

THE SEPARATION OF ALUMINUM FROM BERYLLIUM WITH  
THE AID OF SODIUM HEXAMETAPHOSPHATE

BY

PAUL A. PARENT  
///

*Chem  
LD  
3231  
.M40d  
Parent,  
P. A.  
Folio*

Thesis submitted to the Faculty of the Graduate School  
of the University of Maryland in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy.

1937.

CHEMISTRY LIBRARY  
UNIVERSITY OF MARYLAND

UMI Number: DP70189

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI DP70189

Published by ProQuest LLC (2015). Copyright in the Dissertation held by the Author.

Microform Edition © ProQuest LLC.

All rights reserved. This work is protected against unauthorized copying under Title 17, United States Code



ProQuest LLC.  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106 - 1346

## BIOGRAPHY

Paul Andrew Parent was born in Boston, Massachusetts, July 1, 1912.

Attended North East Catholic High, of Washington, D. C., now known as St. Anthony's High School, from September, 1923 to June, 1927. Entered the Catholic University of America, at Washington, D. C. in September, 1927, and received the degree of Bachelor of Chemical Engineering in June, 1931.

Has attended the University of Maryland from June 1933 to June 1937 where the degree of Master of Science was received in Inorganic Chemistry in June 1935. The title of the Master's Thesis was: The Preparation and Determination of the Solubility of Tertiary Strontium Phosphate and Tertiary Strontium Arsenate.

Candidate for the degree of Doctor of Philosophy in Inorganic Chemistry at the University of Maryland in June, 1937. The title of the dissertation: The Separation of Aluminum from Beryllium with the Aid of Sodium Hexameta-phosphate.

## ABSTRACT

A method is given for the separation of aluminum from beryllium using the reagent sodium hexametaphosphate, which, although five years ago was a laboratory curiosity, is on the market today as an inexpensive chemical.

Essentially the process consists in a preliminary removal of about 60% of the aluminum at a pH of 3.93 by the addition of 5.92 grams sodium hexametaphosphate for each gram of  $\text{Al}^{+++}$  present. A small beryllium loss is experienced. After filtering and washing the precipitate, the filtrate is made more alkaline until a final pH of 5.4 is attained. At this pH, 1.78 grams of  $(\text{NaPO}_3)_6$  are added for each gram of aluminum originally present. Precipitates obtained during this latter step are saved and dissolved in acid, and the original separation is repeated. A total yield of 85-88% of the original beryllium results.

An alternative procedure is offered in which 60% of the aluminum is removed at a pH of 3.93, and the solution boiled with an excess of sodium hydroxide to precipitate the beryllium. This results in a recovery of 86.2% of the beryllium.

The method has been shown to possess certain advantages over the alum process, chief of which are economy of heat, time, and precipitating reagent.

### ACKNOWLEDGMENT

The author is grateful to Dr. Charles E. White for encouragement, and for devoting a liberal amount of time to many problems which arose. Acknowledgement is also due Dr. Malcolm M. Haring for loan of apparatus, and to Mr. William Hart, a student of Dr. Haring's, for several pH measurements made by use of his glass electrode.

## TABLE OF CONTENTS

	Page
I. INTRODUCTION .....	1
II. A HISTORY OF ANALYTICAL AND LARGE SCALE SEPARATIONS OF BERYLLIUM AND ALLUMINUM .....	3
Analytical .....	3
Large Scale .....	8
III. RECENT PATENT LITERATURE.....	14
IV. THE CHEMISTRY OF THE ALKALI METAPHOSPHATES....	20
V. EXPERIMENTAL PART	
Purity of Materials .....	25
Methods of Analysis .....	26
Beryllium-Aluminum Separations .....	30
VI. CONCLUSIONS .....	46
VII. LITERATURE CITED .....	50

## LIST OF TABLES

	Page
TABLE I. Influence of $(\text{NaPO}_3)_6$ on the Separation of $\text{Be}^+$ and $\text{Al}^{3+}$ with an Excess of $\text{NaOH}$ .....	33
TABLE II. Effect of Acidity on the separation of $\text{Be}^{++}$ and $\text{Al}^{+++}$ with $(\text{NaPO}_3)_6$ (0.50 g.) .....	36
TABLE III. Effect of Varying Amounts of $(\text{NaPO}_3)_6$ on the Separation of $\text{Be}^{++}$ and $\text{Al}^{+++}$ .....	36
TABLE IV. $\text{Al}^{+++}$ - $\text{Be}^{++}$ Separations in $(\text{NaPO}_3)_6$ Using Successive Precipitation.....	44
TABLE V. Separations by Incomplete Aluminum Removal .....	46

## I. INTRODUCTION

The element beryllium has received a great deal of notoriety during the past few years because of its property of forming many light metal alloys which may have application in various industries. The metal is about one-third lighter than aluminum and has many of the same physical and chemical properties. It is this similarity to aluminum that has retarded the production of beryllium. The two elements occur together in the form of a beryllium aluminum silicate, and the separation from aluminum is extremely difficult. The problem is further complicated by the fact that even after a pure compound is obtained the conversion to the metal is at present rather costly. However, it is believed that if low priced beryllium salts can be produced, the metallurgy may be greatly improved.

The disintegration of the ore is accomplished by a secret heat treatment process which is followed by sulfuric acid extraction. The problem of separating the resulting aluminum and beryllium sulfates has been attacked by using many different reagents. Most of those that produce reasonable results either involve laborious procedures or are prohibitively expensive. Any method of improving this separation must be considered a contribution to the beryllium industry.

About five years ago sodium hexametaphosphate, which had



formerly been a laboratory curiosity, was produced in large quantities and advertised as a solvent for calcium stearate and related compounds. The proximity of calcium and beryllium in the Periodic System suggested the possibility of the salt having distinctive action towards either aluminum or beryllium compounds, which might be useful in effecting a separation. Qualitative experiments indicated the probability that the desired results might be attained, and the research reported in the following dissertation was undertaken.

## II. A HISTORY OF ANALYTICAL AND LARGE SCALE SEPARATION METHODS FOR BERYLLIUM AND ALUMINUM

### I. ANALYTICAL

Probably the first method employed for the separation of beryllium and aluminum was that of Vauquelin,<sup>1</sup> 1798, who discovered the element beryllium. He found that by digesting a mixture of beryllium and aluminum hydroxides in concentrated ammonium carbonate, beryllium hydroxide passed into solution, and the aluminum hydroxide was not attacked. This procedure does not give quantitative results.

