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PROCESS SCALE SEPARATION OF HYDROGEN ISOTOPES BY GAS CHROMATOGRAPHY

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ABSTRACT

The technical feasibility of a gas chromatographic process for separating hydrogen isotopes was demonstrated. In this process, batches of hydrogen isotopes are swept by helium through ferric-oxide-treated alumina at $77^{\circ}K$. The six molecular species of hydrogen which are resolved by the alumina are stripped from the helium by refrigerated charcoal, and the helium is recirculated.

Capacities in the range of hundreds of liters (at STP) per day are feasible.

CONTENTS

LIST OF TABLES AND FIGURES

PROCESS SCALE SEPARATION OF HYDROGEN ISOTOPES BY GAS CHROMATOGRAPHY

INTRODUCTION

Recent articles have reported the analytical (small scale) separation of the six molecular species of hydrogen, i.e., H_2, HD, HT, D_2, DT, and T_2, on a treated alumina column at 77°K by elution gas chromatography.(1,2) Scaleup of this separation by a factor of 1000, or more, could provide a flexible process with the potential for processing materials of widely different compositions to produce high purity products. The feasibility of 10-fold scaleup of analytical separations has been demonstrated for a number of systems but each separation imposes special problems.(3) No report was found of attempts to scale up by factors in the order of 1000.

After the current work was completed, Debbrecht(4) reported successful scaleup to 4-inch-diameter columns using a column design very similar to that described in this report. F & M Scientific Corporation* now markets a preparative scale gas chromatograph that utilizes a single 4-inch-diameter column of this design and has a capacity about 480 times greater than the usual 0.18-inch-ID analytical column.

This report summarizes the feasibility of an elution gas chromatographic process for the separation of hydrogen isotopes. This study includes:

- Laboratory demonstration of the unit processes on an analytical scale
- Laboratory demonstration of a 10-fold scaleup in column capacity above the analytical scale
- Formulation of a proposed separations process
- Theoretical prediction of the applicability of this technique to a variety of feed compositions.

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SUMMARY

The technical feasibility of a gas chromatographic process for separating hydrogen isotopes was demonstrated. Elution chromatography on a column of ferric-oxide-treated alumina at 77°K, with helium as the carrier gas, resolved the six hydrogen molecular species. In the conceptual process, the resolved hydrogen species emerging from the chromatographic column are stripped from the helium carrier by refrigerated charcoal, and the helium is recirculated.

The unit processes of the proposed process were demonstrated on a laboratory scale. The chromatographic resolution in a single pass was sufficient to upgrade an HDT mixture from 17% T to 44% T; 99.2% of the original tritium was recovered. In addition, an HT fraction that contained 0.4% of the original tritium could be recovered for rework. A charcoal trap at 77°K had a capacity of 10 cc (at STP) of hydrogen per gram of charcoal and was >99.96% efficient in stripping hydrogen from helium in the effluent from a chromatographic column.

Factors involved in scaleup from laboratory to process scale were studied. The maximum sample loading per cross-sectional area of column for the resolution of the six molecular species of hydrogen was 200 cc at STP/in^2. A sectional column was superior to a continuous coil for large diameter columns.

Resolving power and capacity were predicted for a typical system employing a single 4-inch-diameter chromatographic column. Calculations indicate that such a system could upgrade a variety of mixtures to high purity tritium (99.5% T) with a capacity of 100-500 liters of feed per day, depending upon the feed composition.

DISCUSSION

THEORETICAL BACKGROUND

Elution gas chromatography is basically a batch process in which a discrete amount of the mixture to be separated is swept through a column by a carrier gas. The resolved components of the mixture appear at the column effluent at times that are characteristic of each component, as shown in Figure 1. In gas chromatography the relative location of the peak maxima along the time axis is defined as the separation factor, α:

$$\alpha = \frac{x_2}{x_1} \tag{1}$$

where x_2 and x_1 are the distances from time "0" to peak maxima. If the sorption isotherms are linear, the separation factor can be shown[3] to be

$$\alpha = \frac{x_2}{x_1} = \frac{K_2}{K_1} \tag{2}$$

where K_1 and K_2 are the distribution coefficients of components 1 and 2 between the solid and gas phases at equilibrium. The separation factor is dependent on the nature of the components, the nature of the sorbent, and the temperature, but is independent of most other operating variables, e.g., amount of solute, amount of sorbent, flow rate, and column length. Therefore, α can be said to be a measure of the column selectivity at a given temperature.

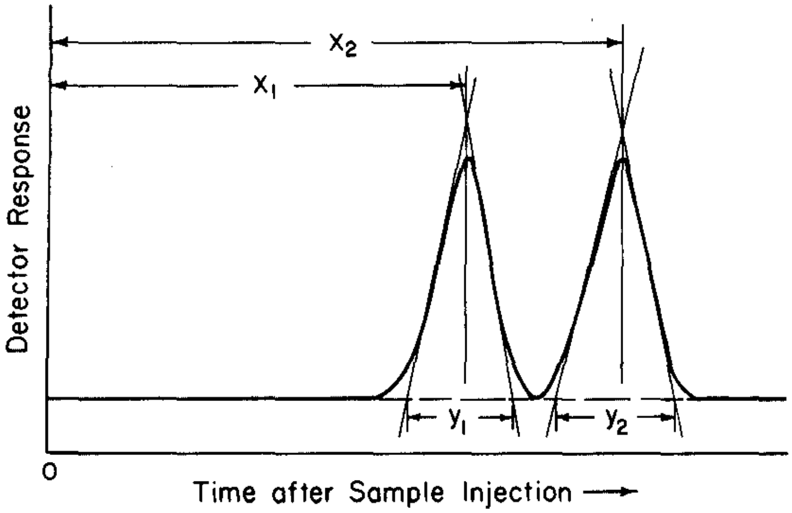

FIG. 1 PARAMETERS FOR CALCULATING ALPHA AND N

If $\alpha \neq 1$, resolution of two solutes is theoretically possible and depends upon the efficiency of the column, N, i.e., the degree of peak broadening relative to the residence times of the peaks in the column. The experimental determination of N is illustrated in Figure 1. Tangents to the curve at the inflection points are extended to intersect the base line, thus defining the "base width," y.

$$N = 16 \left(\frac{x}{y}\right)^2 \tag{3}$$

The definition of N is derived from probability theory and assumes Gaussian-shaped peaks. Many factors affect N, including column dimensions, particle size of the sorbent, flow rates, and quantity of solute.

