# DETERMINATION OF LOW LEVEL HYDROCYANIC ACID IN SOLUTION USING GAS-LIQUID CHROMATOGRAPHY

by

CARL RUDOLPH SCHNEIDER

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APPROVED:

Redacted for privacy

Professor of Chemistry

In Charge of Major

Redacted for privacy

Chairman of Department of Chemistry

Redacted for privacy

Chairman of School Graduate Committee

Redacted for privacy

Dean of Graduate School

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# DETERMINATION OF LOW LEVEL HYDROCYANIC ACID IN SOLUTION USING GAS-LIQUID CHROMATOGRAPHY

## INTRODUCTION

Doudoroff (8) has presented indirect evidence that the toxicity to fish of systems containing heavy-metal cyanides is due primarily to molecular hydrocyanic acid. Studies directed towards a better understanding of this effect and prediction of the toxicity of waters polluted with these compounds required an independent measure of the concentration of hydrocyanic acid. The analytical method was not to displace appreciably the complex equilibria relating cyanide ion, hydrocyanic acid and heavy-metal cyanide complexes.

The use of a solution/air distribution of HCN and analysis of the air for hydrogen cyanide held promise of meeting these requirements. This research was undertaken to study the technique and apply it, if possible, to the problem.

## THEORY AND DISCUSSION

A volatile solute dissolved in water which is in contact with a gas is, when the system is at equilibrium, distributed between the gaseous and liquid phases in a

ratio which is fixed at a given temperature. Glasstone (12, p. 357-358) has given a general treatment of this system, indicating that at high dilution the activity of the solute, $a_2$, is equal approximately to the quantity $(p_2/k)$, where $p_2$ is the partial vapor pressure of the solute and k is a constant.

At high dilution the activity approaches the concentration and the latter becomes equal approximately to $(p_2/k)$. In the systems which are to be analyzed, the hydrocyanic acid level will be low enough for this condition to be valid. One can then write:

$$K = \frac{\text{mg. of HCN per liter of gas}}{\text{mg. of HCN per liter of solution}}$$

$$K = \text{approximately } 3 \times 10^{-3} \ (20^{\circ}C) \ . \ . \ . \ . \quad (1)$$

Lewis and Keyes (19) studied this distribution at 25°C by bubbling nitrogen slowly through the solution, trapping the hydrogen cyanide from the equilibrated gas in sodium hydroxide solution, and analyzing the resultant solution by precipitating and weighing silver cyanide. The distribution constant calculated permitted the analysis for hydrocyanic acid at high concentrations in a system whose thermodynamics was being studied.

Worley and Browne (29) used a similar procedure when studying the hydrolysis of sodium cyanide. Their work involved a continuous "equilibration" in which the color

produced by the hydrogen cyanide when trapped in picric acid, sodium carbonate solution was used as an indication of the concentration of hydrocyanic acid in experimental solutions. The use of three complete equilibration and analysis systems in a single air stream with the unknown between two standards of slightly differing concentration permitted measurement of hydrocyanic acid in the unknown by interpolation. In this way calibration curves and accurate measurement of gas volumes were not necessary.

Harman and Worley (13) pointed out that excessive loss of HCN from the unknown had occurred in the latter work and modified the method to increase sensitivity of hydrogen cyanide detection and thus decrease the volume of gas to be bubbled through the solution to get the same color intensity.

Shirado (25) was the first to study the distribution thoroughly. Electrolytically generated oxyhydrogen gas was passed through consecutive bubblers (containing the same hydrocyanic acid solution) to insure equilibration, and hydrogen cyanide was trapped from the gas stream in potassium hydroxide solution. Readout of cyanide was made with the Liebig titration.

Shirado's results for $p_{HCN}$ as a function of mole fraction of hydrocyanic acid in solution, obtained at 18°C, have been extrapolated to high dilution to obtain a value for k of 3,840 for pressure in mm Hg and concentration in

mole fraction. The value calculated (21, p. 261) from the results of Lewis and Keyes is 4,817 at 25°C. Interpolation gives the constant at 20°C which, after conversion to the proper units, is given in equation (1).

It is evident from the equation that if, as is necessary, aqueous hydrocyanic acid levels as low as 0.025 mg./l are to be determined, measurement of 0.1 microgram of hydrogen cyanide per liter of air is required. Also, the equilibration of one liter of air with an equal volume of solution will result in a loss of about 0.3% of the hydrocyanic acid in the latter. Thus multi-liter gas volumes can be equilibrated with moderate volumes of solution without the loss of appreciable amounts of hydrocyanic acid.

The method chosen for readout of the hydrogen cyanide was gas-liquid chromatography. "Chromatography is a physical method of separation, in which the components to be separated are distributed between two phases, one of these phases constituting a stationary bed of large surface area, the other being a fluid that percolates through or along the stationary bed." (15, p. 2) The moving phase can be a liquid or gas and the stationary phase a solid or liquid. Thus, there are four chromatographic systems: liquid-solid, gas-solid, liquid-liquid and gas-liquid. The second and fourth are often combined under the designation, gas chromatography.

Three techniques of chromatographic separation can be employed. The first, elution development, consists of adsorbing the sample at the top (beginning) of the column and eluting it with the moving phase, the eluent. Components with a greater affinity for the moving phase than the stationary one will move down (through) the column at a faster rate, and the sample components will tend to separate. With a suitable column and eluent, and under the proper operating conditions quantitative separation of the components may occur. These will be eluted consecutively from the column as bands of dissolved component in the eluent. In frontal analysis, the second technique, the sample is fed continuously into the head of the column, components possessing the greater affinity for the stationary phase lagging behind the others. Although separation of the components into bands does not occur, this method has found extensive application in the concentration of trace constituents from a large quantity of sample. Eventually the second component being trapped will break through and the column effluent will become the same as the influent. The third method, displacement development, is similar to elution development in that the sample is first trapped at the head of the column and then eluted. It differs, however, in that the eluent is a substance more strongly adsorbed on the column than any

of the components. Here the components do not leave the column separated by a band of nearly pure eluent, as with elution development. The bands however, are not contaminated with eluent and for this reason this technique has found use in isolating a component in concentrated form.

Although chromatography has been applied most widely in analytical and preparitive techniques, it is often used as a method for determining partition coefficients and adsorption isotherms.

The basic components of a gas chromatograph are a tank of the compressed carrier gas, a pressure regulation device, provision for the injection of a gaseous or liquid sample into the carrier gas stream, the column, and finally the detector. If fractions of the effluent gas stream are to be taken, a freeze-out trap may follow the detector. Tracing through the operation of the instrument in the normal mode of elution development, the carrier gas continually flows through the system, the column (and perhaps the detector) is maintained at the desired operating temperature, and the sample is injected. It is trapped initially at the beginning of the column and eluted in the carrier gas stream. Those components having a higher distribution coefficient between the moving and stationary phases will move along the column faster. Depending on the differences in coefficients between the various

components, the length of the column and operating conditions, separation into discrete bands may occur. The detector normally gives an output which is a d.c. voltage and which varies linearly with the concentration of the component in the effluent stream. Strip-chart readout can then be made, the length of chart being related to the total volume of carrier gas passed through the column. The "chromatogram" will then appear as a number of peaks, each representing a component of the sample (or components if inadequate resolution is obtained). Ideally a peak should approximate a Gaussian distribution, its area being proportional to the amount of the component in the sample. The air in the sample is often used as a reference peak since it usually remains unresolved and is held up but little in the column. The length of chart by which a component follows this peak is a measure of its retention volume in the column.

The theory and practice of gas chromatograph have been treated by Keulemans (15) and Pecsok (23).

Selection of a detector (or set of detectors) is often done when the chromatograph is purchased. Thus one is usually faced with the problem of "making-do" with the one available. In the present case the chromatograph was equipped with a thermistor bridge thermal conductivity detector.

Thermal conductivity is used most commonly since the apparatus required is simple, inexpensive, and capable of detecting most substances. The device consists of two heated sources (hot wires or thermistors) in opposite arms of a Wheatstone bridge circuit. One source is immersed in a stream of pure carrier gas, the other in the column effluent. A difference in the rates of heat dissipation from the two sources results in a difference in their resistance and thus an unbalance across the previously balanced bridge. The sensitivity of detection, the d.c. output per unit concentration of the component to be measured in the effluent stream, thus depends to a great degree on the difference in thermal conductivity of the component from that of the carrier gas. For this reason hydrogen and helium, which have very high thermal conductivities as compared to other gases, are often used as the carrier gases when thermal conductivity is employed for detection. At temperatures below about 75°C a bridge employing thermistors is more sensitive than one with hot wires. Furthermore, whereas the sensitivity of the latter increases nearly linearly with decreasing temperature, the thermistor bridge's sensitivity increases almost exponentially. In work with thermistor bridge detectors low temperatures are necessary if highest sensitivity is to be obtained. Because of the differential detection

extraneous factors, such as fluctuation of flow rate, have a minimum effect on the detector response.

Because the nature of the carrier gas does not play a significant part in determining column resolution, the gas is usually chosen to give optimum detector performance.

Certainly, the most important component in a chromatograph is the column, for high sensitivity and stability of detection are useless unless accompanied by suitable resolution of the components. The separation to be achieved in a column, for two components, is dependent on the separation factor (separation per theoretical plate) and the number of theoretical plates per column. Two approaches can be made in maximizing column selectivity: a more selective stationary liquid can be used (greater separation factor) and the number of theoretical plates can be increased by lengthening the column. The most suitable column liquid is often chosen empirically from a group of promising substances. Sample components, generally speaking, are separated on the bases of boiling points and compatibility with the stationary phase.

The greater the solubility of a component in the stationary liquid, the longer it will be retained in the column. Affinity of this type is often related to the

stationary phase possessing chemical groups similar to the substance to be resolved. Thus, benzene preceeds aliphatic compounds of similar boiling point from a paraffin oil column. Polar compounds would be eluted almost instantaneously. Conversely, the hydrocarbons would be eluted before benzene from a tricresyl phosphate column. Some column liquids contain aromatic, aliphatic and polar groups and are therefore non-specific, separation occurring approximately according to the boiling points of the components in a sample. This type of stationary phase was chosen in the present case, since it gave good resolution of hydrogen cyanide from water.

The solid support for the stationary phase should be inert and possess a high surface area upon which the liquid can be distributed as a very thin film. Since usually 15 to 50 parts by weight of the liquid are used per 100 parts of solid support, non-porous solids are of little value. Crushed firebrick supports (30-80 mesh) are preferred to Celite (diatomaceous earth, ca. 300 mesh) because of the high permeability necessary for desirable column performance. A sufficiently high flow rate is obtained with a moderate pressure head and the variation of flow rate along the column is minimized. With polar compounds appreciable adsorption on the support will occur and a tailing of the peaks will result. This can

be reduced by pre-treatment of the support to deactivate most of the adsorption sites. A support like Chromosorb "W" then results. Ground Teflon sponge, such as Fluoropak 80, is inert, but unfortunately its properties make the uniform packing of a column a difficult task.

The variation of the height equivalent to the theoretical plate, H. E. T. P., with gas velocity, u, is given by the following equation of Keulemans (15, p. 148):

$$H.\ E.\ T.\ P. = A + B/u + Cu \qquad (2)$$

The (A + B/u) term is the sum of eddy and molecular diffusivity. These are band-broadening effects resulting from irregularity of gas flow through the column and from the superposition of molecular diffusion upon the flow rate of the gas. (A) varies from about 2 to 16 times the particle diameter as the particle size of the packing decreases from 20-40 mesh to 200-400 mesh. (B) increases, approaching one, as the particle size is increased. The term (Cu) represents the resistance to mass transfer between the moving and stationary phases. C increases with an increase in film thickness and decreases with the diffusivity of the component in the stationary phase. It also contains the liquid/gas distribution coefficient for a component, and thus changes with temperature and from component to component. The (Cu)

term becomes important only at high gas velocities.

It can be seen from the equation that at low flow rate the H. E. T. P. becomes large and thus the number of theoretical plates per column is small. With increasing flow the quantity decreases, approaching the value of the (A) term, and at still higher velocities it again increases due to the effect of the (Cu) term. Here, the rate of decrease with increase in flow is relatively small.

It is evident that if too much liquid phase is employed per weight of solid support, the column efficiency at high flow rates will be significantly impaired. Too little liquid phase will lead, on the other hand, to appreciable tailing of the peaks due to adsorption effects on the solid support. A good compromise seems to be about 20% by weight.

Usually the temperature is chosen from practical considerations. Keulemans (15, p. 22) recommends that the temperature should be about equal to or a few tens of degrees above the normal boiling point of the constituent. This will insure that, under usual conditions, the component will be eluted within 30 minutes, a not inconveniently long time.

It is evident that not much can be done about the magnitude of the (A) term. Use of a large particle size however cuts down the resistance to flow and permits

less variation of flow rate within the column.

The range over which operating conditions may be varied (to obtain a minimum H. E. T. P.) is often limited by instrumental factors. The present case will serve as an example. A commercially available column was used, in the maximum length obtainable, 18 feet. The packing, 20 weight percent dinonylphthalate on Chromosorb "W" (40-60 mesh), was contained in quarter inch stainless steel tubing. This diameter has been shown to give optimum performance.

The pressure head, 30 p.s.i., was chosen to give maximum flow rate, 135 cc.He/min. The hydrogen cyanide peak is then eluted in less than 30 minutes at an oven temperature of 44°C. The temperature was kept low to permit high detector sensitivity. Variation of the flow rate and temperature indicated that maximum resolution was being obtained near the conditions chosen. Since the operating conditions were chosen on the basis of necessity it is fortuitous that high resolution was obtained.

## APPROACH TO THE PROBLEM

The basic techniques of distribution and analysis are illustrated in Figure I. Air at a precisely regulated flow rate is bubbled through the sample. The "equilibrated" air then passes into a line where it is dried and then sampled. In one position of the valve a sample volume tubing is purged with the air, and in the other is put into series with the carrier gas stream of the chromatograph for readout of the hydrogen cyanide as a peak. The peak area can be related to the concentration of hydrocyanic acid in solution through previously prepared calibration curves. However, with the maximum sample size that can be injected into the chromatograph without severly reducing column separation (approximately 5 cc.) solutions in the concentration range of interest will not give detectable peaks. This is because the thermal conductivity detector, even with voltage amplification prior to readout, will not permit the detection of less than a few tenths of a microgram of hydrogen cyanide. Hydrogen cyanide, as will be shown later, is not well suited for detection by recently developed high sensitivity detectors. Clearly, some method was necessary to permit the concentrating of the HCN from large volumes of gas into a volume small enough for chromatographic injection,

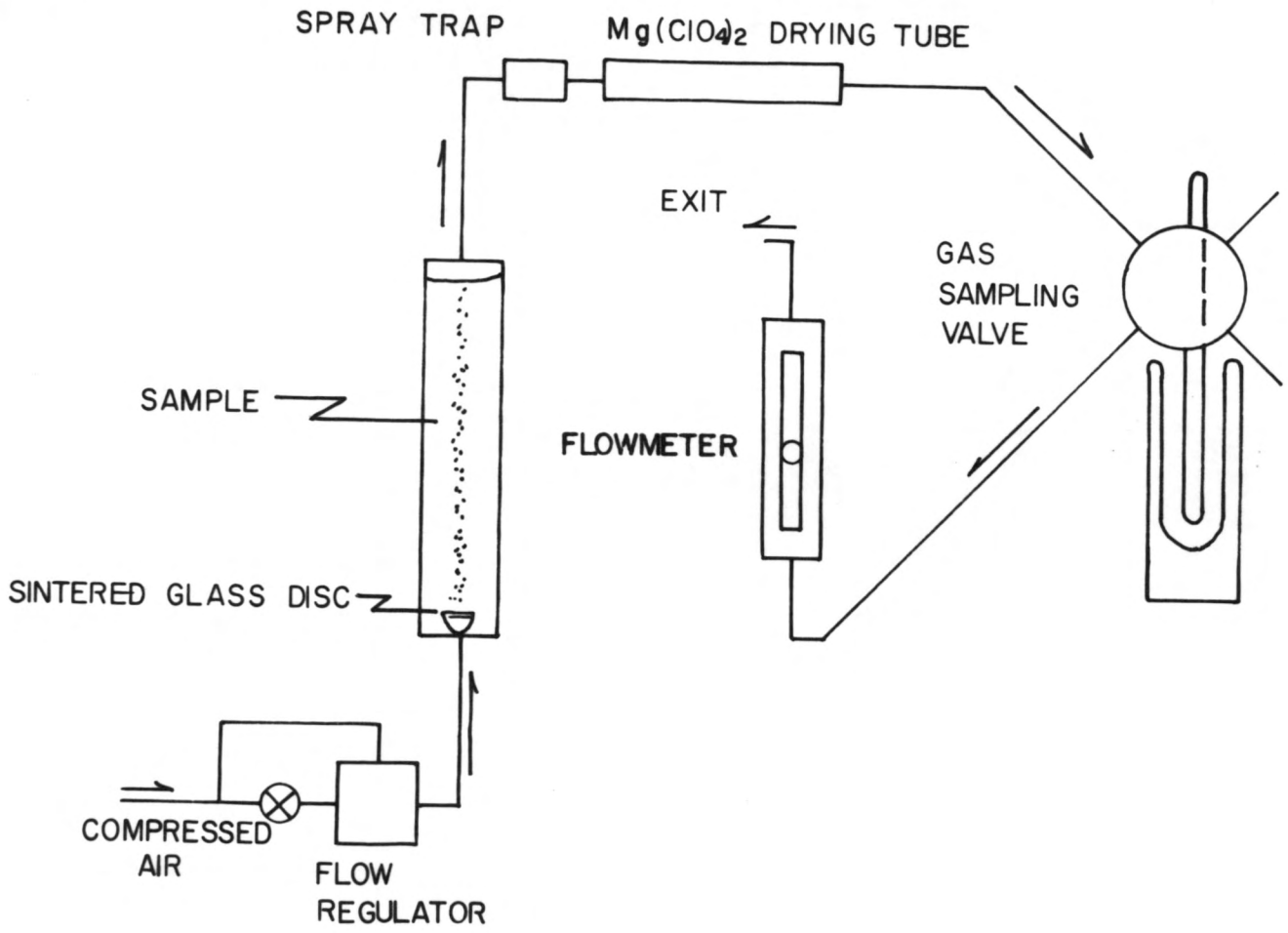



Figure I System for Distribution and Concentration

The following discussion will describe the development and evaluation of the characteristics of the equilibration, drying and concentration steps.