Another early process of separating beryllium and aluminum was developed by Gmelin<sup>2</sup>, in 1840. This method consists in treating a suspension containing beryllium and aluminum hydroxides in a volume of 30 c.c. with enough concentrated sodium hydroxide to give a clear solution. On dilution to 500 c.c. and boiling 2-3 minutes,  $\text{Be}(\text{OH})_2$  precipitates in granular form, while aluminum stays in solution. Although there are certain ratios of  $\text{Al}^{+++} / \text{Be}^{++}$  which do not permit good analytical results, it is claimed that if aliquots of a standard  $\text{Be}^{++}$  solution are added to all unknown solutions, the method may be used successfully. The proportions which do not give results are all high Al to Be ratios. In the manner described, the ratio of Al/Be is reduced and rather accurate results are obtainable.

Among early methods which have received adverse criticism there may be mentioned that of Berzelius<sup>3</sup>, who advocated treating the hydroxides with saturated ammonium chloride solution,

and then boiling until all free ammonia gas was liberated. Berthier<sup>4</sup> proposed boiling a solution of aluminum and beryllium hydroxides in sulfurous acid, or concentrated ammonium hydroxide saturated with sulfur dioxide, to expel sulfur dioxide and precipitate aluminum hydroxide. Hart<sup>5</sup> used a strong solution of sodium carbonate to precipitate the greater part of aluminum hydroxide, beryllium remaining in solution, from which it could be precipitated on diluting and boiling.

In 1855, Debray found that aluminum could be precipitated as basic sulfate by the addition of zinc to a sulfuric acid solution of beryllium and aluminum<sup>6</sup>.

In 1864, Gibbs fused a mixture of the two oxides with KHF. The fused mass was leached with boiling water containing a little hydrofluoric acid, to extract the beryllium as a double fluoride, which crystallized out on cooling<sup>7</sup>.

Rosler in 1878 was able to precipitate beryllium as a double ammonium phosphate by the addition of ammonium phosphate in the presence of citric acid. This method is extremely limited in practice; only when small amounts of aluminum are present will the beryllium completely precipitate<sup>8</sup>.

Vincent, in 1880, proposed a method which has as its basis the fact that beryllium hydroxide is insoluble in excess dimethylamine, while aluminum hydroxide is soluble. Renz later showed that either methylamine, monoethylamine or diethylamine could be used for precipitating beryllium

hydroxide, leaving aluminum in solution<sup>9,10</sup>

Haven's method, which is used somewhat even today, was worked out in 1897, and depends on the insolubility of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  in concentrated hydrochloric acid and ether saturated with HCl gas. This involves double precipitations for even small quantities of BeO and  $\text{Al}_2\text{O}_3$  (as little as 0.1 g.) and if larger quantities are present may involve even more precipitations. The use of small samples for analysis seems to be imperative, and the strongest commendatory point of the procedure is the crystalline character of the aluminum precipitate produced.

Haber and VanCordt found that basic beryllium acetate, which could be crystallized from glacial acetic acid, was soluble in chloroform, while aluminum acetate was not. This procedure is useful for the preparation of pure beryllium for standard samples.<sup>12</sup>

Parsons and Barnes<sup>13</sup> modified Hart's sodium carbonate method, by substituting sodium bicarbonate,  $\text{NaHCO}_3$ ; these investigators found that on boiling beryllium and aluminum hydroxides in 10%  $\text{NaHCO}_3$ , beryllium dissolves and aluminum is unaffected. Britton<sup>14</sup> reviewed the method, and believes it satisfactory provided that the quantities of BeO and  $\text{Al}_2\text{O}_3$  do not (each) exceed 0.1 gram and provided that very efficient stirring is used. Parsons and Barnes themselves give figures which show that double precipitations are necessary.

Wunder and Wenger fused a mixture of the oxides, and

with an excess of sodium carbonate. Water extraction put aluminum in solution as sodium aluminate, while beryllium remained undissolved as an oxide or carbonate. This method has received favorable comment by later investigators.<sup>14,15,16</sup>

Kling and Gelin found that basic beryllium acetate could be distilled under reduced pressure, any aluminum remains in the residue. This method according to Britton gives results accurate to within 2%.<sup>14,17</sup>

More recent methods proposed for analytical separation of beryllium and aluminum include the following: Probably the best of these methods for analytical purposes is the 8-hydroxyquinoline method, due to Kolthoff and Sandell, later modified by Lundell and Knowles, still later by Knowles, in which aluminum is precipitated from a very slightly acid solution, buffered with ammonium acetate, as aluminum oxyquinolate, which may be weighed as such after drying at 135°C. Beryllium, left in the filtrate, is then precipitated as  $\text{Be}(\text{OH})_2$  by the addition of ammonia. Certain precautions are necessary in this latter step to recover the beryllium completely.

Fischer developed a colorimetric procedure for the determination of beryllium in the presence of aluminum, using quinalizarin (1,2,5,8 tetrahydroxyanthraquinone) In absence of beryllium, and presence of sodium hydroxide this indicator is violet; beryllium colors it blue. Aluminum causes no interference, but iron is objectionable, and special procedures must be followed at

different Fe/Be ratios. The method has not become very popular, although quinalizarin has become a standard qualitative test for beryllium, in the presence of aluminum.

Adami states that beryllium may be separated from iron and aluminum by converting to formates by evaporating to dryness twice with formic acid. The resulting formates are then placed in a platinum boat and heated with formic acid in a long glass tube sealed at one end and connected at the other to a vacuum pump. Ignited under vacuum at 180-200°, beryllium formate sublimes and crystallizes in the cold part of the tube.<sup>21</sup>

Willard and Fowler believe it possible to separate beryllium and aluminum by thermal decomposition of the sulfates. They cite some data showing very good analytical results.<sup>22</sup>

Guanidine carbonate is the reagent advocated by Jilek and Kota for beryllium aluminum separation. Ammonium tartrate is used to hold up aluminum, and with certain modifications in case ammonium salts are in high concentration, the solution is made faintly acid to methyl red, and 4% guanidine carbonate added. The beryllium precipitate is ignited to BeO.<sup>23</sup>

Moser uses tannin for beryllium aluminum separations. To the slightly acid solution of the sulfates, containing about 0.1 g. Al<sup>+++</sup> and not much more Be<sup>++</sup>, hot water is added to make the volume 500 c.c. Then quickly while

stirring 3 g. tannin in 100 ml. saturated ammonium acetate solution is added. The mixture is then digested at  $80^{\circ}$  and finally boiled for two minutes, filtered and washed with ammonium nitrate solution. The precipitate is ignited and weighed.

Minnig has an analytical method which uses the insolubility of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  in a 4-1 mixture of acetone and acetyl chloride. Beryllium chloride is soluble in this reagent. Double and triple precipitations are usually necessary.

