nature of the eluite itself. Data from a wide variety of probes will be needed to formulate a more complete picture of the separation mechanism in reversed-phase liquid chromatography.

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Suppression of Boron Volatilization from a Hydrofluoric Acid Solution Using a Boron–Mannitol Complex

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Volatilization and mass fractionation of boron during evaporation of the hydrofluoric and hydrochloric acid solutions were investigated with varying mannitol/boron ratios. The degree of volatilization and mass fractionation decreases with increasing mannitol/boron mole ratio, and the boron volatilization is completely suppressed when the ratio is more than unity. These results indicate that the final stable compound is an equimolar complex of boron and mannitol. The formation of this complex in the acid solutions allows the use of hydrofluoric and hydrochloric acids for the dissolution of silicate rock samples and for the subsequent chemical separation of boron from the samples adopting anion-exchange chromatography in F⁻ form.

INTRODUCTION

Boron in acidic solutions is easily volatilized during evaporation to dryness relative to neutral or alkaline solutions. This property of boron prohibits the use of acids in the separation of boron from natural samples. Boron in hydrofluoric and hydrochloric acids produces gaseous boron fluoride (BF_3) and chloride (BCl_3), which have boiling points of -101 and $+12.5\ °C$, respectively. Hence they easily escape from the solutions and cause boron isotopic fractionation even at room temperature. Due to the above reasons, the most widely used techniques to separate boron for isotopic analysis are methyl borate distillation (1–4), ion-exchange chromatography (3, 5–7), and pyrohydrolysis (5). None of these techniques employ acid treatments and/or evaporations without rendering the solution alkaline, usually by using sodium hydroxide to form borax.

It is widely known that boric acid reacts with many hydroxy compounds such as alcohol or phenol to form stable complexes. In particular, mannitol has been adopted commonly to the quantitative determination of boron (8, 9), because it forms the mannitol–boric acid complex by the reaction with boric acid and drastically raises the degree of electrolytic dissociation. Furthermore, some previous studies have revealed that mannitol suppressed the volatilization of boron from solutions of water, hydrochloric acid, and nitric acid during evaporation (10, 11). In these studies the experiments were carried out at pH 3–11 with a small amount of boron (around 1 μg) or with concentrated acids with considerably large amounts of boron (>500 μg). However, the volatilization of boron and resulting isotopic fractionation have not been examined for the boron–mannitol complex in the hydrofluoric acid and concentrated hydrochloric acid solutions with small amounts of boron.

In this paper, we report that the boron–mannitol complex traps even small amounts of boron (<5 μg) in the hydrofluoric and hydrochloric acid solutions without any volatilization and isotopic fractionation during evaporation. We also stress that this provides a great advantage in the development of new analytical techniques for boron separation from natural silicate

samples and solutions using hydrofluoric and hydrochloric acids, allowing us to develop a new field of stable isotope geochemistry for boron.

EXPERIMENTAL SECTION

Instrumentation. *Mass Spectrometer.* A first-order, stigmatic focusing thermal ionization mass spectrometer, MAT 261, controlled by an HP 9835A computer was employed for all the measurements of boron isotopic composition. Its resolving power is normally about 500. The accelerating voltage was adjusted to 10 kV. A single Faraday cup collector and a 10^{11}-Ω resistor are attached, and ion currents of 10^{-14}–10^{-10} A are available for the isotopic determination. V-Shaped single tantalum filaments (2 mm top × 0.025 mm × 0.75 mm) previously degassed were used.

Reagents. *Water.* Water deionized with mixed-bed ion-exchange resin was subboiled by using a pure-quartz subboiling still (*12*) and subsequently subboiled by using a two-bottle Teflon still (*13*).

Hydrofluoric Acid. Analytical grade 46% hydrofluoric acid, in which several grams per liter of mannitol was dissolved, was subboiled in a two-bottle Teflon still, and then the distillate was diluted to an appropriate concentration with the twice-distilled water previously described.

