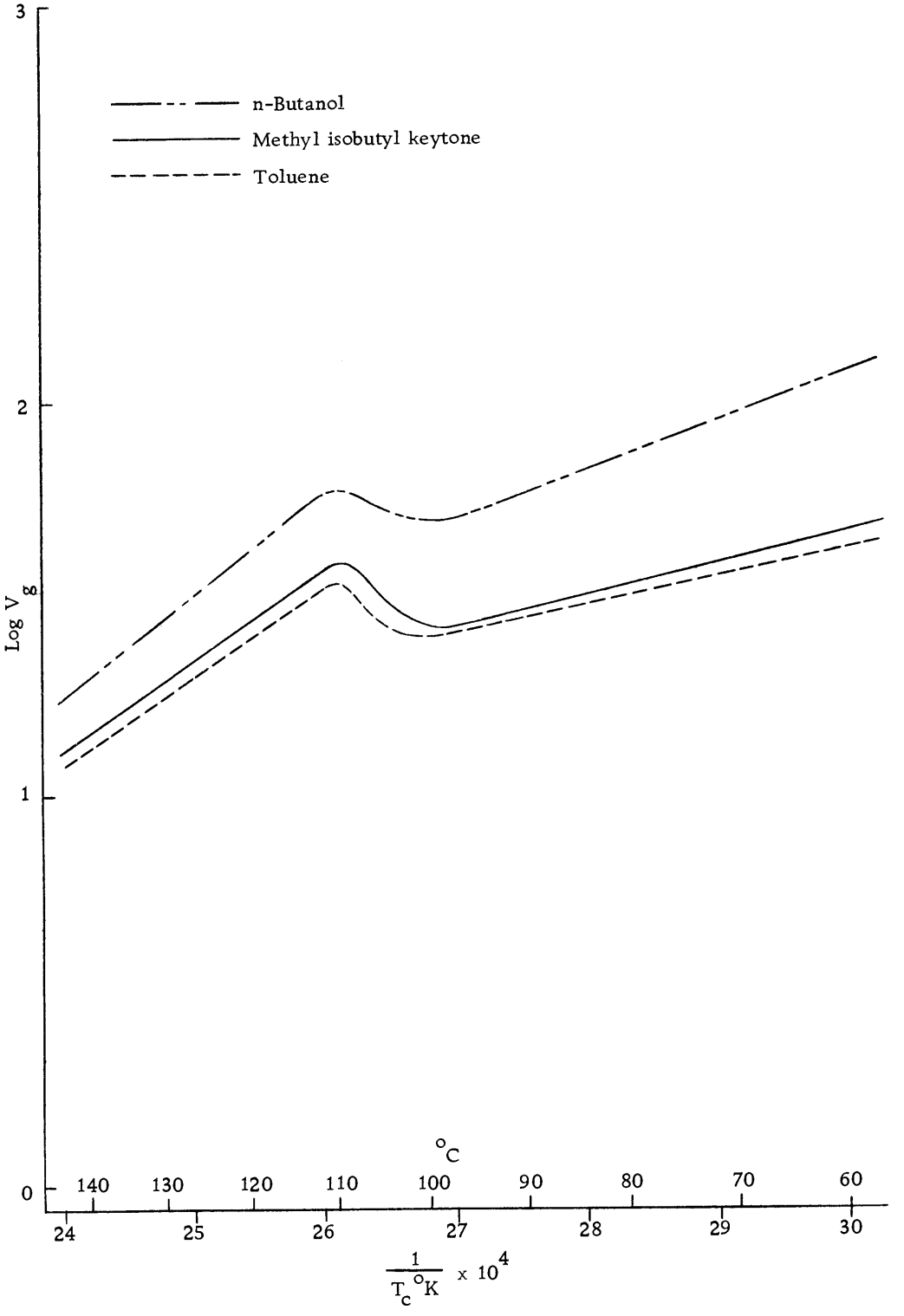


Figure 23. Specific retention volumes on column 5, ethylene glycol succinate.

Column 6, Carbowax 1540

In view of the discontinuities found at the melting point of the stationary phases investigated, the lack of discontinuity of Carbowax 1540 appeared to be unique. A new column with new packing was prepared using rotary evaporation of the solvent and vacuum drying of the coated support at 50° C. The specific retention volume is plotted as a function of temperature in Figure 24. Contrary to column 2, column 6 shows a large discontinuity near the freezing zone similar to Carbowax 20M. Column 6 has the same elution order as column 2 at 25°C and that of Carbowax 20M at 85° C.

