



The separation of boron isotopes using ion-exchange chromatography
by Gerald Thomas Paulson

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemical Engineering
Montana State University
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Abstract:

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The parameters investigated included resin type, length of the resin column, column temperature, volume of boric acid fed to the column, concentration of the feed solution, and flowrate through the column. A model was developed to predict the extent of separation. The model indicates that column length is the most significant parameter. Column temperature and resin type are also significant parameters.

Large scale production of enriched boron was considered. The major issue with the use of ion-exchange chromatography to produce enriched boron is the large amounts of water produced in the product.

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APPROVAL

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Gerald Thomas Paulson

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

The separation of boron isotopes by ion-exchange chromatography of boric acid was investigated. Two commercially available ion-exchange resins were tested. The maximum separation produced a product containing 24.2 atom percent boron-10 using a feed stream containing 18.4% boron-10. The maximum extent of separation obtained was 0.104 as compared with a previously published maximum of 0.07.

The parameters investigated included resin type, length of the resin column, column temperature, volume of boric acid fed to the column, concentration of the feed solution, and flowrate through the column. A model was developed to predict the extent of separation. The model indicates that column length is the most significant parameter. Column temperature and resin type are also significant parameters.

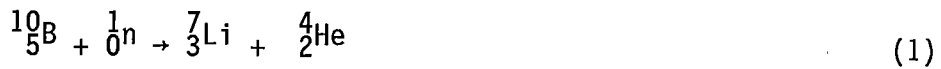
Large scale production of enriched boron was considered. The major issue with the use of ion-exchange chromatography to produce enriched boron is the large amounts of water produced in the product.

INTRODUCTION

One of the basic requirements associated with the production, handling, and use of fissionable material is the control of neutrons. For a system containing fissionable material a neutron balance can be calculated.¹ If the neutron production rate is less than the loss rate, the system is defined as subcritical. If the production rate equals the loss rate, the system is critical. If the production rate exceeds the loss rate, the system is supercritical. The production rate for neutrons is strongly dependent upon the type and quantity of fissile material present. The loss rate for neutrons is a function of the rate of neutrons "leaking" from the system and the rate of neutron absorption. Neutron leakage is strongly dependent on system geometry and density. The absorption rate is dependent on the chemical constituents present in the system. Specific additives such as boron in solid or solution form are used to raise the absorption rate significantly.

The symbol for elemental boron is B. Boron consists of two stable isotopes with mass numbers of 10 (boron-10 or ^{10}B) and 11 (boron-11 or ^{11}B). The natural isotopic abundance is approximately 20% boron-10 and 80% boron-11. The natural isotopic distribution is known to vary based on the location of the deposit.^{2,3}

The boron-10 absorption process occurs by the reaction:



The reaction is exoergic releasing 2.79 MeV.⁴ Both reaction products, lithium (${}^7_3\text{Li}$) and helium (${}^4_2\text{He}$) are stable nonradioactive isotopes. The rate at which absorption occurs is a strong function of the neutron's energy.

The nuclear cross section is a measure of the probability of occurrence for a reaction and largely determines the rate of a nuclear reaction. The unit used for cross sections is the barn ($1 \times 10^{-24} \text{ cm}^2$). In general, adsorption cross sections decrease as neutron energy increases. Effective neutron absorbers have a cross section of at least 1,000 barns in the energy range below one electron volt and about 1 barn with a neutron energy of 10^5 electron volts. At an energy of 0.025 electron volts, boron-10 has a cross section of 4,000 barns while boron-11 has a cross section of 0.05 Barn.⁵ At an energy of 10^5 electron volts, boron-10 has a cross section of 2 barns.⁴

Enriched Boron-10

Research in the area of boron isotope separation within the United States began in 1943 at Columbia University as a portion of the Manhattan Project. Seven separation schemes were considered.

One method was based on gaseous diffusion of BF_3 . All other methods were based on distillation of various boron compounds. The distillation of $(\text{CH}_3)_2\text{O}\cdot\text{BF}_3$ was finally selected.

The Standard Oil Company of Indiana designed and operated the first large scale plant for separating boron isotopes as a part of the Manhattan Project in 1944.⁶ The initial plant was shutdown in 1946 and dismantled. In 1953 a larger plant was constructed by Hooker Electrochemical Company at Model City, New York. The plant produced 460 kilograms per year of boron-10 at an enrichment of 92% boron-10.⁷ The facility consisted of eight columns resulting in 580 theoretical plates. Operating problems included thermal decomposition, corrosion and leakage. The Model City plant was purchased by Eagle Picher Industries and moved to Quapaw, OK. The plant has operated in Oklahoma since 1973 and currently produces 1,000 kilograms per year.