Hydrochloric Acid. Analytical grade 35% hydrochloric acid was diluted to 6 M with deionized water and subboiled by using a quartz boiling flask with an Alihn-type condenser. This was again subboiled by using the two-bottle Teflon still with mannitol in the same way as used for hydrofluoric acid.

Boric Acid. National Bureau of Standards standard reference material (NBS SRM) 951 boric acid was used as a standard for all the boron isotopic measurements. NBS SRM 952, boric acid enriched in ^{10}B, was also employed as a spike for the isotope dilution mass spectrometry (IDMS). These boric acids were dissolved in the twice-distilled water to obtain 6.0013 and 4.08 ppm boron concentrations for SRM 951 and 952, respectively.

Mannitol Solution. Analytical grade mannitol was dissolved in the twice-distilled water to obtain a 1000 ppm (5.49×10^{-3} M) solution.

Cesium Solution. Analytical grade cesium carbonate was dissolved in the twice-distilled water to give a 9.25×10^{-3} M cesium solution.

Graphite. Spectroscopic grade graphite, the same as that used by Xiao et al. (*7*), was mixed with a 50% ethanol/50% water (v/v) solution to give 40 mg/mL graphite.

All reagents used were stored in PFA Teflon bottles.

Procedure. *Mass Spectrometry.* The thermal ionization mass spectrometric technique using the dicesium metaborate cation $Cs_2BO_2^+$ emitted from the stable compound $Cs_2B_4O_7$ (*5, 7, 14*) was applied for the determination of boron isotopic composition. Cesium solution was added to the sample containing boron and mannitol to produce a B/Cs mole ratio of 2 and then loaded onto the V-shaped tantalum filament previously coated by 30 μg of graphite. After drying under the heating lamp, the sample was introduced into the mass spectrometer. When the vacuum reached 3×10^{-7} Torr, the filament current was raised to 0.9 A and then the ratio between $Cs_2^{10}BO_2^+$ (308 m/e) and $Cs_2^{11}BO_2^+$ (309 m/e) was measured against the base line at 306.5 m/e. Data collection was performed by peak hopping. The integration time for each mass peak was 4 s, and 90 ratios were collected in 10 blocks. Measured ratios were corrected for oxygen isotopes to exclude the interference of $Cs_2^{10}B^{16}O^{17}O^+$ as follows: $^{11}B/^{10}B$ = (measured 309/308 ratio) − 0.00079 (*5*). Boron with mannitol loaded onto the graphite-coated tantalum filament resulted in a slight reduction of the signal intensity and stability compared with the condition using graphite alone. Nevertheless, the ion current of $Cs_2^{11}BO_2^+$ was typically 1×10^{-11} A, which was about 1 order of magnitude higher than that obtained without graphite and mannitol. No isotopic fractionation was observed during the measurement, as reported in the previous studies (*5, 7, 14*). Ten separate analyses of SRM 951 (0.9×10^{-7} mol of B) gave a mean $^{11}B/^{10}B$ ratio of 4.0513 ± 0.0004 ($2\sigma_{mean}$). The value obtained in this study is distinguishably higher than the certified value of 4.04362 ± 0.00137 (*15*). However, $(^{11}B/^{10}B)_{cert}/(^{11}B/^{10}B)_{measd}$ for SRM 951 was 4.04362/4.0513 = 0.99810, which is identical with the Xiao et al. result (0.99833) determined by the $Cs_2BO_2^+$ method with graphite alone (*7*).