Results similar to column 6 were obtained by "in place" coating of the support (5). Repeated preparation of column packings by steam bath removal of the solvent and final drying at different temperatures indicate air oxidation of Carbowax 1540 can occur at temperatures above 70° C. This may result in a higher melting point. The column temperatures studied with column 2 may be below the melting point of the oxidized stationary phase; hence no discontinuity is observed.

Table 13 lists the specific retention volumes of each solute of the polarity mixture at 80.0° C. Note the large retention volumes for the cetyl alcohol column versus Halocarbon 6-00.

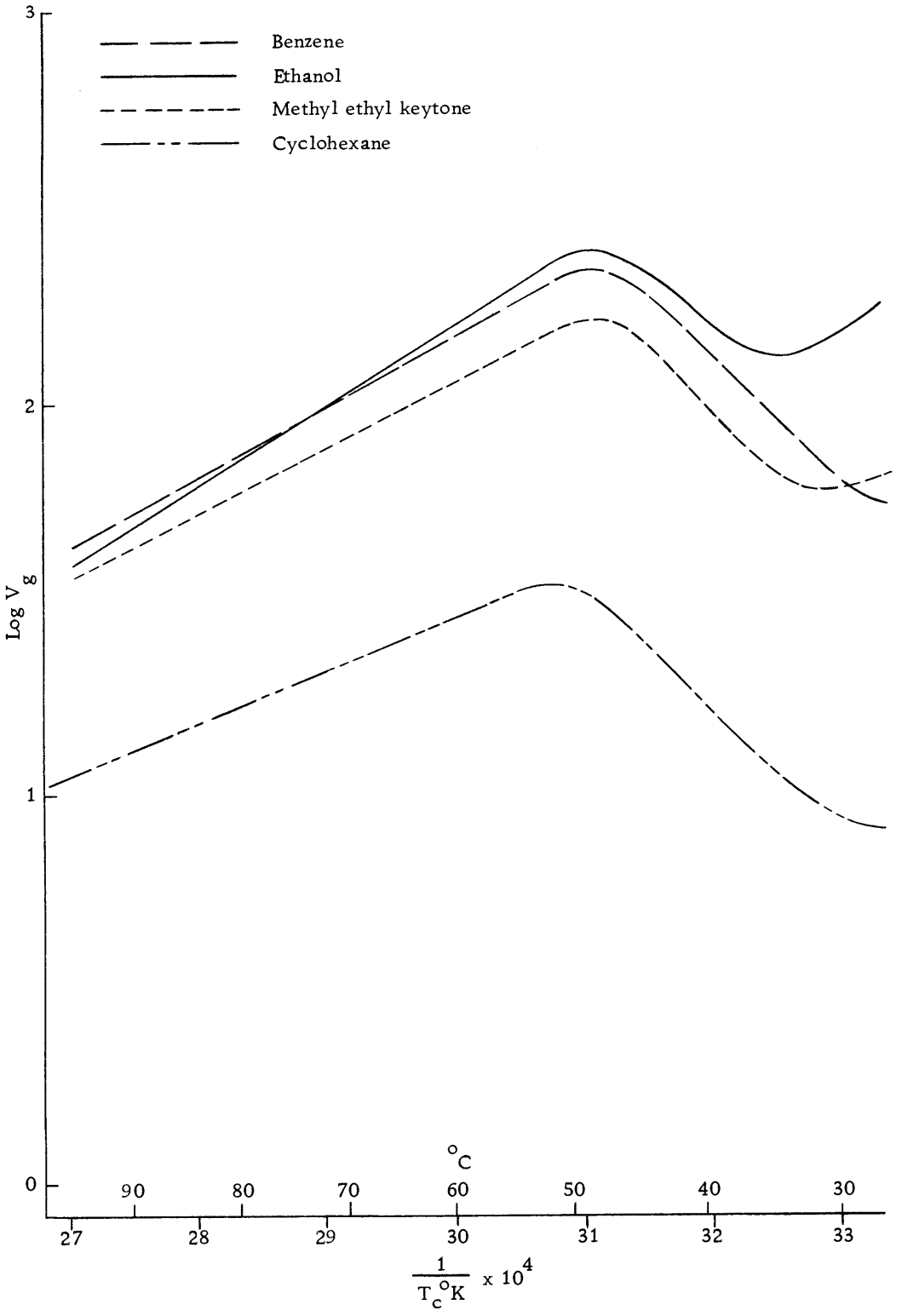


Figure 24. Specific retention volumes on column 6, Carbowax 1540.