Another isotopic exchange reaction using $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$ was used in England to produce 2 kilograms of boron-10 per year.⁷

The enrichment of boron by the distillation of BF_3 has been used commercially by the Soviet Union (0.5 kilograms per year of 83 percent boron-10) and England (26.5 kilograms per year of 95 percent boron-10). The separation factor for the distillation of BF_3 is only 1.0075.⁷ A separation factor is a dimensionless

index used to compare separations. A value of one indicates no separation.

Recent work has identified three novel methods for enriching boron. In 1974, the Los Alamos Scientific Laboratory reported a 14 percent enrichment in the ratio of $^{10}\text{B}/^{11}\text{B}$ by the use of a CO_2 laser in a photochemistry process.⁸ In 1975, the University of Kentucky reported on the separation of boron isotopes by direct mode thermal parametric pumping.⁹ The separation is based on the thermal dependence of the exchange reaction between gaseous BF_3 and solid $\text{BF}_3 \cdot \text{DMSO}$ (dimethyl sulfoxide). Separation factors ranged from 1.020 and 1.028. In 1989, Montana State University reported the separation of boron isotopes by gas phase membrane permeation of BF_3 .¹⁰ Separation factors of 1.020 and 1.090 were determined for phenyl ether modified polyvinylidene fluoride membranes.

Enriched boron-10 is used in certain nuclear applications that require the rate of neutron absorption to exceed a maximum physical limit for the quantity of natural boron that can be added. Since 1943 the nuclear weapons program has required the production of enriched boron. The current boron-10 plant was designed to provide material for the weapons program. The price per gram of boron-10 at an enrichment of 75% boron-10 is \$5.00.¹¹ The cost of boron-10 in common boric acid is \$0.17 per gram.¹² The cost difference of 2800% reflects the difficulty associated with the separation.

The introduction of enriched boron at a reduced cost would generate two major new uses. The first deals with commercial pressurized-water reactors. All such reactors are equipped with emergency core cooling systems that uses soluble boron in water. The water is heated to maintain the boron solubility above the concentration required. The speed at which injection systems introduce appreciable quantities of boron-10 into the core is usually slow and is a result of limited solubility, system capacity and pumping rates. The Electric Power Research Institute has studied the use of enriched boron in reactors.¹³ Virginia Power studied the use of enriched boron for its reactors and decided against converting due to the current high cost of the enriched boron.¹⁴

A second major use of enriched boron at a reduced cost would be in nuclear fuel reprocessing. The Department of Energy dissolves spent reactor fuel in several processes that use natural boron. During the dissolution of fuel, soluble boron-10 is necessary to maintain a subcritical system. The boron is added to the acid during the reagent makeup process in the form of naturally occurring boric acid. Naturally occurring boron is typically 19.6 atom percent boron-10 and 80.4 atom percent boron-11.

After the complete dissolution of the fuel, the uranium is in the form of uranyl nitrate solution and is critically safe because of the uranium concentration without any neutron poison. In the following

extraction system, boron remains in the aqueous solution with the fission products and other fuel components. This waste is eventually processed in a calcining process. The calcining process evaporates and solidifies liquid radioactive wastes within a heated bed of fluidized particles. The calcine generated is stored in stainless steel bins contained in concrete vaults.

A reduction in the total boron concentration would result in a reduction in reagents used and total waste processed. Using 100% enriched boron-10 waste production would decrease the volume of high level radioactive waste produced by 15%.