## II. LARGE SCALE SEPARATIONS

Fogg and Coughlin reported a method of extracting beryllium, caesium and rubidium from beryl. The mineral is fused with  $\text{CaO}$ , then sulfuric acid added to the slag, and water. By evaporation, silica is dehydrated, and removed, and calcium sulfate along with it. The filtrate is allowed to crystallize; and the alums of potassium, caesium and rubidium are separated. Ammonium sulfate is added to the mother liquor, and alum A separated out. The mother liquor is concentrated, and alum B crystallizes. Ammonium hydroxide is now added to the mother liquor, and iron and aluminum hydroxides precipitated. Hydrogen sulfide is passed in, and ferric and cupric sulfides precipitated. To the filtrate ammonium hydroxide and ammonium carbonate are added, and the solution boiled, basic beryllium carbonate precipitates. After evaporating the filtrate, and filtering off ammonium sulfate, sodium carbonate is added, and lithium

carbonate precipitated.

Lebeau volatilized much of the silica in beryl by intensely heating in an electric furnace. The ore residue dissolved readily in  $\text{H}_2\text{F}_2$ . Lebeau's apparatus was quite expensive however, and required large power consumption. After Lebeau had driven off the  $\text{SiO}_2$  by evaporation, he had left  $\text{Al}_3\text{C}$ ,  $\text{BeC}$ ,  $\text{FeSi}$  and  $\text{CSi}$ . He subjected the mass to weathering conditions, and followed this with a treatment of  $\text{H}_2\text{F}_2$  in  $\text{H}_2\text{SO}_4$  which expelled  $\text{SiF}_4$ . The residue of  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{BeSO}_4$  and  $\text{K}_2\text{SO}_4$  dissolved in water was partially neutralized with  $\text{K}_2\text{CO}_3$ , and potassium alum crystallized. After filtration the filtrate was saturated with ammonia gas and an excess of ammonium carbonate was added.

Most methods of attacking beryl consist in use of fluxes such as calcium fluoride ( $\text{CaF}_2$ ), potassium fluoride, ammonium acid fluoride ( $\text{NH}_4\text{HF}_2$ ), sodium or potassium hydroxide, sodium or potassium carbonate, or sodium fluosilicate,  $\text{Na}_2\text{SiF}_6$ . The finely ground ore is intimately mixed with the particular flux, and the mixture heated to the fusion point.

Parsons fused with  $\text{KOH}$ ; then treated the melt with sulfuric acid, and heated to render  $\text{SiO}_2$  insoluble, leaching the melt with hot water dissolved the beryllium, iron and aluminum as sulfates. Potassium alum was then crystallized from the solution. The remainder of the aluminum, and most of the iron was precipitated from the solution by boiling with



saturated sodium bicarbonate. The resulting filtrate was diluted and boiled to precipitate beryllium hydroxide. A second  $\text{NaHCO}_3$  treatment is usually necessary for complete iron and aluminum removal.

Engle and Hopkins used alkali carbonates for fluxes. The ratios used were 500 g. beryl, 400 g.  $\text{Na}_2\text{CO}_3$ , 400 g.  $\text{K}_2\text{CO}_3$ . They obtained good decomposition of the ore.

These investigators also used sodium fluosilicate. This compound decomposes at  $750^\circ$ , giving  $\text{SiF}_4$  and  $\text{NaF}$ . The former is very reactive and at  $850^\circ$  it decomposes beryl.  $\text{Na}_2\text{BeF}_4$  and  $\text{Na}_3\text{AlF}_6$  are formed. Some  $\text{SiO}_2$  is converted to  $\text{SiF}_4$  and volatilized.  $\text{Na}_3\text{AlF}_6$  is very slightly soluble in water.  $\text{Na}_2\text{BeF}_4$  is fairly soluble. Engle and Hopkins recovered 80-90% of the beryllium theoretically obtainable by extracting with hot water<sup>26</sup>.

Sloman used  $\text{Na}_2\text{SiF}_6$  as flux, extracted the beryllium with water and then treated with sulfuric acid to volatilize  $\text{H}_2\text{F}_2$ . He then divides his solution in four parts and treats one-fourth with ammonia, precipitating  $\text{Be}(\text{OH})_2$  and impurities, as  $\text{SiO}_2$ ,  $\text{Fe}(\text{OH})_3$ , etc. He then stirs this precipitate into the remaining three quarters of the  $\text{BeSO}_4$  solution; the  $\text{Be}(\text{OH})_2$  and a very small amount of impurities precipitate  $\text{SO}_4$ . By repeating this process, very pure  $\text{Be}(\text{OH})_2$  was obtained.<sup>27</sup>

Britton uses  $\text{KOH}$  fusion in a nickel crucible. To the melt, sulfuric acid is added to decompose the silicoaluminate of beryllium and potassium. The precipitated  $\text{H}_2\text{SiO}_3$  is

rendered amorphous by heating on a sand bath, and then the solution diluted and filtered. The acidity of the filtrate is now adjusted to 5N by KOH addition. The solution is now saturated with potassium sulfate while boiling and set to crystallize at 0°C. The BeO is extracted from the mother liquor by adding a concentrated solution of sodium hydroxide in the cold in such quantity that the last drop just causes re-resolution of the precipitated hydroxides. The solution is then diluted with water, and boiled. It may be mentioned here that if the initial volume, where addition of KOH is made, is not small, then the yields will be low. Yields of 90% or better should be obtained by this process. Britton recommends in the potassium alum crystallization process that the solid phases obtained be tested. It is not unusual for small amounts of  $\text{BeSO}_4 \cdot \text{K}_2\text{SO}_4$  to crystallize out here. Presumably if the solution has too small a volume during this crystallization, large beryllium losses may be experienced.<sup>28</sup>

Dyson speaks of fusing beryl with calcium carbide, followed by  $\text{H}_2\text{F}_2$  and  $\text{H}_2\text{SO}_4$  treatment. He also mentions passing phosgene ( $\text{COCl}_2$ ) into molten beryl whereby the metals are converted to chlorides, which sublimes. Beryllium is then separated by the carbonate method.<sup>29</sup>

Minerals of beryllium, listed by Negru<sup>30</sup> are the following: Bertrandite ( $4 \text{BeO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ , 42% BeO), found in Bohemia, France and the United States; Beryl ( $3 \text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ , 14% BeO), found all over the world; Beryllonite

