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GAS-CHROMATOGRAPHIC SEPARATIONS OF RARE GASES

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ADMINISTRATIVE INFORMATION

This work was done as part of a project sponsored by the Office of Naval Research. The project is described in this Laboratory's USNRDL Technical Program for Fiscal Years 1960 and 1961, Revision #2, 1 November 1959, where it is designated as Program A-5, Problem 1.

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## ABSTRACT

A procedure was developed for the separation of the rare gases argon, krypton, and xenon from mixtures containing oxygen and nitrogen by use of gas-chromatographic columns packed with molecular sieve type 5A. Helium was the carrier gas. The method is applicable to mixtures which have been considerably enriched in the rare gases. The procedure involves:

- a. Separation of xenon from oxygen, nitrogen, argon, and krypton on a short column at or above room temperature;
- b. Separation of krypton from oxygen, nitrogen, and argon on a long column at  $-20^{\circ}\text{C}$ ;
- c. Separation of argon from oxygen on the long column at  $-50^{\circ}\text{C}$ .

The net reduced retention volumes and heats of adsorption were determined for oxygen, nitrogen, argon, krypton and xenon on molecular sieves types 4A, 5A and 13X.

Voltage output of the differential thermal conductivity detector was measured as a function of the quantity of gas being measured. It is estimated that the presence of about  $6 \times 10^{-11}$  mole, or 0.1 ppm in 25 cc of sample, can be detected. Quantitative measurements can be made down to about  $5 \times 10^{-9}$  mole, or 10 ppm in 25 cc of sample.

## SUMMARY

### The Problem

Accurate determination of the amount of radioactive contamination released to the atmosphere in the vicinity of nuclear reactors, and from the detonation of nuclear explosives, requires knowledge of the contributions made by radioactive isotopes of the rare gases argon, krypton and xenon. Several processes have been devised and are in use for the separation of these radionuclides from their atmospheric diluents. The gas-chromatographic method has proven useful and economical when applied to a broad range of previously difficult chemical separations. The availability of the remarkable synthetic zeolite adsorbents known as "molecular sieves" has made possible the application of these materials to the gas-chromatographic technique. A complete study of the properties of several different types of molecular sieves with respect to their ability to separate the rare gases from other atmospheric constituents has not previously been made.

### Findings

The retention properties of gas-chromatographic columns packed with three types of molecular sieve materials were determined with respect to the gases oxygen, nitrogen, argon, krypton, and xenon. A separation scheme was developed which can be used to separate individual rare gases from an enriched mixture of impure rare gases. Net reduced retention volumes and heats of adsorption of oxygen, nitrogen, argon, krypton and xenon on the molecular sieve materials were measured. The lower limit at which the rare gases can be detected by the differential thermal conductivity method was determined.

## INTRODUCTION

The atmosphere in the vicinity of nuclear detonations and nuclear reactors contains radioactive isotopes of argon, krypton, and xenon. Krypton and xenon are products of nuclear fission, while radioargon is formed by the capture of neutrons by naturally occurring stable argon. The amount of contamination produced in the atmosphere in this manner can be determined by separating the gaseous radioisotopes from large samples of air collected in the vicinity of the nuclear events.

The problem of quantitatively separating rare gases from air samples of the order of a thousand liters in size essentially involves two steps:

- a. Concentration of the rare gas fraction by removal of extremely large quantities of  $N_2$  and  $O_2$ ;
- b. Separation and purification of the components of the rare gas fraction.

Existing gas chromatographic equipment cannot handle the enormous sample sizes required for Step a. It is also unlikely that necessarily expensive attempts to develop a gas chromatograph capable of handling such large samples could produce much advantage over methods currently being used for the initial bulk separations. Such methods include removal of oxygen and nitrogen by chemical combination with hot reactive metals, concentration of rare gases in large charcoal beds at low temperatures, and fractional distillation of liquid air. These methods are in routine use at other laboratories. However, it is likely that gas chromatographic techniques could be used to great advantage in Step b. Therefore, efforts were concentrated on Step b and were directed toward developing a procedure by which an enriched rare gas mixture could be chromatographically separated into the pure components.

The gas-solid chromatographic technique was chosen as best suited for the separation of atmospheric gases. These gases undergo negligible absorption in gas-liquid partition columns, and in fact are often used in direct measurements of the dead volume of such columns. On the other

hand, the materials used in gas-solid adsorption columns possess much greater adsorptive capacities with respect to the atmospheric gases, and separations based on the different adsorptive characteristics of the gases become feasible.

The literature contains numerous references to the use of charcoal as a gas-chromatographic separating agent. For example, Gleuckauf, Barker, and Kitt<sup>1</sup> separated neon isotopes at  $-196^{\circ}\text{C}$ ; Arrol, Chackett, and Epstein<sup>2</sup> purified xenon and krypton evolved during the chemical treatment of neutron-irradiated uranium; Janak<sup>3</sup> investigated the separation of helium, neon, argon, krypton, and xenon using carbon dioxide as the carrier gas; Turkeltaub and co-workers<sup>4</sup> performed experiments similar to those of Janak;<sup>3</sup> and Gleuckauf and Kitt<sup>5</sup> measured the amounts of krypton and xenon obtained in the distillation of atmospheric air. However, these separations were often difficult to make, and no one has reported the separation of argon from oxygen on charcoal columns.

The rather remarkable adsorptive properties of the artificial zeolites known as "molecular sieves" seemed to offer promise of more useful chromatographic applications than could be obtained from charcoal. Attention was then focussed on the use of these materials in a separation scheme.

Prior to the beginning of these studies data pertaining to the use of molecular sieves in rare gas separations was sparse. Some experimental work had been done by Barrer and Robins,<sup>6</sup> by Greene,<sup>7</sup> by Janak,<sup>8</sup> by Kyryacos and Boord,<sup>9</sup> and by Greene and Pust,<sup>10</sup> among others. However, within the last two years a number of further significant contributions have been made. Janak, Krejci, Dubsy, and Tesarik<sup>11-15</sup> investigated several gas separation problems such as the determination of krypton in the presence of hydrogen and methane, analysis of mixtures of helium, neon and hydrogen, and analysis of mixtures of hydrogen, oxygen, nitrogen, carbon monoxide, and methane; Jay and Wilson<sup>16</sup> used molecular sieves to separate the components of respiratory exhalations; separations of argon from oxygen were reported by Vizard and Wynne,<sup>17</sup> by Mosen and Buzzelli,<sup>18</sup> and by Lard and Horn;<sup>19</sup> and analyses of gases in the environment of nuclear reactors were performed by Malgiolio, Limoncelli, and Cleary,<sup>20</sup> and by Kritz.<sup>21</sup> All of the above cited investigations involved the use only of molecular sieve type 5A.

In the present work the properties of molecular sieve types 4A, 5A, and 13X were studied to determine their applicability to the separation of the atmospheric gases. Preliminary experiments were performed, involving evaluations of the relative separating powers of charcoal versus the molecular sieves, and evaluations of the benefits, if any, from the

use of carrier gases other than helium. These experiments indicated that the most fruitful course for the investigation was to develop a separation scheme based on the use of molecular sieves with helium as the carrier gas. Accordingly, a systematic investigation was made of the retention properties of these materials; the information thus obtained was then used to construct a separation scheme. As a by-product of the investigation, the heats of adsorption of the various gases on the molecular sieve materials were determined; since the heats of adsorption themselves may be of interest to other investigators, they are discussed also. Finally, measurements of peak area as a function of the quantity of gas in an eluted peak were made and estimates are given of the lowest concentrations at which a component of a gas mixture can be detected and measured with a thermal conductivity detector.

## PROCEDURE

### APPARATUS AND TECHNIQUE

The apparatus consists of three main sections (see Figs. 1a and 1b): the sampling system, the chromatographic apparatus, and the collection system. In the sampling system, gas samples were prepared and introduced to the chromatographic apparatus, in which the separations took place. After leaving the chromatographic apparatus, the separated gas fractions entered the collection system, where they were adsorbed on small charcoal traps. The fractions were subsequently desorbed from their traps and either were pumped into evacuated storage bulbs, or were reintroduced to the chromatographic apparatus for further analysis.