Glueckauf(5) has derived an expression that relates the column efficiency, N, and separation factor, α, to the degree of separation between two solutes which are present in any proportions. This expression, derived from distribution theory, permits a prediction of the degree of mutual contamination in adjacent peaks. The Glueckauf derivation is complex; however, the utilization of his expression is straightforward and is given in the Appendix.

The capacity of a chromatographic system is limited by the effect of batch size on resolution (peak broadening) and the transport time of the components through the column. The effects of the amount of feed material on resolution are discussed in detail by Dal Nogare and Juvet(3), and Glueckauf.(5) In short, these authors conclude that there is a maximum loading per unit of cross-sectional area of the column for a given resolution.

Increasing the column diameter should permit an increase in quantity of feed proportional to the increase in cross-sectional area of the column. However, increasing the column diameter results in a decrease in efficiency, N. This effect has been treated in detail by Giddings,(6,7) who suggests techniques for minimizing the loss in efficiency. Techniques are presently available whereby column ID may be increased to 3-4 inches without severe losses in efficiency. Techniques have been suggested, but no results reported, whereby the column ID may be increased to 10-15 inches.(6)

Another approach to increased capacity is to arrange small-diameter columns in parallel. In this technique the problem of matching the transport time of the solutes through each column becomes more significant as the number of columns is increased. Up to 120 columns have been arranged in parallel in a commercial gas chromatographic unit.(8) The choice, therefore, is between a large number of small-diameter columns or a small number of large-diameter columns. Although no detailed study has been made of the relative economics of these alternatives, it appears that for process equipment, scaleup of column ID to 3-4 inches is more economical than a parallel arrangement of smaller diameter columns. However, if additional scaleup is required, parallel arrangement of these larger columns appears to be the best approach because a further increase in column diameter would require development of untried techniques.

To be useful as a separations process, the gas chromatographic technique requires that the separated molecular species of hydrogen be quantitatively stripped from the helium carrier. (The maximum hydrogen concentration in the effluent is about 1%.) Ideally, a rapid stripping step is desired in which the individual molecular species are completely separated from the flowing helium. Rapid stripping and complete separation appear to be mutually exclusive in this case, therefore the objective of this operation was to obtain rapid, quantitative stripping of hydrogen and recovery of a product that was at least 20 vol % hydrogen and 80 vol % helium. The hydrogen in each such product could then be stripped of helium by a slower process, such as diffusion through palladium.

EXPERIMENTAL

A schematic diagram of the equipment used in evaluating the gas chromatographic separation is shown in Figure 2. A measured volume (at 1 atm pressure) of the material to be separated was transferred via the Toepler pump to the sample loop of the multiport valve, and then was introduced into the flowing helium carrier. The carrier swept the sample through the column and two detectors arranged in series. The first detector measured the difference in thermal conductivity (all molecular hydrogen peaks) between the column effluent and the carrier and the second measured the radioactivity (tritium only) of the column effluent.

The column material was prepared according to Moore and Ward.(9) Activated alumina was washed first with ferric chloride solution, then with ammonium hydroxide, and finally with water. At least 20 successive volumes of water per volume of alumina were necessary for the best column performance. The alumina was then dried at 120°C for 24 hours. To avoid significant variations(1) in retention characteristics of columns prepared from different batches of alumina, each step was carefully controlled.

All columns used in this work were 24-feet long. Small-diameter columns were wound into 5-inch-OD coils to fit into a 4-liter Dewar. The packing material was loaded into these coils by applying about 50 psig pressure with dry air and vibrating the coil.