Preliminary experiments were necessary to evaluate the efficiency of a bubbler employing a sintered glass disk. Both the variation of efficiency with flow rate and depth of the disk were to be studied, the latter being especially important since the unit was to be immersed in shallow containers which limited the depth of the disk to about 11 inches.

Equilibrations were carried out using hydrocyanic acid solutions of relatively high concentration in order that the gas could be analyzed directly. Direct sampling of 5cc. gas volumes was made. A special equilibration apparatus designed for these studies consisted of a 48 inch glass tube (50 mm O.D.) oriented vertically, stoppered at both ends, and filled nearly completely with the solution. Two 6 mm O.D. glass tubes passed through the top stopper, one leading to a "fine" porosity sintered glass disk, whose depth in the solution could be varied, and the other to the air space above the solution. When a suitable nitrogen pressure head was applied to the disk the gas bubbled through the solution and passed out at the top of the apparatus through the second tube. A spray trap and small, unheated magnesium

perchlorate drying tube were interposed between the apparatus outlet and the gas sampling valve. A flowmeter was placed in the line either directly before or after the valve. After a sufficient time had elapsed for purging of the line and attainment of equilibrium in the drying tube, samples of the gas were taken.

The chromatograph was equipped and operated as described in the experimental section. The oven temperatures were 46 and 41.6°C and the flow rates 125 and 126 cc.He/min. in the first and second studies respectively. The gain was set to 5 and the sensitivity to ½.

To determine the absolute efficiency of equilibration at the maximum depth, as a function of flow rate and pressure head, a 500 ppm hydrocyanic acid solution was prepared by diluting 3.75 grams of potassium cyanide and 15.31 grams of potassium dihydrogen phosphate to about three liters. Most of this was used to fill the equilibration apparatus, but a few hundred milliliters were placed in a closed container and shaken thoroughly with the air above it to provide a gas actually equilibrated with the solution. This was sampled by raising a reservoir of the solution and forcing the air via a tube through the gas sampling valve and the 5cc. tubing. The resultant hydrogen cyanide peak area was an average of 23.6 square centimeters in area. Results for samples of

the air from the "equilibration apparatus are given in Table I.

To determine the variation of this efficiency with depth, another 500 ppm hydrocyanic acid solution was prepared by diluting 2.45 grams of potassium cyanide and 10.00 grams of potassium dihydrogen phosphate to about 2 liters. This solution was added to the equilibration apparatus and the peak area for hydrogen cyanide measured on samples of the equilibrated air as depth and flow were varied. The results are given in Table II. Pressure values are only approximate since they were read directly from the reducing valve on the nitrogen tank.

The difference in peak areas between the two tables can be attributed, at least in part, to the different chromatograph oven temperatures employed. A moderate flow rate of 50 cc./min. (11 inch depth) was chosen so as to allow sufficient time for thermal equilibrium to be approached in the cooled concentration column. The efficiency of equilibration under these conditions can be seen to be about 85% from a comparision of the ratio of peak areas for runs 2 and 5 of Table II to the percent efficiency for run 4 of Table I. The use of a "very fine" porosity sintered glass disk should raise this value. At the shallow depth the efficiency apparently does not vary significantly with flow rate. Over

TABLE I

Efficiency of the Equilibration Apparatus With Pressure and Flow Rate at a 40 Inch Disk Depth

23.6 $cm^2$ Equivalent to 100% Efficiency
24.4°C

| Nitrogen Pressure (p.s.i.) | Flow Rate (cc./min.) | Peak Area ($cm^2$) | Efficiency (calc'd) (%) |
|---|---|---|---|
| 12.4 | 13 | 19.8 | 83.9 |
| 13.1 | 31 | 20.6 | 87.3 |
| 13.2 | 31 | 19.3 | 81.8 |
| 13.3 | 50 | 21.9 | 92.8 |
| 14.0 | 95 | 21.1 | 89.4 |

TABLE II

Hydrogen Cyanide Peak Area With Depth of Disk, Flow Rate, and Pressure

20°C

| Disk Depth (in.) | Nitrogen Pressure (p.s.i.) | Flow Rate (cc./min.) | Peak Area ($cm^2$) |
|---|---|---|---|
| 40 | 12.8 | 25 | 26.2 |
| | 13.5 | 57 | 34.2 |
| | 14.0 | 82 | 35.0 |
| 11 | 10.5 | 25 | 29.9 |
| | 12.0 | 49 | 31.4 |
| | 12.3 | 68 | 32.0 |
| | 12.7 | 83 | 30.6 |
| | 13.5 | 124 | 35.5 |

the range 11 to 40 inches in depth the efficiency does not appear to change greatly. Depth is then not critical. Due to the relatively crude methods used, these results should be considered qualitative rather than quantitative.

Because of the high water to hydrogen cyanide ratio in the equilibrated air and nearness of the water peak to that of hydrogen cyanide, it is necessary to remove water prior to concentration. Water is undesirable also since it tends to decompose both di-n-butyl phthalate and dinonylphthalate.

A spray trap was designed to remove bulk water. Subsequent work has shown that this water is deposited in the glass tubing leading from bubbler to accessory board, making the spray trap superfluous.

Farrington, Pecsok, Meeker and Olson (9) have indicated that potassium carbonate is especially suited to removing water prior to chromatographic readout since it does not adsorb organic compounds significantly, even at 25°C. Hydrogen cyanide would be retained by this basic material. West, Sen and Gibson (27) have shown that water is retained completely on an anhydrous magnesium perchlorate desiccant at 100°C but organic compounds pass through with high efficiency. Magnesium perchlorate was chosen as the desiccant for the present

studies. Heating was found necessary to minimize hydrogen cyanide holdup. The internal volume and heating rate of the drying tube were chosen as a compromise between minimum hydrogen cyanide retention and maximum water holdup. The temperature is high enough to permit equilibration of the hydrogen cyanide in the gas with the desiccant, but yet not so high as to allow enough water to get through to block the concentration column on freezing out, or to interfere with hydrogen cyanide chromatographically. The application of 5 and 3 volts (rms) to the drying tube winding at 25°C results in internal temperatures of 100 and 53°C respectively inside the bulb at a flow rate of 50 cc./min. To maintain the temperature constant at 53°C over the range of 20 to 30°C in ambient temperature, the applied voltage must vary linearly from about 3.3 to 2.3 volts. These characteristics were obtained by packing a Chromel-Alumel thermocouple into the bulb of the drying tube with the desiccant, and reading the temperature on a 0-1200°C Brown strip-chart recorder. Thermal equilibrium is attained in about 15 minutes after switching on the a.c. voltage.

When 2 liter gas volumes are to be concentrated the 100°C temperature is used, since rapid adsorption equilibrium is attained. When the hydrogen cyanide from

10 liters of air is to be concentrated the lower temperature is employed. Here, a longer time is required for the hydrogen cyanide in the gas to equilibrate with the desiccant, but the vapor pressure of water in the drying tube effluent is greatly decreased permitting concentration of the larger volume without frozen water blocking the concentration column.

Normally a drying tube can be used for carrying out two concentrations, before refilling.

The possibility of using one of the recently developed hypersensitive methods of chromatographic detection was considered. Those described by Keulemans (15, p. 79-81) permit the detection of $10^{-11}$ to $10^{-12}$ moles as compared to $10^{-8}$ gram (4) for the most sensitive thermal conductivity detectors and $10^{-7}$ gram for the detector used in the present work. Because of its high ionization potential, hydrogen cyanide is not well suited for detection by the argon ionization detector. The use of helium would permit detection but until quite recently this gas has not been available in sufficient purity. There are, in addition, more subtle problems. For, in order for the detector to be of value, hydrogen cyanide must be adequately resolved from air and water. Here, a capillary type column would be needed, and to prevent flooding the column, gas volumes of a maximum of

a few tenths of a milliliter would be injected. A concentration step would still be needed, and would be made difficult to design since only a small dead space would be allowable. Flame ionization would be expected to present similar problems (the ionization potential of hydrogen is even lower than that of argon).

The trapping of trace constituents from large volumes of gas is often done by passage of the gas through a cold trap. The simplest trap is a narrow diameter glass tube immersed in a coolant. The efficiency of trapping would depend on the vapor pressure (at the temperature of the coolant) of the substance to be concentrated.

Data from several sources (1) (20) (24) have been combined in the vapor pressure versus temperature relationship shown in Figure II. The bend in the curve at about 170°K is associated with a change in crystal structure, apparently. (11) At the temperature of liquid air (83°K) the vapor pressure of hydrogen cyanide is seen to be about $10^{-8}$ mm Hg (by extrapolation) corresponding to $1.5 \times 10^{-11}$ gm/l. The direct trapping of hydrogen cyanide from air when it is present at a $10^{-7}$ gm/l level could be made efficiently at liquid air temperature. Furthermore, hydrogen cyanide adsorption on the glass walls would lead to a still lower vapor pressure. Unfortunately, liquid air is not a common laboratory

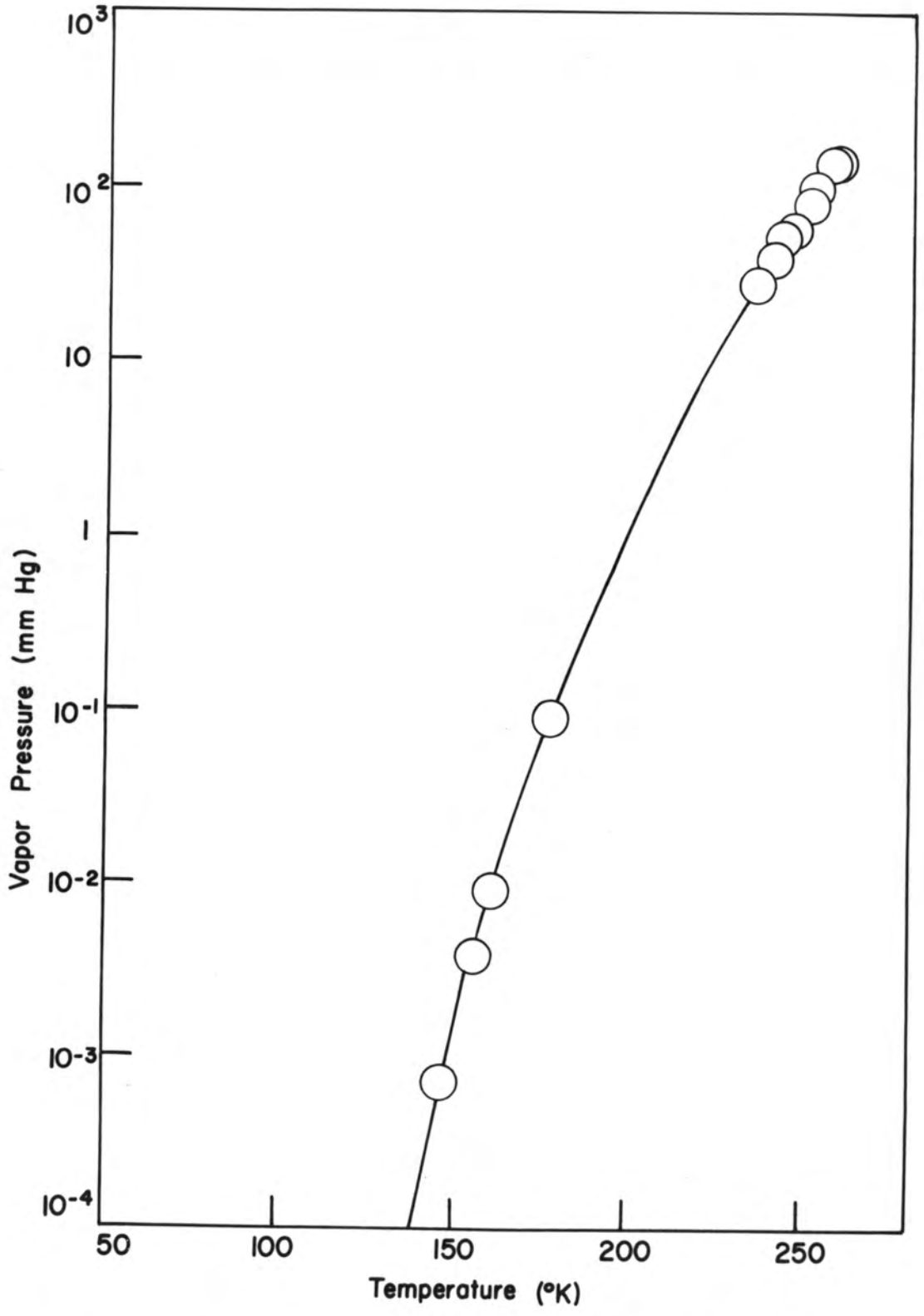



Figure II Vapor Pressure of Solid HCN with Temperature

reagent. At this university the liquid air machine has been converted recently to the production of liquid nitrogen. The use of the latter would result in the liquification of air within the trap.

A mixture of dry ice and acetone provides a temperature of about 195°K, at which the vapor pressure of hydrogen cyanide is 0.6 mm Hg or $10^{-4}$ gm/l. At this temperature efficient trapping of hydrogen cyanide at the expected levels in air could not be made directly. Because of the convenience of the coolant it was felt desirable to develop a suitable packing for the cold trap, and concentrate the hydrogen cyanide by the frontal analysis chromatographic technique. The packing would have to bind HCN strongly at the low temperature, but readily release it at a convenient warm temperature (that of hot water). Two types of material were considered: solid packing (silica gel, crushed firebrick and charcoal) upon which hydrogen cyanide would be adsorbed, and liquid-solid packing in which it would be dissolved.

A number of such "concentration columns" have been designed for the trapping of trace constituents from a large volume of gas prior to readout. West, Sen and Gibson (27) have proposed methods by which air pollutants can be collected on cold activated charcoal from volumes on the order of 20 liters and eluted at 200°C into the

helium carrier gas stream of a chromatograph. Very small amounts of charcoal (0.2 gm) were used in order to minimize the size of the air peak and make the elution time from the column as short as possible. The efficiency of concentration was about 80 percent. For polar substances there was pronounced tailing of the recorded peaks, in some cases for twice as long as for direct injection of the components. Of course, the tailing was due to the slow desorption of the substances from the charcoal.

Lawrey and Cerato (18) have employed a concentration step in conjunction with a special high-sensitivity thermal conductivity bridge with d.c. amplification prior to readout, and were able to determine as little as 1 ppm methane in air. The ten-fold concentration step consisted of trapping out the methane on a two foot by one-quarter inch charcoal column (wetted with di-butyl phthalate to reduce tailing) at dry ice-acetone temperature, and elution at about 175°C (oil bath) at reduced pressure. A splitter column was used in readout. A 20 cc. air sample was injected into the first column in a helium stream, the main portion of the air being shunted directly to the detector as it left this column. Its peak could then be used for calculation of the concentration of methane using the ratio of peak areas. After a

predetermined time, a stopcock was turned to allow the methane on elution from the first column to pass into a second, four foot one, and thence to the detector. Apparently $10^{-7}$ gramø could be determined with this procedure.

A third method, that of Farrington, Pecsok, Meeker and Olson (9), has been developed for the analysis of components in polluted air down to a few hundredths of a part per million. Their concentration step involved the trapping of components from a 16 liter air sample (by drawing the sample through the column and into a previously evacuated tank) at liquid air temperature. A 0.5 by 130 cm dibutylphthalate column was used, with a flow rate of 500 cc./min. At this temperature the trapping was said to be mechanical, by condensation. The trap was flushed with helium to remove the large amount of air and then the remaining gaseous contents were transferred to another column by heating and freezing in order to remove water on intermediate potassium carbonate drying tubes. Finally the gases were transferred to still a third column, an extension of the readout chromatographic column, and injected into the analyzing stream at 25°C. An ionization gauge detector permitted a sensitivity of $10^{-7}$ gramø.

Brenner and Ettre (5) have described a method for the analysis of trace constituents at the parts per million level in gases, using a "condenser" column which can be attached directly to a commercial gas sampling valve. The column consisted of a one-quarter inch by 50 cm stainless steel tube into which was packed one of a variety of adsorbants (silica gel, organic stationary phases on Chromosorb, and molecular sieve) and which was cooled to dry ice-acetone temperature.

