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Production of ^{13}C by Chemical Exchange Reaction between Amine Carbamate and Carbon Dioxide in a Solvent-Carrier System

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Abstract

The chemical exchange reaction between amine carbamate and CO_2 has been investigated for the purpose of using it as a practical method to concentrate ^{13}C. The effects of solvent, concentration of amines, catalysts, flow rate, and diameter of the column have been studied for a number of amines. Of the solutions studied, di-*n*-butylamine (DNBA) in triethylamine (TEA) as a solvent proved to be the most favorable for use in the preparation of highly enriched ^{13}C. The overall separations obtained as a function of the concentration of DNBA using 2.5 cm i.d. × 100 cm column ranged from 2.05 at 1 *M* to 1.69 at 2.84 *M*. For 2 *M* DNBA the maximum separation was 1.94. At this concentration of DNBA the overall separation as a function of flow rate ranged from 1.94 at 0.845 ml/cm^2-min to 1.31 at 2.9 ml/cm^2-min. Neither the rate of exchange nor the overall separations were improved by use of catalysts. Increasing the diameter twofold resulted in little or no loss in overall separations. On the basis of the properties of the system and the data obtained with respect to the above variables, design calculations were made for a six-stage tapered cascade. These calculations were based on a flow of 40 ml/min of 2 *M* DNBA in TEA, giving a maximum transport of 7.1×10^{-3} mmole/min or a maximum production rate of 130 mg ^{13}C/day. The cascade was operated for about 5 months during which period gram quantities of 67% ^{13}C were produced.

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INTRODUCTION

Isotope effects for carbon, oxygen, nitrogen and deuterium in exchange distillation of several low boiling amine carbamates have been studied by Holmberg (*1*, *2*). Yeatts (*3*) and Bown (*4*) have investigated these systems further and have determined the effect of temperature on the separation factors. Most of the current production of ^{13}C is carried out either by low-temperature distillation of carbon monoxide or by thermal diffusion method. Low-temperature distillation of carbon monoxide can produce large quantities of ^{13}C, but it requires rather sophisticated equipment and substantial capital investment (*5*, *6*). The thermal diffusion method is capable of producing only small quantites of enriched ^{13}C. Another class of separation process is the chemical exchange method. Chemical exchange method with chemical reflux, such as exchange of ^{13}C between HCN and CN^-, developed by Urey and co-workers (*7*), was used for a number of years by Eastman Kodak Co. (*8*). The toxicity of the chemicals and their tendency to polymerize required special precautions in using the system. In addition, chemical reflux required large quantities of chemicals.

Among the chemical exchange methods, solvent-carrier systems with thermal reflux, developed in these laboratories, are rather attractive for both laboratory and large-scale operations. Studies on the exchange of carbon dioxide with a variety of amine carbamates in different solvents (*9*, *10*) such as methanol indicated that either a greater exchange rate or a large value of separation factor (α) was required for a practical use of the system. During further investigations of solvent-carrier systems to concentrate ^{13}C, it was found that the exchange between CO_2 and amine carbamate of di-*n*-butylamine (DNBA) dissolved in triethylamine (TEA) was promising (*11*, *12*), even though the single-stage separation factor (α) was rather low. This system allowed significantly higher throughput rates and gave substantially higher overall separation of ^{13}C.

In order to design a cascade of exchange columns for the concentrations of ^{13}C, studies were made on such variables as type of solvent, concentration of amine (DNBA), effect of flow rate, catalyst, and diameter of the column on the performance of the column. Based on these studies, a six-section cascade was designed and operated. The results of the above studies along with the performance of the six-stage cascade are reported in this article.

EXPERIMENTAL

The exchange system consists of an exchange column packed with Heli-Pak packing, a reboiler with a stripping section, and an amine saturator. The dimensions of each of these components depend upon the flow rates of gas and liquid that are to be used. A typical reboiler with a stripping section is shown in Fig. 1. It consists of a boiler B, a stripping section S, a drip-tip T, and a cooling condenser C. The cooling condenser is fitted with a Nichrome wire coil in order to conduct the liquid in a stream around the surface of the condenser. This feature aids in the prevention of any solid deposit that may form due to a drop in temperature of the cooling water. The liquid that leaves the boiler goes through a small bend with a stopcock. This small bend collects the small amount of heavy decomposition products that form after a long period of operation and thus prevents them from entering the exchange column. A typical complete exchange system with its associated equipment is shown in Fig. 2.

Level Controller

It was observed that the drop in liquid level in the boiler is mainly due to the loss of solvent vapors in the exit stream of wate CO_2. As a result, it was

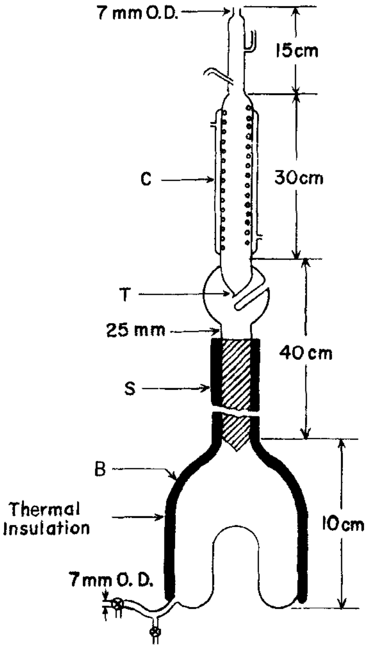

FIG. 1. A typical boiler used for a 25-mm i.d. exchange column in the cascade for the concentration of ^{13}C. B, boiler; C, condenser; S, stripping section; and T, drip-tip.