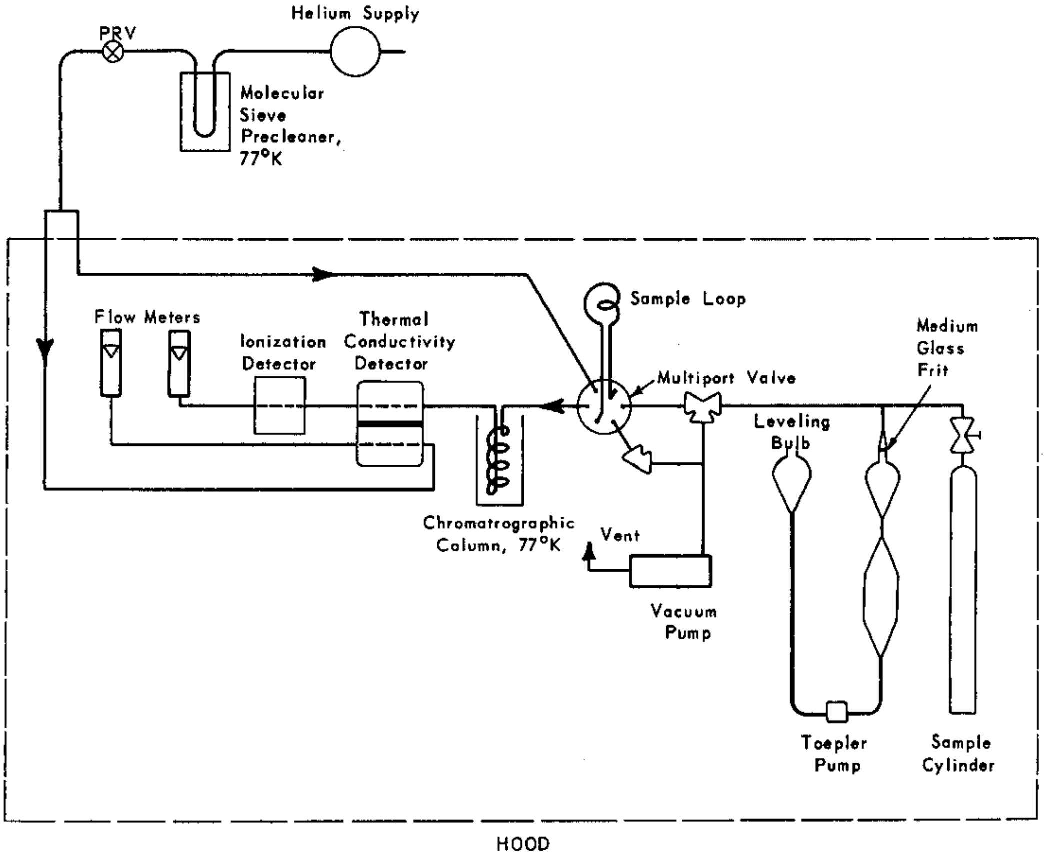

FIG. 2 SCHEMATIC DIAGRAM OF CHROMATOGRAPHIC SYSTEM

The limiting design feature for large-diameter columns was the size of the Dewar required to maintain the column at 77°K. The largest Dewar available for the current studies was a cylinder, 17-inches ID and 36-inches deep. Therefore, for 24-foot columns of large diameter two different column designs were employed:

1. Coiled design: A straight piece of tubing, 24-feet long, was packed with treated alumina and then wound into a tight coil that was 15-inches OD.

2. Sectional design: Straight pieces of tubing, 2-feet long, were packed with treated alumina and the sections were connected in series by unpacked, small-diameter tubes (Figure 3).

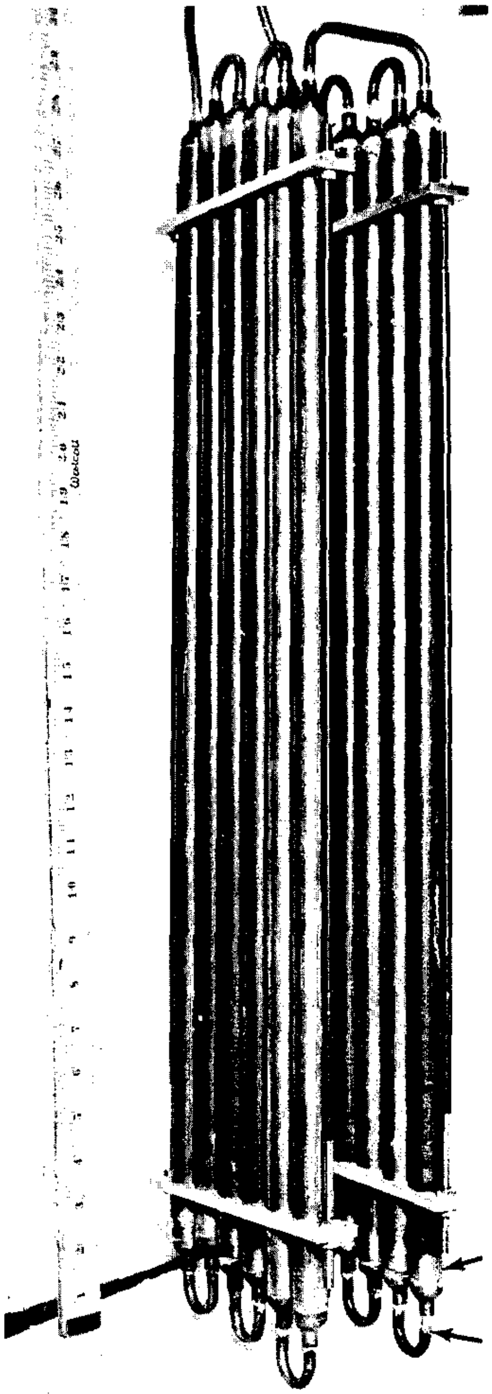

FIG. 3 SECTIONAL COLUMN

RESULTS AND CONCLUSIONS

Column Loading Characteristics

The effect of column loading on resolution is illustrated in Figure 4. The maximum sample loading consistent with adequate resolution of the six hydrogen molecular species was estimated to be 200 cc (STP)/in.^{2} of cross-sectional area of column. The resolution of a mixture of H_2-HD-HT-D_2-DT-T_2 near this loading (140 cc/in.^{2}) is illustrated in Figure 5b.