Table I. Recovery Yields of Boron from Acid Solutions

starting conditions				B recovery yield	
boron, nmol	mannitol, nmol	mannitol/B mole ratio	acid	nmol	%
276.2	0	0	3 M HF	24.5	8.9
277.2	46.3	0.167	3 M HF	160.1	57.8
270.8	75.1	0.277	3 M HF	173.1	63.9
265.1	133.8	0.505	3 M HF	253.4	95.6
276.5	144.1	0.521	3 M HF	251.2	90.8
262.5	171.5	0.653	3 M HF	246.0	93.7
266.3	207.9	0.781	3 M HF	267.9	100.6
259.7	282.3	1.087	3 M HF	261.7	100.8
261.6	342.9	1.311	3 M HF	260.8	99.7
258.5	417.5	1.615	3 M HF	260.7	100.8
271.7	562.7	2.071	3 M HF	268.9	99.0
265.1	544.2	2.053	46% HF	262.9	99.2
268.9	833.6	3.100	6 M HCl	269.3	100.1

Table II. Measured $^{11}B/^{10}B$ Values of B Residues Resulting from Evaporation of Acid Solutions

starting conditions				residue	
boron, nmol	mannitol, nmol	mannitol/B mole ratio	acid	$^{11}B/^{10}B$	2σ
293.0	0	0	3 M HF	3.9463	±0.0009
298.7	0	0	6 M HCl	3.9240	±0.0007
274.5	75.6	0.275	3 M HF	4.0352	±0.0007
276.4	141.3	0.511	3 M HF	4.0486	±0.0005
278.0	329.3	1.185	3 M HF	4.0492	±0.0009
269.8	531.6	1.968	3 M HF	4.0507	±0.0005
271.7	556.3	2.047	46% HF	4.0509	±0.0006
274.6	550.3	2.004	6 M HCl	4.0511	±0.0009

Recovery Yield of Boron. In order to confirm whether or not mannitol actually suppresses the volatilization of boron from the hydrofluoric and hydrochloric acid solutions, recovery yields of boron during the evaporation to dryness were examined by varying the amount of mannitol. A 0.5-mL aliquot of SRM 951 boric acid solution containing about 3 μg of boron (2.8×10^{-7} mol) was transferred into a 5-mL concave-bottom beaker made of PFA Teflon and weighed precisely (Table I). Various amounts of mannitol solution were added by weighing into the beakers, resulting in the mannitol/boron mole ratio ranging from 0 to 3 (Table I). Afterward, 2 mL each of 3 M HF, 46% HF, and 6 M HCl was added one by one to the prepared samples, and the solutions were then evaporated to dryness by using a hot plate with an infrared lamp at a steady-state temperature of 65–70 °C. To avoid extra heating of the residue after evaporation to dryness, heating was stopped within 30 min after the evaporation was completed. Subsequently, a precisely weighed 0.5-mL SRM 952 spike solution (2.0×10^{-7} mol of boron) was added to each residue. Appropriate amounts of cesium solution to give a B/Cs mole ratio of 2 and 50 μL of mannitol solution (2.2×10^{-7} mol) were added to the spiked samples, and the solutions were again evaporated to dryness in the above manner. Their boron isotopic compositions were measured by using the mass spectrometric technique described previously. The recovery yields of boron in the first evaporation were calculated from the given $^{11}B/^{10}B$ ratios by IDMS. The boron blank from the reagents was typically less than 700 pg, and analytical error in the determination of recovery yield was less than 1%.

Examination of Isotopic Fractionation. Isotopic compositions of residual boron after the evaporation of solutions were measured to investigate the isotopic fractionation resulting from the volatilization of boron. SRM 951 solution containing 3 μg of boron (2.8×10^{-7} mol) was taken into eight individual Teflon beakers together with various amounts of mannitol up to 5.5×10^{-7} mol (Table II). A 2-mL aliquot of 3 M HF was added to five of the beakers, 2 mL of 46% HF to one of the beakers, and 6 M HCl to the remaining 2 beakers. The evaporation of the solutions was subsequently carried out in a way similar to that of the former experiment. Boron isotopic compositions of the residues were then determined.
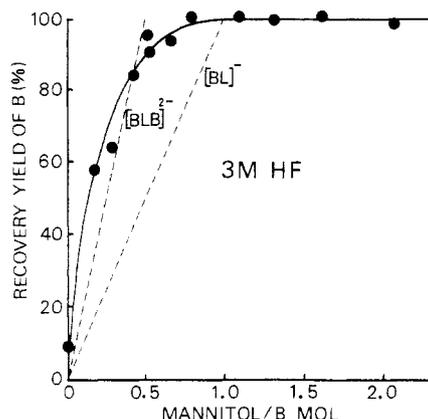
Figure 1. Boron recovery yield after evaporation of the 3 M HF solution vs varying mannitol/boron mole ratio. Analytical errors are within the symbol. Broken lines with [BL]⁻ and [BLB]²⁻ represent the theoretical recovery lines expected when the [BL]⁻ and [BLB]²⁻ type complexes are independently formed.