Mosen and Buzzelli (22) have developed a method for the determination of trace impurities in helium based upon their adsorption on an activated charcoal column (0.75 cc. coconut charcoal in a 2 mm diameter glass tube) at liquid nitrogen temperature, and elution at 90°C (hot water) into the carrier gas stream. Oxygen, nitrogen, carbon monoxide, carbon dioxide and methane have been determined in the range of about 1 to 1000 parts per billion.

A chromatograph manufacturer (28, p. 8) has described a concentration step similar to those above, for use with his instruments. Liquid nitrogen is used as a coolant for a 1/8 inch by 10 inch column packed with hexadecane on 30-42 mesh crushed firebrick to trap out parts per billion of volatiles. Injection is made after warming in warm water.

Allmand and Chaplin (1) and Barrow (3) have studied the adsorption of hydrogen cyanide on charcoal. It would appear from their work that activated or ordinary charcoal would be suitable for use as packing.

Studies, in the present work, have indicated that while hydrogen cyanide is apparently adsorbed at dry ice-acetone temperature, it can not be eluted readily at high temperatures. Similar results were obtained with silica gel. Crushed firebrick permitted elution, but slow desorption led to extensive tailing of the resulting peak. Replacement of adsorbed air by the helium carrier gas resulted in the hydrogen cyanide peak riding on the steep tail of the air peak.

Of the compounds selected as possible liquids for a liquid-solid packing, only di-n-butyl phthalate met the requirements:

1. There must be holdup of hydrogen cyanide at dry ice-acetone temperature, but rapid elution at hot water temperature.

2. The substance should remain liquid at the low temperature but not be appreciably volatile at the high one.

The dimensions of the column used were chosen to give a maximum retention of hydrogen cyanide with a minimum elution volume and free air space. The elution

of hydrogen cyanide is complete in three minutes (135 cc.He/min.) at 57°C. The free air space is about 2 cc.

To estimate the variation of the efficiency of concentration of the column (see experimental section) with the volume of air from which the hydrogen cyanide is concentrated, a 5 ppm hydrocyanic acid solution was prepared and added to the apparatus used in the studies of the bubbler efficiency. Twenty-five milliliters each of a 1 gm/l potassium cyanide solution and a 1 gm/l potassium dihydrogen phosphate solution were diluted to two liters in a volumetric flask. The hydrogen cyanide was concentrated from successively greater volumes of the "equilibrated" gas (flow rate about 50 cc./min.) and warmed in water at 60°C and its contents injected into the chromatograph. The chromatograph was equipped and operated as described in the experimental section, the oven temperature being 42°C. The gain was set to five and the sensitivity decreased from 1/1, in steps, to bring the peaks on-scale. For each run the ratio of peak area to volume was calculated, and divided by the sensitivity and gain to permit comparison of the results. Since at the high sensitivity settings the impedance of the detector affected the gain of the amplifier, it was necessary to calculate a gain for each sensitivity setting. The results are given in Table III.

No significant loss of efficiency occurs up to about 2 liters. A small drop from the fourth to the fifth runs does occur, the drop from the average to the first four being about 2.5%. The last two runs were on a new solution and had best be considered separately. A net drop to 79% efficiency occurs between these.

With the use of this column attached to the gas sampling valve the hydrogen cyanide can be trapped from large volumes of equilibrated air. Stopping the flow of gas, warming the concentration column in hot water, and turning the sampling valve permits readout of the trapped hydrogen cyanide. The peak area can be related to the hydrocyanic acid concentration in solution with a knowledge of the total volume from which the hydrogen cyanide is concentrated and suitable calibration curves.

TABLE III

Variation of the Efficiency of the Concentration Column With the Gas Volume

5 ppm HCN Solution ($20^{o}C$)

| Volume Conc'd ($cc. \times 10^{3}$) | Peak Area ($cm^{2}$) | Sensitivity | Gain | $\frac{\text{Peak Area}}{\text{Vol. Conc'd}}$ ($cm^{-1} \times 10^{2}$) |
|---|---|---|---|---|
| 0.280 | 24.3 | 1/1 | 4.28 | 2.03 |
| 0.523 | 50.2 | 1/1 | 4.28 | 2.24 |
| 1.070 | 51.6 | 1/2 | 4.60 | 2.17 |
| 2.070 | 54.2 | 1/4 | 4.78 | 2.19 |
| 4.020 | 51.2 | 1/8 | 4.88 | 2.09 |
| 1.092 | 47.1 | 1/2 | 4.60 | 1.88 |
| 8.980 | 40.9 | 1/16 | 4.93 | 1.48 |

# EXPERIMENTAL

## Apparatus for Distrubution and Concentration

Borosilicate glass is used throughout.

The system used for distribution and concentration is shown in Figure I. Compressed air flow rate is regulated at approximately 50 cc./min. by means of the series arrangement; 1) conventional two stage reducing valve, 2) Moore Products Co., Model 63 BU-L constant differential flow controller and 3) Hoke 2RB281 metering valve equipped with a vernier adjustment. The gas is then sparged through the solution in the bubbler shown in Figure III. The unit is designed so that the rising bubbles will provide adequate circulation of solution through it and the container, so that significant local cyanide depletion will not occur. Three holes are put in the side of the bubbler.

The drying tube illustrated in Figure IV is operated at two temperatures. The first, 53°C, is employed when ten liter gas volumes are concentrated; 3.3 volts (rms) are applied to the winding at room temperature of 20°C. The second, 100°C, results from the application of 5 volts (rms) at 25°C, and is used when two liter gas volumes are to be concentrated. The voltages applied are obtained from a variable transformer, or a fixed output transformer and voltage

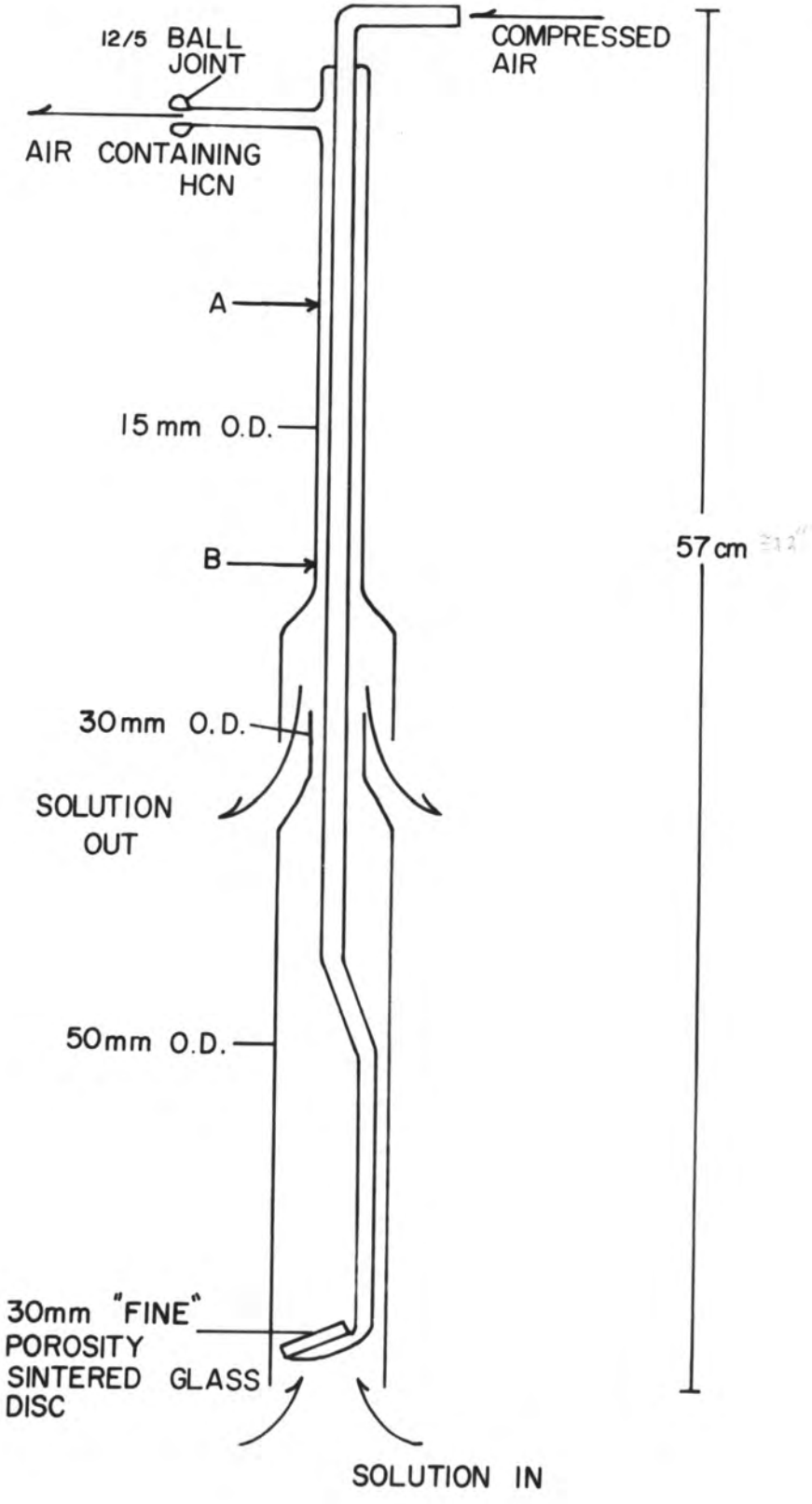



Figure III Bubbler

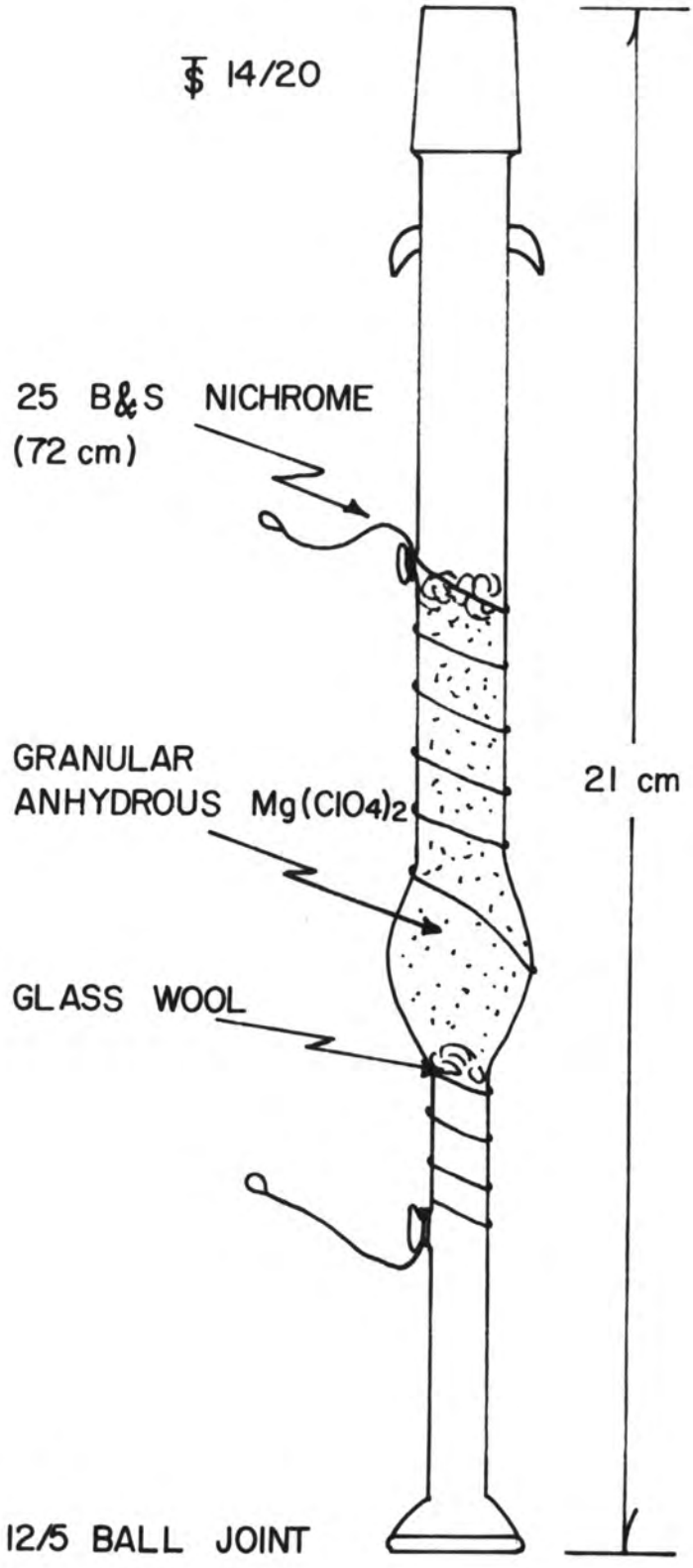



Figure IV Drying Tube

divider.

The concentration column is illustrated in Figure V. The packing, 19.4 wt. % di-n-butyl phthalate on 40/60 mesh crushed firebrick, occupies a length of about 7" in 6 mm glass tubing. Capillary tubing (1 mm I.D.) is used when possible in the concentration column in order to keep the volume injected into the chromatograph small. It is necessary on the input side to use a 2 mm I.D. x 6 cm length capillary tubing to prevent ice from blocking the column. The glass column container can be replaced by a stainless steel concentration column available commercially, eliminating the need for the metal fitting on the concentration column.

The column is cooled in dry ice-acetone mixture. It may be cut into the gas stream through the use of the gas sampling valve as in Figure I. If the concentration step is carried out remotely from the chromatograph, as in the application of this method to field measurements, a four-way stopcock and stainless steel adaptor block may be employed. This block is shown in Figure VI while Figure VII shows the corresponding remote "accessory board".

A Matheson #T-600 flowmeter with stainless steel float was used for flow measurements.