A Perkin-Elmer Model 154-B Vapor Fractometer equipped with a gas sampling valve was modified to allow the use of external columns and to bypass the carrier gas pressure regulator. The carrier gas pressure was regulated at the helium supply tank. The carrier gas was passed through a drying tube filled with activated molecular sieve material, and then through two large activated charcoal traps cooled in liquid nitrogen to remove gaseous impurities. Helium was used as the carrier gas in most of the work; a few experiments were performed with nitrogen and oxygen carriers. Flow rates were measured with a rotameter in the chromatographic unit. The gas sampling valve was connected to a manifold in which gas mixtures were prepared, and from which the samples were admitted to a sample loop of known volume.

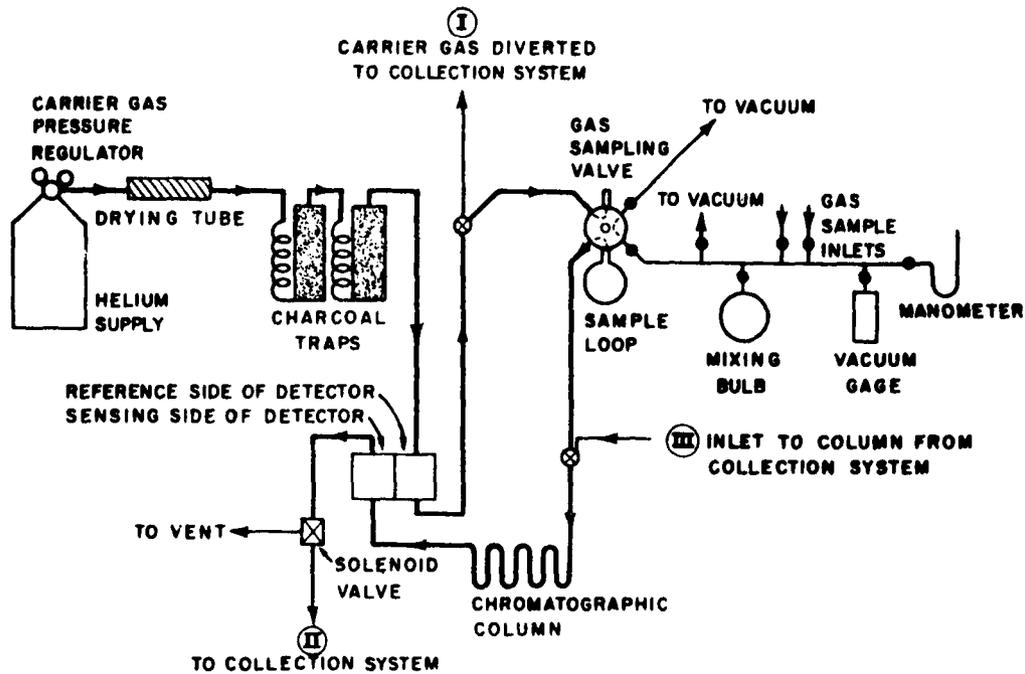


Fig. 1a Schematic Diagram of Sampling System and Chromatographic Apparatus

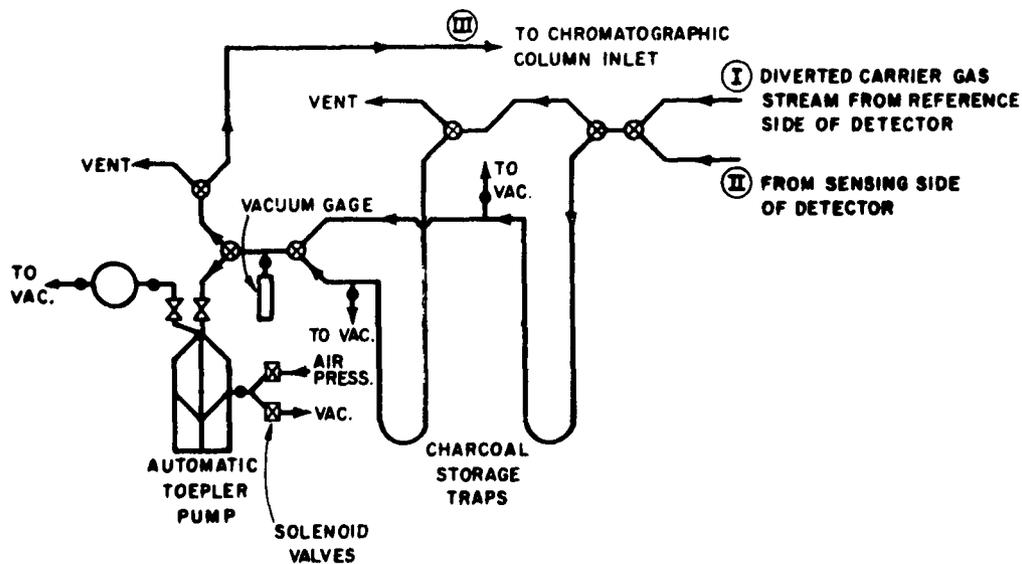


Fig. 1b Schematic Diagram of Collection System

The charcoal column used in the earliest part of this work was supplied by the Perkin-Elmer Corp.; the stationary phase was contained in a helically coiled aluminum tube 10 ft long by 3/16 in. in internal diameter. The author prepared the molecular sieve columns which were used to develop a separation scheme and to gather retention data for the gases involved in the investigation. The molecular sieve material was supplied by the Linde Co. in cylindrical pellets about 1/16 in. long and 1/32 in. in diameter. The pellets were dried overnight at 110°C, pulverized, and the powder was separated into several particle size ranges (12-20, 20-60, 60-80, 80-100 U.S. mesh) by shaking through sieves. The 20-60 and 60-80 mesh fractions were dried for 6 to 8 hrs at 300°C while being purged with dry nitrogen. The dry material was stored in a vacuum dessicator while still hot. The columns were constructed from copper tubing 3/16-in. in internal diameter with 1/32-in. walls. The molecular sieve material was shaken down into the straight tubing while the tubing was vibrated to ensure good packing. The last 6 in. at each end were filled with dry Chromosorb, 60-80 mesh. When the columns were full, the ends were plugged and the tubing was coiled into a series of parallel straight sections, each about 6 in. long. When in use the straight sections were vertical, so that if further settling occurred the formation of channels would be minimized. Each column was dried again at 300°C for 6 to 8 hrs and cooled before using.

The columns were weighed at room temperature before and after filling to determine the weight of the stationary phase.

When in use, the column was immersed in a constant temperature bath. Several cooling media were used, depending on the temperature at which the column was to be operated:

- a. 70° to 0°C: water
- b. 0° to -20°C: NaCl-ice mixtures
- c. 0° to -55°C: CaCl<sub>2</sub>-ice mixtures
- d. -55° to -100°C: methanol cooled with liquid nitrogen.

Eluted fractions which were to be saved for further analysis or for storage were collected on small charcoal traps cooled with liquid nitrogen. To desorb a fraction, helium was pumped off and the traps were warmed to 80-100°C. If the fraction was to be analyzed further, the carrier stream was diverted through the trap after leaving the reference side of the detector. If the fraction was to be stored, it was transferred to an evacuated storage bulb with an automatic Toepler pump.

A novel feature of the control unit for the automatic Toepler pump is the use of a latching relay to activate two solenoid valves

which regulate the application of air pressure and vacuum to the lower chamber of the pump.\*

The detector was of the standard thermal-conductivity type, consisting of thermistor beads in each chamber connected as arms of a balanced bridge circuit. The voltage output was recorded by a graphic recorder with ranges of 0-1, 0-10, 0-100, or 0-1000 mv. In the case of an extremely small eluted peak, the detector output was amplified by a DC amplifier with a 1-v output. In this way detector signals in the micro-volt region could be recorded.

The samples run for the purpose of determining retention parameters were 0.25 cc in volume and consisted of binary or ternary mixtures with roughly equal quantities of components. These samples were run at a column inlet pressure of 10 psig.

Detector sensitivity was determined by measuring the area of recorded peaks as a function of the quantity of rare gas being analyzed. The samples were run through a 10-ft by 3/16-in. internal diameter column packed with Chromosorb, and the detector was thermostatted at 40°C. This was done for argon samples ranging in size from  $10^{-3}$  to  $3 \times 10^{-10}$  moles, for krypton from  $10^{-3}$  to  $2 \times 10^{-5}$  moles, and for xenon from  $10^{-3}$  to  $3 \times 10^{-8}$  moles. The larger samples were introduced into the carrier stream from a 25-cc sample loop, the sample pressure being varied to change the quantity of sample. The smaller samples were introduced in the same manner, but using a 0.25-cc loop. Below  $10^{-7}$  mole, the argon was diluted with helium in order to obtain reliable sample pressure measurements. However, at the  $10^{-8}$  mole level, contaminants in the helium, which are not separated from argon on Chromosorb, began to make significant contributions to peak areas. Corrections were made by subtracting the peak areas obtained from blank helium samples. The helium was found to be contaminated to the extent of about 0.08 %, probably air.