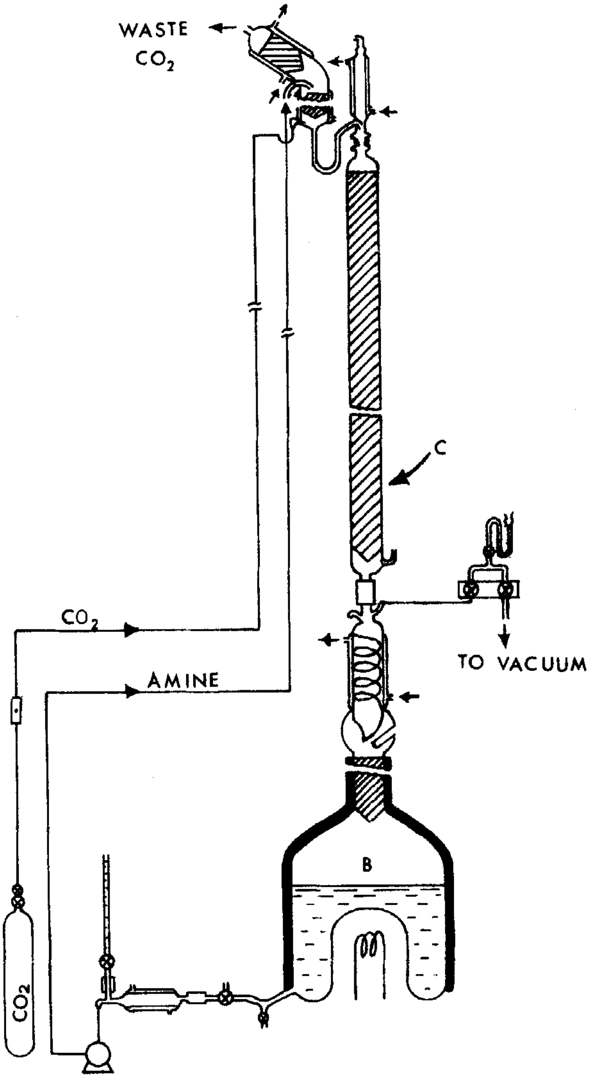

FIG. 2. Schematic diagram of a single column exchange system. C, exchange column; B, boiler.

necessary to control the liquid level in the boiler to maintain the concentration of DNBA at a constant value. Various types of level controlling devices were tried. The one described below is versatile, simple, and reliable. It makes use of thermistors as the sensing elements. Thermistors are semiconductors having large negative temperature coefficients of resistance. If a constant voltage is applied to the thermistor, its temperature will be lower and its resistance higher in the liquid than in air due to better heat transfer in the liquid. This property of thermistors was utilized to control the liquid level by using two thermistors in a standard bridge circuit with some modifications. In Fig. 3 part of the level controller is shown schematically. When the level of the liquid is below T_1, the balance of the bridge is set so that solenoid valve V_1 is open and solvent flows into the boiler. The flow of solvent through V_1 is controlled by a throttle valve V_2. When the level of the liquid rises to T_1, the balance of the bridge is changed and this closes the solenoid valve V_1. The function of thermistor T_2 is to compensate for changes in room temperature.

Procedure for a Run

Before starting a run the column is flooded with DNBA solution in a desired solvent to ensure proper wetting of the packing. Then the column

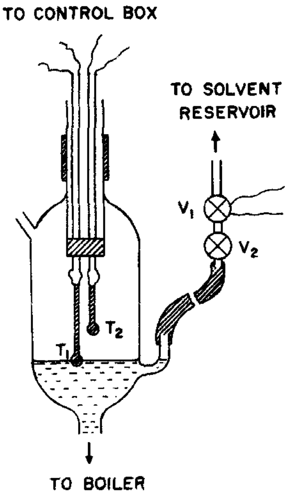

FIG. 3. Level controller. T_1 and T_2, thermistors; V_1, solenoid valve (normally closed); and V_2, throttle valve.

is allowed to drain slowly while the feed of amine solution is being pumped into the amine saturator. After draining the excess fluid from the column, the liquid flow is adjusted to the operating value. The column is allowed to operate under this condition to obtain steady flow of liquid through the packing and to adjust the liquid level in the boiler. Then the feed of CO_2 is started to the amine saturator. After a predetermined time the boiler heater is turned on. This time depends upon the hold-up in the column and the flow rate at which amine solution is pumped into the amine saturator. The voltage of the boiler heater is so adjusted that the temperature near the drip-tip T is about 70°C. Then the level controller is connected to the boiler. Attainment of a constant temperature and boiling rate is necessary since fluctuations result in erratic changes of the liquid level in the controller. The progress of separation is followed by withdrawing small gas samples at different time intervals and analyzing them mass spectrometrically.

Mass Spectrometric Analysis

The gas sample collected in the sample bulb is first frozen with liquid nitrogen and then opened to the vacuum system to pump out noncondensible impurities. Then liquid nitrogen is replaced by Dry Ice to keep the water and solvent vapors condensed. The gas sample is then introduced into the mass spectrometer and a scan of the mass spectrum is taken from mass 12 to 46. From the peak heights at mass 44 and 45, the separation S_{13} is calculated as follows:

$$S_{13} = \frac{R \text{ tank } CO_2}{R \text{ sample}}$$

where

$$R = \frac{\text{peak height of mass 44}}{\text{peak height of mass 45}}$$

Determination of the Composition of the Amine Solution

The overall separations are influenced by the concentration of DNBA. Since this may vary because of loss or an addition of solvent, it is essential that the composition of liquid in the boiler be monitored. Various volumetric methods were tried but none was satisfactory. Consequently, it was decided that a gas chromatographic method should be investigated.

Different types of columns under various conditions were tested, and the one which was reasonably satisfactory consisted of Gas-chrom-Q as a column support and silicone QFl as a stationary phase. A typical gas chromatogram of a 2-*M* DNBA in TEA is given in Fig. 4. For day to day analysis a calibration curve for standard solutions of DNBA is obtained first, then a sample from the boiler is analyzed. Over long periods of time it was found that concentration of DNBA in the boiler remained within the range of 1.9 to 2 *M*. Larger variations in concentration were corrected by addition of DNBA or solvent TEA as needed.

RESULTS AND DISCUSSION

The chemical reaction between an amine and carbon dioxide to form a carbamate can be represented as

$$2R_2NH + CO_2 \rightleftarrows R_2NCOO^{-}\text{---}{}^{+}H_2NR_2 \qquad (1)$$

where R is an alkyl group. The isotopic equilibrium between the carbamate and carbon dioxide is

$$R_2N^{12}COO^{-} + {}^{13}CO_2 \rightleftarrows R_2N^{13}COO^{-} + {}^{12}CO_2 \qquad \alpha \approx 1.01 \qquad (2)$$

Thus ^{13}C concentrates in the carbamate at the lower end of the exchange column.