$(\text{Na}_3\text{PO}_4 \cdot \text{Be}_3\text{P}_2\text{O}_8, 19.7\% \text{ BeO})$  found in Maine; Chrysoberyl  
 $(\text{BeO} \cdot \text{Al}_2\text{O}_3, 19.8\% \text{ BeO})$  found in Brazil, Ireland, Siberia,  
 Ceylon, Moravia, United States; Gadolinite  $(2\text{BeO} \cdot \text{FeO} \cdot$   
 $2\text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2, 10\% \text{ BeO})$  found in Greenland, Ireland, Norway,  
 United States, Siberia, Sweden; Danalite  $(\text{Be}, \text{Fe}, \text{Zn}, \text{Mn})$   
 $\text{Si}_3\text{O}_{12}\text{S}, 14\% \text{ BeO})$  found in Colorado, Massachusetts and New  
 Hampshire; Helvite  $(\text{Mn}, \text{Fe})\text{S} \cdot 3(\text{Be}, \text{Mn}, \text{Fe})\text{SiO}_4, 13.5\% \text{ BeO}$  found  
 in Finland, Hungary, Norway, Saxony, United States; Herderite  
 $(\text{CaF} \cdot \text{BePO}_4, 15.4\% \text{ BeO})$  found in Saxony and United States;  
 Phenacite  $(2\text{BeO} \cdot \text{SiO}_2, 45.6\% \text{ BeO})$  found in the Urals, France,  
 Mexico, Switzerland and United States; Euclase  $(2\text{BeO} \cdot 2\text{SiO}_2 \cdot$   
 $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}, 17.3\% \text{ BeO})$  found in Brazil, the Urals, Austria and  
 the Alps; Hambergite  $(4\text{BeO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}, 53.3\% \text{ Be})$  found in  
 Norway; Leucophane  $(\text{NaF} \cdot 3\text{BeO} \cdot 3\text{CaO} \cdot 5\text{SiO}_2, 10.3\% \text{ BeO})$  found in  
 Norway; Meliphanite  $(\text{NaF} \cdot 2\text{BeO} \cdot 2\text{CaO} \cdot 3\text{SiO}_2, 13.1\% \text{ BeO})$  found in  
 Norway, and Trimerite  $(\text{Mn}, \text{Ca})_2\text{SiO}_4 \cdot \text{Be}_2\text{SiO}_4, 16.6\% \text{ BeO})$  found  
 in Sweden.

Negu also mentions the following methods of separation:  
 Vauquelin, who discovered beryllium used KOH fusion in  
 conjunction with the ammonium carbonate process. Scheffer  
 introduced zinc into the acid solution of sulfates, which  
 formed zinc sulfate, and basic aluminum sulfate was precipitated.  
 In dilute solution, aluminum is completely precipitated, but  
 beryllium stays in solution. Zinc is later thrown out of  
 solution by adding potassium sulfate, a double sulfate being  
 precipitated. Hydrogen sulfide is later passed in, to remove

the last traces of zinc, in the presence of ammonium acetate.

Wyrouboff fused beryl with KOH, separated  $\text{SiO}_2$  in the usual way. The solution of chlorides was then evaporated to a small volume, and treated with a concentrated solution of potassium oxalate. A crystalline precipitate of oxalates was formed. On treating with a small quantity of water, only  $2\text{BeC}_2\text{O}_4 \cdot 3\text{K}_2\text{C}_2\text{O}_4$  remains.

Pollock used caustic soda fusion and HCl evaporation for silica removal. The solution was treated with ammonia and the precipitates dissolved in hydrochloric acid. He now saturated this HCl solution with hydrogen chloride gas;  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  precipitated. The filtrate was concentrated to a sirup and saturated ammonium carbonate solution added with stirring. Beryllium remains in solution and iron and aluminum are precipitated.

## III. RECENT PATENT LITERATURE

Bucher patented a process, U. S. Pat. 2,010,844, 1935, for rendering silica dehydrated in the treatment of beryl. He digested the fused ore with concentrated sulfuric acid, and added a controlled amount of water so as to generate enough heat for conversion of the oxides of beryllium and aluminum to sulfates, and at the same time not enough to hydrate the silica present.

Ferkel and Ellis, in U. S. Pat. 1,986,567, 1934, seems to use more than enough sodium hydroxide to dissolve the hydroxides of aluminum and beryllium. They speak of a "suitable excess" whereby they believe that aluminum is definitely eliminated in the  $\text{Be}(\text{OH})_2$  obtained on boiling the diluted solution of these hydroxides. They use as a fusing flux soda ash. It is interesting that they provide a means of recovering silica in the form of water glass.

Clafflin, in U. S. Pat. 2,022,404 gives a method of obtaining metallic beryllium by electrolysis of a fused mixture of ammonium beryllium fluoride and alkali or alkaline earth fluorides, at a temperature below  $1000^\circ\text{C}$ . In U. S. Pat. 1,861,656 he chlorinates beryllium oxide, or beryllium carbonate, mixed with C, by feeding chlorine into a vertical silica tube which is externally heated and contains the beryllium oxide-carbon mixture. Carbon monoxide, and gaseous beryllium chloride result. These

are passed into a molten electrolyte bath of sodium chloride; beryllium chloride condenses, and carbon monoxide escapes. Metallic beryllium is obtained by the electrolysis of the molten material.

Many patents for producing coherent beryllium have been issued. Cooper, in U. S. Pat. 1,775,589 presses beryllium powder to a coherent body and melts it with halides of alkaline earth metals. Stock and Goldschmidt in No. 1,427, 919 electrolyze a fused bath containing essentially an alkaline earth metal fluoride and a beryllium compound, the bath having a high melting point (1200-1300°). Dickinson, 1,511,829 patents a very similar process. Kroll, in 1,740,657 obtains compact beryllium by chemical decomposition. He reacts fluorides of beryllium with an alkaline earth metal under anhydrous conditions. A temperature of 1300° is produced by the heat evolved in the reaction. The product of the reaction, beryllium metal, is removed, and melted again with a mixture of beryllium fluoride and alkaline earth metal fluoride. Beryllium salts used here are of course anhydrous, and are diluted with other fluorides (more electropositive) to render the reaction less violent.

Pries and Cooper, U. S. Pat. 1,710,840 decompose beryllium minerals by heating with twice the weight of ore of equal parts calcium oxide and calcium fluoride. Sulfuric acid is added to dehydrate silica. Solution of soluble sulfates in water follows, then the solution is

evaporated to a specific gravity of 1.31, when calcium sulfate is filtered off; the solution is again evaporated to a specific gravity of 1.41, and  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{BeSO}_4$  are allowed to crystallize. The mixture of these sulfates is ignited and fused with sodium carbonate. This is followed by water extraction leaving beryllium in the residue and putting sodium aluminate in solution.