The maximum sample size that could be handled efficiently by the 10-ft by 3/16-in. columns was 25 cc. Above 25 cc, peak broadening and flattening became increasingly severe, and above 100 cc the columns began performing frontal analyses rather than elution analyses.

A larger column, 20 ft long by 3/8-in. in internal diameter and packed with 10-40 mesh molecular sieve 5A, tolerated samples as large as 100 cc. However, because of its size, this column was operated only at room temperature and gave very poor resolution. Samples as large as one liter produced typical frontal analyses on the large column.

\*The use of a latching relay was suggested by Mr. P.R. Werp, and the control unit was constructed by Mr. Bruce Euler.

## TREATMENT OF DATA

### Retention Volumes

The raw data consist of graphic recordings of the detector voltage output as a function of the elapsed time since the instant of sample injection. The time required for the appearance of the maximum of a chromatographic peak includes not only the time spent on the column stationary phase, but also the time required for the sample to travel from the injection point to the beginning of the column, through the column dead space, and from the end of the column to the detector. Due to the adsorptive properties of the stationary phases used in this work, the column and apparatus dead times were not measured directly.

The observed retention time,  $t_R$ , defined as the time between injection of the sample and the appearance of the peak maximum, is converted to the reduced retention volume,  $V_o$ , by the relationship

$$V_o = \frac{273}{T} j t_R F_c$$

where  $T$  is the column-operating temperature in degrees Kelvin,  $j$  is the pressure-drop correction factor, and  $F_c$  is the volumetric flow rate of the carrier gas corrected to the column outlet pressure and column temperature. The quantity  $V_d$ , the reduced dead volume, is defined by

$$V_d = \frac{273}{T} V'_m$$

where  $V'_m$  is the corrected dead volume. (The derivations of the equations for  $V_o$  and  $V_d$  are given in detail in Appendix A.)

It can be shown<sup>10</sup> that the variation with temperature of the quantity  $(V_o - V_d)$ , the net reduced retention volume, is given by

$$V_o - V_d = V_s e^{-\Delta H_a/RT} \quad (1)$$

where  $V_s$  is a constant,  $\Delta H_a$  is the heat of adsorption of the sample gas on the stationary phase, and  $T$  is the column temperature. A similar expression can be derived for the case of gas-liquid partition chromatography.<sup>22</sup> Then assuming that  $\Delta H_a$  remains constant over the temperature

range considered, the plot of  $\ln (V_G - V_d)$  versus reciprocal temperature will be a straight line with intercept equal to  $\ln V_G$  and slope equal to  $-\Delta H_0/R$ . In order to construct such plots for a given column, the value of  $V_M^i$  for that column must be known. Since  $V_M^i$  was not obtained experimentally, a mathematical analysis of the data, based on the method of least squares, was used to determine  $V_M^i$  for each column, and  $V_G$  and  $\Delta H_0/R$  for each gas on each stationary phase. (Argon and oxygen were not retained by molecular sieve 4A between  $-95^\circ$  and  $25^\circ\text{C}$ , and krypton and nitrogen were not retained above  $-40^\circ\text{C}$ . These data were fitted to the dead volume equation,  $V_d = 273/T V_M^i$ .) The procedure used in the analysis is set forth in detail in Appendix B.

### Peak Resolution

The expression for resolution suggested by Phillips<sup>23</sup> was used. If two peaks are eluted in sequence under identical operating conditions, the resolution,  $R$ , is given by

$$R = \frac{t_{R_2} - t_{R_1}}{\frac{1}{2} w_1 + \frac{1}{2} w_2}$$

where  $t_{R_1}$  and  $t_{R_2}$  are the retention times, and  $\frac{1}{2} w_1$  and  $\frac{1}{2} w_2$  the peak half-widths measured in units of time. Since the peak shapes obtained in this work were usually slightly asymmetrical, peak half-widths were obtained in the manner illustrated in Fig. 2. Tangents to the peaks at the inflection points of the adjacent sides of the two peaks were extended to the base line; the half-width for each peak was then taken to be the distance along the base line between the intersection of the tangent with the base line and the time of appearance of the peak maximum.

### Peak-Area Measurements

Peak areas were measured directly from the graphical recordings with a compensating polar planimeter. These areas were then converted from units of square inches to millivolt-cubic centimeters by using the formula:

$$A = \frac{r \cdot F}{w \cdot V} \cdot S$$

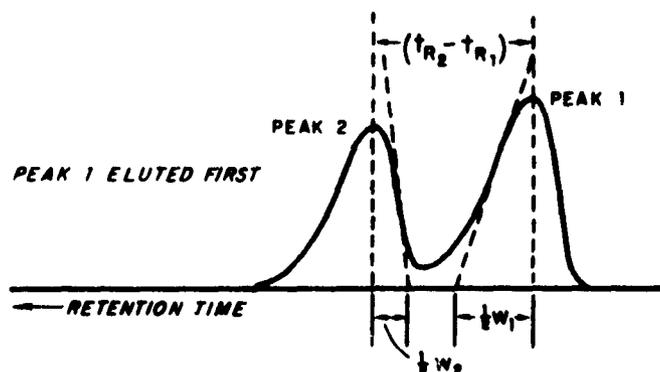


Fig. 2 Method of Determining Peak Half Widths

where  $A$  is the derived area in millivolt-cubic centimeters,  
 $S$  is the measured area in square inches,  
 $r$  is the recorder span in millivolts,  
 $F_c$  is the carrier gas flow rate in cubic centimeters per minute,  
 $w$  is the width of the chart paper in inches,  
 $V$  is the chart speed in inches per minute.

## RESULTS AND DISCUSSION

### PRELIMINARY EXPERIMENTS

Preliminary qualitative experiments with the charcoal column and with a column containing coarsely ground (about 20-60 mesh) molecular sieve type 5A showed that the latter type of column could provide better and more useful separations, although it did not have as high a capacity as the charcoal column. Also, the charcoal column would not separate argon from oxygen, while it was anticipated that these gases could be separated on a molecular sieve column. Because of these considerations, subsequent work was directed toward the use of molecular sieves. The separating properties of the three types of molecular sieve investigated, 4A, 5A, and 13X, were determined, and the usefulness of each in a separation scheme evaluated.

The particle size range of 60-80 mesh was found to be the optimum range for the stationary phase. The particles in this size range are small enough to give reasonably symmetrical peaks with a minimum of tailing, yet they are large enough so that very high column inlet pressures and low flow rates can be avoided.

The use of oxygen and nitrogen as carrier gases was investigated. These gases produced slightly poorer resolution than did helium, and they frequently gave rise to spurious detector responses which obscured the appearance of genuine peaks. These spurious responses were attributed to flow surges in the exit of the column caused by a temporary increase in pressure accompanying the desorption of a gaseous fraction from the column stationary phase.

#### RETENTION DATA

Tables 1, 2, and 3 list the values obtained for the retention parameters  $V_M$ ,  $V_S$ , and  $\Delta H_a$ , for the three molecular sieve columns used most frequently during the investigation. The carrier gas was helium. Values are also given for  $S_n$  and  $n_n$ .  $S_n$  is defined in Appendix B as the sum of the squares of the deviations of the observed from the calculated net reduced retention volumes; the observed net reduced retention volumes were obtained by subtracting the calculated dead volumes  $V_d$  from the experimentally determined reduced retention volumes  $V_o$ .  $n_n$  is the number of experimental points used in the analysis.

The heats of adsorption of argon, oxygen, krypton, and nitrogen on molecular sieve type 5A have also been measured by Greene and Pust;<sup>10</sup> the results are reproduced in Table 4.

These values are consistently lower than those determined in this work, which are given in Table 2. Both sets of values are within the range (~ 1-5 kcal/mole) expected for adsorption due to van der Waals interactions between adsorbent and adsorbate.

Greene and Pust dried their columns for 2 hr at 150°C; the columns used in the present work were dried for 6 to 8 hr at 300°C. It seems likely that the treatment used by Greene and Pust did not completely purge the molecular sieve material of entrapped water. Janak, Krejci, and Dubskey<sup>11</sup> have shown that the presence of very small amounts of water can radically change the adsorptive properties of molecular sieves. Entrapped water could prevent other gases from diffusing through the porous, cage-like structure<sup>24</sup> of the sieve material.