In the exchange system shown in Fig. 1, the isotopic exchange reaction (2) is utilized as follows. The amine carbamate solution from the saturator A flows down the exchange column C_2 through the stripping section C_1 to reboiler B. The hot vapors of the solvent decompose the carbamate to

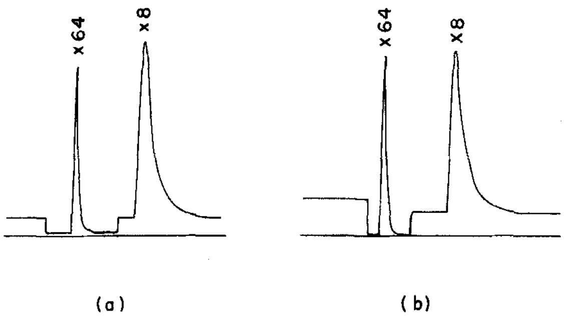

FIG. 4. Gas chromatogram of (a) 2 *M* DNBA in TEA and (b) a sample from the boiler after 3 days of operation.

amine and carbon dioxide in the stripping section. Carbon dioxide rises countercurrently in the exchange column where it is contacted with the carbamate, and the amine solution is pumped back to the saturator at the upper end of the exchange column.

The effectiveness of the system in concentrating ^{13}C depends upon a number of factors which require investigation to select the optimum operating conditions. These include such factors as α, the nature of the amine, the solvent, the concentration of the amine, and the flow rate. Although previous investigations (*9*, *10*) had shown some significant differences among the amines in the same solvent, the choice of the amine is in part dependent upon the solvent selected. For proper operation of the stripping section it is desirable, for example, that the boiling point of the amine be somewhat higher than that of the solvent. The solubility of its carbamate in the solvent, the viscosity of the solution, and the absorption of carbon dioxide are also of importance. Since the differences among solvents had been found to be greater than the differences among most amines, consideration was given first to the effect of different types of solvent.

Effect of Solvent

Since methanol had been used as a solvent in many of the previous experiments (*9*, *10*), it was selected as a reference solvent. Besides the boiling point, the solubility of the amine and the carbamate, the viscosity, etc., two other properties were given consideration in selecting a solvent. These were the basicity and the solubility of carbon dioxide in the solvent. Triethylamine (TEA) and pyridine have significantly different basicities and were found to have suitable solvent properties otherwise. The results of the effect of these solvents on overall separation of 1 *M* di-*n*-butylamine (DNBA) solution are summarized in Table 1.

It can be seen from these results that DNBA in triethylamine ($S_{13} = 2.05$) is considerably more effective than DNBA in methanol ($S_{13} = 1.43$), DNBA in pyridine ($S_{13} = 1.74$), or MEA in methanol ($S_{13} = 1.39$). That is, with 1 *M* DNBA the concentration of ^{13}C was increased by 105% with TEA as solvent compared to 74% for pyridine and 43% for methanol. A small amount of methanol mixed with TEA did not affect the overall separation ($S_{13} = 1.99$), but when the solvent was 50% by volume methanol the overall separation dropped to $S_{13} = 1.52$.

A measure of the total volume of CO_2 absorbed per milliliter of solution could be obtained by measuring the milliliters per minute of amine solution

TABLE 1

Effect of Solvent on Overall Separation in a 2.5-cm i.d. × 100 cm Column with 1 *M* DNBA

Solvent	Flow rate $\frac{ml}{min}$	 $\frac{ml}{cm^2\text{-}min}$	 $L^a \left(\frac{mmoles\ CO_2}{cm^2\text{-}min}\right)$	S	$\ln S$	HETP (cm)
Methanol	4.00	0.800	0.640	1.43	0.358	2.77
TEA	4.17	0.835	0.668	2.05	0.718	1.38
Pyridine	4.15	0.830	0.664	1.74	0.554	1.78
1 *M* Methanol in TEA	4.15	0.830	0.664	1.99	0.688	1.44
50: 50 (v/v) Methanol + TEA	4.15	0.830	0.664	1.52	0.419	2.56

[a] Moles of CO_2 absorbed per mole of DNBA is taken as 0.80 and $\alpha = 1.01$.

pumped to the saturator. This assumes that the amine solution was completely saturated with CO_2 in the saturator. From the CO_2 feed required by the saturator, saturation appeared to be complete. These results are in agreement with the static measurements of the solubilities of CO_2 in amine solutions performed in these laboratories (*13*).

Effect of Amine Concentration on Separation

Because of the small single-stage separation factor ($\alpha \cong 1.01$), it is desirable to use a high concentration of DNBA, large diameter columns, or fast flow rates to increase the interstage flow for large isotope transport. At higher concentrations, due to increased viscosity of carbamate, the advantage gained by higher throughput is reduced by the loss in overall separation. The results obtained in 2.5 cm i.d. × 100 cm exchange column for the DNBA–TEA system are given in Table 2. The concentration of DNBA was varied from 1 to 2.84 *M*. It can be seen that overall separation S_{13} is not greatly affected in the concentration range of 1 to 2 *M*. At concentrations higher than 2 *M* DNBA, the overall separation is affected significantly as seen from the drop in overall separation from 1.94 at 2 *M* to 1.69 at 2.84 *M*. Use of concentrations higher than 2 *M* DNBA not only results in loss of separation but also creates other problems such as deposition of solid carbamate on colder parts of the exchange system. From the practical point of view it was felt that 2 *M* DNBA would be the optimum concentration to be used in the preparation of enriched ^{13}C.

TABLE 2

Effect of Amine Concentration on Overall Separation in a 2.5-cm i.d. × 100 cm Column with DNBA in TEA

DNBA conc (M)	Flow rate						
	$\frac{ml}{min}$	$\frac{ml}{cm^2\text{-min}}$	L^a $\left(\frac{mmoles\ CO_2}{cm^2\text{-min}}\right)$	S	ln S	HETP (cm)	$\frac{HETP}{L}$
1.00	4.17	0.835	0.668	2.05	0.718	1.38	2.07
1.40	4.00	0.800	0.905	2.02	0.703	1.40	1.55
2.00	4.17	0.835	1.338	1.94	0.663	1.50	1.12
2.84	4.00	0.800	1.820	1.69	0.525	1.89	1.04

[a] Moles of CO_2 absorbed per mole of DNBA is taken as 0.80 and $\alpha = 1.01$.

Effect of Catalyst

Because of the relatively slow exchange rate of the amine carbamate–CO_2 system, attempts were made to catalyze the exchange reaction between the carbamate of monoethanol amine in methanol and carbon dioxide using transition metal ions such as Cu^{2+}, CO^{2+}, and Zn^{2+} (*14*). With other amines and solvents they were not very effective as catalysts. Most salts of these elements are not very soluble in DNBA–TEA solutions. However, it was found that anhydrous cupric acetate and zinc acetylacetonate were sufficiently soluble to determine their effect on overall separation. The results obtained in a 2.5-cm i.d. × 90-cm exchange column are summarized in Table 3. It can be seen from these results that neither 0.02 M cupric acetate nor 0.05 M zinc acetylacetonate made a marked improvement in the overall separation.