RESULTS AND DISCUSSION

Boron Volatilization from the Acid Solutions in the Presence of Mannitol. Recovery yields of boron after the evaporation of the hydrofluoric and hydrochloric acid solutions containing various amounts of mannitol are listed in Table I. Recoveries for the 3 M HF solutions are plotted against the mannitol/boron mole ratio in Figure 1. The recovery yield from the mannitol-free 3 M HF solution is only 9%. However, it drastically rises with increasing amounts of added mannitol and reaches about 90% when the mannitol/boron mole ratio is more than unity. Similar results were also obtained for the 46% HF and 6 M HCl solutions.

Feldman (10) showed that mannitol suppressed the volatilization of boron from water, HCl, and HNO₃ solutions when more than 500 μg of boron was accompanied by a 10-fold molar excess of mannitol. On the other hand, Kuwada et al. (11) asserted that even a 30-fold molar excess of mannitol to low levels of boron (0.3 μg) was not sufficient to resist such a loss from water and quasi-neutral solutions without the addition of base. These previous observations do not agree with the results obtained in this study. Feldman (10) revealed that about 90% of the boron was volatilized from solid H_3BO_3 by continuous heating at 80 °C for 12 days. Nevertheless, in Feldman's (10) experiment with mannitol, dried residues were heated overnight (16 h) at 75–77 °C. Although the temperature during evaporation of the solution was strictly maintained lower than 80 °C in the previous studies, little attention was paid to the extra heating after complete evaporation of the solution. It was often observed in the present experiment that such an extra heating of the residue over several hours distinguishably lowered the recovery yield of boron even if the mannitol/boron mole ratio was more than unity. However, the effect was negligible when the heating was stopped within 30 min after the complete evaporation. Therefore, the disagreement between the previous studies and ours is probably derived from boron volatilization by the extremely long extra heating after dryness in the previous studies.

Isotopic Fractionation of Boron during the Evaporation. Boron isotopic compositions of the evaporated residues from the acid solutions containing NBS SRM 951 boric acid are presented in Table II and plotted against the mannitol/boron mole ratio for the 3 M HF solution in Figure 2. Without mannitol, residual boron shows an extremely low $^{11}B/^{10}B$ ratio, indicating the preferential enrichment of ^{11}B into the gas phase in the form of BF_3 or BCl_3 during the evaporation of solution. Figure 2 indicates that the $^{11}B/^{10}B$ ratio of the resulting residue increases with increasing amount of mannitol relative to boron and becomes constant when the
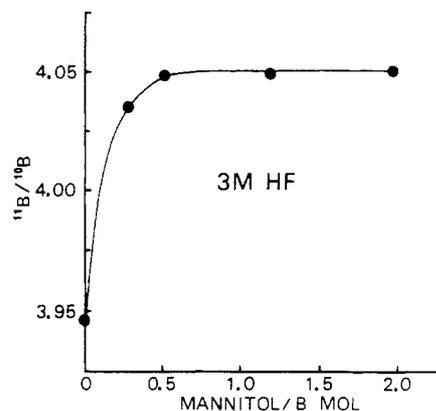
Figure 2. Boron isotopic compositions of the evaporated residue from the 3 M HF solution vs changing mannitol/boron mole ratio. Analytical errors are smaller than the symbol.
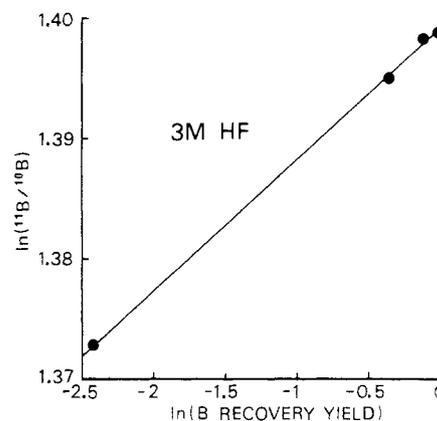
Figure 3. Logarithmic plot of boron recovery yields vs $^{11}B/^{10}B$ ratios of evaporation residues from the 3 M HF solution. The solid line represents a regression line: ln ($^{11}B/^{10}B$) = 0.01089 ln (B recovery yield) + 1.399.