Chromatography

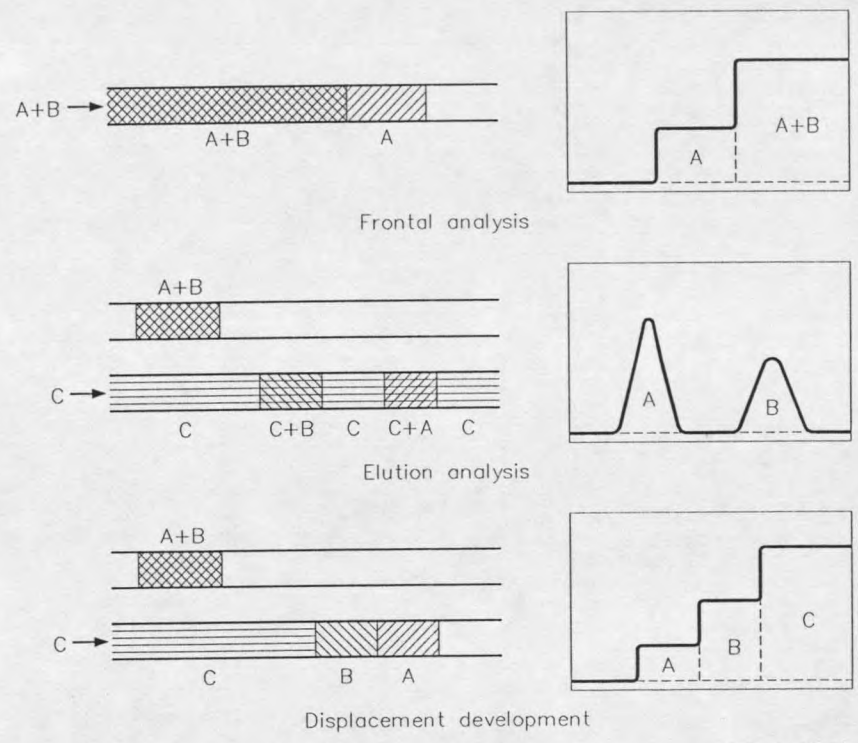
In 1906 a Russian scientist, M. S. Tswett, published a paper dealing with the separation of plant pigments. In the paper he coined the term "chromatographic method" to describe his technique. He selected the name by combining two Greek words, chroma (color) and grapheme (write) to indicate the development of individual colored bands in a column. However, he also noted that colorless substances could likewise be separated. Chromatography is best defined as a physical method of separation in which the components to be separated are distributed between a stationary and a mobile phase. The separation occurs as a result of repeated sorption/desorption steps.

Chromatography can be divided into a variety of classifications.¹⁵ Liquid chromatography and gas chromatography become two major classes based on the mobile phase of the system. The stationary phase is either a liquid or solid. Liquid-liquid, liquid-solid, gas-liquid, and gas-solid chromatography become the four subclasses of chromatography.

Chromatography can be classified based on the physical equipment used. Column chromatography is based on flow through a packed column. Paper chromatography is based on the selective migration of compounds across a plane of paper. Thin-layer chromatography is based on the flow of a mobile phase through a small gap created by two planes of stationary material. Four column chromatography subclasses can likewise be defined based on column packing. Ion-exchange chromatography substitutes an ion-exchange resin for the adsorbent. Gel chromatography uses a controlled porosity gel as a packing. Affinity chromatography is based on a unique packing which is capable of separating certain proteins based on protein-ligand interactions.

Chromatography is also classified based on technique. The three techniques are shown in Figure 1. Frontal analysis involves a step function change at the inlet. The least adsorbed component exits first. In elution analysis a pulse of a mixture is added to a column. Each component moves through the column with the least

Gold Crest Botts
25% COTTON CONTENT



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Figure 1. Types of Chromatography

adsorbed component exiting first. Displacement development adds a pulse of a mixture to a column followed by the addition of a more powerfully adsorbed component. The final component "pushes" the mixture through the column with the least strongly adsorbed compound exiting first.

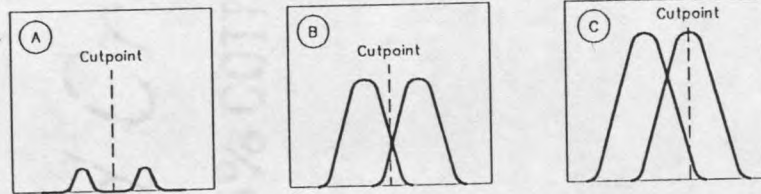
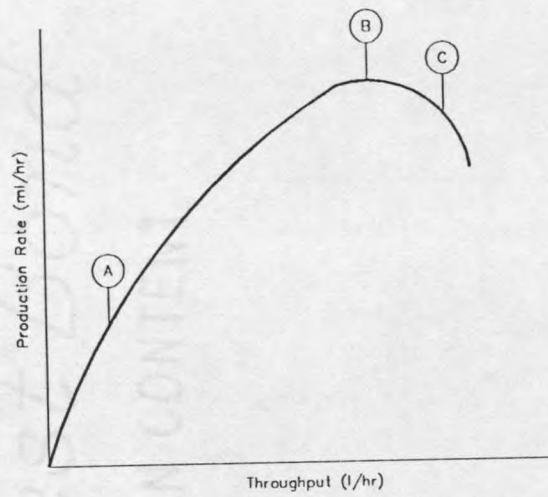
A final classification for chromatography is based on purpose. Analytical chromatography is used for the qualitative identification of sample components and for a quantitative assessment of relative concentration. In analytical chromatography, speed and the resolution of various compounds are the major requirements. Preparative chromatography is used to produce a quantity of purified material by chromatographic means. In preparative chromatography throughput and purity are the major requirements.