TABLE 3

Effect of Catalyst on Overall Separation in a 5.2-cm i.d. × 90 cm column using 2 M DNBA in TEA

Flow rate $\left(\frac{mmole\ CO_2}{cm^2\text{-min}}\right)$	Catalyst	S	HETP (cm)
1.15	—	1.61	1.87
1.28	Zn-acetylacetonate	1.55	2.04
1.21	0.02 M Cu-acetate	1.56	2.00

Effect of Flow Rate on Separation

The interstage flow can be increased by increasing the flow rate or concentration of the feed material. In order to determine the optimum flow rate at which various sections in the cascade can be operated, experiments using different diameter columns were carried out. These columns were packed with Heli-Pak 3013 packing and were operated at various flow rates. Typical results obtained in a 5.2-cm i.d. × 90-cm and in a 2.5-cm i.d. × 100-cm exchange column are summarized in Tables 4 and 5.

TABLE 4

Effect of Flow Rate on the Performance of a 5.2-cm i.d. × 90 cm Column with 1 and 2 *M* DNBA in TEA[a]

Flow rate								
$\frac{\text{ml}}{\text{min}}$	$\frac{\text{ml}}{\text{cm}^2\text{-min}}$	L $\left(\frac{\text{mmoles CO}_2}{\text{cm}^2\text{-min}}\right)$	S	ln S	HETP (cm)	$1/L$	$\frac{\text{HETP}}{L}$	$k_Ta \times 10^5$ $\left(\frac{\text{moles CO}_2}{\text{cm}^3\text{-sec}}\right)$
			1 *M* DNBA					
16.0	0.75	0.60	1.70	0.531	1.69	1.67	2.78	0.60
24.0	1.13	0.90	1.49	0.399	2.24	1.11	2.49	0.67
30.0	1.41	1.13	1.41	0.344	2.60	0.88	2.30	0.72
39.2	1.85	1.48	1.35	0.300	2.99	0.68	2.02	0.83
			2 *M* DNBA					
16.0	0.75	1.20	1.63	0.489	1.83	0.83	1.53	1.09
23.5	1.11	1.78	1.45	0.372	2.41	0.56	1.35	1.23
29.4	1.38	2.21	1.37	0.315	2.84	0.45	1.29	1.30
39.2	1.85	2.96	1.25	0.223	4.01	0.34	1.35	1.23

[a] For this table the moles of CO_2 absorbed per mole of DNBA is taken as 0.80 and $\alpha = 1.01$.

TABLE 5

Effect of Flow Rate on the Performance of a 2.5-cm i.d. × 100 cm Column with 2 *M* DNBA in TEA

Flow rate L								
$\frac{\text{ml}}{\text{min}}$	$\frac{\text{ml}}{\text{cm}^2\text{-min}}$	$\frac{\text{mmoles CO}_2}{\text{cm}^2\text{-min}}$	S	ln S	$1/L$	HETP (cm)	$\frac{\text{HETP}}{L}$	$k_T \times 10^5$ $\left(\frac{\text{mole CO}_2}{\text{cm}^3\text{-sec}}\right)$
4.2	0.85	1.3	1.94	0.663	0.77	1.49	1.15	1.43
8.4	1.7	2.7	1.54	0.432	0.37	2.30	0.85	1.85
14.5	2.9	4.6	1.31	0.270	0.22	3.68	0.81	1.98

The effect of flow rate L on overall separation S can be expressed by the equation developed by Cohen (*15*). According to this equation, the variation of overall separation S with flow rate is expressed as

$$\ln S_\infty = \frac{(k_T a)Z(\alpha - 1)}{L} \tag{3}$$

where Z is the length of the column and L is the interstage flow expressed as mmoles CO_2/cm^2-min. The specific transfer rate k_T (moles CO_2/cm^2-sec), when multiplied by the interfacial area (a) in a 1-cm length of column per cm^2 of cross-sectional area, gives an interphase transfer rate $k_T a/cm^3$ of the column.

At the steady state with no product withdrawal, Eq. (3) indicates that $\ln S$ should vary linearly with $1/L$ provided the quantities $(\alpha - 1)$ and $k_T a$ remain constant. Alternatively, Eq. (3) can be put in the form

$$\frac{L}{k_T a} = \frac{Z(\alpha - 1)}{\ln S_\infty} = \text{HETP} \tag{4}$$

so that HETP should vary linearly with flow rate L. In Figs. 5 and 6, plots of HETP vs L, $\ln S$ vs $1/L$, and interphase transfer rate $k_T a$ vs flow rate L are shown. It can be seen from these plots that, at lower flow rates, HETP varies linearly with L, and $\ln S$ varies linearly as $1/L$, but at higher flow rates there is a significant deviation from the linear relationships. The rather rapid increase in HETP with flow rate probably results from a decrease in interfacial area with a corresponding decrease in interphase transfer rate $k_T a$. This is not unreasonable since the viscosity of 2 *M* DNBA in TEA saturated with carbon dioxide is rather high (1.10 cP) as compared to 0.59 cP for 1 *M* DNBA (*13*).

Another measure of the optimum concentration and flow rate is the relative volumes of the single column required for a given overall separation S and the initial transport T for a feed containing atom fraction N_0 of the desired isotope. The volume required is

$$V \approx \frac{T \ln S_\infty}{(N_0)(1 - N_0)} \frac{\text{HETP}}{L(\alpha - 1)^2} \tag{5}$$

or

$$V \approx \text{constant} \frac{\text{HETP}}{L(\alpha - 1)^2}$$

If $(\alpha - 1)$ is constant, the volume required is proportional to the ratio of HETP/L. On this basis, the values of HETP/L tabulated in Table 4 show