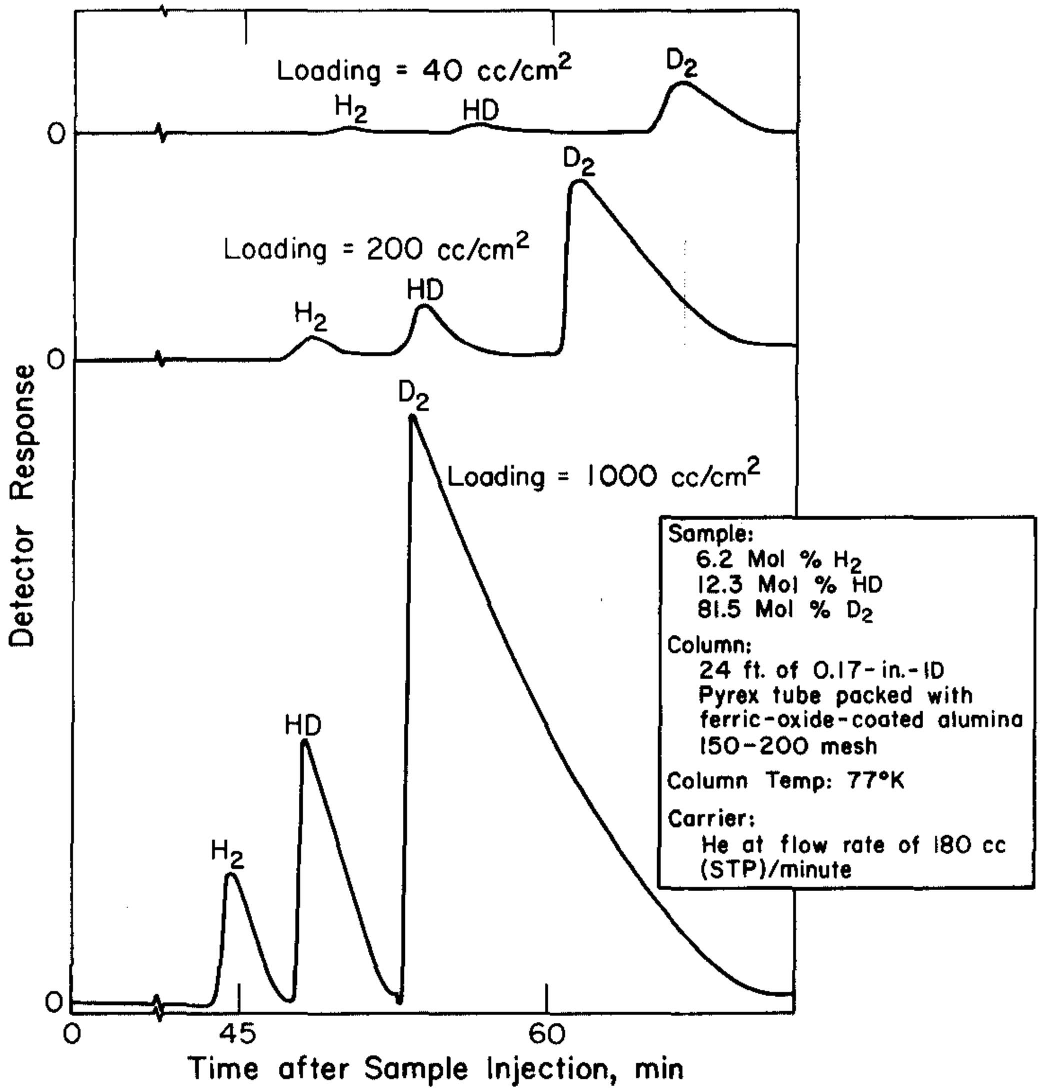

FIG. 4 EFFECT OF COLUMN LOADING ON RESOLUTION

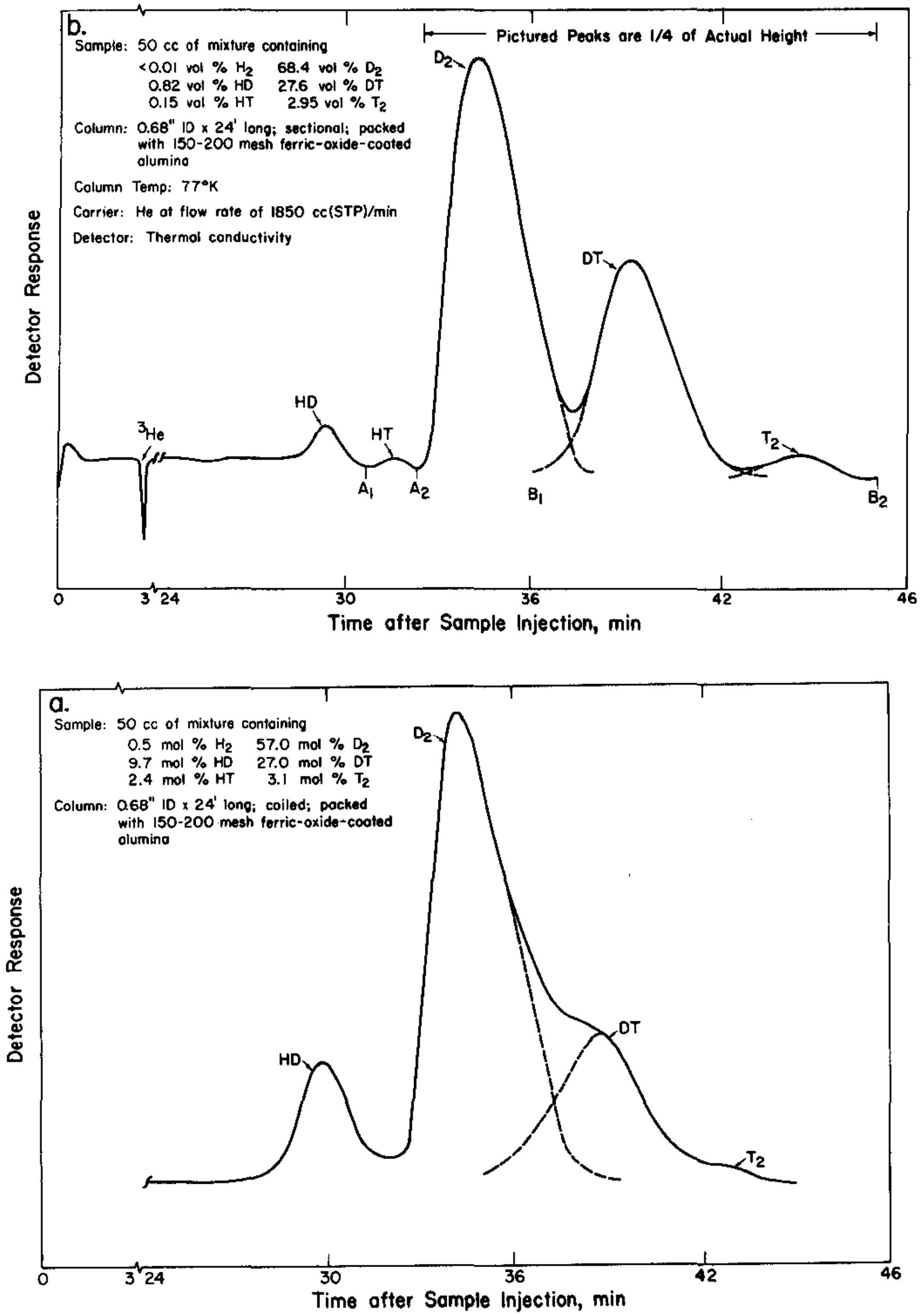

FIG. 5 EFFECT OF COLUMN DESIGN ON RESOLUTION

Scaleup of Column Diameter

A tenfold scaleup in batch size was achieved without loss of resolution with a sectional column, whereas a significant loss in resolution was experienced with a coiled column. The effect of column design on relative efficiencies is shown in Table I. A fivefold loss in efficiency resulted on scaleup with the coiled configuration, whereas no loss resulted with the sectional column. No changes in the separation factors, α, were expected or observed since the columns were packed with the same material and operated at the same temperature.