Lowenstein, in U. S. Pat. 1,777,122 fuses beryl with pyrite and carbon, and does this by means of an electric furnace under reduced pressure. Volatile oxides and sulfides of aluminum and beryllium are produced. He obtains these as sublimates, and extracts them with hot alkali solutions, sometimes with addition of sulfides or polysulfides. Extracts are filtered, and treated by careful addition of acids. Flakelike deposits form, containing beryllium and sulfur, not aluminum. In another patent, 1,777,267, Lowenstein separates  $\text{BeO}$  and  $\text{BeS}$  from  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{S}_3$  by fractional condensation.

Fischer in U. S. Pat. 1,815,056 heats beryllium bearing minerals with silicofluoride to incandescence. He comminutes the fused mass and leaches with cold water. He then adds, to the cold water solution, an alkaline earth hydroxide, subjects the resulting precipitate to further treatment with acid (HX), leaches the product with cold water to separate the resulting  $\text{BeX}_2$  from  $\text{CaF}_2$ , etc. In U. S. Pat. 1,820,655, he fuses with alkali carbonate in excess, only to sintering, not fusion, then adds HX, to form a paste.

The paste is added to a solution of alkali metal carbonate, or of sodium bicarbonate. The clear solution is separated from the precipitate and hydrofluoric acid added, forming  $\text{BeF}_2$ . The beryllium fluoride solution is treated with ammonium sulfide which removes the iron precipitate, and separates the beryllium fluoride from solution.

Kangro, U. S. Pat. 1,893,331 uses chlorine gas to decompose beryl, obtaining volatile  $\text{BeCl}_2$ .

Zisch, U. S. Pat. 1,966,371, finds that by fusing beryl with a very large excess of calcium oxide, or compounds furnishing calcium oxide on ignition, (in the proportion 1 mol beryl to 11 mols  $\text{CaO}$ ) he puts Al, Fe, Cr, etc., in a form soluble in hydrochloric acid. Beryllium, presumably as oxide, is left in insoluble form. He then heats the beryllium residue with  $\text{H}_2\text{SO}_4$  to dehydrate silica, beryllium sulfate formed is then soluble in water.

Brush, U. S. Pat. 1,656,660, makes mixtures of aluminum and beryllium oxide of different  $\frac{\text{Al}_2\text{O}_3}{\text{BeO}}$  ratio. He heats the ore with alkaline flux, decomposes the mass with sulfuric acid, dissolves the sulfates of aluminum and beryllium, removes  $\text{SiO}_2$  and iron, and ignites the mixture of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{BeSO}_4$  to obtain a corresponding mixture of the oxides. He varies his  $\text{Al}_2\text{O}_3/\text{BeO}$  ratio by controlling aluminum removal as sodium alum,  $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

Sawyer and Kjellgren in U. S. Pat. 1,823,864, use



heat treatment to render beryl attackable by fairly concentrated sulfuric acid. They find that heating above  $1000^{\circ}$  rapidly decreases the resistance of beryl to acids, if melted at  $1500^{\circ}$ , there is practically no resistance, provided the molten beryl is quenched in water. Beryllium and aluminum may be either extracted successively or simultaneously, as desired, depending on the degree of modification of the beryl, the concentration of the acid used, the temperature and time of reaction between the acid and comminuted beryl. Silica is left completely dehydrated if the temperature is sufficiently high. A complete separation of aluminum is claimed, based on the fact that an alum such as ammonium alum or potassium alum is substantially insoluble in an aqueous solution of suitable concentration and temperature, containing a mixture of beryllium sulfate and for example ammonium sulfate or an alkali sulfate. The beryllium sulfate solution should be saturated, and contain 6% of the weight of beryllium sulfate of ammonium sulfate.

Zimmerman, U. S. Pat. 1,851,476, heats beryl with gaseous  $\text{H}_2\text{F}_2$  to a temperature of  $100-900^{\circ}\text{C}$  until no  $\text{SiF}_4$  escapes, extracts the reaction mass with water at  $10-100^{\circ}\text{C}$ , filters and precipitates the beryllium from the filtrate with ammonium hydroxide.

In this brief review of the patent literature on beryllium, no attempt has been made to include all the patents which have been issued, but it is believed that the most pertinent of them have been reviewed.

#### IV. THE CHEMISTRY OF THE ALKALI METAPHOSPHATES

It has long been known that several different forms of sodium metaphosphate existed. Graham found that by gradual heating of microcosmic salt, sodium acid pyrophosphate was first formed:



On further slow gradual heating, a vitreous cake was formed. Graham stopped heating at this point, which appears to have been, when other investigators' work is considered, about a temperature of  $350^\circ$ . Graham found that by treating the cooled cake with water, a portion was found soluble, and another portion insoluble. The names "Graham's soluble salt" and "Graham's insoluble salt" have been used by later investigators to denote these salts. Graham believed the soluble salt was a trimetaphosphate,  $(\text{NaPO}_3)_3$ ; he believed that the insoluble salt was the monometaphosphate,  $\text{NaPO}_3$ . Graham's insoluble salt is identical with "Maddrell's salt". Maddrell prepared the same salt later. It is interesting that Pascal by electrical conductivity measurements, using the rule for determining basicity of acids, verified Graham's soluble salt as the trimetaphosphate ( $\text{Na}_3\text{P}_3\text{O}_9$ ), but believes his insoluble salt, because of freezing point measurements, is a complex of high molecular weight.

Pascal's method of preparing sodium dimetaphosphate

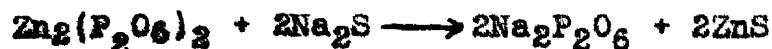
is as follows:<sup>31</sup>

Sirupy phosphoric acid ( $H_3PO_4$ ) is heated for a limited time at moderate temperatures ( $320^\circ$ ) and heating is stopped at the first appearance of ill defined crystals of an insoluble polymer. The product is dissolved in ice water to avoid rehydration (to pyrophosphoric acid,  $H_4P_2O_7$ ). Addition of the theoretical amount of sodium hydroxide gives a pure solution of the neutral salt. Excess alcohol precipitates an oil which rapidly crystallizes as a hydrated salt,  $Na_2(PO_3)_2 \cdot 3H_2O$ . This salt,  $Na_2P_2O_6 \cdot 3H_2O$  is very soluble in water, much more so than Maddrell's salt, so that Maddrell's salt should not be considered a dimetaphosphate.

Travers and Chu<sup>32</sup> claim that Pascal's method always gives a product containing a little  $Na_2H_2P_2O_7$ . Pure  $Na_2P_2O_6$  is obtained on heating to  $250^\circ$  in vacuo for eight hours a mixture of five parts  $Na_2HPO_4 \cdot 12H_2O$ , one part  $NH_4NO_3$  and one part  $NH_4Cl$ , when, after slow cooling, solution, neutralization and recrystallization, well crystallized  $Na_2P_2O_6 \cdot 3H_2O$  is obtained, any very soluble  $Na_2H_2P_2O_7$  formed simultaneously remaining in solution.