TABLE 1

## Retention Parameters for 4A Column

Dimensions: 10-ft long by 3/16 in. in internal diameter.  
 Stationary phase: 42 gm molecular sieve type 4A, 60-80 mesh.  
 Carrier gas: Helium

	Ar <sup>a</sup>	O <sub>2</sub> <sup>a</sup>	Kr <sup>b</sup>	N <sub>2</sub> <sup>b</sup>	Xe
V <sub>s</sub> (cc)	-	-	1.8 x 10 <sup>-5</sup>	3.83 x 10 <sup>-4</sup>	1.54 x 10 <sup>-3</sup>
-ΔH <sub>s</sub> (cal/mole)	-	-	5770	4340	4830
S <sub>h</sub> (cm <sup>6</sup> )	477		49	55	391
n <sub>h</sub>	15		4	4	7
V <sub>M</sub> <sup>i</sup> = 130 cc					

a. Ar and O<sub>2</sub> not retained over temperature range studied; data were fitted to

$$V_0(\text{Ar} + \text{O}_2) = \frac{273}{T} V_M^i$$

b. Kr and N<sub>2</sub> not retained above -40°C; data above -40°C were fitted to

$$V_0(\text{Kr} + \text{N}_2) = \frac{273}{T} V_M^i$$

TABLE 2

## Retention Parameters for 5A Column

Dimensions: 10 ft long by 3/16-in. in internal diameter.  
 Stationary phase: 39 gm molecular sieve type 5A, 60-80 mesh.  
 Carrier gas: Helium.

	Ar	O <sub>2</sub>	Kr	N <sub>2</sub>	Xe
V <sub>s</sub> (cc)	0.254	0.183	0.463	0.0270	0.462
-ΔH <sub>s</sub> (cal/mole)	3540	3800	4140	5790	5310
S <sub>h</sub> (cm <sup>6</sup> )	780	1482	867	637	184
n <sub>h</sub>	8	8	6	6	3
V <sub>M</sub> <sup>i</sup> = 216 cc					

TABLE 3

## Retention Parameters for 13X Column

Dimensions: 10 ft long by 3/16 in. in internal diameter.  
 Stationary phase: 32 gm molecular sieve type 13X, 60-80 mesh.  
 Carrier gas: Helium.

	Ar	O <sub>2</sub>	Kr	N <sub>2</sub>	Xe
V <sub>g</sub> (cc)	0.103	0.111	0.324	0.0498	0.573
-ΔH <sub>a</sub> (cal/mole)	3540	3570	3910	4790	4760
S <sub>h</sub> (cm <sup>2</sup> )	3567	5051	3189	5835	13491
n <sub>h</sub>	9	18	8	14	4
V <sub>M</sub> ' = 209 cc					

TABLE 4

## Heats of Adsorption on Molecular Sieve 5A\*

Gas	-ΔH <sub>a</sub> (cal/mole)
Ar	1510
O <sub>2</sub>	2040
Kr	3150
N <sub>2</sub>	4170

\*Data taken from Table IV of reference 10.

Brunaue,<sup>25</sup> in his discussion of heats of adsorption, cites evidence to show that heats of adsorption are considerably larger, due to effects associated with surface tension in capillaries, if the adsorption occurs in crevices, tubes or cells of the adsorbent, than if it occurs on plane surfaces. Also, dispersion forces would be expected to play a more important role in increasing the heat of adsorption in the interior of the crystal where the adsorbate molecule can come in contact with a larger number of lattice ions than on the outside.<sup>26</sup>

Therefore, the higher heats of adsorption measured in this work are attributed to the effects resulting from greater penetration of the molecular sieve crystal structure by the adsorbate atoms, due to the more drastic drying treatment to which the molecular sieve material was subjected.

Graphs showing  $\ln (V_0 - V_d)$  plotted against reciprocal temperature, using the parameters listed in Tables 1, 2, and 3, are presented in Figs. 3, 4, and 5. Figure 3 also shows plots of  $\ln V_0$  versus reciprocal temperature for the five gases on the 4A column. Although a cross-over in the  $\ln (V_0 - V_d)$  curves is shown at  $-70^\circ\text{C}$ , krypton and nitrogen were not actually separated above this temperature.

In Fig. 5, although the curves for argon and oxygen indicate that these gases might be separated from each other over the whole temperature range, no separation was actually observed above  $-40^\circ\text{C}$ .

Similarly, referring to Fig. 4, no separation of argon from oxygen was observed above  $0^\circ\text{C}$ .

The shaded and hatched areas indicate regions in which resolution varied from zero to unity, and from unity to two, respectively. Open areas between curves indicate resolution greater than two. Since resolution depends to some extent on the relative sample sizes, the resolution values indicated in the figures are strictly valid only for mixtures in which the components are present in approximately equal amounts (about 0.10 cc of each gas); the values are intended to serve only as an indication of the kind of separations that can be obtained on the types of columns used here.

#### DEVELOPMENT OF SEPARATION SCHEME

Three general requirements are imposed on a rare gas separation scheme by the fundamental characteristics of gas-solid chromatography:

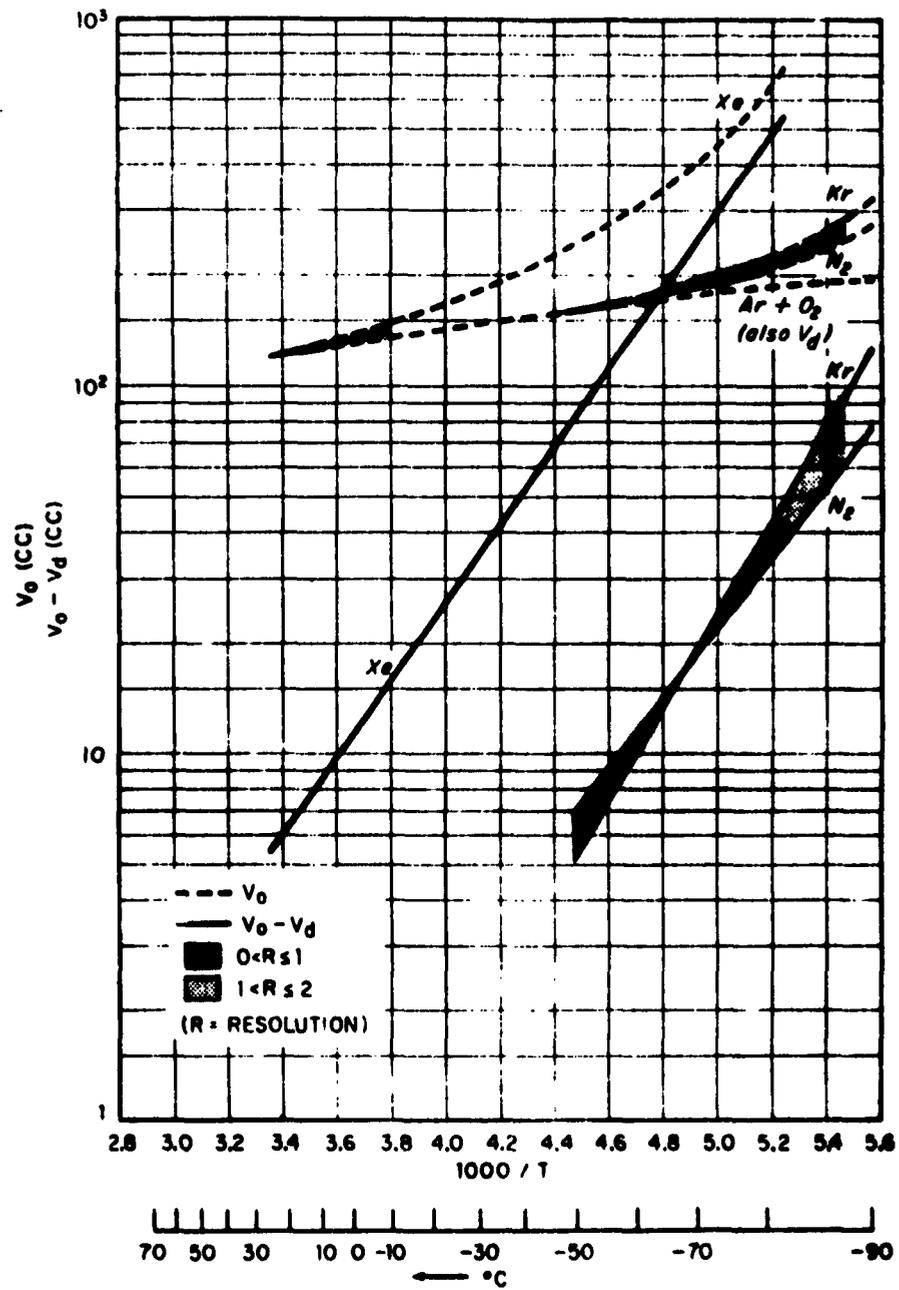


Fig. 3 Reduced Retention Volumes of Ar, Kr, Xe, O<sub>2</sub>, N<sub>2</sub> and Net Reduced Retention Volume of Kr, Xe, N<sub>2</sub> Through 42 Grams of Molecular Sieve Type 4A