TABLE I

Efficiencies of Large and Small Diameter Columns

Alumina Packing	Sample Size, cc STP	Column ID, in.	Theoretical Plates[a], N	Relative Efficiency, large/small column
Lot "A"	5	0.18 (coiled)	3.0×10^3	0.2
	50	0.68 (coiled)	0.6×10^3	
Lot "B"	5	0.18 (coiled)	1.8×10^3	1.0
	50	0.68 (sectional)	1.8×10^3	

(a) Theoretical plates calculated for D_2 peak.

Direct comparison of the efficiencies of the two columns of the same diameter is not meaningful because they were packed with different lots of treated alumina. The lot "A" was 150-200-mesh alumina whereas lot "B" was 100-150 mesh.

The data in Table I were determined from H-D mixtures; however, the superiority of the sectional column for H-D-T mixtures can be seen by comparing Figure 5a with 5b. This superiority is attributed to a more uniformly packed column because:

- two-foot sections were easier to pack
- crushing of the column material that may have occurred on coiling was avoided.

Recovery of Separated Products

Refrigerated (77°K) charcoal was selected to strip the resolved hydrogen species from the helium carrier gas. The experimental work was designed to measure:

- efficiency of the bed

- capacity of the bed

- specificity of the bed (He/hydrogen ratio in the sorbed phase)

- desorption characteristics of the bed.

The efficiency of a charcoal bed for stripping hydrogen from helium was demonstrated with a complete system. A charcoal bed at 77°K, with a residence time* of about 15 sec, was attached to the effluent of a small-diameter gas chromatographic column. Five successive 0.25 cc samples of a 17% T - 83% D mixture were swept through the column to the trap in a manner simulating a continuously operated batch process (1 sample introduction/20 minutes). The effluent from the trap was monitored for radioactivity with a flow-through ionization chamber of the type described by Nystrom.(10) The detector provided a signal that was proportional to the concentration of tritium in the trap effluent. No tritium was detected during the two-hour period in which the samples were fed to the system. Comparison of the integrated signal (over the two-hour period) with the observed signal from samples without a charcoal trap showed that >99.96% of the tritium was retained on the charcoal. When the trap was warmed to room temperature with helium carrier still flowing through it, the detector went off scale and returned to 10^{-3}% of scale within 3 minutes. Thus, the tritium was easily desorbed at room temperature.

The capacity of charcoal was determined by breakthrough experiments with the apparatus shown in Figure 6. Purified He and D_2 were flow-blended to a concentration of 0.17 vol % D_2 and fed to the charcoal trap at a rate of 200 cc/min. The D_2 concentration of the feed was determined at the start and at the finish of each run by mass spectrometric and thermal conductometric analyses. Samples of the effluent gas were collected in bulbs at appropriate intervals during the run and analyzed by conventional mass spectrometry, or transferred via the multiport valve to the thermal conductivity analyzer.

Deuterium breakthrough curves determined for charcoal at 77°K with a feed that was 0.17 vol % D_2 in He showed a sharp wave front on breakthrough (Figure 7). The capacity of a bed with a 3-sec residence time for the gas was about 10 cc D_2 (STP) per gram of charcoal. No breakthrough was detected until the loading reached about 9.8 cc D_2 (STP) per gram of charcoal. (Thermal conductivity analysis could detect breakthrough at 0.01 vol % D_2.)

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* Residence time is the length of charcoal bed divided by the linear velocity of the gas going through the bed.