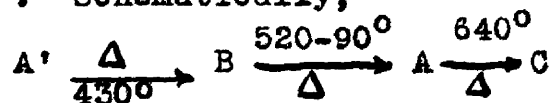
Mellor<sup>33</sup> states that if the oxide or other salt of copper, manganese, zinc or cobalt be heated between  $316^\circ$  and  $400^\circ$  with excess  $H_3PO_4$ , the dimetaphosphates are formed in each case. Barium, lead, cadmium, silver and bismuth, however, give hexametaphosphates. It is possible

to prepare dimetaphosphates of other metals by double decomposition reactions such as:



Pascal has stated that the dimetaphosphates claimed here are really tetrametaphosphates, by the electrolysis rule, in solution.

Boullé, in two articles,<sup>34,35</sup> in one of which he studies X-ray spectra of different sodium metaphosphate polymers, and the other in which he studies these polymers by means of thermal analysis, finds that  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ , dehydrated below  $250^\circ$  gives insoluble Maddrell's salt,  $\text{Na}_3\text{P}_3\text{O}_9$ \*, designated A'. A' heated to  $400-550^\circ$  forms an insoluble, and unknown polymer  $\text{B}_n(\text{NaPO}_3)_n$ . A' (which is  $(\text{NaPO}_3)_3$ ) or B, heated above  $550^\circ$  but below the melting point ( $640^\circ$ ) gives a soluble product A with spectrum identical with A', and therefore  $(\text{NaPO}_3)_3$ . A, A' B, fused and cooled quickly form vitreous, soluble sodium hexametaphosphate,  $(\text{NaPO}_3)_6$ , designated C. C, if reheated at  $300-625^\circ$  passes into A, the more quickly the higher the temperature. Knorre's  $(\text{NaPO}_3)_3$  is identical with A, which is unaltered by heating at  $300-625^\circ$ . Schematically,



where  $\text{A}' = \text{A} = (\text{NaPO}_3)_3$ ; B is unknown, C is  $(\text{NaPO}_3)_6$ , and all changes are irreversible. Note that Boullé does not find  $(\text{NaPO}_3)_4$ , sodium tetrametaphosphate.

---

\* Note inconsistency with statement on Page 20.

Travers and Chu<sup>38</sup> maintain that Knorre's so-called sodium trimetaphosphate is really identical with their sodium dimetaphosphate. Knorre heated  $\text{NaNH}_4\text{HPO}_4$  (microcosmic salt) or  $\text{NaH}_2\text{PO}_4$  at  $245^\circ\text{C}$ . Note that A' and A would then be sodium dimetaphosphate, not trimetaphosphate as Boullé claims.

The dimetaphosphate (Travers and Chu, and Pascal's method of preparation used) in solution passes into  $\text{H}_4\text{P}_2\text{O}_7$  (which must be why Pascal believed the dimetaphosphates of Mellor, were tetrametaphosphates). Pascal<sup>31</sup> states that all other polymetaphosphoric acids go directly to orthophosphoric acid, the dimetaphosphate alone forming the acid pyrophosphate. Here Pascal must reconcile his former statement that dimetaphosphates in solution were salts of a tetrabasic acid.

It appears that tetrametaphosphates are really dimetaphosphates which in solution are changed to pyrophosphates. Flatmann had claimed the tetrametaphosphates could be prepared by heating mixtures of orthophosphates of metals with excess  $\text{H}_3\text{PO}_4$  at  $300^\circ$ . The mass was extracted with water and digested with  $\text{Na}_2\text{S}$  or  $\text{K}_2\text{S}$  (sodium or potassium sulfide), and small crystals of the sodium or potassium salt are obtained. Electrical conductance of the sodium salt corresponds with that required for a tetrabasic acid.

Pentametaphosphates have been claimed. If one heats ammonium dimetaphosphate at  $200\text{--}250^\circ\text{C}$ , and extracts with water, he obtains presumably  $(\text{NH}_4\text{PO}_3)_5$ . If he treats the

solution with NaCl or LiCl he obtains  $\text{Li}_4\text{NH}_4\text{P}_5\text{O}_{15}$  and  $\text{Na}_4\text{NH}_4\text{P}_5\text{O}_{15}$ , the electrical conductance of which indicates five cations<sup>33</sup>.

There seems to be no dispute concerning the existence of sodium hexametaphosphate,  $\text{Na}_6\text{P}_6\text{O}_{18}$ , obtained by heating  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ,  $\text{NaH}_2\text{PO}_4$  or  $\text{NaNH}_4\text{HPO}_4$  to above  $640^\circ$  and rapidly cooling the fused mass.

Higher polymers have been claimed<sup>33</sup>.

## V. EXPERIMENTAL PART

### Purity of Materials

Beryllium nitrate was obtained from the Brush Beryllium Company of Cleveland, and was shown by the Pontachrome Blue Black R test<sup>36</sup> to be free of aluminum. Iron was proved absent by the thiocyanate test.

The potassium alum used was a recrystallized product made by recrystallizing ordinary C.P. potassium alum from 1% sulfuric acid solution. It was shown by the thiocyanate test to be free from iron.

C.P. aluminum nitrate (A.C.S. reagent quality), free from iron was also employed as a source of aluminum.

The 8-hydroxyquinoline used for determining aluminum gave no residue on ignition and melted at 76°C. This was a product of the Eastman Kodak Company.

The sodium hexametaphosphate was donated by Calgon, Inc., of Pittsburgh. It is a white flaky substance of a high degree of purity. This salt contains a trace of iron but not sufficient to interfere with Al or Be determinations. One mol of it prevents two mols of trivalent metal from precipitating with ammonium hydroxide. It decolorizes  $\text{Fe}(\text{CNS})_3$  readily.



### Methods of Analysis

Aluminum. Aluminum was analyzed by the 8-hydroxyquinoline method as recently modified by Knowles<sup>19</sup>. This consists in precipitating aluminum in a volume of 200 ml. from a slightly acid solution (PH = 6.8) in the presence of ammonium acetate.

Beryllium. Beryllium was determined by the standard method of precipitation, with ammonium hydroxide, as a hydroxide from a solution containing sufficient ammonium salts. A concentration of at least 2% ammonium nitrate, or acetate is required. In the presence of 8-hydroxyquinoline, an excess of ammonium hydroxide is required, and it is also necessary to allow the solution to stand overnight (covered). Filtrates were always tested with more ammonium hydroxide to see if precipitation was complete.