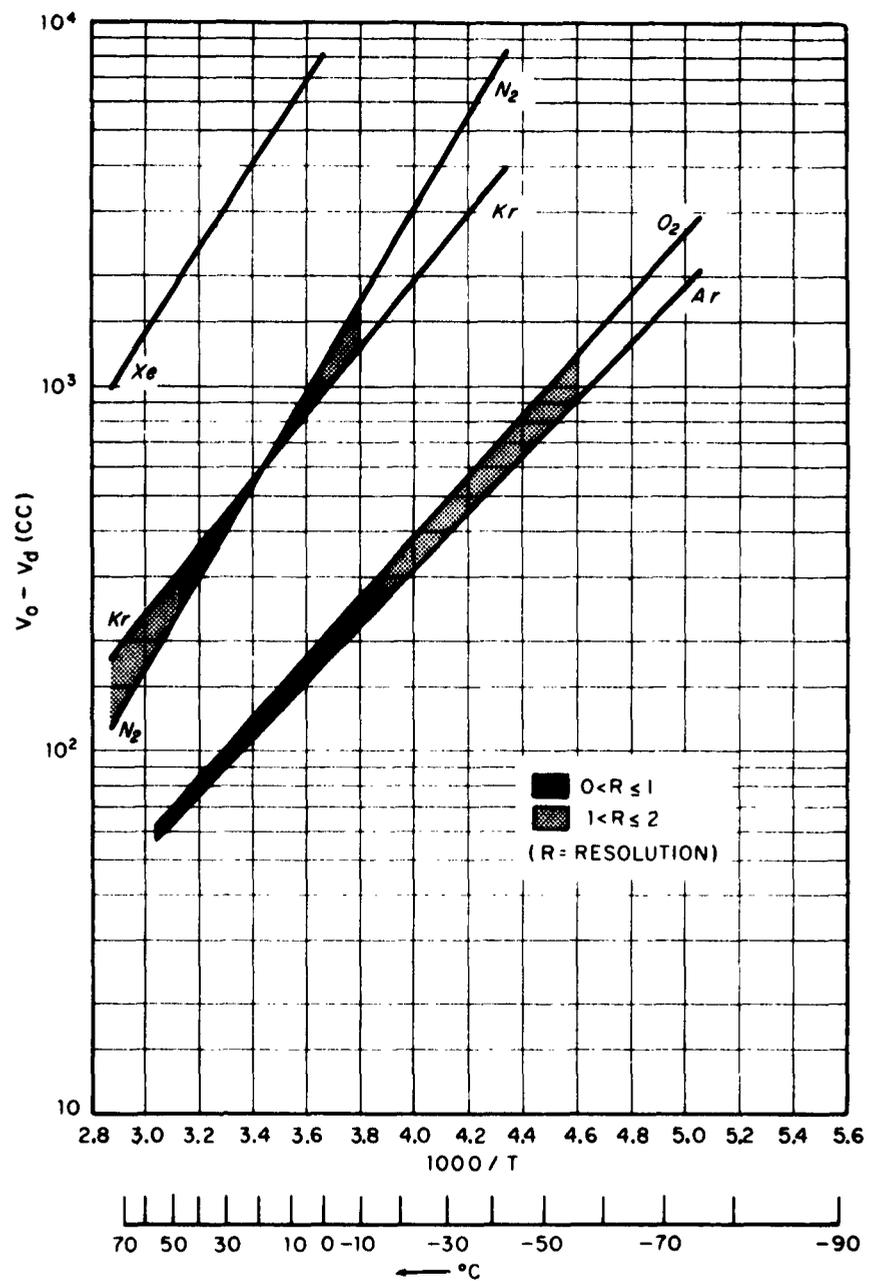


Fig. 4 Net Reduced Retention Volumes of Ar, Kr, Xe, O<sub>2</sub>, N<sub>2</sub> Through 39 Grams of Molecular Sieve Type 5A.

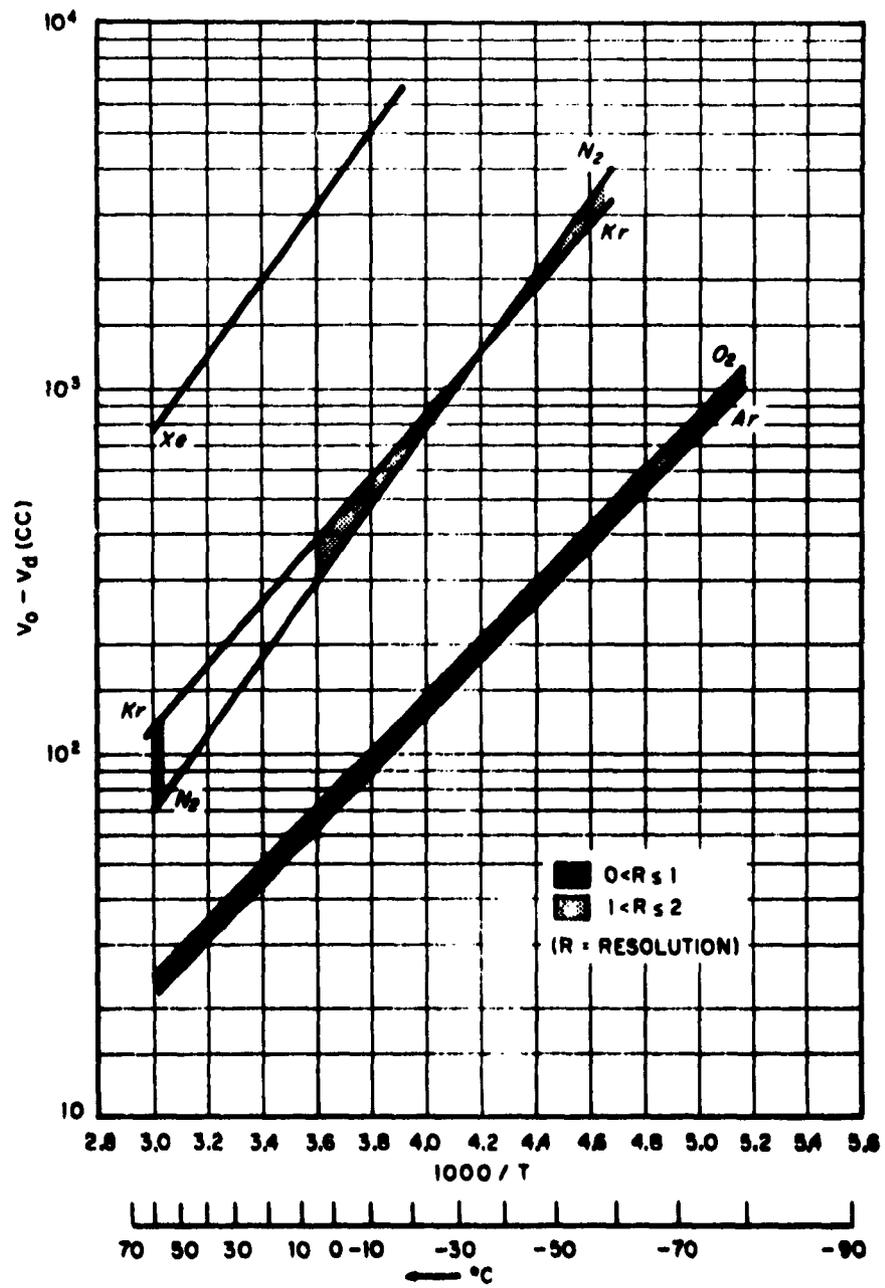


Fig. 5 Net Reduced Retention Volumes of Ar, Kr, Xe, O<sub>2</sub>, N<sub>2</sub> Through 32 Grams of Molecular Sieve Type 13X

- a. Due to the nature of the phenomena that occur in a gas-solid column, the eluted peaks will generally exhibit sharply rising fronts and more slowly decreasing tails. Since a minor component is liable to be obscured by the tail of a closely preceding major component, the column stationary phase and operating temperature should be chosen so that the minor component is eluted before the major component.
- b. Retention volumes should be kept small to reduce peak broadening associated with large volumes.
- c. The column should have a capacity high enough to perform efficiently with the sample sizes to be used.