mannitol/boron mole ratios exceed unity, as predicted in Figure 1. The constant boron isotopic compositions within the experimental errors were obtained for the residues with a mannitol/boron mole ratio >1 regardless of acid concentration. These isotopic ratios firmly agree with our $^{11}B/^{10}B$ value (4.0513 ± 0.0004) for SRM 951, which was determined without any use of strong acids. Although the recovery yield expected from Figure 1 is around 90% at a mannitol/boron mole ratio ≈0.5, the difference in boron isotopic composition between the residue and the unfractionated SRM 951 is only 0.6 per mil.

Figure 3 shows a logarithmic plot of $^{11}B/^{10}B$ values of residues in Figure 2 against the corresponding boron recovery yields estimated from the smoothed curve in Figure 1. A tight linear correlation between them indicates that the boron isotopic fractionation during evaporation of the hydrofluoric acid solution is controlled by a Rayleigh-type distillation, which is expressed by the equation

$$\ln R = (\alpha - 1) \ln f + \ln R_0$$

where R_0, R, f, and α are the initial and fractionated $^{11}B/^{10}B$ ratios of residues, boron recovery yield, and the kinetic isotope separation coefficient, respectively. The α in this study is defined as $(^{11}B/^{10}B)_{BF_3}/(^{11}B/^{10}B)_{B-mannitol}$ at 70 °C and is calculated to be 1.011 from the slope of the regression line in Figure 3. The α obtained is fairly close to the estimated value of 1.013 from the observation of kinetic isotope fractionation between BF_3 and the BF_3-anisole complex at 50–100 °C (16).

Structure of the Boron–Mannitol Complex in the Hydrofluoric Acid Solution. In general, boric acid easily

reacts with hydroxy compounds which have a hydroxyl group in the cis position. Mannitol, $CH_2OH-(CHOH)_4-CH_2OH$, one of the polyhydric alcohols, has two pairs of cis OH groups; thus it is considered that the boron–mannitol complex is constructed by occupying these sites. In spite of its broad chemical utilization, however, the molecular structure of the boron–mannitol complex has not been well understood.

According to Barbier and Rosset (17), the structure of the boron–mannitol complex in an aqueous solution is strongly affected by the mannitol/$B(OH)_3$ mole ratio based on the affinity of the boron–mannitol complex to the anion-exchange resin as follows: (1) when the mannitol/$B(OH)_3$ mole ratio is <1, boron exists as the [BL]⁻ complex, where L is mannitol, as well as borate and polyborate ions; (2) when the ratio is from 1 to 2, both [BL]⁻ and [LBL]⁻ complexes are formed and the proportion of the [LBL]⁻ complex progressively increases with increasing mannitol/$B(OH)_3$ mole ratio; (3) when the ratio is >2, all boron behaves as the [LBL]⁻ complex.