Preparative chromatography has been integrated into the chemical industry within the last three decades. P. E. Baker and G. Gauetos have recently published a complete review of production scale chromatography systems.¹⁶ The goal of preparative chromatography is to maximize throughput at a defined purity and minimize capital and operating costs. Different scale-up approaches have produced a variety of physical systems with the intent of minimizing capital cost. All systems can be classified as either a batch or continuous operation. The concepts for separation using chromatography can be classified as co-current, counter-current, or cross-current flow

systems. Ten industrial types of columns are in use.

Once a concept is chosen for use, optimization focuses on maximizing throughput and purity. Guiochon and Colin¹⁷ define production rate as the amount of a compound produced at a given purity per unit time. Additionally, throughput is defined as the amount of feed injected per unit time (averaged over a number of cycles). Figure 2 illustrates the relationship between production rate and throughput. The amount of feed injected per pulse is increased in the three cases shown. The cutpoint is defined by a minimum purity requirement. The maximum production rate is typically found at an intermediate throughput. Jones¹⁸ has analyzed the optimization of process scale liquid chromatography. He introduces the term "process scale preparative" column to identify columns with diameters greater than 10 cm. His specific experimentation dealt with separating o-, m-, and p- nitro-anilines in a 15 cm diameter column using a silica packing. Sixteen variables were considered and seven were determined to be statistically significant. The seven were particle size, column length, packing method, differential pressure across the column, solvent type, flowrate, and the use of a precolumn.

Hupe and Lauer¹⁹ likewise studied optimization of preparative chromatography. They concluded that the parameters for a preparative separation should be selected based on selectivity, column length,



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Figure 2. Production Rate as a Function of Throughput

column diameter, particle size, flowrate, injection system, and product dilution.

The two optimization reports address preparative chromatography in a slightly different manner. However, both studies document rigorous methods for optimization.

The result of a specific preparative chromatography study is the definition of a separation column of specific dimensions. The largest column diameter in current use is 4.7 meters. The longest column is 12 meters. Figure 3 provides a scatter plot of the dimensions of preparative chromatography columns in use.¹⁶

Scope And Objectives

The scope of this work is to determine if large quantities of enriched boron can be produced economically using elution ion-exchange chromatography. The specific objectives consist of the following:

1. Demonstrate the enrichment of boron using ion-exchange chromatography.
2. Collect and compare the various theories for isotope enrichment using ion-exchange chromatography.