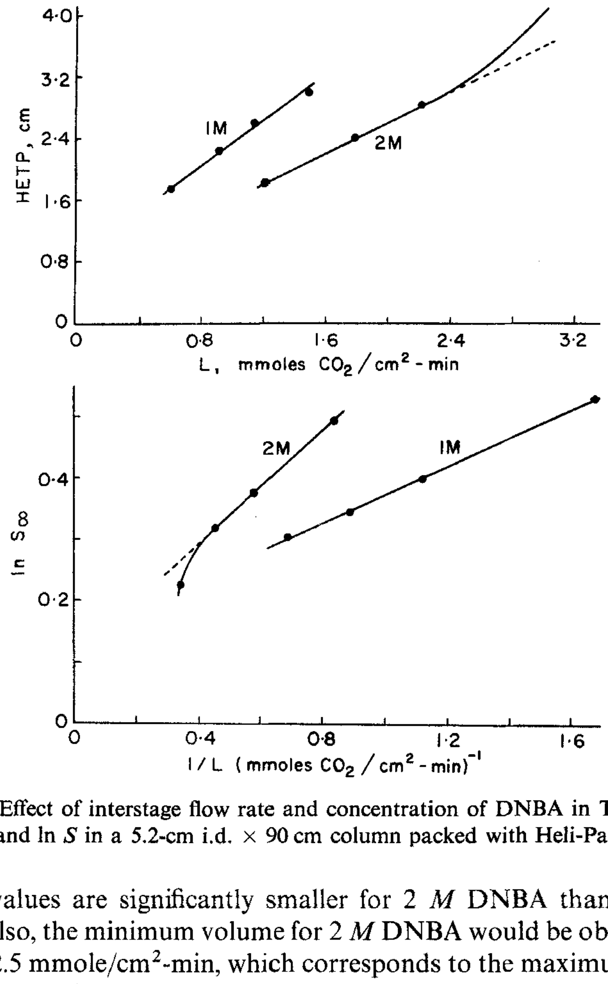

FIG. 5. Effect of interstage flow rate and concentration of DNBA in TEA on HETP and ln S in a 5.2-cm i.d. × 90 cm column packed with Heli-Pak 3013.

that the values are significantly smaller for 2 M DNBA than for 1 M DNBA. Also, the minimum volume for 2 M DNBA would be obtained for a flow of 2.5 mmole/cm^2-min, which corresponds to the maximum for the interphase transfer rate $k_T a$. However, this concentration is too high because of the practical consideration of deposition of solid in the cooler parts of the system, causing obstruction for the free gas flow.

Calculations for a Cascade to Enrich ^{13}C

With the information gathered from the preliminary studies and using known equations, calculations for a multistage exchange system were carried out. The overall separation needed to obtain the desired enrichment in such a system is given by

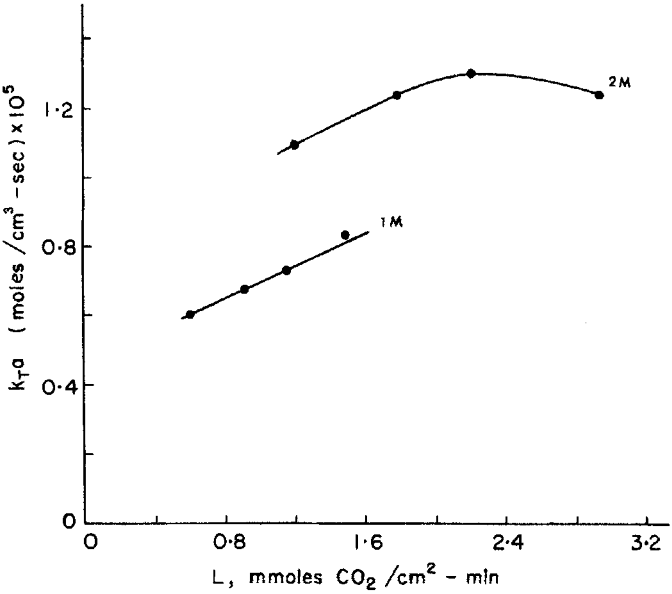

FIG. 6. Effect of interstage flow rate on interphase transfer rate k_Ta in a 5.2-cm i.d. × 90 cm column packed with HeliPak 3013.

$$S = \frac{N_p}{1-N_p} \Big/ \frac{N_f}{1-N_f} = \alpha^n \tag{6}$$

where S is the overall separation, N_p and N_f are the mole fractions of the desired component in the enriched material and feed material, respectively; α is the single-stage separation factor; and n is the total number of theoretical plates. This equation is for operation at equilibrium with no production.

In the present case the single stage separation factor (α) for the chemical exchange

$$R_2N^{12}COO^- + {}^{13}CO_2 \rightleftarrows R_2N^{13}COO^- + {}^{12}CO_2 \tag{7}$$

is assumed to be approximately 1.01. If 90 mole-% ^{13}C ($N_p = 0.90$) is to be obtained from natural feed material with a concentration of 1.13 mole-% ^{13}C ($N_f = 0.0113$), an overall separation S of 786 would be required. According to Eq. (6), this corresponds to 672 theoretical plates for equilibrium operation. For a practical system with production, about 1.5 times the theoretical plates for equilibrium operations are usually provided, which would be about 1000 plates for this system.

When a large number of plates is required, a tapered cascade of several columns is used to reduce the hold-up of the system and thus the time required for steady state. Such an arrangement is particularly important for this system because the transport of isotope is low as a result of the small single-stage separation factor (α) and the slow rate of exchange. Due to the physical limitations of the laboratory, the packed length of the columns was limited to 250 cm. Six columns would provide a total length of 1500 cm.

A column 6.4 cm i.d. × 250 cm long filled with Heli-Pak 3013 was selected for column 1 of the cascade. The area is 32.2 cm^2 so that a liquid flow rate of 1.24 ml/cm^2-min of 2 M DNBA gives a total flow of 40.0 ml/min or an interstage flow L_f of (40 ml/min) (2 M) (0.8 mole CO_2/ml) = 64 mmoles CO_2. This flow rate is somewhat greater than the optimum of 0.8 to 0.9 ml/cm^2-min, but the higher flow rate in the initial column increases the transport of isotope into the system and consequently the rate of production of the isotope.