Conclusions

Large discontinuites in the retention volumes of solutes may be anticipated where distinct phase changes occur. Carbowax 1540 and 20M, ethylene glycol succinate, and cetyl alcohol have a crystalline appearence as a solid and show large discontinuities in their log Vg vs 1/T plots. Halocarbon 6-00 has a broad melting range and only small changes in the specific retention volumes occur at the melting zone.

Changes in the elution order may occur below the freezing point. This may be used to an advantage in separating small impurities from a major component where the loss in column efficiency below the freezing point is not prohibitive.

Where large discontinuities exist at the freezing point the column efficiency drops abruptly and the solute peak becomes highly skewed. At temperatures well below the freezing point an improvement in column efficiency is generally observed. With HCN the loss of column efficiency below the freezing point of Carbowax 1540 or 20M was small.

Carbowax 1540 packing prepared by steam bath evaporation coating procedure may be degraded at temperatures above 70^{o} C. Volatile solvents and low drying temperatures are recommended in the preparation of Carbowax 1540 packings.

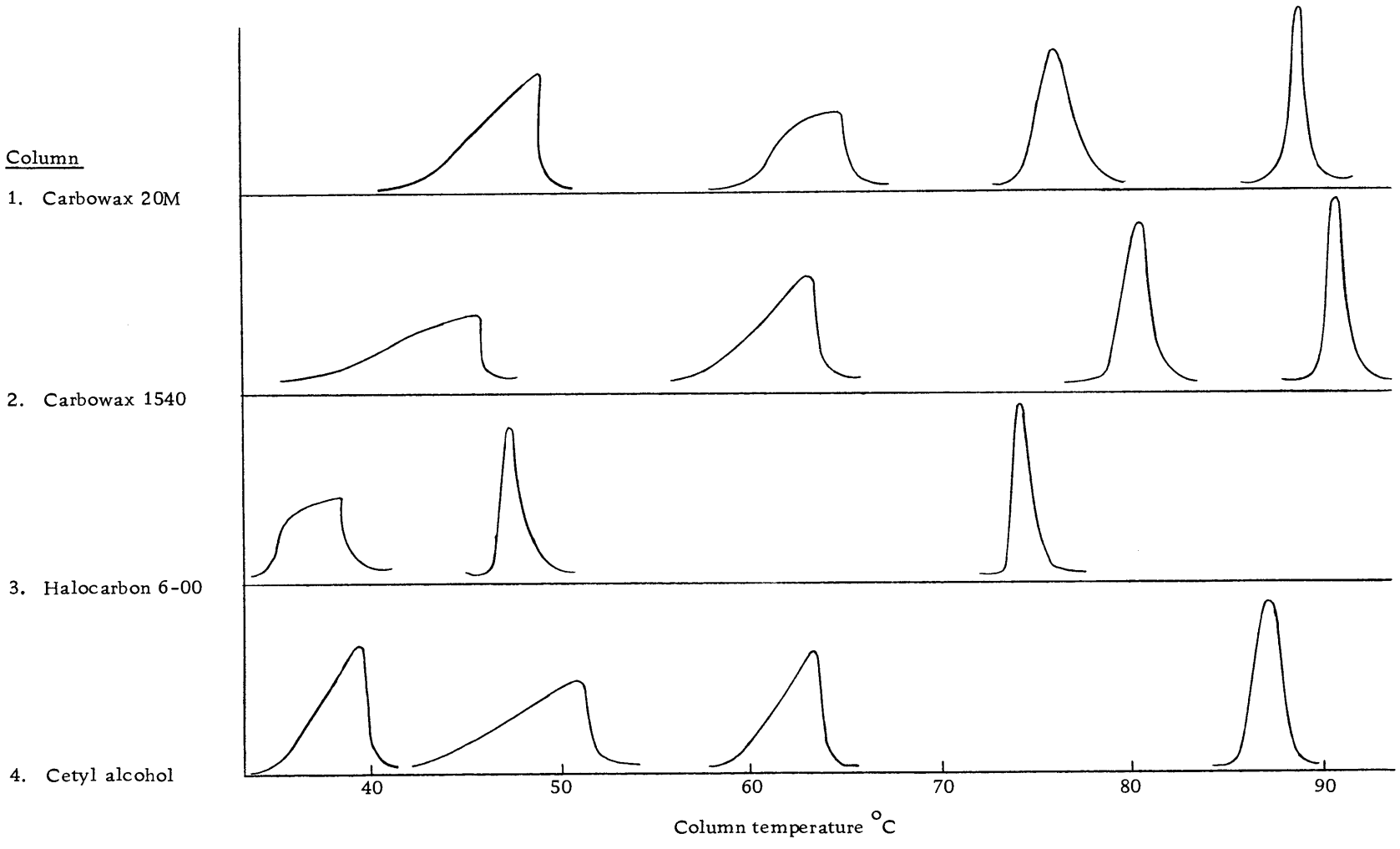


Figure 25. Peak profile for ethanol.