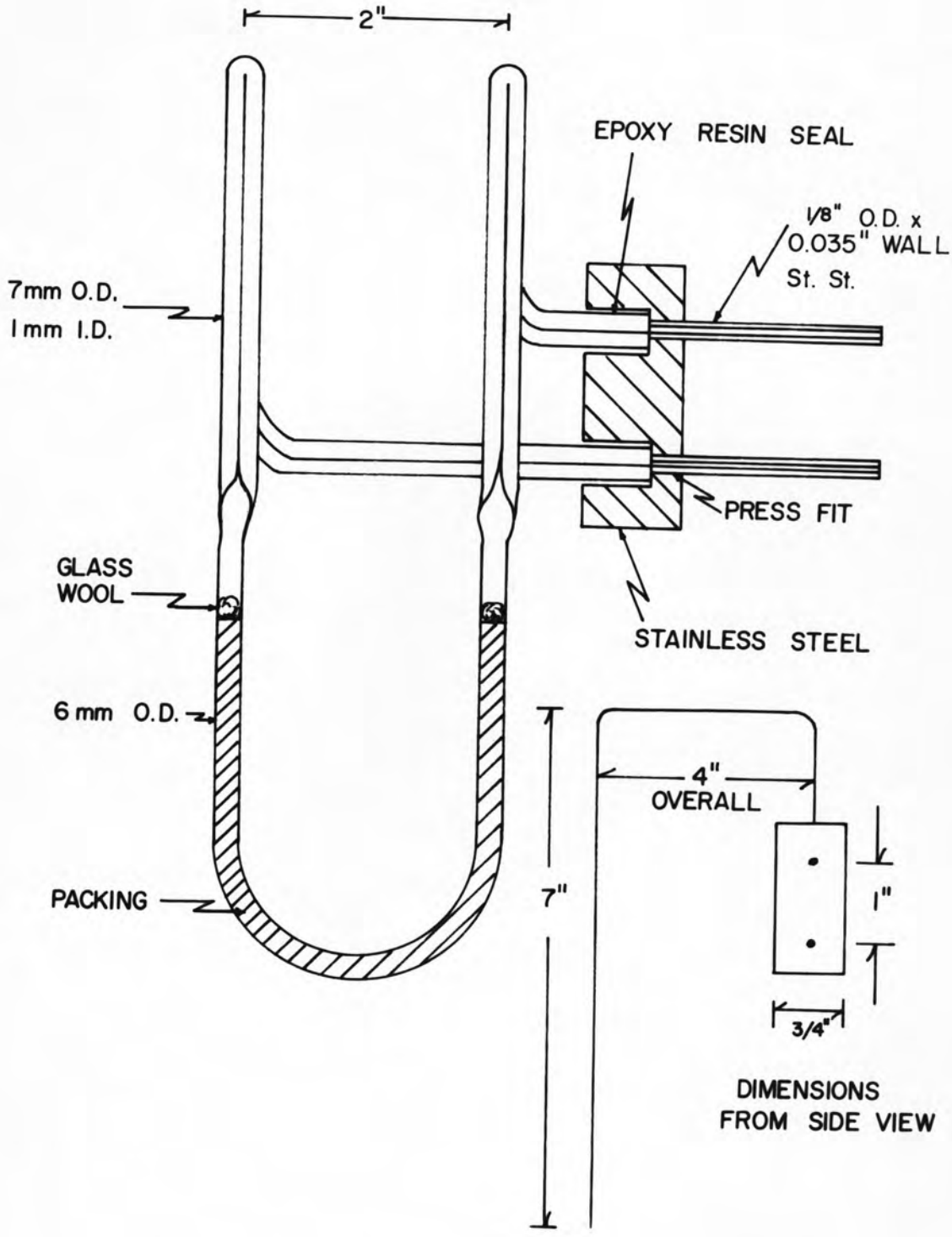



Figure V Concentration Column

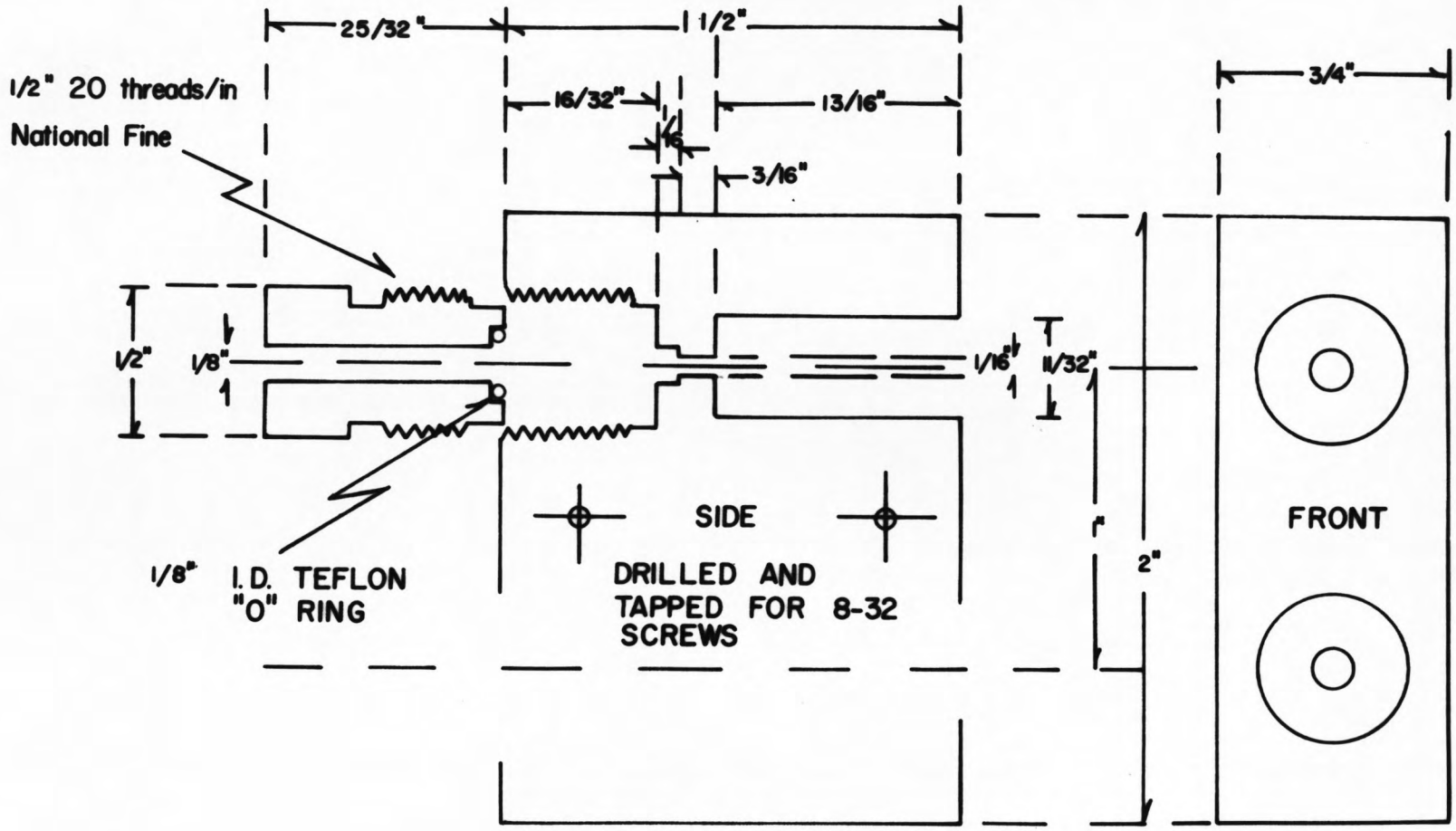



Figure VI Stainless Steel Adaptor Block

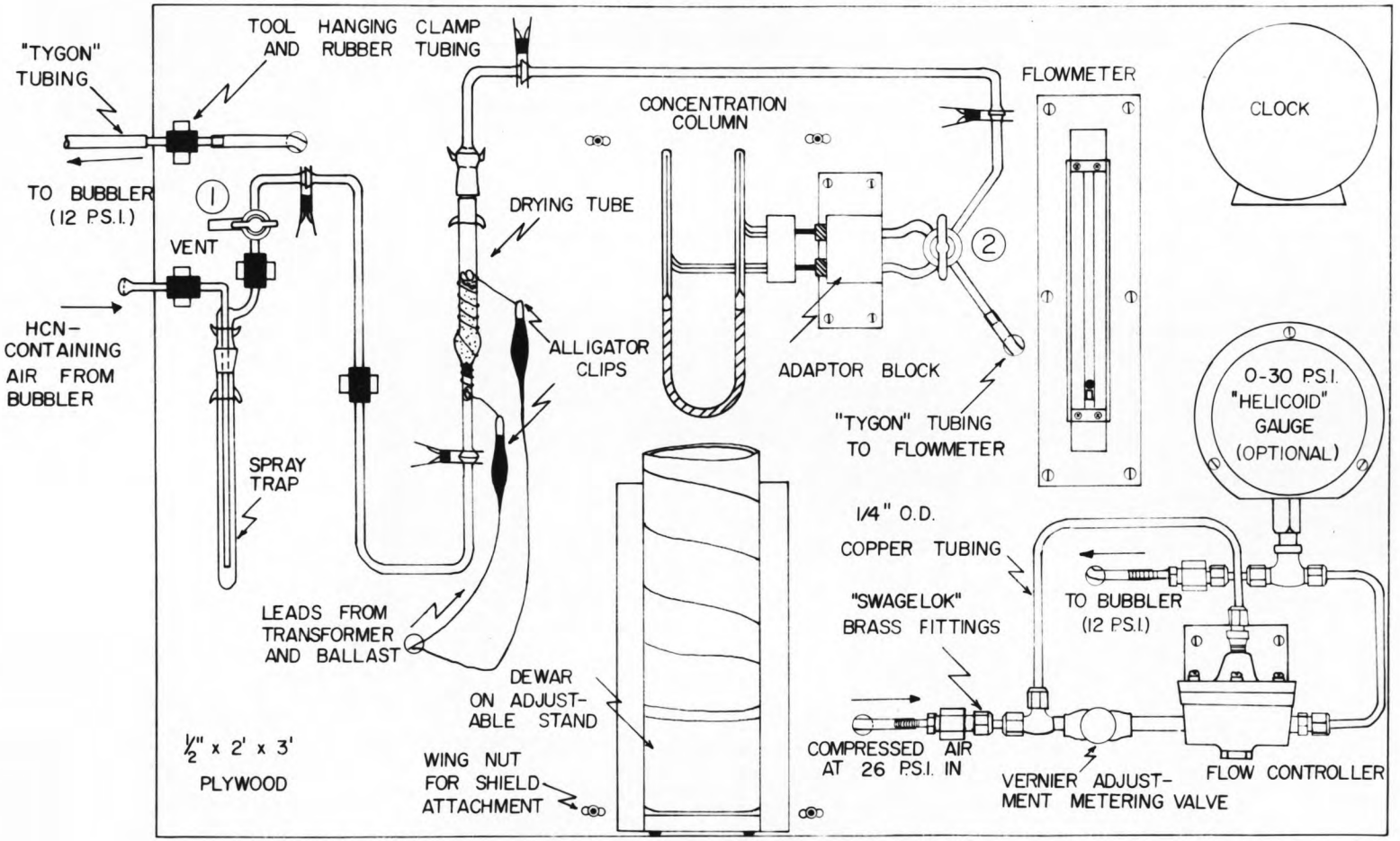
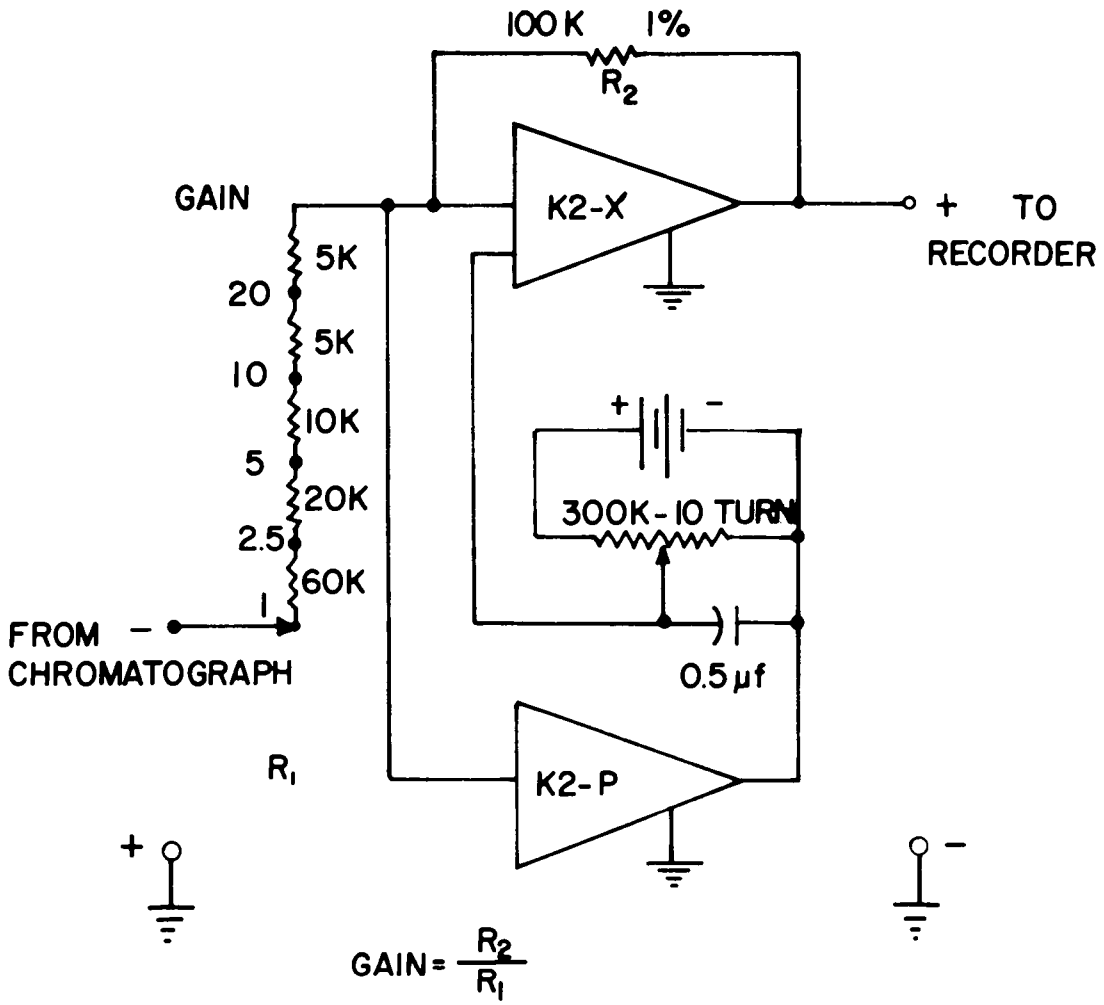



Figure VII Accessory Board

Apparatus for Readout

A Perkin-Elmer 154B Vapor Fractometer with gas sampling valve is equipped with an 18 ft., 20 wt. % dinonylphthalate-Chromosorb "W" in ¼" stainless steel tubing column obtained from Wilkens Instrument and Research, Inc. Helium carrier gas is from the Matheson Co., Inc.

The D.C. Amplifier in Figure VIII is constructed with available analog computor components obtained from George A. Philbrick Researches, Inc. and is used between the thermistor bridge and a 2.5 millivolt, 4½ second Brown recording potentiometer. Precision wire-wound resistors are used throughout. The high-gain direct-coupled K2-X amplifier is stabilized by feed-back and by the K2-P chopper-modulated high-gain a-c amplifier. Amplifier zero is set by adjustment of the 300K ohm potentiometer. Nominal gain settings of 1, 5, and 20 are used with the chromatograph sensitivity set to maximum. Because of the detector resistance, true gains are somewhat less than these values. Amplifier noise varied from about 5 to 20 microvolts referred to input and generally increased during the course of these investigations. Noise can be minimized by tube replacement. Commercially available D.C. amplifiers




PHILBRICK HKR MANIFOLD

Figure VIII D.C. Amplifier

particularly designed for such applications should eliminate the noise problem.

Base line drift is minimized by a long warmup time and installation of the chromatograph in a room whose temperature can be maintained reasonably constant.

Operating conditions chosen as a compromise between resolution and sensitivity, and retention time are:

| | |
|---|---|
| Oven Temperature | 44°C |
| Pressure | 30.0 p.s.i.g. |
| Bridge Voltage | 8.0 volts |
| Flow Rate | 135 cc./min. |

Preparation of Standards

Analytical reagent and CP grade chemicals were used throughout.

Stock 0.1 M potassium cyanide was standardized against 0.05 M $AgNO_3$ according to Kolthoff and Sandell (17). Because of cyanide decomposition, a fresh solution was prepared at least every two weeks. Standardization at the beginning and end permitted interpolation for intermediate concentrations. Dilute stock potassium cyanide solutions 0.02, 0.004 and 0.001 molar were prepared by quantitative dilution of the 0.1 M solution with boiled, cooled distilled water.

Stock buffer, 0.2 M in total phosphate, was prepared by diluting 4.26 gm $NaHPO_4$ and 23.15 gm $KH_2PO_4$ to one

liter.

Standards in the concentration range $5 \times 10^{-6}$ to $5 \times 10^{-4}$ M are prepared in 2 liter volumetric flasks. To each flask is added 25 ml of buffer and enough distilled water to nearly fill the flask. The required aliquot of dilute stock potassium cyanide is then added and, after shaking and dilution to volume, the solution is mixed thoroughly. Such a procedure minimizes loss of hydrogen cyanide by volatilization. The two identically prepared solutions are combined in a 100 mm x 20 inch cylinder to provide sufficient volume for analysis. When 10 liter gas volumes are to be concentrated, solution volumes of 20 liters are used. Here, preparation is made in a calibrated 20 liter jug, to which 100 ml of buffer is added. The resulting pH of the standard solutions was 6 to 7. Redistilled water is used in the preparation of all solutions lower than $3 \times 10^{-5}$ M. Both dilute stock and standard solutions are prepared within a day or two of use.

## Procedure for Distribution and Concentration

After the standard is brought to the temperature of the constant temperature bath, the bubbler is immersed, positioned vertically, and connected with a glass tube to the accessory board shown in Figure VII.

To provide a pressure head sufficient for a flow of 50 cc. of air per minute through the concentration column, a solution height differential must be present at the bubbler. A trial run will ascertain the point to which the bubbler must be immersed (point A in Figure III) so that when the internal liquid level is brought to B the desired flow rate will be obtained.

The vernier metering valve on the flow controller is set to the required position to give a flow rate of 50 cc./min. and the bubbling is started. The initial part of the line is purged for 10 minutes with equilibrated air, shunting it out through stopcock 1 in Figure VII.

The drying tube should be heated for at least fifteen minutes prior to passing air through it and the concentration column should be bypassed via stopcock 2 until sampling is begun.

After the equilibrated air is led into the rest of the line by turning stopcock 1, about 30 minutes (75 minutes when 10 liter gas samples are concentrated) should be allowed before concentration is begun. This will ensure that equilibrium HCN adsorption is attained in the drying tube. During this period final adjustment of flow rate to the desired value should be made and stopcock 2 turned slightly to provide a pressure

drop sufficient to bring the water level in the bubbler down to point B.

The column is immersed in the coolant at least 5 minutes before beginning concentration. A thermal shield around the Dewar flask may be necessary to prevent condensation of water in the gas line.

Stopcock 2 is then turned to put the column in series with the air stream and time and flow rate are recorded. After the required period (40 or 200 minutes for concentration of hydrogen cyanide from 2 and 10 liters of gas respectively), the column is cut out and again time and flow rate are recorded. Flow rate should drift only slightly during the concentration period. The column should be sealed with a polyethylene cap and stored in dry ice until readout.

Procedure for Readout

Initially the recorder is zeroed using the amplifier bias control, with the chromatograph attenuation control set to the shorting position. Zero adjustment later in the run can be made with the chromatograph control. The column is attached to the gas sampling valve and is immersed in hot water at 57°C (or there abouts). At this temperature the HCN has been found to be completely eluted within 3 minutes. Because of the volatility of

the di-n-butyl phthalate higher temperatures are not recommended. Five minutes later the gaseous contents are injected into the chromatograph by turning the gas sampling valve. After three minutes the concentration column is cut out of the stream. With the gain set to the desired value the chromatograph attenuation control is used to bring the air peak on scale. Excessive base line drift at high gain settings may require upscale or downscale setting of zero a few minutes prior to the HCN peak to prevent the peak going off scale. However, if this occurs downscale, immediate rezeroing and a back extrapolation method can be used.

## Standard Curves and Determination of Concentration Efficiency

Standards were run in a constant temperature bath of 75 gallon volume, regulated to 20 $\pm$ 0.05°C.