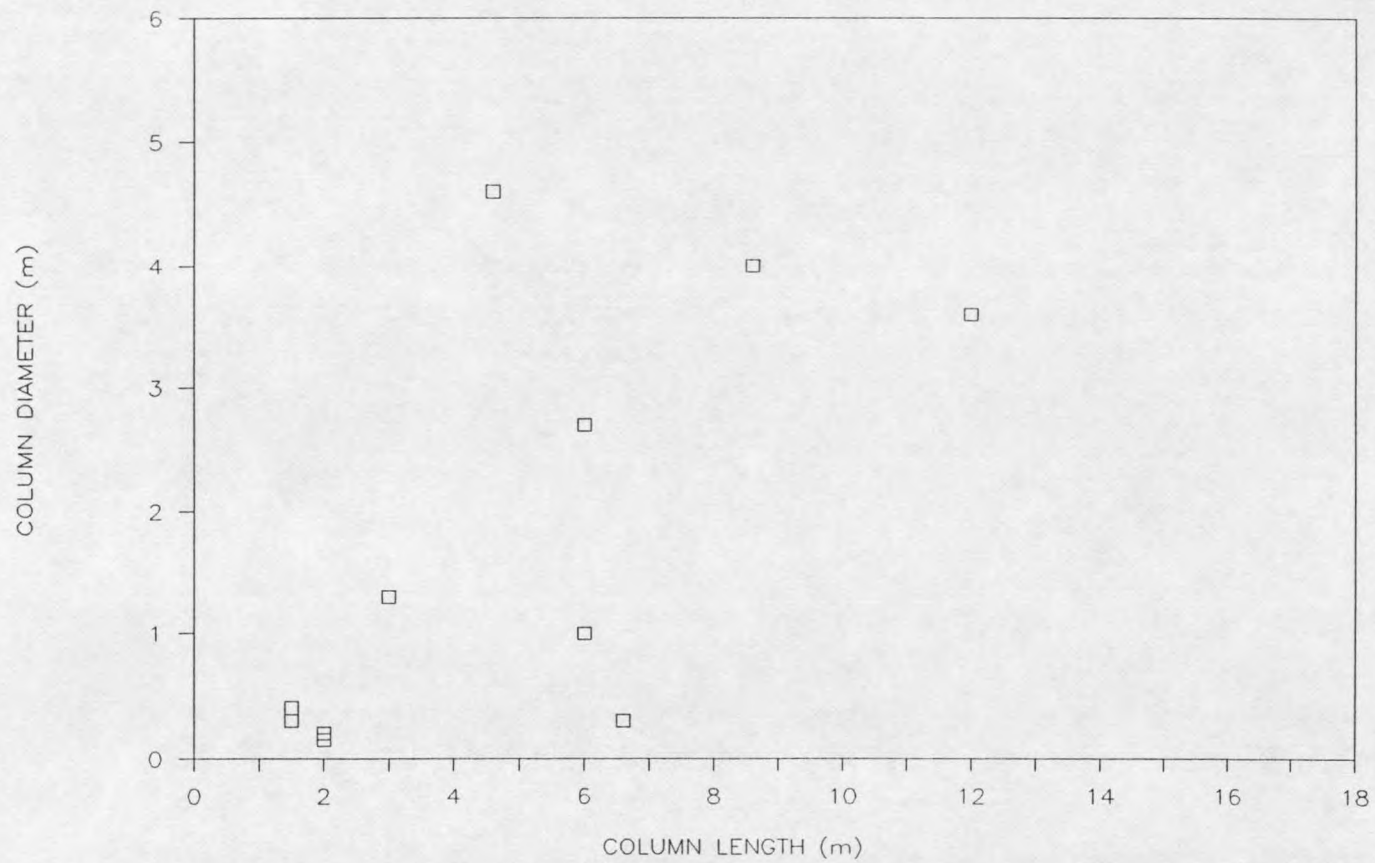


Figure 3. Dimensions of Columns in Use

3. Develop a simulation model for boron enrichment.
4. Perform a parametric study for both the quality and quantity for enrichment. The variables studied will include feed concentration and temperature, feed quantity, flowrate, resin type and column length.
5. Compare the simulation model to the various theories.
6. Determine the scale-up economics of production based on the simulation model.

A REVIEW OF PUBLISHED WORK

The scope for this work is limited to liquid column chromatography with an ion-exchange packing using the elution technique for a preparative purpose. The restrictive nature of the scope is based on published results which provides substantial insight into the separation of the boron isotopes. The most encouraging work was reported by the Research Laboratory for Nuclear Reactors at the Tokyo Institute of Technology.²⁰ A pulse of common boric acid was fed into a column packed with weakly basic anion exchange resin. Both boron-10 and boron-11 were adsorbed onto the resin. The adsorbed boron was eluted by displacement with water. With a migration length of 256 meters, the enrichment changed from 19.8% to 91.0% boron-10.

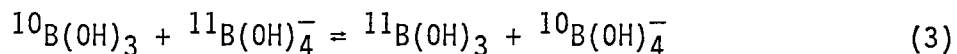
The Enrichment Phenomena

To understand the enrichment phenomena, the chemistry of boron needs to be discussed. When boric acid is dissolved in water there is a slight dissolution as shown in equation 2.

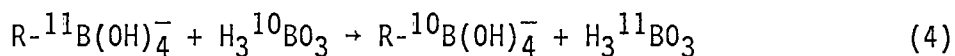


It should be expected that this dissociation would occur for both the boron-10 and boron-11 isotopes. What may not seem obvious is that an

isotope exchange equilibrium is maintained in the form of equation 3.



Kakihana²¹ calculated the equilibrium constant of the reaction given in equation 3 to be 1.0186 at 300⁰K. He²² later developed the equilibrium constant as a function of temperature that varies from 1.0206 at 273⁰K to 1.0177 at 333⁰K. Because the equilibrium constant of equation 3 is greater than unity, boron-10 preferentially remains as an anion. One should expect that when a boric acid solution is in contact with an anion exchange resin boron-10 would preferentially adsorb onto the resin. Such adsorption can be represented by the reaction shown in equation 4 with R- representing a resin.