From material balance considerations, the maximum production PN_p or the transport of ^{13}C is given by

$$PN_p = T = \frac{[L_f N_f(\alpha - 1)(1 - N_f) + PN_f]}{1 + (\alpha - 1)(1 - N_f)} \tag{8}$$

or for the low concentrations of ^{13}C at the feed end of the first column,

$$\begin{aligned} PN_p = T \approx {} & L_f N_f(\alpha - 1)(1 - N_f) \\ & (64)(0.0113)(0.01)(0.9887) \\ & 7.1 \times 10^{-3} \text{ mmoles } ^{13}\text{C/min} \\ & (7.1 \times 10^{-3})(1440)(13) = 131 \text{ mg } ^{13}\text{C/day} \end{aligned}$$

In the above equations, T = transport rate in millimoles of ^{13}C, L_f = flow in millimoles of CO_2 as carbamate and dissolved CO_2, α = single-stage separation factor, N_f = mole fraction of ^{13}C in the product, and P = millimoles of "carbon dioxide" withdrawn as product. A constant transport of 7.1×10^{-3} mmoles of ^{13}C/min as calculated above was used in determining the size and operating conditions for the other five columns of the cascade. Because of fluctuations, losses, etc., only a fraction of the above maximum transport is usually withdrawn as product. It is hoped that at about 75%, 100 mg of ^{13}C/day can be withdrawn from the system.

One of the advantages of the solvent carrier system is that the concentration of the active solute (DNBA) can be varied, and this allows independent changes in the liquid flow rate and the interstage flow L. Thus adjustments for the diameters of the columns used for the cascade can be made by changing the flow rate of 2 *M* DNBA or by changing the concentration of DNBA. The diameters, flow rates, and the estimated concentration of ^{13}C of the six columns used for the cascade are given in Table 6. Columns 1 through 4 were packed with Heli-Pak 3013, and the two smaller columns were packed with Heli-Pak 3012.

Preliminary experiments on the operation of individual columns to near equilibrium indicated that the HETP for the 6.4-cm column at the relatively high flow rate of 1.24 ml/cm^2-min of 2 *M* DNBA would be about 2.3 cm. The approximate values of HETP for the other columns when operated to near their equilibrium separations are 2.0 cm for column 2 and 1.5 cm for columns 3, 4, 5, and 6. These values for HETP correspond to the following numbers of theoretical plates for equilibrium operation with no production: column 1 = 109; column 2 = 125; and columns 3, 4, 5, and 6 = 167. This is a total of 902 instead of the 1000 plates calculated previously. The cascade of six columns provides 902/672 = 1.34 times the minimum number of theoretical plates so that the values for HETP for production will be (1.34)(2.3) = 3.1 cm for column 1; 2.5 cm for column 2; and 2.0 cm for columns 3, 4, 5, and 6 as summarized in Table 6.

An HETP of 3.1 cm for column 1 would result in 250/3.1 = 81 plates or an overall separation ($S = \alpha^n$) of 2.23. The mole fraction N_p of ^{13}C at the product end of this column would be $N_p = SR_f/(1 + SR_f) = (2.23)(0.0114)/(1.025) = 0.025$, where R_f for the feed material with mole fraction N_f of ^{13}C $N_f(1 - N_f) = (0.0113)/(0.9887) = 0.0114$. As calculated previously, a total flow of 40 ml/min (1.24 ml/cm^2-min) of 2 *M* DNBA results in a maximum transport of 7.1×10^{-3} mmoles ^{13}C/min or a maximum produc-

TABLE 6

Diameters of Columns, Flows, and Estimated Concentration of ^{13}C Based upon Steady-State Operation in the Tapered Casade of Six Columns Using 2 *M* DNBA in TEA. Each Column Is 250 cm Long

Column no.	i.d. (cm)	Cross section (cm^2)	HETP (cm)	Mole fraction ^{13}C	L_f $\left(\frac{\text{mmoles}}{\text{min}}\right)$	F liquid flow (ml/min)	F $\left(\frac{\text{ml}}{\text{cm}^2\text{-min}}\right)$
1	6.4	32.2	3.1	0.025	64.0	40.0	1.24
2	5.2	21.2	2.7	0.061	28.6	18.7	0.87
3	3.4	9.1	2.0	0.18	11.7	7.3	0.81
4	2.5	4.9	2.0	0.43	3.8	2.4	0.49[a]
5	1.5	1.77	2.0	0.73	1.5	0.95	0.54[a]
6	1.18	1.09	2.0	0.90	0.61	0.38	0.37[a]

[a] These flows can be increased, if necessary, for proper wetting of the packing by decreasing the DNBA concentration.

tion rate $P = T/N_p = 7.1 \times 10^{-3}/0.90 = 7.9 \times 10^{-3}$ mmoles of "carbon dioxide"/min at 90% ^{13}C.

The product material from column 1 with mole fraction 0.025 for ^{13}C enters the feed end of column 2. With an HETP of 2.7 cm, there will be 93 plates in the 250-cm column and the separation in this column will be 2.5. The total separation at the bottom of column 2 will then be (2.23)(2.5) = 5.6 or a ^{13}C concentration of 0.061. In order to maintain a constant transport T of ^{13}C, the flow L_f required can be obtained as follows from a rearranged form of Eq. (6):

$$L_f = \frac{T[1 + (\alpha - 1)(1 - N_f)] - PN_f}{(N_f)(1 - N_f)(\alpha - 1)} \tag{9}$$

$$= \frac{(7.1 \times 10^{-3})[1 + (0.01)(0.975)] - (7.9 \times 10^{-3})(0.025)}{(0.025)(0.975)(0.01)}$$

$$= \frac{7.17 \times 10^{-3} - 0.197 \times 10^{-3}}{2.47 \times 10^{-4}} = \frac{6.97 \times 10^{-3}}{2.47 \times 10^{-4}}$$

$$= 28.6 \text{ mmoles/min}$$

Since 1 ml of 2 M DNBA in TEA absorbs 1.6 mmoles of CO_2, a liquid flow rate of $F = L_f/1.6 = 28.6/1.6 = 18.7$ ml/min.

The diameter of column 2 is 5.2 (area = 21.2 cm^2), so that the flow of 2 M DNBA in ml/cm^2-min is 18.7/21.2 = 0.87. This is near the optimum flow rate of 2 M DNBA in this column as determined in the preliminary experiments.

Similar calculations were made for the four remaining columns and the results are summarized in Table 6. For optimum flow of 0.8 to 0.9 ml/cm^2-min in column 4, it would be desirable to use a smaller diameter column but a column 2.5 cm i.d. was already available. If the 0.50 ml/min is too low for proper wetting of the packing (Heli-Pak 3013) in column 4, the concentration of DNBA can be decreased to 1 to 1.5 M DNBA with a corresponding increase in the flow rate to give the required interstage flow for constant transport T of ^{13}C. Columns 5 and 6 with the smaller size packing (Heli-Pak 3012) may operate properly at the lower flow rates and give even shorter values for HETP. If they do not, as will be shown by the data for the start-up of the system, the concentrations of DNBA and the flow rates can be changed.