Typical chromatograms are shown in Figure IX. Peak area, flow rate, concentration time and known concentration are used to construct the standard curves in Figure X. With these, analysis for HCN down to $5 \times 10^{-6}$ M is possible in unknowns run in the same manner as the 4 liter aqueous standards. The data used to prepare the curves are given in Table IV.

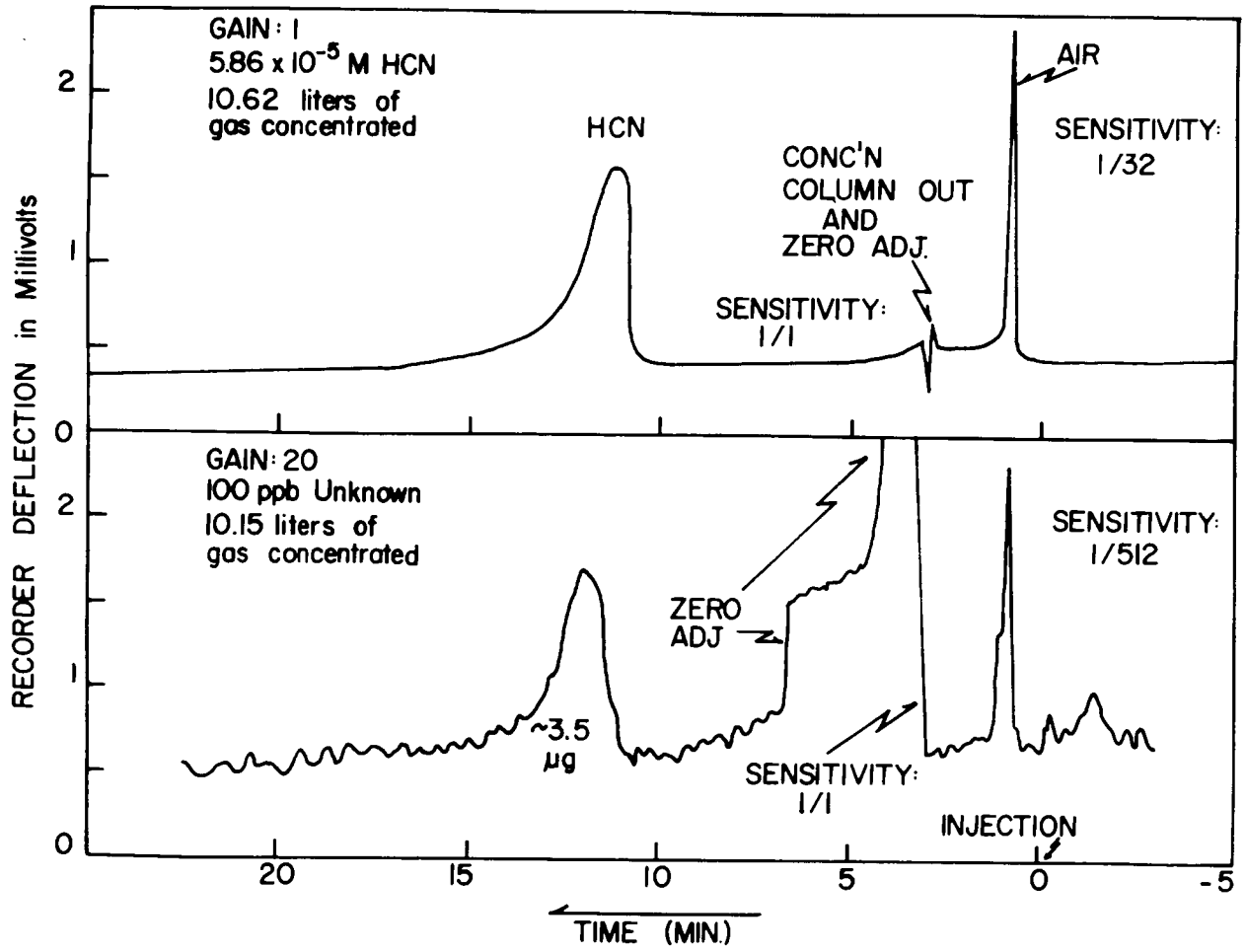



Figure IX Typical Chromatograms

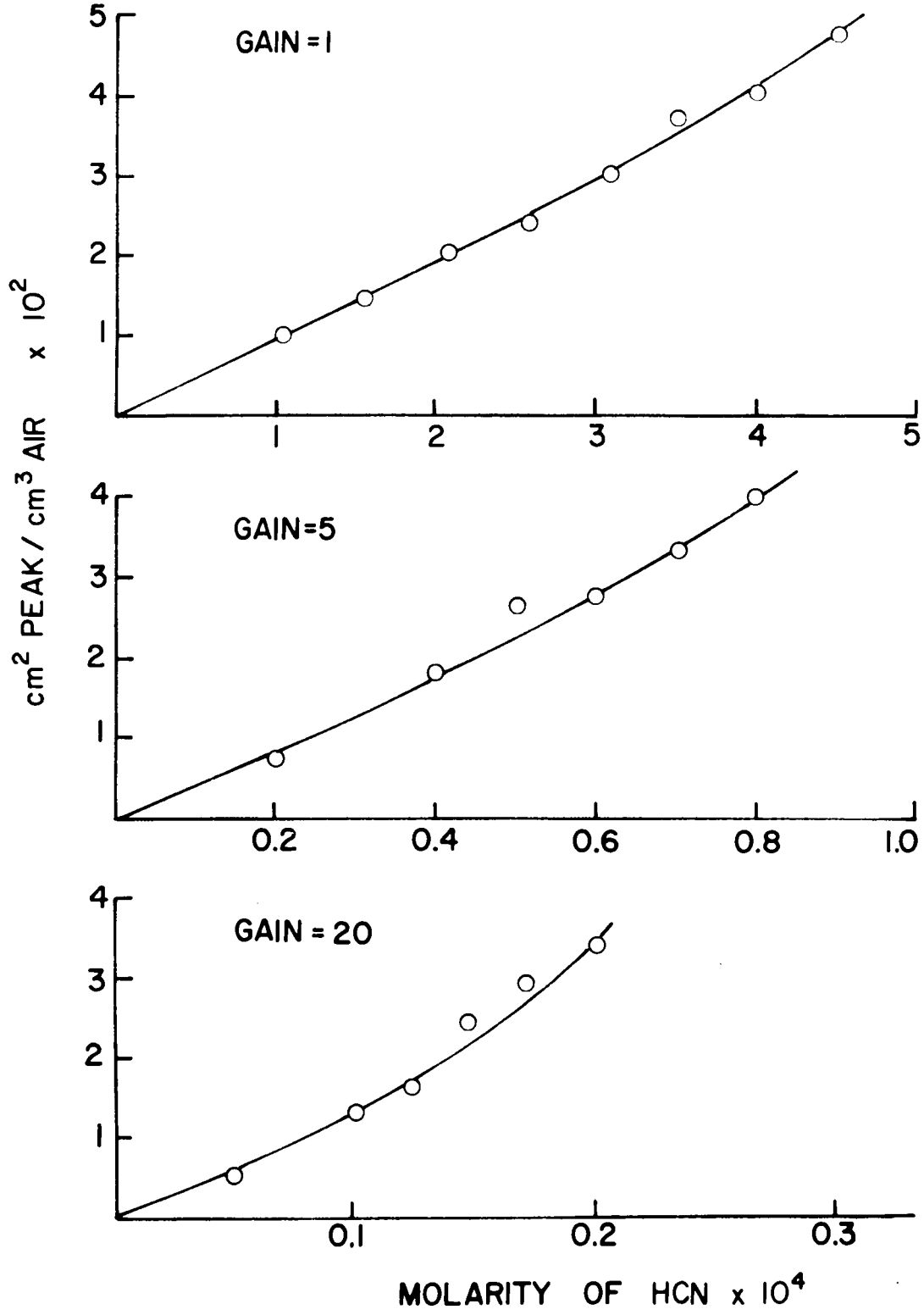



Figure X Standard Curves for Two Liter Gas Volumes

TABLE IV

Data For Construction of Standard Curves

| Molarity of HCN x $10^5$ | Volume Concentrated ($cm^3$ x $10^3$) | Peak Area ($cm^2$) | Peak Area / Vol.$^{-1}$ Conc'd ($cm^{-1}$ x $10^2$) |
|---|---|---|---|
| **Gain of 1** | | | |
| 10.32 | 2.060 | 20.9 | 1.02 |
| 15.46 | 2.016 | 29.4 | 1.46 |
| 20.63 | 2.148 | 44.5 | 2.07 |
| 20.63 | 2.176 | 43.6 | 2.00 |
| 25.88 | 2.140 | 51.6 | 2.41 |
| 31.05 | 1.976 | 59.3 | 3.00 |
| 34.9 | 2.056 | 76.4 | 3.72 |
| 39.9 | 2.144 | 85.8 | 4.00 |
| 44.9 | 1.964 | 93.1 | 4.74 |
| **Gain of 5** | | | |
| 1.99 | 2.069 | 16.1 | 0.78 |
| 3.99 | 1.984 | 35.5 | 1.84 |
| 5.00 | 2.056 | 53.9 | 2.62 |
| 5.99 | 2.068 | 57.1 | 2.76 |
| 5.99 | 2.180 | 53.0 | 2.43 |
| 5.99 | 2.083 | 60.9 | 2.92 |
| 6.99 | 2.000 | 67.7 | 3.39 |
| 6.99 | 2.051 | 67.0 | 3.27 |
| 7.98 | 1.980 | 79.2 | 4.00 |
| **Gain of 20** | | | |
| 0.50 | 2.016 | 10.4 | 0.51 |
| 1.00 | 2.104 | 27.7 | 1.32 |
| 1.03 | 2.076 | 34.4 | 1.65 |
| 1.03 | 2.128 | 35.1 | 1.65 |
| 1.47 | 2.232 | 54.8 | 2.46 |
| 1.71 | 1.980 | 58.3 | 2.94 |
| 2.00 | 2.160 | 73.7 | 3.41 |

To extend the lower limit and to provide more accurate analysis, larger gas volumes were concentrated. The concentration column efficiency, now less than 100%, was determined as follows:

Hydrogen cyanide from 10 liter gas volumes, drawn from 20 liter aqueous standards, was concentrated and passed into the chromatograph. Dividing the peak area by 2000 cc., and using the previously determined standard curves, an apparent concentration of hydrocyanic acid was obtained. Multiplication of the apparent concentration by the fraction (2000/cc. of air concentrated) then yielded the measured hydrocyanic acid concentration. These results are shown in Table V.

In further runs in which 10 liter gas volumes are concentrated, results were calculated in the manner just described, correcting the value found for concentration efficiency.

TABLE V

Determination of Efficiency of Concentration of 10 Liters
(Gain = 1)

Concentration Column II

| Molarity of HCN x $10^5$ | Volume of Gas Concentrated $cm^3 \times 10^3$ | Peak Area $cm^2$ | Molarity of HCN Found x $10^5$ | Percent Efficiency |
|---|---|---|---|---|
| 3.88 | 9.92 | 30.6 | 3.13 | 80.7 |
| 3.88 | 10.28 | 30.3 | 3.00 | 77.3 |
| 5.79 | 10.12 | 49.1 | 4.98 | 86.0 |
| 5.86 | 10.39 | 47.8 | 4.76 | 81.2 |
| 5.86 | 10.62 | 50.0 | 4.80 | 81.9 |

Mean Efficiency = 81.4 Rel. S.D. = 3.8%

Concentration Column III

| | | | | |
|---|---|---|---|---|
| 5.79 | 10.09 | 46.5 | 4.71 | 81.3 |
| 5.79 | 10.11 | 47.3 | 4.81 | 83.0 |
| 5.79 | 10.29 | 48.3 | 4.84 | 83.6 |
| 5.79 | 10.42 | 46.3 | 4.55 | 78.6 |

Mean Efficiency = 81.6 Rel. S.D. = 2.7%

## Effect of Ionic Strength

To evaluate the effect of ionic strength on the method (through the distribution constant or equilibration efficiency) 10 ppm hydrocyanic acid solutions of differing ionic strength were prepared. Twenty milliliter aliquots of 2.51 gm/l potassium cyanide solution, 50 ml aliquots of 4 gm/l potassium dihydrogen phosphate solution, and 0, 10 or 100 ml aliquots of 2 M sodium chloride solution were added to 2 liter volumetric flasks. The resulting ionic strengths were 0.0015, 0.0115 and 0.112. The solutions were run in the same manner as the 4 liter aqueous standards. The gain was 1 and the sensitivity, $\frac{1}{2}$. Table VI presents the results. The decrease in the molar concentration of water due to the addition of 0.1 molar salt is negligible, and one would then expect little effect of ionic strength. The results bear this out. Furthermore, the work of Shirado (25) indicates that the vapor pressure versus concentration relationship becomes non-linear only at rather high levels of hydrogen cyanide.

TABLE VI

Effect of Ionic Strength on Peak Area to Volume of Gas Concentrated Ratio

10 ppm Hydrocyanic Acid Solution

| Ionic Strength | $\frac{\text{Peak Area}}{\text{Vol. Conc'd}}$ ($cm^{-1}$) |
|---|---|
| 0.0015 | 2.04 |
| 0.0115 | 2.09 |
| 0.112 | 2.09 |

## Determination of Hydrogen Cyanide in Air

As a side aspect of these investigations studies were made of the feasibility of developing a method for the analysis of hydrogen cyanide gas, at relatively high levels in air, using gas chromatography.

Pure hydrogen cyanide was prepared according to the method of Wade and Panting (26). All glassware was 24/40 standard taper borosilicate unless otherwise noted. Joints were sealed with a small amount of Vaseline.

Cold, 50 volume percent sulfuric acid was added dropwise to fifty grams of sodium cyanide to produce hydrogen cyanide. The reaction was carried out in a three-neck, 500 ml round-bottom flask. One neck was stoppered, another held the dropping funnel and the third was fitted with a Claisen head. The latter was attached to a series of two condensers, a connecting tube and a round bottom 250 ml collecting flask (19/38 adapted to 24/40) cooled in an ice-salt mixture at about $-10^{\circ}C$. The first condenser was 300 mm long and packed with 20 mesh reagent anhydrous calcium chloride. The hydrogen cyanide in passing through the first condenser (heated with hot water) was dried and was condensed out in the second (water cooled, 400 mm) one and collected in the cooled flask. After the equivalent amount of

dilute sulfuric acid (117 ml) had been added, the reaction vessel was heated until its contents just started to boil. Heating was discontinued and the 250 ml flask was removed from the apparatus, stoppered and stored on dry ice. Re-distillation of the hydrogen cyanide was made from this flask after it was fitted to the Claisen head. The gas passed through two 300 mm condensers in series, the first being heated with hot water and the second cooled with tap water, and was collected in a round bottom 50 ml flask (19/38 adapted to 24/40) cooled in the ice-salt mixture. The first condenser was packed with a mixture of phosphorous pentoxide and glass beads. The hydrogen cyanide passed over in the range of 25.6 to 26.2°C, the weight of the collecting flask increasing by 11 grams. The distillation was repeated, the product passing over in the range 25.6 ± 0.2°C. This value agrees well with that of Perry and Porter (24). Again storage was in dry ice.

The flask containing the hydrogen cyanide was warmed carefully until all of the solid has melted. One end of a 6 mm glass tubing fitted with two stopcocks was immersed in the liquid and the HCN drawn up to partially fill the space between the stopcocks using a pipetting bulb. The stopcocks were closed and the excess hydrogen cyanide allowed to drain back into the flask after

which the tube was removed and the flask re-stoppered and placed back on the dry ice.

The tube was weighed before and after the addition of the hydrogen cyanide, and the weight added calculated by difference. A stoppered glass jug of 8.52 liters internal capacity was used for preparing the master HCN gas standard. Through its stopper passed a 6 mm glass tube fitted with a stopcock, a tube with stopcock connected to an aspirator, and a long capillary tube with a stopcock at its end. The jug was evacuated partially and the device containing the liquid hydrogen cyanide attached to the first tube. The two stopcocks (one on the HCN container, the other on the first tube) were opened to allow the hydrogen cyanide to evaporate into the 8.52 liter volume. Then the other stopcock on the HCN container was opened and air allowed to enter the jug to equalize pressures, after which all three stopcocks were closed and the HCN container removed. In this way gas mixtures of about 2% HCN in air were prepared. Data on the preparation of these mixtures are given in Table VII.

Gas burets were constructed by fitting 50 ml volumetric burets with stopcocks on the open ends. They were calibrated to relate the 50 ml scale to actual

TABLE VII

Preparation of Standard Mixtures of

Hydrogen Cyanide With Air

8.52 Liter Volume

| HCN Taken (gm) | Temperature (°C) | Pressure (mmHg) | Water Vapor (mmHg) | HCN by Volume (%) | HCN by Weight (%) |
|---|---|---|---|---|---|
| 0.1675 | 26 | 757.6 | 11.9 | 1.79 | 1.68 |
| 0.1851 | 25 | 759.8 | 15.8 | 1.97 | 1.85 |
| 0.1898 | 30 | 756.4 | 14.2 | 2.03 | 1.91 |

volume. Samples of the master standard were taken by raising a mercury reservoir attached to the lower end of the buret until the buret was filled with mercury, attaching the upper end to the capillary tube leaving the standard jug, opening both stopcocks (the one on the buret and the one on the capillary tube), lowering the mercury reservoir to nearly fill the buret with the gas, equalizing the mercury levels and closing the two stopcocks. The capillary line would have been purged previously with the standard using a similar technique. Pressure inside the jug was maintained at that of the outside by adding mercury from the dropping funnel to replace the gas volume removed.