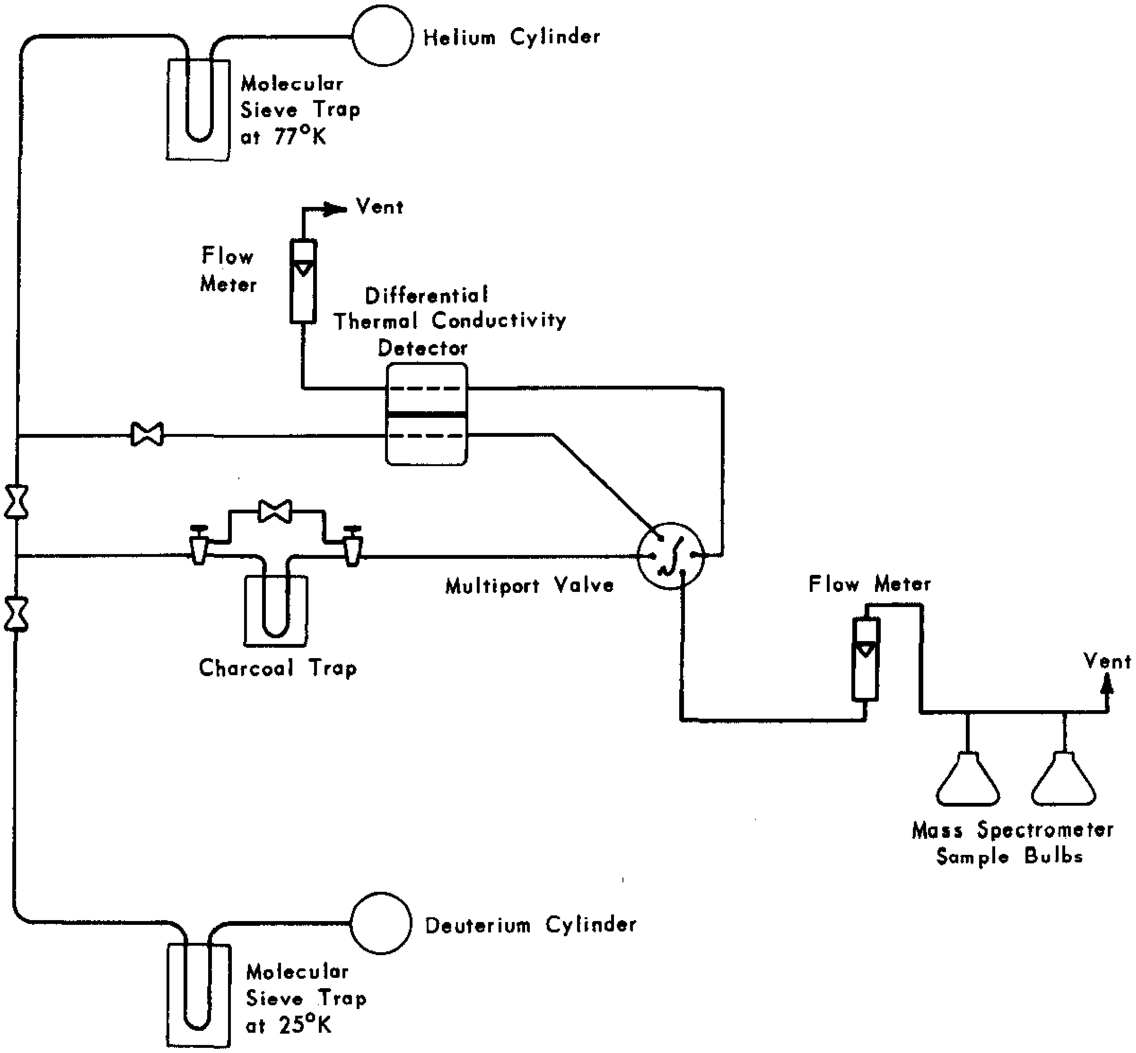

FIG. 6 SCHEMATIC DIAGRAM OF BREAKTHROUGH APPARATUS

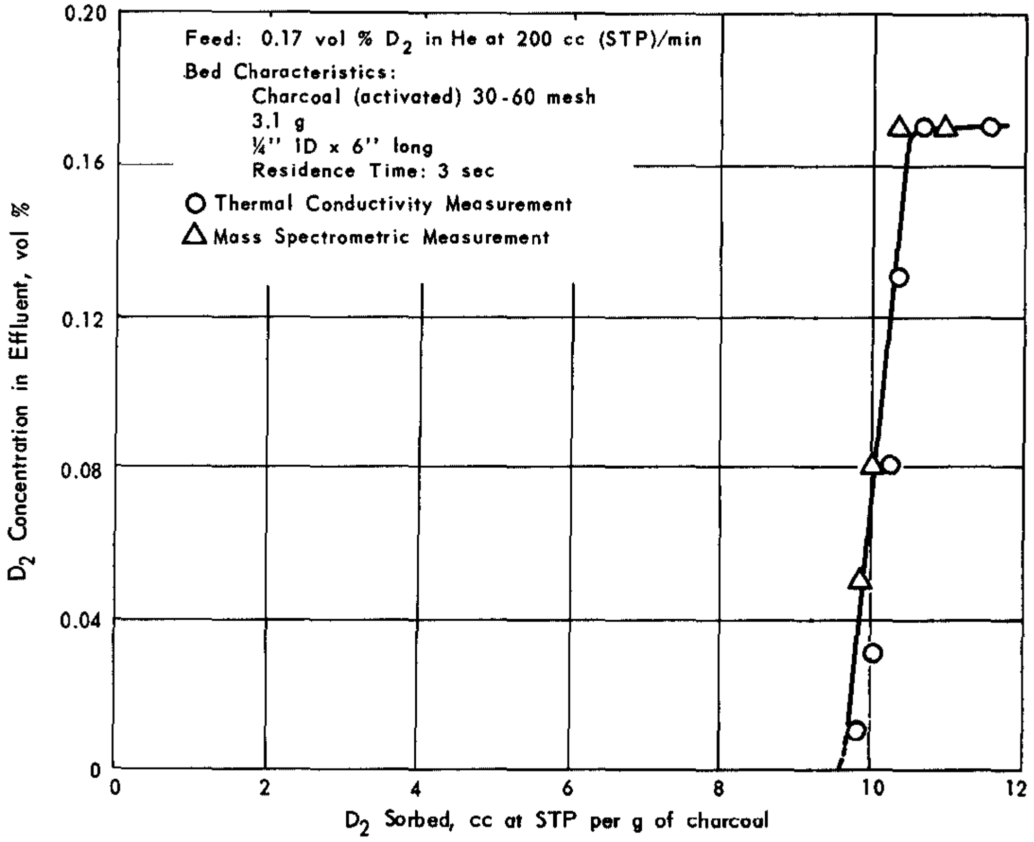

FIG. 7 BREAKTHROUGH CURVE FOR DEUTERIUM ON CHARCOAL AT 77°K

Specificity for hydrogen and the desorption characteristics of charcoal were determined by successive evacuations on a loaded charcoal bed. A bed (1.9 g of charcoal) was loaded to about half its capacity (12 cc D_2), swept with He to remove the unsorbed D_2 from the void spaces; then the desorbed gases were collected during five successive evacuations at different temperatures. Two 1-second pumpoffs at 77°K were employed in an effort to remove most of the unsorbed He without significant loss of sorbed D_2. These were followed by 10-minute pumpoffs at 77°K, 298°K, and 500°K.

Desorption data in Table II show that 99.8% of the D_2 was contained in fractions 3 and 4 whose combined composition was 39% D_2 - 61% He. By increasing the number of short-term pumpoffs at 77°K, it appears that a higher D_2 purity could have been obtained in the subsequent fractions. Higher D_2 concentration would facilitate the subsequent palladium diffusion removal of He. The first two fractions contained primarily He from the void volume of the trap. The volume of He in voids was estimated to be 30 cc at STP. The trace of D_2 in

TABLE II

Desorption of Gases from Charcoal by Successive Evacuations

Fraction No.	Pumpoff Time	Temperature of Bed, °K	Desorbed Gas, cc at STP	
			He	D_2
1	1 sec	77	13.3	0.015
2	1 sec	77	8.6	<0.001
		Total, 1 & 2 →	21.9	0.015
3	10 min	77	13.7	0.28
4	10 min	298	0.8	9.1
		Total, 3 & 4 →	14.5	9.38
5	10 min	~500	0.007	0.005
		Total, 1-5 →	36.4	9.40

the first evacuation was attributed to residual D_2 in the gas phase rather than desorbed D_2 because no D_2 was detected in the second pumpoff. Fraction 5 shows that only a trace (0.05%) of the D_2 was retained after pumpoff at room temperature.