The single stage separation factor, α , for boron isotopes in contact with a resin is given in equation 5,

$$\alpha = \frac{\left[\begin{array}{c} \overline{10\text{B}} \\ \text{---} \\ \text{---} \end{array} \right] \left[\begin{array}{c} 11\text{B} \\ \text{---} \\ \text{---} \end{array} \right]}{\left[\begin{array}{c} \overline{11\text{B}} \\ \text{---} \\ \text{---} \end{array} \right] \left[\begin{array}{c} 10\text{B} \\ \text{---} \\ \text{---} \end{array} \right]} \quad (5)$$

where $\left[\begin{array}{c} \overline{} \\ \text{---} \\ \text{---} \end{array} \right]$ and $\left[\begin{array}{c} \\ \text{---} \\ \text{---} \end{array} \right]$ denote the concentration of each species in the resin phases and external solution, respectively. Three experimenters have determined separation factors for six resins and

are listed in Table 1. In addition, Christoph²⁵ calculated a maximum theoretical separation factor of 1.032.

TABLE 1. Experimentally Determined Separation Factors

| <u>Resin</u> | <u>Condition</u> | <u>α</u> | <u>Reference</u> |
|-----------------------|------------------|----------------------------|------------------------|
| Amberlite CG-400-I | 0.03M | 1.010 | Yoneda ²³ |
| Dowex 1-X-8 | 0.1M | 1.0272 | Urge11 ²⁴ |
| Dowex 1-X-8 | 0.03M | 1.0262 | Urge11 ²⁴ |
| Dowex 1-X-8 | 0.015M | 1.0269 | Urge11 ²⁴ |
| Dowex 2-X-8 | 0.1M | 1.0285 | Urge11 ²⁴ |
| Dowex 2-X-8 | 0.5M | 1.0354 | Urge11 ²⁴ |
| Diaion WA-21 | 0.0107M | 1.015 | Kakihana ²¹ |
| Diaion WA-21 | 0.102M | 1.013 | Kakihana ²¹ |
| Diaion WA-21 | 0.518M | 1.011 | Kakihana ²¹ |
| Diaion WA-10 | 0.0101M | 1.016 | Kakihana ²¹ |
| Diaion WA-10 | 0.0991M | 1.012 | Kakihana ²¹ |
| Diaion WA-10 | 0.501M | 1.007 | Kakihana ²¹ |
| Diaion PA-310 | 0.0104M | 1.019 | Kakihana ²¹ |
| Diaion PA-310 | 0.109M | 1.013 | Kakihana ²¹ |
| Diaion PA-310 | 0.501M | 1.007 | Kakihana ²¹ |

Past Enrichment Experiments

With the understanding that preferential adsorption of boron-10 occurs, two different experiments using an ion-exchange column can be

used to study the effect. They are elution analysis and frontal analysis. In elution analysis experiments boron is introduced as a short pulse and is displaced through the column. In frontal analysis boron is introduced continuously until the column is completely saturated followed by elution. Frontal analysis can be considered as a step function change to the input of the column. Experimenters have also used two basic types of resins: strong base resin and weak base resin. With a weak base resin the boron can be displaced through the column solely with water. A strong base resin requires displacement of the boric acid with another acid such as hydrochloric or acetic acid. Figure 4 provides a time line of the literature that documents the four types of boron enrichment experiments using ion-exchange resins.

Figure 5 is a scatter plot of all reported data. An increase in enrichment was calculated from the difference of the highest enrichment of a given product fraction (E_f) and the initial enrichment (E_0) and plotted versus the length of the resin column.

An itemization of published conclusions is given in Table 2. There is general agreement between authors that the separation improves with increasing column length, increasing concentration of the feed and increasing amount of the feed.