The hydrogen cyanide in the buret was either run directly, by using 20 to 50 cc. to purge out the gas sampling valve, or diluted and then run.

Dilution consisted of equalizing the mercury levels, opening the upper stopcock, carefully raising the reservoir to sweep put a fraction of the gas, again equalizing the levels, reading the buret, lowering the reservoir to draw in air until the desired total volume had been reached, again equalizing the mercury levels, closing the stopcock and reading the final volume. For high dilutions of the master standard, a sample of this diluted standard was transferred to another gas buret,

and again diluted. In this way more than one "very dilute" standard could be obtained from a single dilute standard.

Five cc. gas volumes of the master and dilute hydrogen cyanide standard gas mixtures were injected into the chromatograph for readout of hydrogen cyanide. The instrument was equipped with a six foot Perkin-Elmer "A" chromatographic column (didecylphthalate) and operated at 66°C, 10 p.s.i., 24 cc.He/min. and 8.00 volts bridge voltage. A somewhat different d.c. amplifier circuit permitted a gain setting of ½.

The results in Table VIII indicate that levels of hydrogen cyanide on the order of 0.3 to 2% in air can be analyzed accurately. Deviation from linear response occurs at lower concentrations, perhaps due to adsorption of hydrogen cyanide in the sampling valve or the reaction of the gas with the mercury in the presence of moisture of the air.

TABLE VIII

Results With Hydrogen Cyanide Mixtures

In Air

| Gain | Sensitivity | Standard Diluted (wt% HCN) | HCN by Weight (%) | Peak Area ($cm^2$) | Peak Area / wt% HCN ($cm^2$/wt%) |
|---|---|---|---|---|---|
| 1/2 | 1/8 | 1.85 | 1.85 | 19.5 | 10.54 |
| | | | 1.85 | 19.8 | 10.70 |
| | | 1.91 | 1.91 | 18.7 | 9.79 |
| | | | 1.91 | 19.0 | 9.95 |
| | | | 1.91 | 19.0 | 9.95 |
| | | | 1.91 | 19.3 | 10.10 |
| | | | 1.91 | 19.6 | 10.26 |
| | | | | mean | 10.18 |
| | | | | s.d. | 0.334 |
| 1/2 | 1/4 | 1.68 | 0.883 | 16.6 | 18.8 |
| | | | 0.883 | 16.7 | 18.9 |
| | | | 0.911 | 18.1 | 19.9 |
| | | | 1.31 | 25.3 | 19.3 |
| | | | 1.31 | 25.8 | 19.7 |
| | | | 1.68 | 33.3 | 19.8 |
| | | | 1.68 | 33.5 | 19.9 |
| | | | 1.68 | 33.7 | 20.1 |
| | | | | mean | 19.4 |
| | | | | s.d. | 0.53 |
| 1/2 | 1/2 | 1.68 | 0.513 | 20.3 | 39.6 |
| | | | 0.519 | 18.8 | 36.2 |
| | | | | mean | 37.9 |
| | | | | s.d. | 2.4 |
| 1 | 1/2 | 1.91 | 0.310 | 23.8 | 76.8 |
| | | | 0.310 | 25.9 | 83.5 |
| | | | | mean | 80.15 |
| | | | | s.d. | 4.7 |

TABLE VIII - Cont.

| Gain | Sensitivity | Standard Diluted (wt% HCN) | HCN by Weight (%) | Peak Area ($cm^2$) | Peak Area / wt% HCN ($cm^2$/wt%) |
|---|---|---|---|---|---|
| 1 | 1 | 1.68 | 0.209 | 29.0 | 139 |
| | | | 0.209 | 29.4 | 141 |
| | | 1.85 | 0.149 | 21.9 | 147 |
| | | | 0.149 | 22.5 | 151 |
| | | 1.91 | 0.0593 | 4.6 | 78 |
| | | | 0.0995 | 9.5 | 95 |
| | | | 0.136 | 13.1 | 96 |
| | | | 0.136 | 15.1 | 111 |
| 2 | 1 | 1.85 | 0.0375 | 5.0 | 133 |
| | | | 0.0375 | 5.0 | 133 |
| | | | 0.0846 | 20.6 | 243 |
| | | 1.91 | 0.0593 | 12.0 | 202 |
| | | | 0.0995 | 25.3 | 254 |

# RESULTS AND DISCUSSION

## Correction For HCN Loss

It is evident from equation (1) that a loss of 0.3% of HCN will occur when a volume of gas equal to that of the solution is sparged. On this basis, using the value for the volume of air sparged to the mid-point of concentration, HCN loss for each run can be calculated. In the preparation of the standard curves the average losses were 0.5% for Gain = 1, 0.4% for Gain = 5 and 0.5% for Gain = 20. When the loss from an unknown solution differs appreciably from 0.5% a correction should be applied to the result.

Runs used to calibrate the concentration columns (Table I) had an average HCN loss of 0.3%. If the actual loss differs appreciably from this a correction should be applied to the result. In both cases the corrections would normally be negligible.

## Analysis of Synthetic Unknowns

Synthetic unknowns were prepared and run in the same manner as standards used in the preparation of the standard curves. The results are shown in Table IX.

TABLE IX

Analysis of Synthetic Unknowns

| Molarity of HCN x $10^5$ | Volume Concentrated $cm^3 \times 10^3$ | Peak Area $cm^2$ | Molarity of HCN x $10^5$ Found | Percent Error |
|---|---|---|---|---|
| **Gain 1** | | | | |
| 29.9 0.80 mg/l | 2.152 | 64.1 | 30.0 | +0.3 |
| 29.9 | 2.044 | 62.8 | 30.8 | +4.4 |
| | 2.096 | 63.6 | 30.5 | +3.4 |
| | 2.088 | 66.0 | 31.6 | +7.1 |
| 19.9 | 2.076 | 40.6 | 19.9 | 0.0 |
| **Gain 5** | | | | |
| 6.99 | 2.036 | 71.7 | 7.13 | +2.0 |
| 4.99 | 2.056 | 50.6 | 5.15 | +3.2 |
| 3.00 | 1.984 | 27.5 | 3.15 | +5.0 |
| **Gain 20** | | | | |
| 0.478 0.13 mg/l | 10.71 | 71.8 | 0.461 | -3.6 |
| | 11.07 | 68.2 | 0.434 | -9.2 |
| | 10.27 | 75.1 | 0.501 | +4.8 |
| | 10.42 | 72.2 | 0.479 | +0.2 |
| | 10.05 | 64.5 | 0.466 | -2.5 |

The result of the second run on the $0.478 \times 10^{-5}$ M unknown was not used in calculating a mean value since the volume differed significantly from those used in the determination of concentration column efficiency (mean volume = 10.25 liters). The average volume concentrated in the remaining four runs is 10.36 liters. Alternatively a plot of percent efficiency versus volume concentrated using the data in Table V can be made and the concentration efficiency for an unknown read from this. See the detailed procedure.

## Interferences

A substance which has significant vapor pressure above its solution, low enough vapor pressure at dry ice temperature to be held appreciably on a concentration column and a boiling point in the proper range to be eluted chromatographically with HCN will interfere if present in great enough concentration in the sample. None of the substances normally expected in natural waters will interfere. Water, itself, if present in appreciable amounts in the drying tube effluent will interfere chromatographically with HCN.

Water pollutants listed by the California State Water Pollution Control Board (6) (7) and by Klein (16) have been considered as possible interferences. Most

were eliminated from consideration because of very high or very low boiling points relative to HCN. The rest were studied when available. Liquid or gaseous samples of these substances were injected via hypodermic needle into the chromatograph. The position of their peaks relative to that of HCN gave indication of interference. The results are listed in Table X.

The lower amines (to diethylamine), pentane, pentene, methanol, methanethiol and lower mercaptans and high levels of hydrogen sulfide will interfere chromatographically. Lacking information on water/air distribution of these substances it is not possible to determine the degree of over-all interference.

If one or more interferences are present in a sample, as indicated by distortion of the HCN peak, they might be eliminated by selective removal prior to concentration or by use of a more selective chromatographic column.

## Application to Metal-Cyanide Systems

To demonstrate the applicability of the method to solutions in which only a fraction of the total cyanide exists as hydrocyanic acid, analyses were carried out in nickel- and silver-cyanide systems.

TABLE X

Chromatographic Interferences

| Compound | Boiling Point (°C) | Interference |
|---|---|---|
| hydrogen sulfide | -61.8 | no[a] |
| ammonia | -33.4 | —[b] |
| methylamine[c] | - 6.5 | yes |
| trimethylamine[d] | 3.5 | yes |
| dimethylamine | 7.4 | not tested[e] |
| methanethiol | 7.6 | not tested[e] |
| cyanogen chloride | 13.8 | not tested[e] |
| ethylamine | 16.6 | not tested[e] |
| acetaldehyde | 21.0 | no |
| pentenes | (30) | yes |
| ethanethiol[d] | 34.7 | not tested[e] |
| pentanes | (36) | yes |
| carbon disulfide | 46.3 | no |
| diethylamine | 55.5 | yes[e] |
| acetone | 56.5 | no |
| methanol | 64.7 | yes |
| chloroform | 61.3 | no |
| cyanogen bromide | 61.6 | not tested[f] |
| butyraldehyde | 75.7 | not tested[f] |
| butylamine | 77.8 | not tested[f] |
| ethanol | 78.5 | no |
| acrylonitrile | 79.0 | no |

a) Tailing caused interference only at high $H_2S$/HCN ratios.

b) Probably reacted with column contents.

c) 40% aqueous solution.

d) Not listed as potential pollutant.

e) Expected to interfere on basis of results with other compounds.

f) Not expected to interfere on basis of results with other compounds.

Stock 0.1 M nickel nitrate was standardized with dimethylglyoxime (14). Standard silver nitrate, 0.05 M, was prepared by weight.

Experimental solutions were prepared in a manner similar to that employed for the 4 liter aqueous standards. The required aliquot of 0.1 M nickel nitrate was added prior to the addition of cyanide, while the aliquot of 0.05 M silver nitrate was added after addition of cyanide. The nickel solutions were buffered with a 0.01 M total phosphate buffer, a 0.01 M total acetate buffer being used for the silver system. Measurements at 20.0 ± 0.05°C were carried out as described previously. In the readout step a Philbrick UPA-2 operational amplifier and R-100B power supply replaced the K2-X, K2-P, HKR manifold combination used in the previously described amplifier. Therefore a new Gain = 1 standard curve was prepared.

The data used for the construction of the new standard curve is given in Table XI, and the results for the complex systems in Table XII.

Except for the first run, a sufficient excess of cyanide exists so that the contribution of free cyanide due to dissociation of the complex is negligible. Thus the hydrocyanic acid level is determined only by the excess of cyanide and the pH. The calculation of the

TABLE XI

Standard Curve at Gain = 1 for Modified Amplifier

| Molarity of HCN x $10^4$ | Volume Concentrated $cm^3 \times 10^3$ | Peak Area $cm^2$ | $\frac{\text{Peak Area}}{\text{Volume Con'c'd}}$ $cm^{-1} \times 10^2$ |
|---|---|---|---|
| 0.980 | 1.976 | 18.3 | 0.93 |
| 1.959 | 2.008 | 36.1 | 1.80 |
| 2.939 | 2.060 | 58.7 | 2.85 |
| 3.918 | 2.024 | 81.7 | 4.04 |

TABLE XII

Analyses in Complex Systems

| Molarity of Total Nickel $\times 10^3$ | Molarity of Total Silver $\times 10^3$ | Molarity of Total Cyanide $\times 10^3$ | pH | Molarity of HCN $\times 10^4$ Cal'd | Measured |
|---|---|---|---|---|---|
| (0.01 M in Phosphate Buffer) | | | | | |
| 1.243 | - | 4.928 | 6.19 | 0.73 | 0.68 |
| 1.243 | - | 5.174 | 6.28 | 2.02 | 1.79 |
| (0.01 M in Acetate Buffer) | | | | | |
| - | 1.235 | 2.559 | 6.45 | 0.89 | 0.90 |
| - | 1.235 | 2.707 | 7.39 | 2.34 | 2.28 |

hydrocyanic acid level in the first run is based upon the total nickel and total cyanide concentrations, the pH, and the thermodynamic constants at 25°C : $K_a$ = 6.1 x $10^{-10}$ (2) and $K_D$ = 5.4 x $10^{-31}$. The latter constant has been recalculated from that recently reported (10) using the new value for the ionization constant of HCN. This calculated HCN level in the first run is only approximate in view of the lack of constants at 20°C. The agreement between observed and calculated results in nickel-cyanide and silver-cyanide systems indicates, as expected, that hydrocyanic acid can be determined in the presence of a large reservior of total cyanide.

Unknowns

Toxicological studies of simple and complex cyanides in a natural water are currently in progress. Analyses of synthetic unknowns prepared with this water indicate continuing reliability.

# CONCLUSIONS

The operations involved in the method are summarized in Figure XI. Operating conditions are summarized in Table XIII. It has been applied extensively in determining hydrocyanic acid *per se* in nearly fifty systems used in the toxicity work. Despite the great many procedural details it has proven reliable and, for the experienced worker, straight forward. Hydrocyanic acid can now be analyzed in solution at levels hitherto impossible and without disturbing equilibria in which it is involved.

The work described here represents probably the first application of gas chromatography, by way of air-solution distribution, to the analysis of a dissolved volatile substance. This type of measurement has far-reaching implications. In the chemical process stream, a volatile component might be present in solution more often in parts per hundred than parts per million. Then, the above method could be carried out (without the use of the complicated concentration step nor of voltage amplification) in minutes instead of hours. Selection of the appropriate chromatographic column, operating conditions and detector would be necessary.

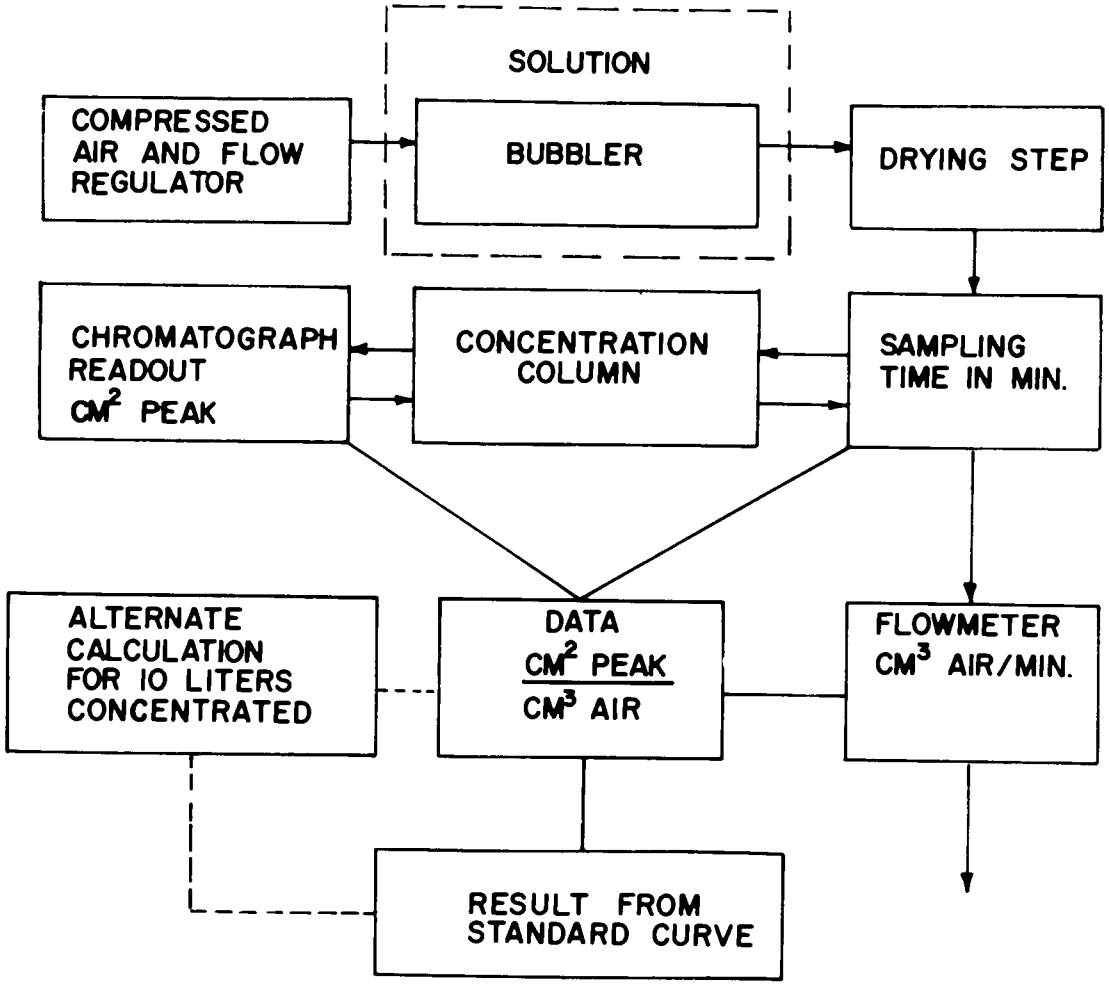



Figure XI Block Diagram of Operations

TABLE XIII

Summary of Operating Conditions

| | |
|---|---|
| **Concentration Step** | |
| Temperature of Solution | 20°C |
| Air Pressure Head | 12 p.s.i. |
| Flow Rate | 50 cc./min. |
| Drying Tube Voltage at 25°C (RMS) | |
| 2 Liters Concentrated | 5 (100°C) |
| 10 Liters Concentrated | 3 ( 53°C) |
| Concentration Column | |
| Dimensions | ¼" o.d. x 7" |
| Liquid Phase | di-n-butyl phthalate |
| Solid Support | 40-60 mesh crushed firebrick |
| Liquid to Solid Proportion | 19.4 wt. % |
| Operating Temperatures | -78 and 57°C |
| **Chromatograph** | |
| Oven Temperature | 44°C |
| Helium Pressure Head | 30 p.s.i. |
| Flow Rate | 135 cc./min. |
| Bridge Voltage | 8.0 volts |
| Column | |
| Dimensions | ¼" o.d. x 18' |
| Liquid Phase | dinonyl-phthalate |
| Solid Support | 40-60 mesh Chromosorb "W" |
| Liquid to Solid Proportion | 20 wt. % |
| Sensitivity | 1/1 |
| Recorder Sensitivity | 2.5 mv. |
| Amplifier Gain | 1, 5 and 20 |

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# APPENDIX I

## Table of Contents

Detailed Procedure

I. Preparation of Standards and Synthetic Unknowns

A. Concentrated KCN Standard (0.1 M)

(1) Weigh out 6.5 gm of Reagent grade KCN. Dilute to one liter in a volumetric flask with distilled water.