The material balance for the desorption experiment was within the experimental error of the analytical techniques. Feed analyses and flow-rate measurements indicated that 12 cc of D_2 was loaded on the bed and that 9.4 cc was recovered on pumpoff; the apparent recovery was 78%. However, the accuracy of the analytical techniques, especially the determination of the concentration of D_2 in the feed, is no better than ±25% relative. Analysis of the trap effluent during sorption clearly indicated that less than 5% of the D_2 passed through the trap, and previous experiments with tritium in the feed showed that less than 0.04% of the tritium passed through the bed.

Isotopic Purity of Products

The isotopic purity of the products (or cuts) that can be successively isolated from the effluent of a chromatographic column is a function of the location of the cuts along the time axis of the chromatogram, the resolution of the column, and the composition of the feed material. The location of the cuts also determines the losses.

The purity of cuts that could be made from the 0.68-inch sectional column was estimated from Figure 5b. Assume that the material from A_1-A_2 is stripped into a trap designated "HT Fraction"; from B_1-B_2 into another, designated the "DT-T_2 Fraction"; and all of the other material into another trap designated "Raffinate". Although the cut lines are at the baseline intercepts of the tritium-containing peaks, assume that the area of the peak represents 99% of that component, i.e., 0.5% of that material is lost to the preceding cut and 0.5% to the following cut. With these assumptions, and from the areas of the peaks, the estimated purity of each cut was calculated and summarized in Table III. These data show that a feed material that was 17% T was upgraded in one pass to a DT - T_2 fraction that was 44% T, 56% D, and contained 99.2% of the feed tritium.

TABLE III

Estimated Composition of Fractions from 0.68-Inch-ID Column

Component	Composition, vol %			
	Feed	HT Cut	DT - T_2 Cut	Raffinate
H	0.5	15	<0.01	0.7
D	83	70	56	99.2
T	17	15	44	0.09
% of Feed Tritium	100	0.4	99.2	0.4

The agreement was determined between the purity of fractions calculated from the peak areas of the chromatogram and those predicted from Glueckauf's equation (Appendix). Because Glueckauf's equation assumes a cut so as to obtain equal fractional impurity in adjacent peaks, the purities estimated from peak areas were recalculated on that basis. There was excellent agreement between predicted and observed values, as shown in Table IV. Therefore, Glueckauf's equation can be used to predict the purity of products from the separation of hydrogen isotopes by this technique. Some modifications of his equation are desirable to permit selection of cuts to minimize losses rather than cuts of equal fractional impurity.

TABLE IV

Comparison of Predicted and Observed Separations

Component	Composition, vol %		
	Feed	DT - T_2 Cut	Raffinate
		Predicted	
D	83	45	99
T	17	55	1
% of Feed Tritium	100	96	4
		Observed	
D	83	46	99
T	17	54	1
% of Feed Tritium	100	96	4

PROPOSED PROCESS

On the basis of the successful demonstration of capacity and resolution in the current work and successful scaleup of other gas chromatographic separations by others,(4,8) a new process for separating hydrogen isotopes is proposed. A simplified schematic diagram of a typical system for such a process is shown in Figure 8. In this system a batch of the mixture to be separated is fed intermittently (one loading every 30 minutes) to the head of a 4-inch-diameter x 24-foot-long column. The effluent is valved to the desired charcoal trap at a time determined by the ion chamber detection of tritium. The helium, flowing at a rate of 10^5 liters/day (~150 cu ft/hr) is recycled.

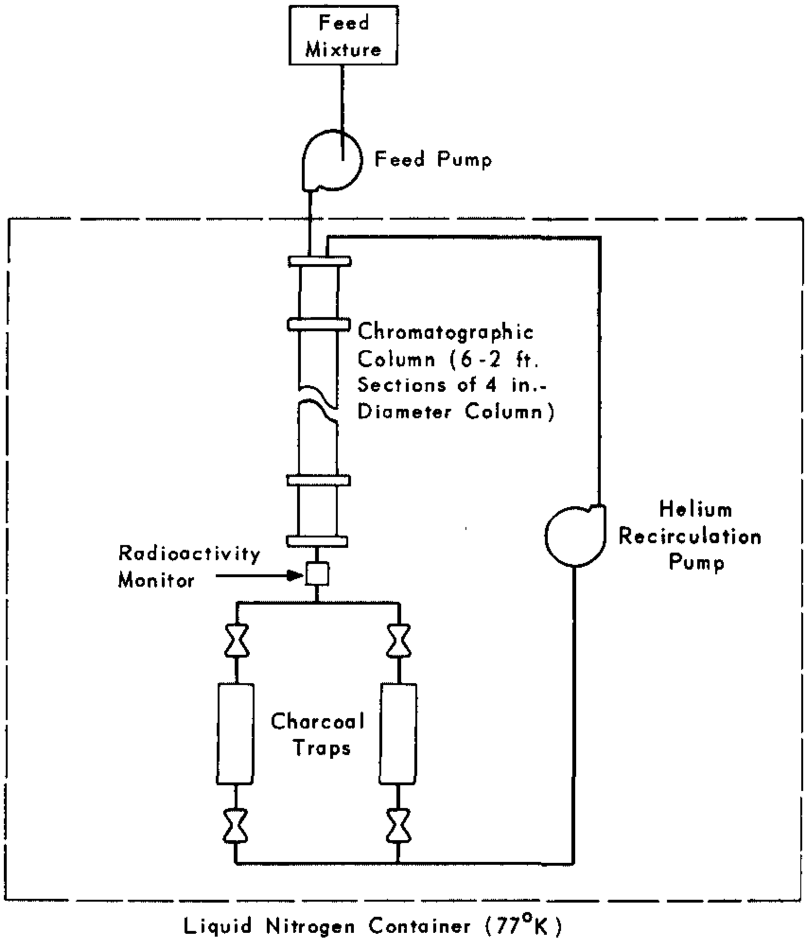

FIG. 8 SCHEMATIC DIAGRAM OF CONCEPTUAL PROCESS

Estimated capacities and resolving powers (dependent upon the feed composition) of this system are shown in Table V. These data were calculated from Glueckauf's expression (see Appendix) using observed separation factors and efficiencies projected from current work on the 0.68-inch-ID column.