Figure 1 illustrates the formation of the boron–mannitol complex vs changing mannitol/boron mole ratio in the hydrofluoric acid solution. The recovery yield of boron implies the magnitude of formation of the boron–mannitol complex in the hydrofluoric acid solution. Achievement of the complete boron recovery at the mannitol/boron mole ratio of 1 suggests that the final stable compound is an equimolar complex of boron and mannitol ([BL]⁻). Nevertheless, the nonlinear and steeper gradient of the boron recovery curve in the range of mannitol/boron ratio <0.5 strongly suggests the formation of the [BLB]²⁻ complex in addition to the [BL]⁻ complex. In the [BLB]²⁻ complex, two pairs of cis OH sites in mannitol are both occupied by boron. The two broken lines in Figure 1 indicate the theoretical recoveries of boron resulting from the formation of [BLB]²⁻ and [BL]⁻ type complexes, respectively. From the above observations, the following aspects can be pointed out in terms of the structure of the boron–mannitol complex: (1) when the mannitol/boron mole ratio is smaller than 0.5, the dominant form of the boron–mannitol complex is [BLB]²⁻, and the reaction formula is given by

(2) as the ratio is increased, the [BLB]²⁻ complex is progressively replaced by the [BL]⁻ complex

and/or the more polymerized form, $[BL]_n{}^{n-}$

and (3) when the ratio is more than 1, all boron occurs as the [BL]⁻ type complex.

The presence of the [LBL]⁻ complex in aqueous solution observed by Barbier and Rosset (17) is not consistent with our results. This disagreement, however, might originate from the difference in boron species existing between aqueous solution and the hydrofluoric acid solution. In the hydrofluoric acid solution, boron occurs entirely as BF_4^-, whereas in aqueous solution, boron exists as $B(OH)_3$, $B(OH)_4^-$, or other borates.

Application to the Boron Isotopic Analysis in Natural Samples. In the course of boron separation from natural samples for the isotopic analysis, any chemical operation accompanied by acid treatment has previously been restricted due to the boron isotopic fractionation during evaporation of the solution. Thus sample decomposition and subsequent chemical procedures have been carried out usually in the presence of excess base. The most general method for the separation of boron from natural rock samples for that purpose is a methyl borate distillation technique after decomposition of the sample with alkali fusion (e.g. refs 2 and 3). In that method, it is often difficult to achieve the high recovery yield of boron; therefore considerable isotopic fractionation arises during the distillation (4). Furthermore, alkali fusion requires a large amount of flux such as sodium carbonate and a high temperature exceeding 800 °C. This sample decomposition method might, therefore, magnify the boron blank and induce the loss of boron from the sample in the crucible through volatilization.

As discussed in the previous section, mass fractionation and volatilization of boron during evaporation of the hydrofluoric and hydrochloric acid solutions are completely suppressed when the mannitol/boron mole ratio is more than unity. This property of mannitol with boron enables us to make use of hydrofluoric and hydrochloric acids in the course of boron separation from the natural samples, especially from silicate rock samples for the isotopic analysis. Sample decomposition can be performed with concentrated hydrofluoric acid generally employed in isotopic analyses such as for Sr and Nd. Since boron exists as BF_4^- in the hydrofluoric acid solution, it is possible to isolate boron from other elements in the natural rock and solution samples adopting anion-exchange chromatography in the F⁻ form. Most of the major elements of rock samples in the hydrofluoric acid solution are not adsorbed in the anion-exchange resin because they behave as cations. Therefore, a large ion-exchange capacity is not required in this method for boron separation. This makes it possible to reduce the volume of resin and eluent and consequently diminish the total blank of boron in the chemical procedure. Accordingly, it is conceivable to separate trace amounts of boron from natural rock samples including basalts, ultramafic xenoliths, and meteorites that have extremely low boron concentrations (<1 ppm). We have successfully developed a new technique that can be applied to determine the precise isotopic composition of a trace amount of boron (≈ 1 μg) in the natural samples by using anion-exchange chromatography with mannitol, which was described elsewhere (18).