Examination of the retention data for the three molecular sieve columns shows that a mixture of nitrogen, oxygen, argon, krypton and xenon will, in general, be eluted in groups in the order oxygen plus argon, nitrogen plus krypton, and finally xenon. This suggested the possibility of making preliminary group separations followed by individual separations of the components of each group, using the optimum conditions for each separation. Efforts were also made to operate the columns at as high a temperature as possible to reduce retention volumes.

The 4A column was the first choice for the xenon separation, primarily because of its speed. However, it was found that the 4A material does not have a capacity large enough to prevent the single peak due to nitrogen, oxygen, argon and krypton from running over into the following xenon peak when 25-cc samples are used. For this reason a short 5A column (3 ft long by 3/16 in. in internal diameter) was constructed and was found quite satisfactory for the separation of xenon in the temperature range +20 to +60°C.

Both the 5A and 13X columns appeared useful for separating the nitrogen-krypton group from the oxygen-argon group. The first approach was use of the 13X column at room temperature. The oxygen-argon group appears first and could be stored on charcoal for subsequent analysis. The next peak to appear is nitrogen, with krypton following on the nitrogen tail. It was anticipated that the major part of the nitrogen peak could be removed and only that part of the tail containing krypton preserved, thus eliminating most of the undesirable major component. The krypton would then be purified in another analysis. This did not prove feasible because of difficulty in detecting the krypton peak.

Krypton can be separated from nitrogen (and other gases) on the 5A column below -20°C. The krypton peak is eluted before the nitrogen peak.

If the oxygen-argon group is present in the initial mixture fed to this column, this group will be eluted well before krypton appears, and can be preserved for subsequent separation of argon.

Argon can be separated from the oxygen-argon group on the 5A column below  $-20^{\circ}\text{C}$ , although good resolution ( $R \geq 2$ ) is obtained only below  $-50^{\circ}\text{C}$ . Argon is eluted before oxygen.

Although the 13X column exhibits lower retention volumes (and less peak broadening) than the 5A column, and has almost as high a capacity, these advantages are outweighed by the disadvantage of obscuration of the krypton peak and by the advantages of the 5A column in producing more complete separation and reversal of elution sequence in the nitrogen-krypton group.

In summary, the final separation procedure is as follows (see Fig. 6):

- a. A 25-cc sample consisting of nitrogen, oxygen, argon, krypton and xenon, and free of water and carbon dioxide,\* is analyzed on a short 5A column (3 ft long by 3/16 in. in internal diameter) at a temperature between  $+20$  and  $+60^{\circ}\text{C}$ . The first peak (actually two incompletely resolved peaks) containing nitrogen, oxygen, argon and krypton is trapped on charcoal at  $77^{\circ}\text{K}$ . The second peak, following some time later, is xenon.
- b. The fraction containing nitrogen, oxygen, argon and krypton is desorbed from its trap at  $100^{\circ}\text{C}$  and is analyzed on a long 5A column (10 ft long by 3/16-in. in internal diameter) at  $-20^{\circ}\text{C}$ . The oxygen-argon group appears first as two closely overlapping peaks. This fraction is trapped on charcoal at  $77^{\circ}\text{K}$ . Krypton appears next. Nitrogen closely follows krypton, and is vented.
- c. The oxygen-argon fraction is desorbed from its trap and is analyzed on the same column used in Step b, at  $-50^{\circ}\text{C}$ . Argon is eluted first, closely followed by oxygen, which is vented.
- d. Each individual pure gas fraction can be trapped separately on charcoal for temporary storage until the procedure is completed.

It will be noted that molecular sieve type 5A is used exclusively in the procedure. This is because of its versatility and usefulness in a procedure involving several difficult separations. The molecular sieve types 4A and 13X can also be quite useful, and in some respects might even be better for other less difficult separations such as argon or krypton from xenon, argon from krypton, oxygen from nitrogen or krypton, and so forth.

~~Water~~ and  $\text{CO}_2$  are irreversibly adsorbed on molecular sieve columns.

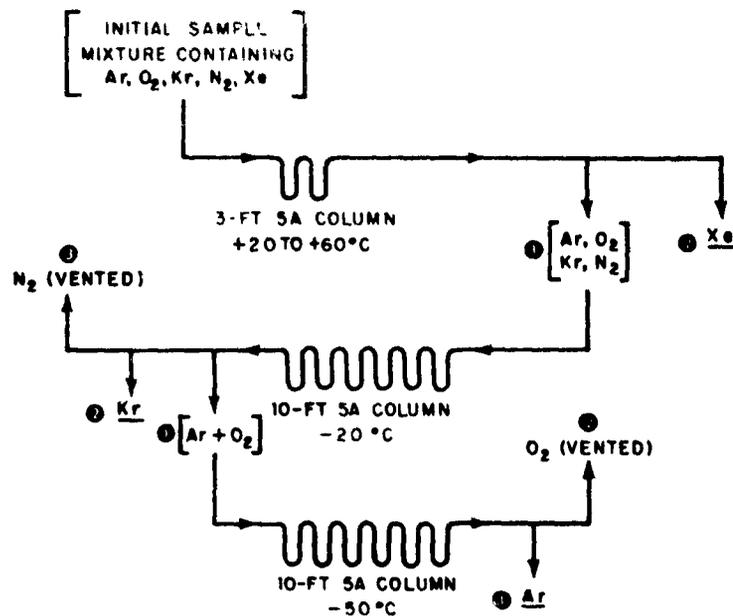


Fig. 6 Flow Chart for Rare Gas Separations (numbers indicate elution sequence)

#### PEAK AREA MEASUREMENTS

Results of peak area measurements are shown in Figs. 7 and 8, where  $\log A$  is plotted as a function of  $\log n$  (where  $n$  is the number of moles of gas giving rise to a peak). Krypton and xenon are detectable at lower concentrations than is argon, since they give slightly larger detector responses when helium is used as the carrier gas; for this reason only argon was studied in the region of very small sample sizes, in order to establish an upper limit to the ultimate response of the detector to these gases.

The relationship between peak area and sample size for argon was found to be linear between  $3 \times 10^{-10}$  and  $1 \times 10^{-5}$  mole. Least squares analysis of the data in Fig. yielded the equation:

$$A = (0.945 \times 10^7) n$$

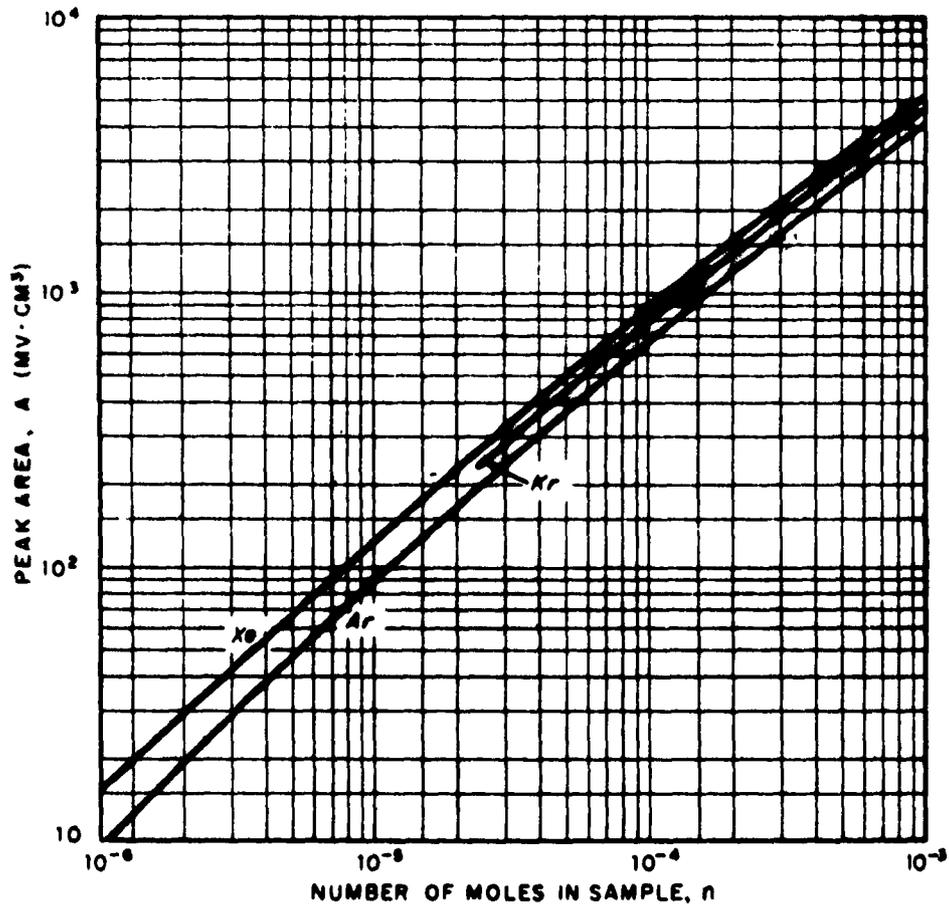


Fig. 7 Peak Area vs Sample Size for Argon, Krypton, Xenon

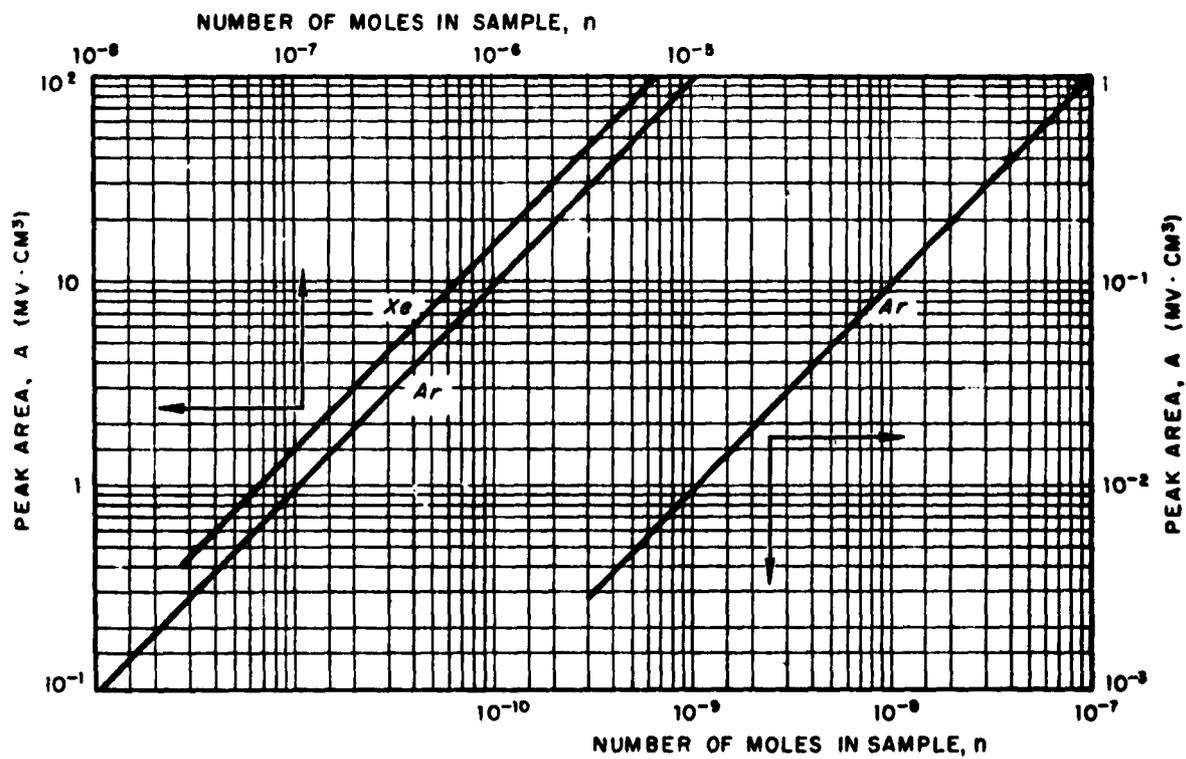


Fig. 8 Peak Area vs Sample Size for Argon and Xenon

where  $n$  is in moles and  $A$  is in millivolt-cubic centimeters. The proportionality constant is valid only for the detector used in this work.

Examination of Fig. 7 shows that the relationship is not linear for sample sizes greater than  $10^{-5}$  mole due to the non-linear relationship between thermal conductivity and composition of gas mixtures at these concentrations.

The peak area measurements indicate that with suitable amplification, quantitative measurements of the quantity of gas in an eluted peak can be made down to about  $5 \times 10^{-9}$  mole. Below  $5 \times 10^{-9}$  mole, noise fluctuations in the detector output render peak area measurements increasingly inaccurate.

However, the presence of a peak can be detected at much lower levels. The smallest sample measured, corresponding to  $5 \times 10^{-10}$  mole of argon, enclosed an area on the strip chart recording of 8.7 in.<sup>2</sup> (very easy to see), with the chart moving at a speed of 8 in./min and a chart span corresponding to 20 $\mu$ v output from the detector. The maximum height of this peak corresponded to 17  $\mu$ v while the noise amplitude was about 2  $\mu$ v. If we say that we can detect a peak only when its maximum amplitude is greater than twice that of the noise, or 2  $\mu$ v above the noise, then we should be able to detect peaks containing as little as  $6 \times 10^{-11}$  mole. This corresponds to about 0.1 ppm of the quantity of gas that occupies a volume of 25 cc at STP. Krypton and xenon will be detectable at slightly lower concentrations. Thus if only small amounts of isotopic carriers for krypton and xenon are added to large air samples, no difficulty should be experienced in seeing the krypton and xenon peaks from enriched chromatographic samples from which most of the oxygen and nitrogen have been removed.

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## APPENDIX A

### CALCULATION OF REDUCED RETENTION VOLUMES FROM OBSERVED RETENTION TIMES

The (uncorrected) retention volume,  $V_R$ , is the volume of carrier gas which has passed through the chromatograph between the time of sample injection and the time of appearance of the peak maximum, and is given by

$$V_R = t_R F_C$$

where  $t_R$  is the observed retention time and  $F_C$  is the volumetric flow rate of the carrier gas corrected to the column outlet pressure and column temperature.  $V_R$  is composed of the apparatus and column dead volume  $V_M$ , and the adjusted retention volume  $V_R^i$ ; thus

$$V_R^i = V_R - V_M$$

The corrected retention volume  $V_R^O$  is given by

$$V_R^O = jV_R = jV_M + jV_R^i$$

The quantity  $j$  is the correction factor for the effect of the pressure gradient through the column, and is given by

$$j = \frac{3}{2} \frac{(p_1/p_0)^2 - 1}{(p_1/p_0)^3 - 1}$$

where  $p_1$  and  $p_0$  are the pressures of the carrier gas at the inlet and the outlet of the column, respectively. During the runs in which data to be used for the determination of retention parameters were collected,

$j$  varied only from 0.562 to 0.564.  $j$  was then considered constant, and the dead volume terms were combined into a single constant term  $V_M'$ , the corrected dead volume, given by

$$V_M' = jV_M$$

$V_R^o$  is then adjusted to 0°C, yielding  $V_o$ , the reduced retention volume:

$$V_o = \frac{273}{T} V_R^o = \frac{273}{T} jV_M + \frac{273}{T} jV_R', \quad (\text{A.1})$$

where  $T$  is the column-operating temperature in degrees Kelvin.