TABLE V

Predicted Gas Chromatographic Separations

	Composition, vol %				Tritium in Raffinate (% of Feed Tritium)	Estimated Capacity of Single 4-inch-ID Column, liters/day
	Feed	HT Cut	DT Cut	T_2 Cut		
T	90	50		99.95	<0.01	500
H	10	50		0.05	-	-
T	84	49	51	99.5	<0.1	100
D	8	2	49	0.5	-	-
H	8	49	<0.01	<0.01	-	-
T	20	44	50	99.95	0.15	100
D	79	10	50	0.05	-	-
H	1	46	<0.01	<0.01	-	-

Considerable sophistication of this system would probably be desirable such as:

- valving to more traps
- provisions for recovery of product and raffinate during operation
- additional monitoring points

Details of these improvements are beyond the scope of the present work.

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APPENDIX

In his theoretical treatment of gas chromatography, Glueckauf(4) demonstrated the column efficiency required to obtain any degree of resolution between two solutes present in any proportion. Complete separation is possible only with an infinite number of theoretical plates. For practical purposes, only enough plates are required to reduce the degree of mutual contamination in the peaks to an acceptable level. Glueckauf's derivation is complex but the application of his conclusions is straightforward and is summarized below.

Referring to Figure A-1, assume a cut between peaks 1 and 2 at line C. Then let Δa_1 be the area of peak 1 from C to ∞, and Δa_2 be the area of peak 2 from 0 to C. Also, let a_1 equal the total area from 0 to C and a_2 the area from C to ∞. As an approximation, let the corresponding fractional impurities, η, be

$$\eta_1 = \Delta a_2/a_1$$

$$\eta_2 = \Delta a_1/a_2$$

Consider the case where $\eta_1 = \eta_2$. The separation factor, α, for the solute pair is x_2/x_1, and the normalized area of each peak is the ratio of its area to the total area, that is,

$$A_1 = a_1/(a_1 + a_2)$$

$$A_2 = a_2/(a_1 + a_2)$$

$$A_1 + A_2 = 1$$

If the detector responds linearly to concentration, or if the appropriate sensitivity corrections are applied, the areas and fractional areas correspond to amounts of solutes.

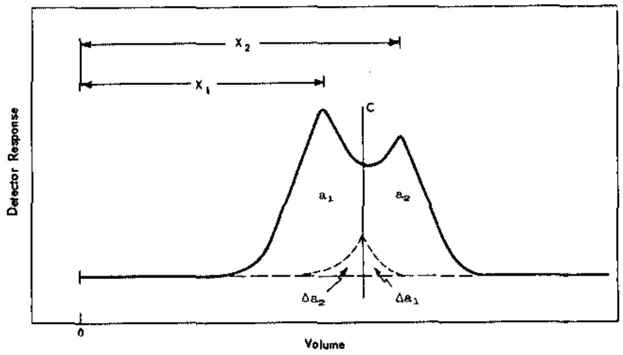

FIG. A-1 OVERLAP OF UNEQUAL AREA PEAKS

By substitution of the assumed values for A_1 and A_2,

$$\eta[(0.7)^2 + (0.3)^2]/2(0.7)(0.3) = 4 \times 10^{-3}$$

$$\eta = 3 \times 10^{-3} = 0.3\%$$

Thus with 2000 theoretical plates, components 1 and 2 can be upgraded from a 70-30% mixture to separate fractions, each 99.7% pure.

With the desired η decided upon and the α and the normalized areas, A_1 and A_2, calculated from the chromatogram, the number of theoretical plates required to obtain the desired η can be determined from the plot in Figure A-2. Likewise the η can be predicted if the other parameters are known. For example, assume two peaks of $A_1 = 0.7$, $A_2 = 0.3$, $\alpha = 1.15$, and $N = 2000$. Determine the fractional impurity in each peak. From the plot, with $\alpha = 1.15$ and $N = 2000$,

$$\eta({A_1}^2 + {A_2}^2)/2A_1A_2 = 4 \times 10^{-3}$$

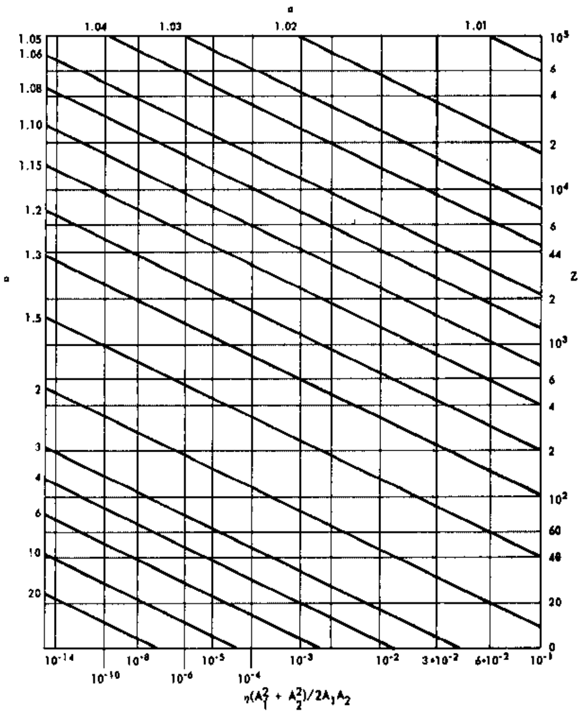

FIG. A-2 GLUECKAUF PLOT OF RESOLUTION AS A FUNCTION OF ALPHA AND N