Schematic Arrangement and Operation of the Cascade

A flow sheet showing the general arrangement of each section of the cascade is shown in Fig. 7. Each section contains a saturator at the top, an exchange column, and a reboiler with a stripping section at the bottom. The dimensions of each of these components of the section were chosen so that the system could be operated under a variety of conditions. These sections were then intercoupled in such a manner that each of them could be isolated from the rest of the system in the event of a breakdown. A typical coupling of two sections is shown in Fig. 8.

The tapered design of the cascade of columns necessitates a progressive decrease in the amine flow rate from section 1 through section 6 (see Table 6). A solution of 2 *M* DNBA in TEA is pumped at the predetermined flow rate from the boiler B_1 into amine saturator S_1 (Fig. 8) where it reacts with a feed of natural CO_2 to form amine carbamate. Excess CO_2 from the saturator passes through the amine trap and is discarded as waste. The amine carbamate solution flows into the exchange column and then to boiler B_1 where it is decomposed completely into amine solution and carbon dioxide.

The whole amount of carbon dioxide is then allowed to enter amine saturator S_2 to form carbamate. Since the flow of amine is less, part of this CO_2 is used and the rest is returned to the bottom of column C_1. The carbamate that flows through column C_2 enters boiler B_2 and is decomposed there into amine and CO_2. The amount of CO_2 formed in B_2 is fed to the saturator S_3 and the excess is returned to the bottom of column C_2.

All the sections are similarly interconnected. The gas that leaves the top of each column is mixed with the excess gas leaving the saturator of that column. Due to this type of coupling, the amount of gas that is entering at the bottom of any column is equivalent to the amount of gas that is leaving the boiler associated with that column.

The advantage of the above type of intercoupling of sections lies in the fact that one does not need additional pumps to transport enriched material in the forward directions. However, it is necessary to balance the flow of solvent vapors in the forward and backward directions by cooling the gases at the proper places. Failure to obtain solvent balance results in changes of the DNBA concentration. Gas chromatographic analysis was used to detect any changes in concentration that occurred so that corrections could be made.

It was convenient to condense the solvent vapors in the waste gases from section 1 and return the required amount of solvent to the system. Therefore, the gases from saturator S_1 and the exchange column C_1 were passed through a cooled amine trap to recover the solvent. The liquid level in boiler B_1 was maintained at a predetermined mark with a thermistor level controller.

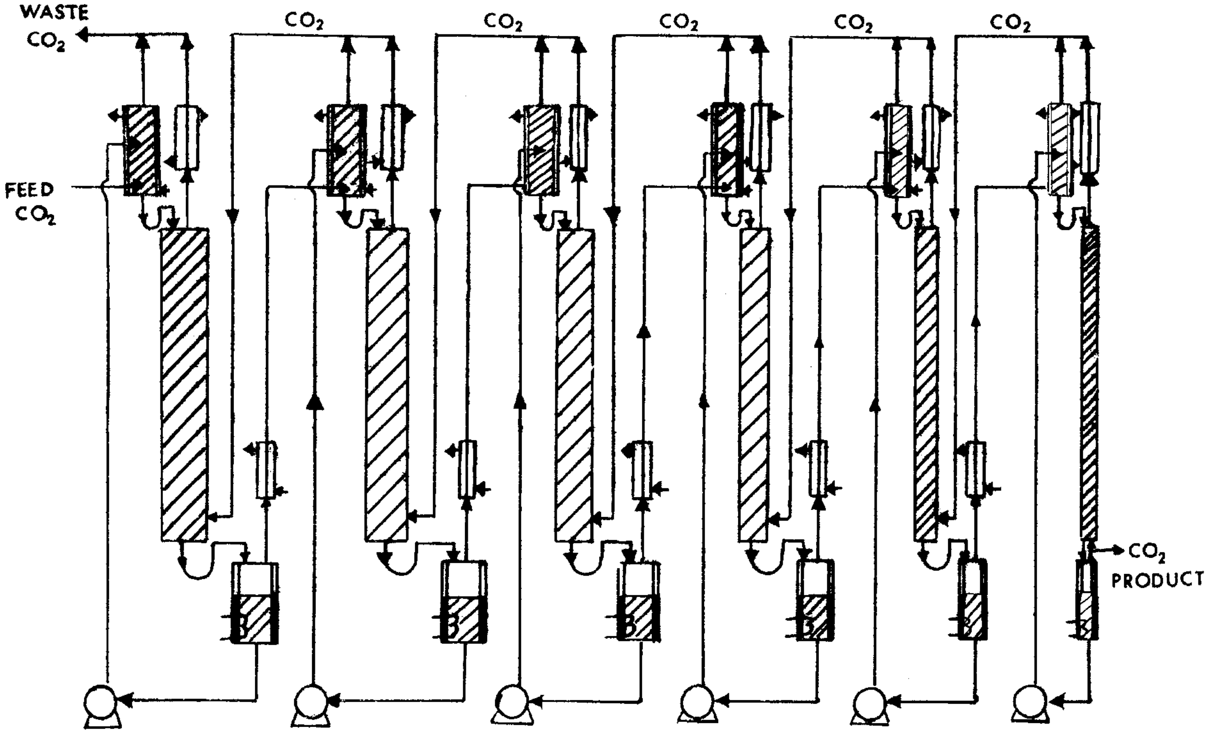

FIG. 7. Flow diagram for a tapered cascade of six sections to concentrate ^{13}C. All the sections are 250 cm long and their diameters are, from left to right, 6.4, 5.2, 3.4, 2.5, 1.5, and 1.18 cm. The first four sections are packed with Heli-Pak 3013 (0.050 × 0.100 × 0.100 in.) and the last two sections are packed with Heli-Pak 3012 (0.030 × 0.070 × 0.070 in.).