The above method of determining beryllium was tried on a pure sample of basic beryllium acetate. A known weight of basic beryllium acetate was treated with dilute sulfuric acid and boiled till it was completely changed to soluble beryllium sulfate. The solution so obtained, now free of acetic acid, was treated with nitric acid and boiled until a clear solution resulted. This final solution was diluted in a volumetric flask. Samples were withdrawn, and precipitated with ammonium hydroxide. To remove the adsorbed sulfate the precipitates were dissolved and re-precipitated in the presence of 2% ammonium nitrate, filtered on ashless

filter paper, washed with slightly ammoniacal ammonium nitrate until sulfate free (barium chloride + acid), and ignited to BeO in platinum crucibles. Following are the results obtained:

#### Analysis of Known Samples of Beryllium

Be Present	Be Found	Diff.
0.0223	0.0225	+0.0002
0.0558	0.0557	-0.0001
0.1116	0.1117	+0.0001
0.2232	0.2224	-0.0008

Mixtures of known concentration of aluminum and beryllium were made up and analyzed by Knowle's modification of the 8-hydroxyquinoline method:

#### Analysis of Known Al<sup>3+</sup>- Be<sup>2+</sup> Mixtures

Al <sup>+++</sup> present	Al <sup>+++</sup> found	Diff.	Be <sup>++</sup> present	Be <sup>++</sup> found	Diff.
0.02614	0.02607	-0.00007	0.0713	0.0713	0.0000
0.01044	0.01041	-0.00003	0.0713	0.0716	+0.0003
0.00524	0.00516	-0.00008	0.0713	0.0711	-0.0002

In later work 8-hydroxyquinoline method had to be employed when the solution contained metaphosphate polymers. The procedure then followed was: Solutions containing Al<sup>+++</sup>, Be<sup>++</sup>, metaphosphate polymers and possibly orthophosphate, were boiled one hour in 10% sulfuric acid, or until fumes were produced. More water was then added and allowed to

evaporate again to  $\text{SO}_3$  fumes. This procedure hydrolyzed all metaphosphate polymers to orthophosphate. The solutions were cooled, acidity adjusted to pH 3-4, ammonium nitrate added to make the solution 1.5 M in  $\text{NH}_4\text{NO}_3$ , and diluted so that sulfate ion was not over 5% by weight. Enough ammonium molybdate reagent was added to completely precipitate all the orthophosphate, then solutions were warmed to  $70^\circ$  in a water bath for one hour. After cooling, the phosphomolybdate precipitates were filtered off and washed five times with cold distilled water; washings were added to the filtrate. Filtrates were now treated with an excess of five to seven drops concentrated ammonium hydroxide beyond litmus blue, whereby beryllium and aluminum hydroxides containing adsorbed molybdate ion were produced. These precipitates were dissolved in dilute nitric or sulfuric acid (10%), and reprecipitated with concentrated ammonium hydroxide, an excess of 3 - 5 drops being used. After solution of these precipitates in hot 10% nitric acid, another re-precipitation with concentrated ammonium hydroxide, using an excess of 1 - 2 drops followed. After resolution in 10% nitric acid, hot, solutions were diluted to 200 c.c., 15 c.c. of ammonium acetate solution (30 g.  $\text{NH}_4\text{OAc}$ , 75 ml.  $\text{H}_2\text{O}$ ) was added, a drop of 0.4% bromocresol purple, and ammonium hydroxide added until the indicator became distinctly purple. An excess of 8-hydroxyquinoline was added, and solutions

heated to boiling. If, on settling, the filtrate was not colored a good distinct yellow, more 8-hydroxyquinoline was added, until a distinct yellow color was obtained. Aluminum precipitates so obtained were filtered on weighed Gooch crucibles and dried at 135° for three hours.

Beryllium was determined in the filtrates by adding a sufficiently large excess of ammonium hydroxide, and allowing to stand overnight. The precipitates obtained were ignited to BeO in platinum crucibles.

This method was tried on known solutions of Al<sup>+++</sup> and Be<sup>++</sup> containing 5.00 c.c. of 10% (NaPO<sub>3</sub>)<sub>6</sub>, and 10 c.c. 18 M H<sub>2</sub>SO<sub>4</sub> with the following results.

#### Analysis of Al and Be in the Presence of (NaPO<sub>3</sub>)<sub>6</sub>

Al <sup>+++</sup> present	Al <sup>+++</sup> found	Diff.	Be <sup>++</sup> present	Be <sup>++</sup> found	Diff.
0.0845	0.0846	+0.0001	0.0049	0.0052	+0.0003
0.0423	0.0423	0.0000	0.0097	0.0093	-0.0004
0.0423	0.0419	-0.0004	0.0244	0.0247	+0.0003

Phosphate. Phosphate was determined by the alkali-metric method for small amounts<sup>37</sup>, and weighing of magnesium ammonium phosphate hexahydrate for large amounts.

pH. Hydrogen ion concentration measurements were taken with the glass electrode and by the colorimetric method.

### Separation of Aluminum from Beryllium

The idea of using sodium hexametaphosphate to separate beryllium and aluminum was conceived while studying the action of this reagent in forming complex ions with certain divalent metals.

Sodium hexametaphosphate has the property of preventing many metals from precipitating on the addition of the usual analytical reagents to their solutions. One mol of this compound will prevent two mols of trivalent metal from precipitating. The undissociated compound  $M_2^{+++}P_6O_{18}$  is thought to be formed. One mol of bivalent metal,  $M^{++}$ , is kept in solution by one mol of sodium hexametaphosphate, with the formation of the complex ion  $[M^{++}P_6O_{18}]^{=}$ . Zinc and beryllium are two bivalent metals which require larger amounts of sodium hexametaphosphate to prevent their precipitation than would be calculated by the above assumption.

Qualitative experiments showed that much greater amounts of sodium hexametaphosphate were necessary to hold  $Be^{++}$  in solution than for  $Al^{+++}$ , when a hydroxide was used as the precipitating reagent. The procedure used in these tests was as follows: (1) Ammonium hydroxide was added to a solution containing 0.0496 g  $Al^{+++}$  and 0.8 g.  $(NaPO_3)_6$  in a volume of 23 ml. until the phenolphthalein end point was reached. The aluminum gave no precipitate. (2) Beryllium solutions at the same volume containing 0.0229 g.