If the quantity  $V_d$ , the reduced dead volume, is defined by

$$V_d = \frac{273}{T} V_M'$$

Eq. A.1 becomes

$$V_o = V_d + \frac{273}{T} jV_R'$$

Also,

$$V_o = \frac{273}{T} j t_R F_c$$

APPENDIX B

ANALYSIS OF RETENTION DATA

Equation 1 can be rewritten as

$$\ln (y - 273 a x) = b + c x \quad (\text{B.1})$$

by taking the logarithms of both sides and using the substitutions

$$\begin{aligned} V_d &= \frac{273}{T} V_M' \\ y &= V_o, & x &= \frac{1}{T} \\ a &= V_M' \\ b &= \ln V_s \\ c &= -\Delta H_a/R \end{aligned}$$

We divide the data\* for all gases on the column of interest into five sets, one for each gas, each set containing  $n_h$  data, and define a group of conditional equations:

$$\ln (y_{n_h} - 273 a x) = b_{n_h} + c_{n_h} x \quad (5 \text{ eq'ns}) \quad (\text{B.2})$$

\*Care must be exercised in choosing the data to be included in the analysis. If a gas is not adsorbed on the column stationary phase; i.e., if  $V_o - V_d = 0$ , the left hand side of Eq. B.1 becomes infinite and the analysis breaks down immediately. This was the case with the 4A column used in this work; argon and oxygen were not retained over the whole temperature range investigated, while krypton and nitrogen were not retained above  $-40^\circ\text{C}$ . These data were fitted to the equation

$$V_o = \frac{273}{T} V_M'$$

where the index h refers to one particular gas. Now we define the functions  $F^h$  by

$$F^h = \ln (y_h - 273 a x) - b_h - c_h x = 0$$

First derivatives of  $F^h$  are represented by

$$F_{y_{hi}}^h = \frac{\partial F^h}{\partial y_{hi}}, F_a^h = \frac{\partial F^h}{\partial a}, F_{b_h}^h = \frac{\partial F^h}{\partial b_h}, F_{c_h}^h = \frac{\partial F^h}{\partial c_h}$$

Let the functions  $F_{oi}^h$  represent  $F^h$  evaluated at each appropriate observed datum  $(Y_{hi}, x_{hi})$ , thus:

$$F_{oi}^h = \ln (Y_{hi} - 273 a_o x_{hi}) - b_{ho} - c_{ho} x_{hi}$$

where  $a_o, b_{ho}, c_{ho}$  are initial estimates of  $a, b_h, c_h$  arrived at by any convenient method. The derivatives of  $F^h$  then become

$$F_{y_{hi}}^h = (Y_{hi} - 273 a_o x_{hi})^{-1}, F_{a_i}^h = -273 x_{hi} F_{y_{hi}}^h$$

$$F_{b_{hi}}^h = -1, F_{c_{hi}}^h = -x_{hi}$$

We define the residuals  $V_{hi}, A, B_h, C_h$  by

$$V_{hi} = Y_{hi} - y_{hi},$$

$$A = a_o - a,$$

$$B_h = b_{ho} - b_h,$$

$$C_h = c_{ho} - c_h$$

We assume that there is no error in x. All data are weighted equally.

We now expand  $F^h$  in Taylor's series around  $a_o, b_{ho}, c_{ho}$ , and  $Y_{hi}$ , retaining only the first order derivatives of  $F^h$ . The expansion yields:

$$F^h = 0 = F_{oi}^h + F_{ai}^h (a - a_o) + F_{bhi}^h (b_h - b_{ho}) + F_{chi}^h (c_h - c_{ho}) + F_{yhi}^h (y_{hi} - Y_{hi})$$

or

$$F_{oi}^h = F_{yhi}^h V_{hi} + F_{ai}^h A + F_{bhi}^h B_h + F_{chi}^h C_h \quad (B.3)$$

Equations B.2, which express a transcendental relationship between  $y_h$ ,  $x$ ,  $a$ ,  $b_h$ , and  $c_h$ , have been reduced to Eqs. B.3, which are linear in the unknowns  $V_{hi}$ ,  $A$ ,  $B_h$ , and  $C_h$ .

We now define the quantities  $S_T$  and  $S_h$ :

$$S_T = \sum_h S_h = \sum_h \left[ \sum_i^{n_h} v_{hi}^2 \right] \quad (B.4)$$

$V_{hi}$  from Eqs. B.3 is substituted into Eqs. (A-4) yielding:

$$S_T = \sum_h \left[ \sum_i^{n_h} \left( \frac{1}{F_{yhi}^h} \right)^2 \left( F_{oi}^h - F_{ai}^h \cdot A - F_{bhi}^h \cdot B_h - F_{chi}^h \cdot C_h \right)^2 \right] \quad (B.5)$$

We require that  $S_T$  be minimized with respect to each of the variables  $A$ ,  $B_h$ , and  $C_h$ . We equate to zero the corresponding partial derivatives of Eqs. B.5 and arrive at the following set of simultaneous equations:

$$\begin{aligned} A \sum_h \left[ \sum_i^{n_h} \frac{(F_{ai}^h)}{L_{hi}} \right] + \sum_h \left[ B_h \sum_i^{n_h} \left( \frac{F_{ai}^h F_{bhi}^h}{L_{hi}} \right) \right] + \sum_h \left[ C_h \sum_i^{n_h} \left( \frac{F_{ai}^h F_{chi}^h}{L_{hi}} \right) \right] \\ = \sum_h \left[ \sum_i^{n_h} \left( \frac{F_{ai}^h F_{oi}^h}{L_{hi}} \right) \right] \quad (1 \text{ eq'n.}) \quad (B.6) \end{aligned}$$

$$\begin{aligned}
A \sum_i^{n_h} \left( \frac{F_{ai}^h F_{bi}^h}{L_{hi}} \right) + B_h \sum_i^{n_h} \frac{(F_{bhi}^h)^2}{L_{hi}} + C_h \sum_i^{n_h} \left( \frac{F_{bhi}^h F_{chi}^h}{L_{hi}} \right) \\
= \sum_i^{n_h} \left( \frac{F_{bhi}^h F_{oi}^h}{L_{hi}} \right) \quad (5 \text{ eq'ns.}) \quad (B.7)
\end{aligned}$$

$$\begin{aligned}
A \sum_i^{n_h} \left( \frac{F_{ai}^h F_{chi}^h}{L_{hi}} \right) + B_h \sum_i^{n_h} \left( \frac{F_{bhi}^h F_{chi}^h}{L_{hi}} \right) + C_h \sum_i^{n_h} \frac{(F_{chi}^h)^2}{L_{hi}} \\
= \sum_i^{n_h} \left( \frac{F_{chi}^h F_{oi}^h}{L_{hi}} \right) \quad (5 \text{ eq'ns.}) \quad (B.8)
\end{aligned}$$

where  $L_{hi} = (F_{yhi}^h)^2$ . Equations B.6, B.7, and B.8 determine the corrections ( $A$ ,  $B_h$ , and  $C_h$ ) that must be made to the estimated retention parameters ( $a_o$ ,  $b_{ho}$ , and  $c_{ho}$ ) to arrive at the second estimates ( $a$ ,  $b_h$ , and  $c_h$ ). If the initial estimates are made carefully and are close to the second estimates, only one run through the procedure should be necessary; if they are not close, the procedure must be repeated, each time using the second estimates from the previous run as the estimated input parameters, until  $A$ ,  $B_h$ , and  $C_h$  become small enough relative to  $a$ ,  $b_h$ , and  $c_h$  so that further analysis is not justified by the accuracy of the data. The amount by which  $S_T$  changes is often another good indicator of when the analysis should be terminated. Careful choice of the initial estimates will save much work.

From Eqs. B.4 we have

$$S_h = \sum_i^{n_h} V_{hi}^2 \quad (B.9)$$

Combination of Eqs. B.9, B.3, B.7 and B.8 yields

$$\begin{aligned}
 S_h = & \sum_1^{n_h} \frac{(F_{oi}^h)^2}{L_{hi}} - 2A \sum_1^{n_h} \left( \frac{F_{ai}^h F_{oi}^h}{L_{hi}} \right) - B_h \sum_1^{n_h} \left( \frac{F_{bhi}^h F_{oi}^h}{L_{hi}} \right) - C_h \sum_1^{n_h} \left( \frac{F_{chi}^h F_{oi}^h}{L_{hi}} \right) \\
 & + A^2 \sum_1^{n_h} \frac{(F_{ai}^h)^2}{L_{hi}} + AB_h \sum_1^{n_h} \left( \frac{F_{ai}^h F_{bhi}^h}{L_{hi}} \right) + AC_h \sum_1^{n_h} \left( \frac{F_{ai}^h F_{chi}^h}{L_{hi}} \right)
 \end{aligned}$$

$S_T$  is given by the first equation in Eqs. B.4.

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gases. The procedure involves:

- a. Separation of xenon from oxygen, nitrogen, argon, and krypton on a short column at or above room temperature;
- b. Separation of krypton from oxygen, nitrogen, and argon on a long column at -20°C;
- c. Separation of argon from oxygen on the long column at -50°C.

The net reduced retention volumes and heats of adsorption were determined for oxygen, nitrogen, argon, krypton and xenon on molecular sieves types 4A, 5A and 13X.

Voltage output of the differential thermal conductivity detector was measured as a function of the quantity of gas being measured. It is estimated that the presence of about  $6 \times 10^{-11}$  mole, or 0.1 ppm in 25 cc of sample, can be detected. Quantitative measurements can be made down to about  $5 \times 10^{-9}$  mole, or 10 ppm in 25 cc of sample.

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