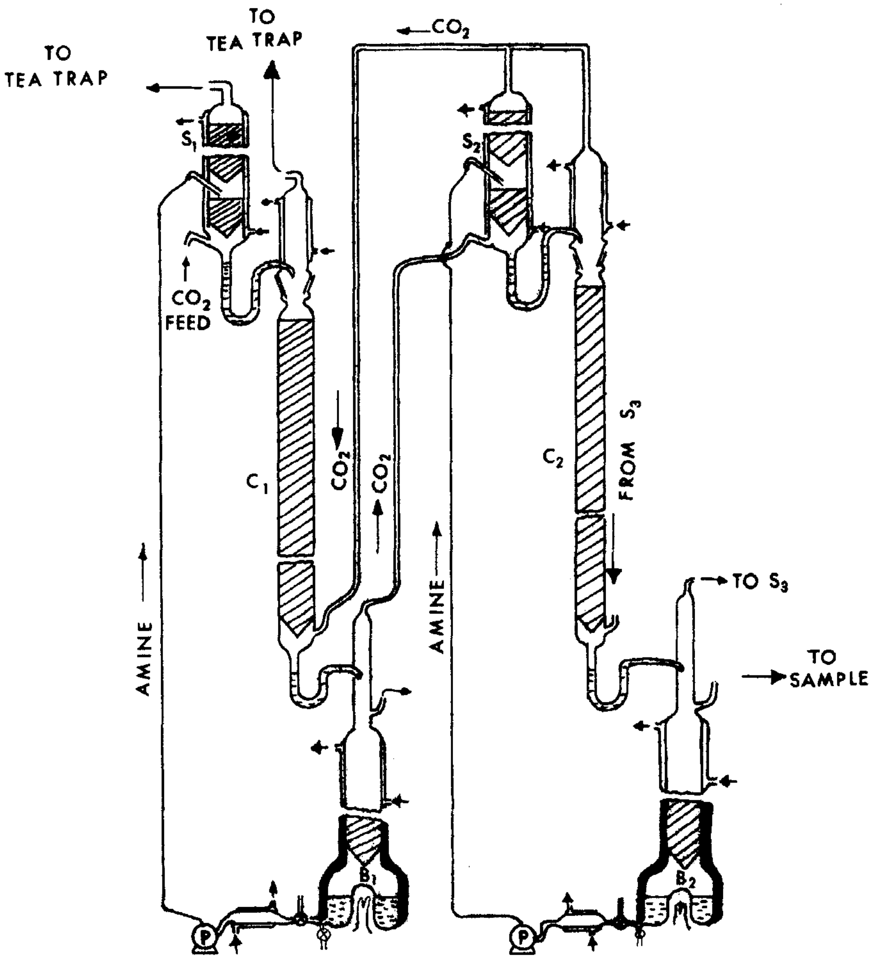

FIG. 8. Schematic diagram showing a typical intersection coupling for two sections of the cascade. P, pumps; B_1 and B_2, boilers; C_1 and C_2, exchange columns; and S_1 and S_2, amine saturators.

Operation of the Six-Stage Cascade

Since the time required to reach steady state for a multistage cascade would be rather long, from the practical point of view it was desirable to try various start-up procedures to reduce the time period to start production. On this basis, the following three procedures were considered:

(a) Start all the stages of the cascade together having CO_2 feed at first stage only.

(b) Start all the stages individually, each having its own CO_2 feed, and after reaching the steady state interconnect them.

(c) Start first stage only, allow it to reach steady state, and then connect it to stage two, allow the second stage to reach steady state, and then connect it to stage three.

The preliminary studies on the start-up procedure indicated that the procedure (a) was the best one, since it minimized time to start production and also eliminated possible loss of product due to coupling and uncoupling of the joints.

In order to start the cascade, all the columns were flooded with 2 *M* DNBA solution in TEA. The solution was then drained slowly while pumping 2 *M* solution of DNBA in TEA to the saturators. When excess solution from all the columns was removed, and all of them were operating at their predetermined flow rates, CO_2 feed to the column 1 was started. After about 30 min when the carbamate was flowing down into boiler 1, the boiler heater was turned on. The CO_2 thus produced in boiler 1 was then fed to saturator 2. Similarly, when the carbamate was flowing down from the bottom of column 2, boiler heater 2 was turned on. This procedure was continued until all six columns were operating properly. The cascade was operated continuously for 141 days. During this period the overall separation in the sixth section, i.e. the product end of the cascade, reached to a value of 177 (66.9% ^{13}C). A typical mass spectrum of the product $^{13}CO_2$ is shown in Fig. 9.

Conclusions

It was observed that the cascade could be operated without any major difficulty with minimal manpower. Even though the exchange reaction has a slower exchange rate and smaller single-stage separation factor, the

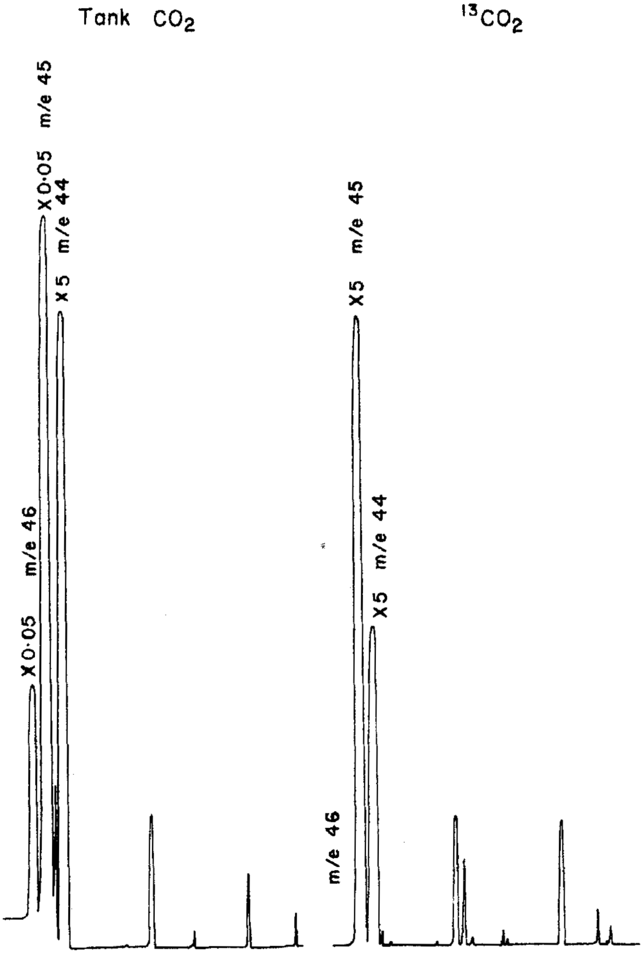

FIG. 9. A typical mass spectrum of a ^{13}C enriched carbon dioxide gas sample.

separation method stands on its merits of low capital investment, ease of operation, and moderate production rate of highly enriched ^{13}C.

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