Table 12. Columns investigated

Column	Length (feet)	%	Stationary Phase	W_L (grams)	Melting Point °C	Conditioning Temp. °C
1	15.0	15	Carbowax 20M	2.30	62-63	190
2	15.0	15	Carbowax 1540	2.37	45-47.5	130
3	15.0	15	Halocarbon 6-00	2.31	57-60	130
4	15.0	15	Cetyl Alcohol	2.31	47-47.5	130
5	9.0	15	Ethylene glycol Succinate	1.32	99-102	160
6	6.0	15	Carbowax 1540	0.803	45-47.5	130

Table 13. Theoretical plates per foot for benzene

Column	Temperature °C	Theoretical Plates
1. Carbowax 20M	74.5	80
2. Carbowax 1540	82.5	88.8
3. Halocarbon 6-00	74.3	32.9
4. Cetyl Alcohol	76.6	87.7
6. Carbowax 1540	74.9	170

Table 14. Specific retention volumes at 80.0° C

Column	Cyclohexane	Benzene	Methyl Ethyl Keytone	Ethanol
1. Carbowax 20M	17.2	85.5	59.6	65.5
2. Carbowax 1540	9.9	65.0	58.5	85.0
3. Halocarbon 6-00	19.9	26.7	20.3	4.1
4. Cetyl Alcohol	102	112	89.5	84.5
6. Carbowax 1540	16.2	69.0	54.5	66.0

An Example of the Calculation of the Specific Retention Volume

Definitions and Experimental Data

a. w_L = weight of the liquid phase = 0.803 grams

b. T_a = ambient temperature = 23.8° C = 297° K

c. T_c = column temperature = 87.5°C = 360.7° K

d. P_i = inlet pressure = 12.5 psig = 27.2 psi = 1406 mm

e. P_o = outlet pressure = 758 mm

f. P_w = vapor pressure of water at ambient temperature = 22.1 mm

g. j = gas compressibility correction factor = $(3/2)\left[(Pi/Po)^2-1\right] / \left[(Pi/Po)^3-1\right]$

h. t_R solute = retention time from injection to the peak maximum = 2.09 min.

i. t_R air = retention time from injection to the peak maximum = 0.65 min.

j. F_a = uncorrected volumetric flow rate of the carrier gas measured at ambient temperature and outlet pressure and corrected for the vapor pressure of water at ambient temperature.

k. F = volumetric flow rate of the carrier gas measured at ambient temperature and outlet pressure and corrected for the vapor pressure of water at ambient temperature.

l. Fc = volumetric flow rate of the carrier gas measured at the outlet pressure and the temperature of the column

m. V_R = retention volume of the solute (uncorrected) and adjusted to the column temperature = $F_c\ t_R$ solute

n. V_A = retention volume of the nonabsorbed solute (air) adjusted to the column temperature = $F_c\ t_R$ air.

o. V_R' = adjusted retention volume of the solute = $V_R - V_A = F_c\ (t_R \text{ solute} - t_R \text{air})$

p. V_N = net retention volume = $j\ V_R'$

q. V_g = specific retention volume = $\frac{V_N}{w_L} \cdot \frac{273.2}{T_c\ ^oK}$

Calculations

1. $F = F_a\left(1 - \frac{P_w}{P_o}\right) = 39.73\left(1 - \frac{22.1}{758}\right) = 38.57$ cc/min

2. $F_c = F\ \frac{T_c\ ^oK}{T_a\ ^oK} = 38.57\left(\frac{360.7}{297.0}\right) = 46.84$ cc/min

3. $j = (3/2)\left[(1406/758)^2 - 1\right] / \left[(1406/758)^3 - 1\right] = 0.680$

4. $V_{R'} = F_c\ (t_R \text{ solute} - t_R \text{ air}) = 46.84\ (2.09 - 0.65)$
$= 67.45$ cc

5. $V_N = j\ V_R' = (0.680) \cdot (67.45) = 45.86$ cc

6. $V_g = \frac{V_N}{w_L} \cdot \frac{273.2}{T_c\ ^oK} = \frac{45.86}{0.803} \cdot \frac{273.2}{360.7} = 43.3$ cc