(2) To a 25 ml aliquot of 0.1 M KCN add 0.085 gm KI, 2.5 ml of 6 M $NH_4OH$ and 15 ml of water. Titrate with standard 0.05 M $AgNO_3$ to the first appearance of a permanent white precipitate.

(3) $$M_{KCN} = \frac{(ml\ AgNO_3)\ (M\ AgNO_3)}{(ml\ KCN)}$$

(4) Prepare anew after 2 weeks. Standardization at beginning and end permits interpolation for intermediate KCN concentration during the 2 weeks.

B. Dilute KCN Standards

(1) The appropriate aliquot of 0.1 M KCN is diluted to volume in a volumetric flask with boiled, cooled, distilled water. By initially almost filling the volumetric flask with water, adding the aliquot, shaking and finally diluting to volume, HCN loss by volatilization can be minimized.

| Conc'n of Dilute Standard | Dilution of aliquot of 0.1 M KCN |
|---|---|
| 0.02 M | 50 ml to 250 ml |
| 0.004 M | 20 ml to 500 ml |
| 0.001 M | 20 ml to 2000 ml |

(2) Prepare anew after a few days.

C. Stock Buffer (0.2 M in Total Phosphate)

(1) 4.26 gm $NaHPO_4$ and 23.15 gm $KH_2PO_4$ are diluted to volume in a 1 liter volumetric flask with distilled water.

D. Preparation of HCN Standards

(1) For HCN concentrations below $3 \times 10^{-5}$ M redistilled water is employed. Above $3 \times 10^{-5}$ M boiled, cooled distilled water is used.

(2) Suggested Use of Dilute Standards

| Dilute Standard (Molarity) | For Use in Prep. of 4 liter Aq. Stds. | 20 liter Aq. Stds. |
|---|---|---|
| 0.02 | $1 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ M | ---------- |
| 0.004 | $2 \cdot 10^{-5}$ to $8 \times 10^{-5}$ M | $2 \cdot 10^{-5}$ to $10^{-4}$ M |
| 0.001 | $0.5 \cdot 10^{-5}$ to $2 \times 10^{-5}$ M | $2 \cdot 10^{-6}$ to $10^{-5}$ M |

(3) Four Liter Aqueous Standards.

(a) Duplicate solutions are prepared in 2 liter volumetric flasks.

(b) Add:

1) The water until 2/3 full.

2) A 25 ml aliquot of stock buffer and shake.

3) An aliquot of the appropriate dilute KCN standard and shake.

(c) Dilute to volume and shake well.

(4) 20 Liter Aqueous Standards

(a) Add:

1) The water to a 20 liter glass jug until 2/3 full.

2) A 100 ml aliquot of stock buffer and shake.

3) An aliquot of the appropriate dilute KCN standard and shake.

(b) Dilute to 20 liter calibration mark and shake well.

(5) HCN standards (or Synthetic Unknowns) are prepared within a day of two of

use.

II. Concentration Step

A. Standards: Two Liters of Air Equilibrated With 3.3 Liters of Aqueous Standard.

(1) Immerse two 2 liter volumetric flasks containing the same aqueous standard in a constant temperature bath at 20.0°C for at least 1 hour prior to sparging.

(2) Mix the contents of the volumetric flasks thoroughly. Use several small portions of the standard solution to rinse out a 100 mm x 559 mm (22 inch) Pyrex cylinder. Fill the cylinder to the red mark, about 63.5 mm, (2½ in.) below the rim, and immerse in the constant temperature bath.

(3) After allowing the sparger to drain, immerse it in the standard solution to a depth given by the red mark on the

narrow part of the barrel (point A, Figure III). The position of the mark is determined by the depth of immersion of the sparger that will make the air/water interface fall 1 cm. above the neck of the sparger (point B, Figure III) when the flow rate is 50 cc./min. Generally the mark will be about 12 cm. below the top of the bubbler. Align it vertically in the cylinder, attach the ball joint, and clamp in position.

(4) Turn stopcock #1 so that the red mark on the handle points down, thereby venting the initially equilibrated air to the outside.

(5) Check to see that:

(a) The needle valve on the flow controller (accessory board) is set so that the vernier reads 0.00. DO NOT CLOSE TIGHTLY.

(b) The needle valve on the reducing valve attached to the air tank is completely clockwise.

(c) The "T" handle valve on the reducing valve attached to the tank is completely counterclockwise.

(6) Open the main tank valve by turning it completely counterclockwise.

(7) Bring the pressure on the left gauge of reducing valve to 26 p.s.i. by turning the "T" handle valve clockwise.

(8) Turn the needle valve on reducing valve completely counterclockwise.

(9) Slowly turn the vernier dial needle valve on the flow controller to bring the setting to 0.05 turns. Try not to overshoot. In this initial step the gauge is brought to about 12.4

p.s.i. If the setting is overshot, turn the needle valve to 0.00 and wait 15 minutes before bringing up again.

(10) After completion of step (9) record the time, $\underline{t_1}$.

(11) Plug in the variable transformer and adjust the voltage across the drying tube heating coil to 5.0 volts. Replace the desiccant after four hours of steady use.
In apparatus equipped with a built in heating circuit merely turn on switch. The adjustment potentiometer will have been set previously.

(12) Wait 12 minutes.

(13) The red mark on the handle of stopcock #2 is pointed up so that the concentration column is bypassed. Next turn stopcock #1 one-quarter turn counterclockwise, aligning the two red marks, and connecting the drying tube-

flowmeter line into the gas stream.

(14) After completion of step (13) note the time, $\underline{t_2}$.

(15) Adjust the main reducing valve to bring the pressure to 26 p.s.i.

(16) Make a fine adjustment of the vernier needle valve by turning it slightly (0.01 unit) counterclockwise or clockwise, to raise or lower the flow to obtain a reading of 70 mm on the stainless steel float. Carry out this adjustment in 0.05 p.s.i. intervals (if the apparatus is equipped with a gauge) allowing a minute for flow equilibration after each adjustment. If the flow rate goes above about 73 mm shut off flow until bubbling stops and slowly raise the pressure again.

(17) Turn stopcock #2 slightly clockwise to build up sufficient pressure drop to bring the air/water interface in

the sparger to 1 cm above the neck (point B, Figure III). Check this setting from time to time during the next few minutes and once or twice later. No further adjustment is permitted after $t_1$ + 35 minutes.

(18) Prepare coolant by adding acetone to a Dewar flask filled with dry ice. Fill another Dewar flask with this coolant to about 2/3 full and place it under the concentration column, raising it to immerse the column. Check the knurled knobs to see that the column is attached tightly. Then fill the Dewar flask to the brim with crushed dry ice and, if necessary, add more cold acetone. Immediately attach aluminum thermal shield (Figure XII). Step 18 should be completed by $t_1$ + 35 minutes.

(19) At $t_1$ + 35 minutes note the flowmeter reading.

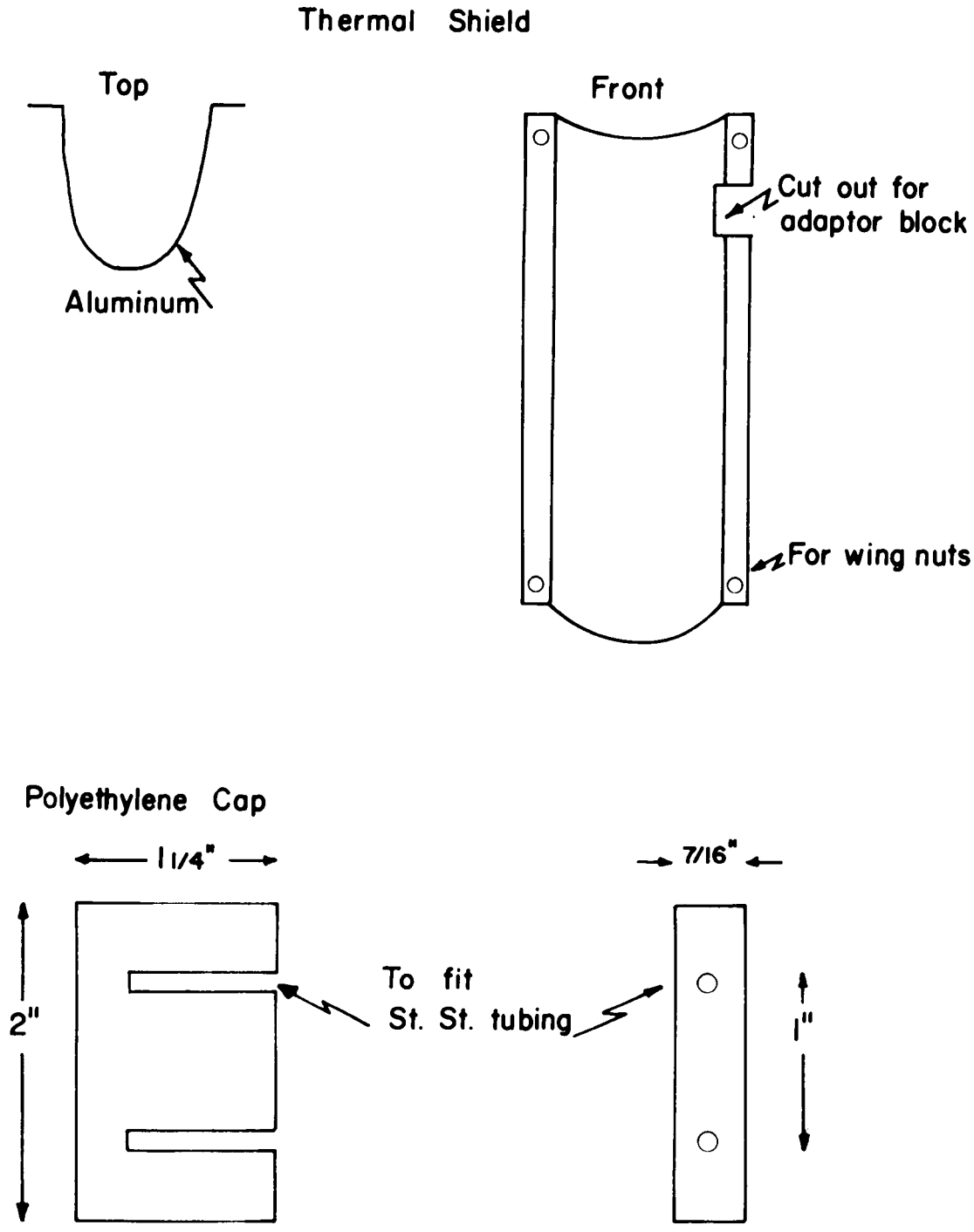


Figure XII Accessory Equipment

(20) At ($t_1$ + 40 minutes) connect the concentration column into the gas stream by turning stopcock #2 one-quarter turn clockwise to align the two red mark marks. Accurately record both the flowmeter readings and times according to the following schedule:

$t_3$, the time of connection

$t_3$ + 2 minutes

$t_4$, the time of cutout.

(21) At exactly $t_3$ + 40 minutes cut out the concentration column by turning stopcock #2 one-quarter turn counterclockwise. Record this time accurately.

(22) Remove the shield and carefully lower and remove Dewar flask, shaking down dry ice. Wipe off excess coolant and, after turning knurled nuts ½ to ¼ turn counterclockwise, remove column from stainless steel block.

B. Standards: Ten Liters of Air: 20 Liter Aqueous Standards (The steps are numbered to correspond to the previous section).

(1)-(2) The sample contained in a 20 liter glass jug is placed in a constant temperature bath several hours before sparging. Sparging is not started until the internal temperature of the solution reaches that of the bath.

(3)-(10) Carry out steps (3) thru (10) as indicated in above instruction for the two liter standards.

(11) Set the voltage across the drying tube heating coil to 3.0 volts. Replace the desiccant after two 10 liter runs.

(12)-(16) Same steps as the previous section.

(17) Same except for last sentence: The adjustment should be completed by $t_1$ + 60 minutes.

(18) Same except the last line should read: 1 hour.

(19) The flowmeter reading is noted as $t_1$ + 1 hour.

(20) At $t_1$ + 75 minutes the schedule should be:

$t_3$ + 2 minutes

$t_4$, time of cutoff.

(21) The cutoff time should read $t_3$ + 200 minutes.

(22) Same steps as previous section.

C. Unknowns

Laboratory Operation

The concentration of HCN in an unknown must be known approximately before the unknown can be run. Either the 2 liter

(II, A., 1.) or the 10 liter (II, A., 2.) concentration step is employed depending on the HCN level in the unknown.

Field Operation

(1) Remove sparger from the storage cylinder and allow it to drain and then immerse it in the water so that the red mark (point A, Figure III) is at the water level.

(2) Align the sparger vertically, clamp it into position and then attach ball joint and clamp it.

(3) Turn stopcock #1 so that the red mark on the handle is downward (thereby venting initial equilibrated air to the outside).

(4) Check to see that:

(a) The vernier needle valve reads "0".

(b) The needle valve at the tank is completely clockwise (CW).

(c) The "T" handle valve on the tank reducing valve is completely counterclockwise (CCW).

(5) Open the main tank valve by turning it completely counterclockwise (CCW).

(6) Bring the pressure on the left gauge at the tank reducing valve to 26.0 p.s.i. by turning the "T" handle valve clockwise (CW). After about a half hour check this setting and, if necessary, adjust it.

(7) Turn the needle valve at the tank completely counterclockwise (CCW).

(8) Turn the vernier needle valve to read 0.05 and wait for the pressure to rise slowly to about 12.4 p.s.i. and record the time ($t_1$) to the nearest minute.

(9) After $t_1$ is noted plug in transformer line plug, attach alligator clip leads to terminals of the windings of the drying tube and switch on switch at the left rear of the accessory board to ON. The drying tube should start heating (the heating rate will have been set earlier to the proper value for ambient room temperature). Approximately 3.5 volts is required across the windings to provide the necessary internal temperature of 53 C for a room temperature of 20 C. The desiccant should be replaced after two runs (approximately two 10 liter volumes concentrated) although in a pinch it might last for 3.

(10) Fifteen minutes after $t_1$ check to see that the red mark on the handle of stopcock #2 is pointed up and then turn stopcock #1 one-quarter turn CCW to align the two red marks.

(11) After completion of step (10) mark

down the time to the nearest minute ($t_2$).

(12) Note the reading of the flowmeter and, if necessary, carefully increase the vernier dial reading in very small increments, waiting a minute after each adjustment until the flowmeter reading for the stainless steel float is brought up to about 70 mm. If a pressure gauge is available one can also follow this on the gauge. (approximately 0.05 p.s.i. increments will result).

(13) Turn stopcock #2 slightly clockwise so as to build up sufficient pressure drop to bring the air/water interface in the sparger down to one centimeter above the neck (point B, Figure III). Check this adjustment from time to time to make sure the interface remains at this level.

(14) Attach concentration column if this

has not yet been done.

(15) Prepare coolant by adding acetone to a large Dewar flask filled with dry ice.

(16) Fill a small Dewar flask with coolant to about 2/3 full. Place it under the concentration column and raise into place. Check the knurled knobs to see that the column is attached tightly. Use pliers if necessary. Fill the Dewar to the brim with crushed dry ice and if necessary add more cold acetone. IMMEDIATELY attach the aluminum shield (Figure XII).
Step (16) should be completed by 1 hour after $t_2$.

(17) At $t_2$ + 75 minutes inject the concentration column into the gas stream by turning stopcock #2 one-quarter turn CW to align the two red marks. Record the following times accurately

as well as the corresponding flow rates.

(a) $t_3$, time of injection

(b) Flow rate (stainless steel float) at beginning and end of concentration.