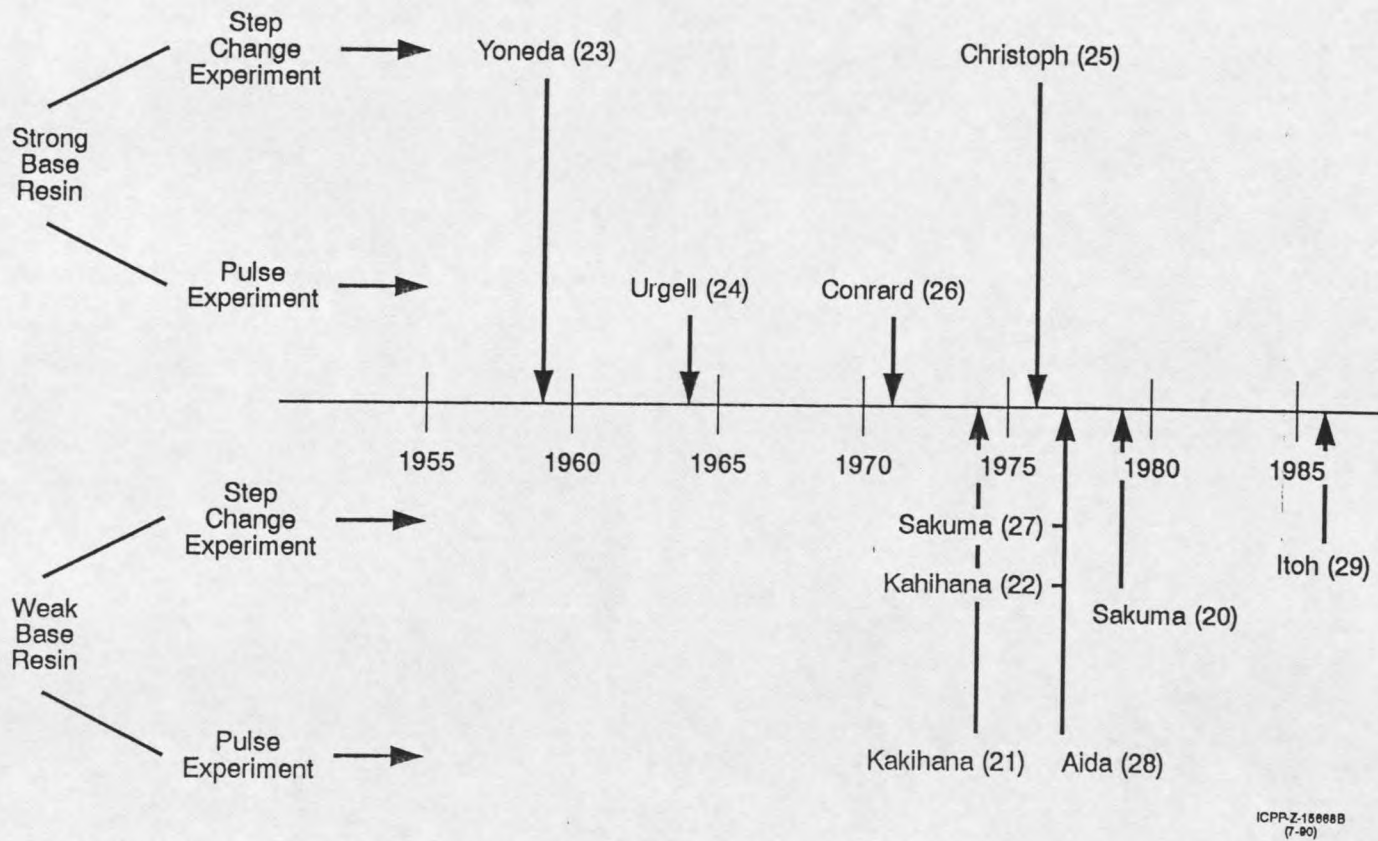


Figure 4. Time Line of Boron Experiments

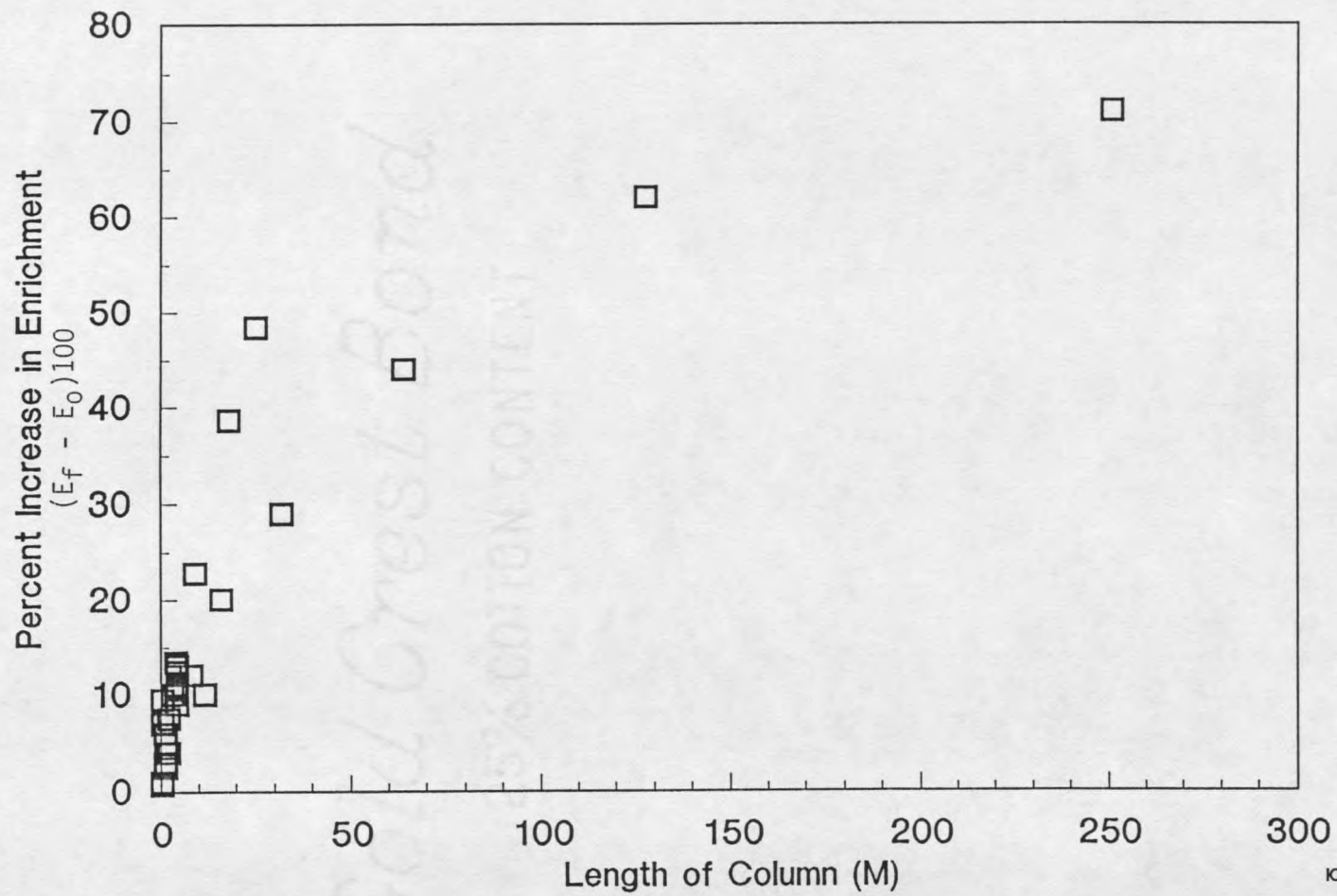


Figure 5. Results Found in the Literature

TABLE 2. Summary Of Published Conclusions

| <u>Author</u> | <u>Reference</u> | <u>Major Conclusions</u> |
|---------------|------------------|---|
| Yoneda | 23 | α increases with an increase in boron concentration |
| Yoneda | 23 | α increases with the addition of glycerine in the feed |
| Urgell | 24 | The highest α occurred with boric acid. α decreased when mannite or glycerine were added. |
| Urgell | 24 | Only a slight separation occurred when sodium borate was used |
| Urgell | 24 | Separation improved when the column length was increased from 9 to 25 meters |
| Kakihana | 21 | Weakly basic resin requires only water as the eluting agent |
| Christoph | 25 | The amount of boric acid adsorbed on the resin increases as the feed concentration increases |
| Aida | 28 | Enrichment increases with increasing concentration and increasing amount of boric acid in the feed |
| Aida | 28 | An optimum flowrate of 10 to 20 ml/cm ² hr exists for the column |
| Aida | 28 | The bulk of the boron exits the column at a constant 19% B-10 |
| Aida | 28 | In concentrations less than 0.3 molar no tailing was observed |
| Sakuma | 20 | Enrichment increases with length |
| Sakuma | 20 | The separation factor is constant irrespective of column length |

Theory Of General Chromatography

There are two general viewpoints for chromatography theory. Rate theory is explained in terms of models involving molecular diffusion, reaction and flow. Phenomenological theory is based on a model that produces an outcome similar to the given system but does not identify the mechanisms within the system. Rate theory models are typically based on the steady-state thermodynamics of molecules and the resins or by the kinetics of the adsorption-desorption steps. Phenomenological theory is based either on the concept of a theoretical plate or by statistical mechanics.

The Mathematical Model

The basis for rate theory is the development of differential equations that describe the mass transfer processes. Figure 6 identifies the starting point of the differential equations.³⁰

Mass transfer is caused by the application of external force and by the internal concentration gradient. The external force, E , is defined in equation 6.

$$\Delta E = \frac{\partial}{\partial x} \left(-V_i(x,t)C_i(x,t) \right) \Delta x \Delta y \Delta z \Delta t \quad (6)$$