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Separation of Permanent Gases by Single-Column Gas–Liquid Chromatography with Liquid Nitrogen as the Stationary Phase

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Mixtures of neon, argon, krypton, nitrogen, carbon monoxide, oxygen, and methane were separated by gas–liquid chromatography at 77 K. The mobile phase was a mixture of nitrogen and helium. The stationary phase was a very thin film (10–20 Å) of "liquid" nitrogen adsorbed onto the surface of an inert solid support. The components were eluted in the order of their boiling points, except for CO and CH$_4$ which adsorbed on some of the solid supports. The systems were very efficient with minimum HETP values of ~500 μm with support particles of 150–180 μm packed in a 40-cm column. The van Deemter curves were essentially flat due to the high density and low diffusion coefficients of the mobile phase and the very low film thickness of the stationary phase. Henry's law constants for the solute gases in liquid nitrogen at 77 K were measured. The gas–liquid solubility measurements are unique because the solutes were all less volatile than the solvent.

INTRODUCTION

The separation and analysis of gaseous mixtures containing some or all of the gases neon, nitrogen, carbon monoxide, argon, oxygen, krypton, and methane is a common analytical problem of interest in the production and analysis of commercial gases, as well as natural, artificial, and even extraterrestrial atmospheres. Gas–solid chromatography with molecular sieves, other zeolites, and porous polymers has been used successfully for such separations (1–5). However, analyses of mixtures of different compositions or concentrations often require specially designed separation strategies, systems, or conditions. Some schemes require subambient temperatures or even subambient-temperature programming. Others require multiple columns, multiple ovens, or multiple injections. In some cases, the oxygen is removed chemically to allow analysis of the remaining gases. In any case, the additional manipulations required diminish the accuracy and convenience usually associated with an isothermal GC analysis.

The chromatographic properties of zeolitic adsorbents are strongly influenced by the particle structure, composition, and surface properties. The type, charge, and number of exchangeable cations and the degree of hydration of the zeolites also affect the performance of the adsorbents. Rigorous and repeated conditioning at high temperatures is often required, and water as well as reducing gases must be excluded from some systems. If these conditions are fulfilled, however, zeolites can resolve the components of such mixtures at ambient or higher temperatures with packed columns in only a few minutes. The elution order of the gases is determined primarily by polarizability; however, the elution order for different zeolite separations varies with the type and water content of the zeolites (1).

Separation of Ar and O$_2$ is particularly difficult because the sizes and polarizabilities of these two gases are almost identical and the boiling points differ by only 3 deg. However, separations of these gases have often been achieved on zeolites.

Porous polymers have also been used for the separation and analysis of atmospheric and permanent gases. The chromatographic properties of the polymers are determined primarily by the composition of the polymer and not so much by the chemical or physical treatment or history of the adsorbents. Such polymers have been used routinely to separate Ar and O$_2$ at ambient or higher temperatures in 5–10 min (2, 3), and this type of polymer was used for the NASA missions to Mars and Venus (4, 5). However, a major problem with the porous polymers is the batch-to-batch variability of the synthetic products. Also, the elution order for the gases is somewhat odd; i.e., the gases elute in the order N$_2$ < O$_2$ < Ar < CO. This order does not correlate with either the boiling points or polarizabilities of the gases.

Recently, a tracer pulse chromatographic method was developed (6) for the determination of nitrogen isotherms and Brunauer–Emmett–Teller surface areas for chromatographic adsorbents. Nitrogen was used as the carrier gas, and the packed columns were immersed in liquid nitrogen at 77 K. Under these conditions, a layer of nitrogen several angstroms thick adsorbed onto the surface of the adsorbent, and this condensed layer was observed to retain inert gases, such as argon (7). The present investigation was undertaken in order to explore the possible chromatographic applications of a condensed, two-dimensional layer of "liquid" nitrogen as a stationary liquid phase for the separation of the permanent gases discussed previously.

EXPERIMENTAL SECTION

Figure 1 shows the experimental instrumentation, which was principally a gas chromatograph/mass spectrometer (Hewlett-