(c) $t_4$, the exact time of cut out of the concentration column

(18) At exactly $t_3$ + 3 hours, 20 minutes, (200 minutes) cut out concentration column by turning stopcock #2 one-quarter turn CW. Record this exact time.

(19) Remove shield, loosen knurled nuts and remove Dewar with column from the apparatus. Immediately cap column with polyethylene cap (Figure XII) and then drain out acetone, add more dry ice and set aside for later transport to chromatograph.

Procedure for Making Successive Runs

(20) In step (18) when cutting out column return stopcock to its position immediately prior to injection in the column. That is, return it to the position where an artificial pressure drop is set up which causes the air/water interface to be 1 cm above sparger neck (point B, Figure III) with flow rate of about 70 mm.

(21) After removal of concentration column put in new column, tighten nuts, immerse in coolant and attach shield.

(22) Check to see that air/water interface in sparger is at the correct position (point B, Figure III) and if it is not then adjust setting of stopcock #2 ro make it so.

(23) Carry out steps (17) on. Column should be injected into gas stream after a wait of at least 5 minutes

after it was immersed in coolant.

(24) After 2 runs on the same drying tube replace desiccant and carry out steps (9) thru (19) again.

When runs are finished for the day and when the sparger is to be used continuously, the following sequence should be carried out.

(25) After completion of step (18) turn stopcock #1 so that the red mark on the handle is downward and then switch off heating to drying tube.

(26) The pressure head at the compressed air tank should be checked and if it is not 26.0 p.s.i. it should be brought to that value.

(27) When a new run is to be run the drying tube should be heated for 15 minutes prior to turning stopcock #1 to cut in the rest of the line. Then steps (11) thru (19) should be carried

out.

When runs are finished and sparging is to be stopped:

(28) Complete step (25).

(29) Close main tank valve by turning completely clockwise CW. Open reducing valve by turning completely CCW. Close needle valve at tank by turning completely CW. Close needle valve by setting to "O".

(30) When all bubbling has ceased sparger can be removed from solution if so desired and placed in cylinder.

Special Note on Continuous Running of Sparger

When sparger runs continuously, there is observed from day to day a drop in the pressure head required to maintain a flow rate of 70 mm stainless steel. Since a pressure range of 12.0 to 12.4 is

desirable it is suggested that the required head be brought up to this value by:

(1) Turning vernier to "0" and allowing sufficient time for bubbling to nearly case and then slowly open vernier needle valve.

(2) Or opening line ahead of sparger after setting vernier to "0" and then sealing back line and slowly opening needle valve to get desired flow value.

## III. Chromatograph Operation

### A. Preliminary

The following warm up times are recommended prior to sample injection:

| Gain | Warm Up Time - Hours |
|---|---|
| 1 | 3 |
| 5 | 4 |
| 20 | 6 |

(1) Amplifier

(a) Remove protective cover.

(b) Check to see that the proper side of the line cord is grounded (for minimum amplifier noise).

(c) Turn on A.C. Then, after a minute switch on D.C.

(2) Chromatograph

(a) Set Variable transformer to 100.

(b) Turn on heater and blower.

(c) WATCH TEMPERATURE CAREFULLY, and when it reaches 64°C turn variable transformer <u>down to 22</u>.

(d) Meanwhile open the helium tank valve (turn full CCW).

(e) MAKE SURE PRESSURE VALVE ON CHROMATOGRAPH IS FULLY COUNTERCLOCKWISE (CCW).

(f) Turn the "T" handle valve on the reducing valve to bring the pressure up to 45 p.s.i.

(g) SLOWLY turn the pressure valve handle on the chromatograph clockwise to raise the pressure to 29.9 p.s.i.

(h) Check to see that step (c) has been carried out - - - the transformer setting should read 22.

(3) Three hours prior to use or after the instrument has been running for about 2 hours:

(i) If the oven temperature is not 44 ± 0.5°C make a slight increase or decrease in the variable transformer setting, waiting ½ hour between adjustments. One scale division change in the setting will

correspond to about 1°C. No further adjustments should be made within one hour of the run.

(j) Set the Bridge Voltage to 8.00 V.

(k) Check to see that the recorder is plugged in with proper side of the line grounded and see that the recorder power is on but the chart drive is off.

(l) Check the recorder ink and paper and see that the pen writes evenly. See that the chart paper is properly aligned and attach a clip to the end (allowing it to hang over the stand shelf.)

Twenty minutes prior to the attachment of the concentration column:

(m) Adjust chromatograph pressure to 30.0 p.s.i.

(n) Check to see that Bridge is at

8.00.V.

Immediately prior to the attachment to the concentration column:

(o) Raise the pressure slowly to 30.1 p.s.i.

B. Chromatographic Readout of HCN on Concentration Column

(1) Have Hot Water Ready (61°C).

(2) Gently shake the dry ice out of the Dewar flask. Remove column and wipe off loose coolant and immediately remove polyethylene cap.

(3) Bring column and water up to the chromatograph.

(4) Place fittings and "O" rings on the concentration column.

(5) Attach the column on the back of the

gas sampling valve and tighten nuts with end wrench. Do not overtighten or the "O" rings may be damaged.

(6) Add sufficient cold water to the Dewar flask to bring the temperature to 57°C.

(7) Immerse the column in the water, holding the Dewar flask in place with suitable block.

(8) Make a note of the time of immersion on the chart paper.

(9) Set the proper amplifier gain.

For 10 liters concentrated:

| ppb HCN | Gain |
|---|---|
| 0- 200 | 20 |
| 200- 600 | 5 |
| 600-3,000 | 1 |

For 2 liters concentrated:

| | |
|---|---|
| 125- 600 | 20 |
| 600- 2,000 | 5 |
| 2,000-12,000 | 1 |

(10) Set the sensitivity switch on the

chromatograph to "S" and zero the recorder to 80 mm from the left hand side USING THE AMPLIFIER ZEROING CONTROL. To carry out this step the chart drive must be on.

(11) Set sensitivity switch to 1 and again set recorder pen to 80 mm from the left hand side USING CHROMATOGRAPH FINE ZERO CONTROL. It may be necessary to use the coarse zero if the fine control has insufficient range. To do this, unlock the coarse zero adjust and move dial 1 small scale division clockwise or counterclockwise and attempt to zero using fine control. After this step is complete, lock coarse zero and note down its new setting on the chart.

(12) Set sensitivity switch to the following:

| For gain of: | Set sensitivity switch to: |
|---|---|
| 20 | 256 |
| 5 | 64 |
| 1 | 16 |

(13) At 5 minutes after the time of immersion of the column (step 8) turn the gas sampling valve all the way counterclockwise and note exact time on chart.

(14) Exactly 3 minutes later cut out the column by turning the gas sampling valve all the way clockwise.

(15) Turn sensitivity to 1 and zero pen to the above position using chromatograph zero adjust.

(16) Check to see that the correct gain is set and that the sensitivity control is set at 1.

(17) For the runs at gains 5 and 1 the zero drift will be small if sufficient time was allowed for

warmup. If the base line does drift significantly, rezero with the chromatograph fine zero according to judgment. DO NOT MAKE any zero adjustment after 8 minutes after the air peak maximum. Note:

This "according to judgment" might be described by the following examples:

If 10 liters from a 300 ppb solution were being run (gain = 5) one could predict that a resultant HCN peak would be about ½ full scale in height. Thus there could be a considerable amount of zero drift and still the peak might remain on scale.

If the base line were drifting to the left, one could then set the pen up scale about ½ to 1/3 the way. The final zero adjust would be made before 8 minutes after the air peak, the zero would drift downscale to the left and still the entire peak might be recorded.

For runs at a gain of 20 the instrument should be thoroughly warmed up or excessive zero drift will result.

(18) Wait as long as possible after the HCN peak in order that sufficient base line be available for back extrapolation.

(19) Shut off chart drive and proceed with shutdown.

Special Note on Chromatographic Readout

With time the pressure control valve on the chromatograph loses its ability to control precisely. This results in large fluctuations of the base line at high gain settings. The "noise" can be eliminated by leaving the pressure at 29.5 p.s.i. and then bringing it up to 30.1 p.s.i. immediately after cutting out the concentration column (step 14).

## IV. Method of Calculation

### A. Experimental Measurements

(1) Flow rate in mm height of the stainless steel float.

(2) Time of concentration in minutes and seconds.

(3) Temperature of the solution.

(4) Air temperature during concentration (within a degree C).

(5) Gain on chromatograph amplifier.

(6) Area of HCN peak.

### B. Calculation of Total Volume of Air Concentrated.

Use of the calibration curve furnished by Matheson for flow rate in mm on the stainless steel float vs cc./min. and of a

correction factor (obtained from another furnished curve) if the air temperature is different from that used in preparing the standard curves (26° C -- mean --- the correction factor for runs at 20° C is x 1.01) gives the true flow rate in cc./min. Multiplication of this by datum (2) in minutes and tenths gives the total volume concentrated in cc. (we shall call this value (7) ).

C. Preparation of Standard Curves.

Divide datum (6) by (7) and plot the resultant value versus known concentration for the run on a separate piece of graph paper for each gain used (5).

D. Analysis of Unknowns.

(1) 2 Liters of Air Concentrated

(a) Select the appropriate standard curve for the gain used (datum 5).

(b) Divide the peak area (6) by (7) and apply the resultant value to the standard curve to read off directly the HCN concentration in the unknown in moles/liter.

(2) 10 Liters of Air Concentrated

Divide the peak area (6) by 2000 and compare to the standard curve to read off an apparent concentration of HCN, (AC). Multiply AC by 2000/(7) to correct for the difference in volumes and get the true concentration uncorrected for inefficiency of concentration (TCU). Read off the concentration efficiency (from the plot of concentration efficiency vs volume concentrated in Figure XIII) by the use of value (7). We shall call this percent concentration efficiency, (8). Multiply (TCU) by 100/(8) to get the true concentration of HCN in the sample. (TC)

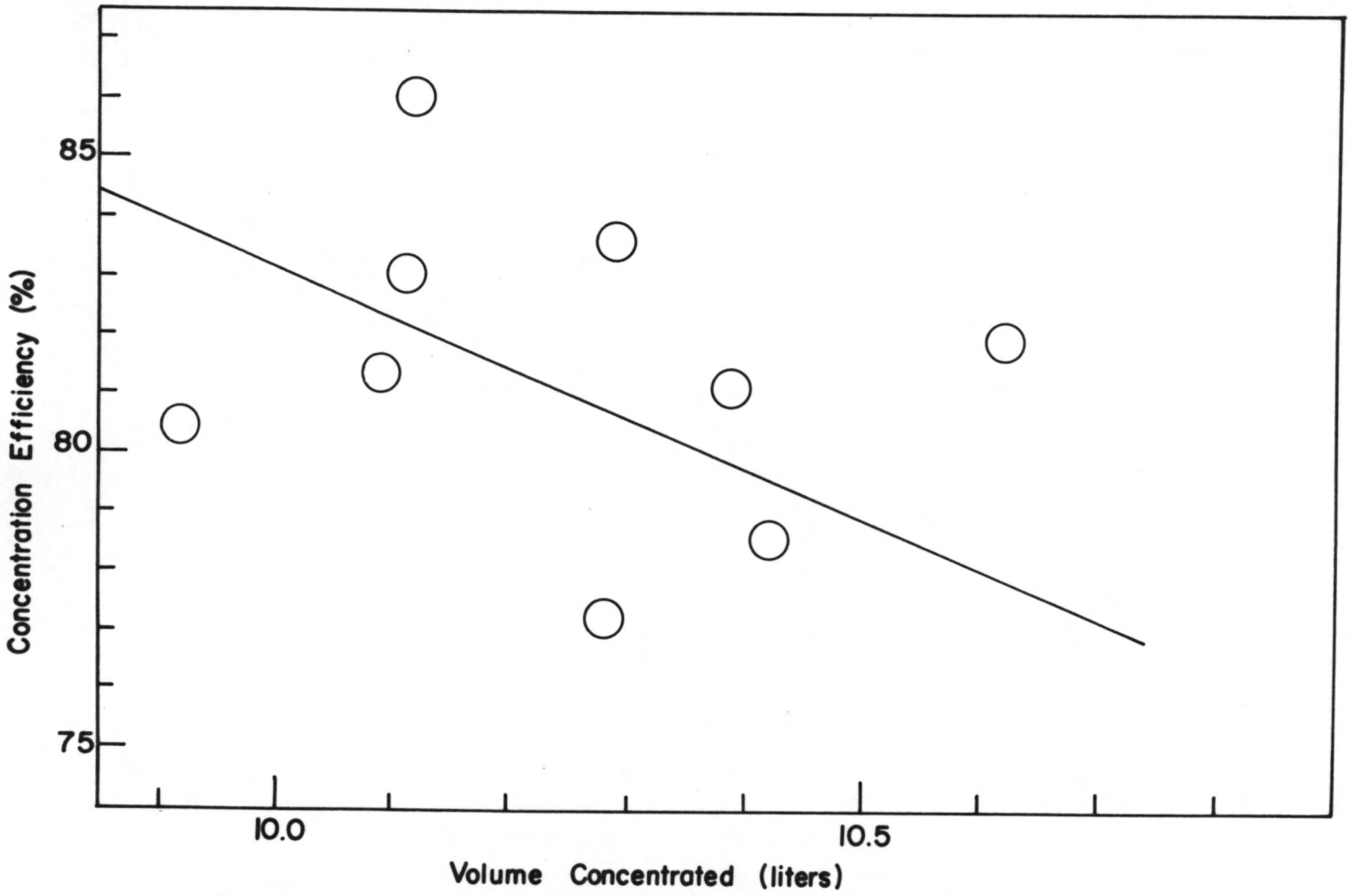


Figure XIII Concentration Efficiency with Volume of Gas

E. Correction for Loss of HCN.

In addition, a small correction may be applied to (TC) to correct for a greater or smaller mean loss of HCN than occurred in the preparation of the standard curves.

(1) Compute the total volume sparged to the mid-point of the concentration step, (9) in cc.

(2) Divide this by the volume of solution in cc. to get a value (10).

(3) Multiply (10) by 0.3% to get the actual percent HCN lost (11).

(4) If (11) is larger than 0.3% increase (TC) by the difference, and if smaller than 0.3% decrease (TC) correspondingly.

F. Example.

1. Unknown No, 1 was prepared and analyzed in the following manner:

An aquarium was filled with 184 liters of a solution of sodium cyanide in creek water. Enough sodium cyanide had been added such that if it hydrolyzed completely the HCN level would be 0.100 ppm. The pH at the beginning and end of the run was 7.4 and 7.8, the mean being 7.6. The calculated HCN level was 0.0985 ppm. Subsequent work has shown that cyanide decomposed (bacterially) in this system at the rate of 0.001 ppm/hr.

The analysis for HCN was carried out as described above (see section II. C. of Procedure), and the resulting chromatogram is shown in Figure IX, above. The base line was obtained by drawing a straight line through the points of intersection of the previous and later slopes with the peak. A planimeter was used to obtain the area in square centimeters.

2. a. Experimental Measurements.

(1) Flow Rate: 70.0 mm, stainless steel float.

(2) Time of Concentration: 201 minutes.

(3) Temperature of Solution: $20^{\circ}$ C.

(4) Air Temperature: $20^{\circ}$ C.

(5) Gain: 20

(6) Area of HCN peak: 45.7 $cm^2$.

b. Calculation of the Total Volume of Air Concentrated

From the calibration curve for the T-600 Matheson Flowmeter (tube: R-2-15-AAA, float: stainless steel), 70.0 mm corresponds to 50.0 cc./min. of air at $70^{\circ}$ C. Correcting this using "Correction Factor Curves for

Matheson Flowmeters" considering the temperature 26° C (that was the average when standards were run) one multiplies by 1.01 to obtain 50.5 cc./min.

Total Volume Concentrated is 50.5 x 201 or 10,150 cc., 10.15 liters.

c. Calculations for 10 Liter Concentration

$\frac{\text{Peak Area}}{2000}$ equals $\frac{45.7}{2000}$ or 0.0228 which when compared to the standard curve for gain of 20 (Figure X) gives an apparent concentration of HCN of $1.465 \times 10^{-5}$ M, AC. Multiplication of AC by $\frac{2000}{10,150}$ gives $2.89 \times 10^{-6}$ M, TCU. The concentration efficiency from page 115 of the procedure is 81.9%, value (8).

Multiplication of TCU by $\frac{100}{81.9}$ gives the true concentration of HCN in the unknown, $3.53 \times 10^{-6}$ M, TC.

d. Correction for Loss of HCN by Sparging

(1) Total Volume Sparged to Run Midpoint

The solution has been sparged for 175 minutes to the midpoint. This, when multiplied by the flow rate, 50.5 cc./min. gives the volume, $8.84 \times 10^3$ cc., (9).

(2) Volume of Solution, is $1.84 \times 10^5$ cc., and division of this value by (9) gives value (10), $4.8 \times 10^{-2}$.

(3) The actual HCN loss is then $4.8 \times 10^{-2} \times 0.3\%$ and is 0.0144%, (11).

(4) Less HCN was lost than in the standardization, the difference being 0.3% and the corrected HCN concentration is then $3.54 \times 10^{-6}$ M. The result is then $3.54 \times 10^{-6} \frac{\text{moles}}{\text{liters}} \times$

27 $\frac{\text{grams}}{\text{mole}}$ or 0.096 ppm.