$\text{Be}^{++}$  and 0.8 g  $(\text{NaPO}_3)_6$  became solid jellies on adding ammonium hydroxide until alkaline. (3) Aluminum solutions containing 0.0992 g.  $\text{Al}^{+++}$  in volumes from 30 to 50 ml., on adding 1.2 g  $(\text{NaPO}_3)_6$  (as 10% solution) and then ammonium hydroxide until alkaline gave a small precipitate which peptized to a turbid solution on boiling; (4) Beryllium solutions containing 0.0092 g.  $\text{Be}^{++}$  in a volume of 30 ml. gave on adding the same quantities of  $(\text{NaPO}_3)_6$  and  $\text{NH}_4\text{OH}$ , a precipitate which remained on boiling. At larger volumes, the precipitate was peptized on boiling.

In light of these results it was thought worth while to obtain some quantitative data, and the following experiments were tried:

(1) To 0.0496 g.  $\text{Al}^{+++}$  and 0.0229 g.  $\text{Be}^{++}$  and 0.8 g.  $(\text{NaPO}_3)_6$  in a volume of 15 ml., 10 ml. of water were added, then some macerated filter paper, and  $\text{NH}_4\text{OH}$  until alkaline. The precipitate was filtered and analyzed. It was found that 56.8% of the original aluminum had precipitated along with 59.0% of the original beryllium. The precipitate carried large quantities of metaphosphate.

(2) To 0.0992 g.  $\text{Al}^{+++}$  and 0.0459 g.  $\text{Be}^{++}$  in a volume of 30 ml., 12 ml. 10%  $(\text{NaPO}_3)_6$  were added, then ammonium hydroxide until alkaline, then some macerated filter paper, and the whole heated to boiling. The precipitate was filtered off and analyzed. 86.9% of the original aluminum had precipitated along with 88.2% of the original beryllium.

These results were somewhat discouraging and wholly unexpected. The aluminum apparently coprecipitated with the beryllium in large amounts.

Another procedure was now tried. It is well known that concentrated ammonium hydroxide has an appreciable solvent action on aluminum hydroxide. An excess of 5 ml. ammonium hydroxide will dissolve 0.007 - 0.01 g. aluminum hydroxide calculated as  $Al^{+++}$ . To see if sodium hexametaphosphate enhanced this effect, the following experiments were performed. 0.0166 g.  $Al^{+++}$  in a volume of 100 ml. when poured into a mixture containing 0.5 - 0.6 ml. 2%  $(NaPO_3)_6$  and 6 ml.  $NH_4OH$ , gave no precipitate on heating to  $80^\circ$ . Even half this quantity of  $Be^{++}$  gave a large precipitate under these conditions. Order of addition of reagents affects these results somewhat. Solutions containing both aluminum and beryllium do not give a precipitate free of aluminum when 0.5 - 0.6 ml. 2%  $(NaPO_3)_6$  and 5 ml. conc.  $NH_4OH$  are used for each 0.0166 g.  $Al^{+++}$  present. In an actual run, with 0.0850 g.  $Be^{++}$  and 0.1668 g.  $Al^{+++}$  in 100 ml. volume, poured into a solution containing 5.1 ml. 2%  $(NaPO_3)_6$  and 51 ml. conc.  $NH_4OH$ , the precipitate obtained contained on analysis 71.3% of the original aluminum and 96.0% of the original beryllium.

These results were of course unsatisfactory and it was decided to next study the effect of the hexametaphosphate on the separation of beryllium and aluminum as proposed by

Gmelin. This was done in the following manner: Solutions containing aluminum and beryllium in a volume of 30 ml. were treated with 2 M NaOH if  $\text{Al}^{+++}$  did not exceed 0.4 g. or 4 M NaOH if it did, until the precipitates dissolved and a clear solution resulted. Solutions were now diluted to 500 ml., and  $(\text{NaPO}_3)_6$ , as 2% solution, added with stirring. After the  $(\text{NaPO}_3)_6$  addition, solutions were heated to boiling for 2-3 minutes. Precipitates were filtered and washed with water until free of sodium, then analyzed. The following table gives the results of these studies.

TABLE I

Influence of  $(\text{NaPO}_3)_6$  on the Separation of  $\text{Be}^{++}$  and  $\text{Al}^{+++}$  with an Excess of NaOH

$\text{Al}^{+++}$ present	$\text{Be}^{++}$ present	$(\text{NaPO}_3)_6$ present	$\text{Al}^{+++}$ in ppt.	$\text{Be}^{++}$ pptd.
0.4000 g.	0.2000 g.	0.00	0.0008	0.1999
0.4176 "	0.0850 "	0.00	0.0108	0.0814
0.4176 "	0.0850 "	0.01	0.0143	0.0736
0.4176 "	0.0850 "	0.02	0.0080	0.0804
0.4176 "	0.0850 "	0.04	0.0183	0.0779
0.4176 "	0.0850 "	0.16	0.0148	0.0705
0.8000 "	0.3370 "	0.00	0.0216	0.3308
0.8000 "	0.3370 "	0.32	0.0210	0.3339

It is seen that the hexametaphosphate may decrease the aluminum coprecipitating, but there is a critical amount which varies depending on the ratio  $\text{Al}^{+++}/\text{Be}^{++}$  and possibly on the amounts of aluminum and beryllium present.



It is doubtful if the aluminum would be completely eliminated. Reprecipitation in the absence of metaphosphate would eliminate the aluminum, and traces of orthophosphate would not be present (as is the case when sodium hexametaphosphate is used).

In carrying out the foregoing experiments it was observed that if sodium hexametaphosphate were added to an  $\text{Al}^{+++}$  solution above a pH of 3, a permanent precipitate was obtained. Qualitative experiments showed that  $\text{Be}^{++}$  solutions gave no precipitate until higher pH values were reached.  $\text{Al}^{+++}$  precipitates analyze  $[\text{Al}(\text{PO}_3)_3]_x$  at lower pH values and become basic salts on an increase of pH. These observations suggested that it might be possible to remove all or a great part of the aluminum by controlling the pH of solutions containing  $\text{Al}^{+++}$  and  $\text{Be}^{++}$ , and adding  $(\text{NaPO}_3)_6$  slowly. Table II shows that separation of beryllium and aluminum may be partially accomplished on the acid side. In all cases, mixtures of beryllium and aluminum solutions were initially at a volume of 100 c.c. The term "apparent acidity" was arrived at in the following way. The standard solutions of beryllium nitrate, and aluminum were individually titrated with standard 0.1 N sodium hydroxide using phenolphthalein. An "apparent" acidity usually near 2N was obtained. This is not the true acidity. The pH values were less than pH 3, an actual acidity of about 0.001 N. In analyses recorded

in the table given, amounts of  $Al^{+++}$  standard solution and  $Be^{++}$  standard solution were always the same. Dilutions to 100 ml. of the standard solutions was in all cases the procedure, followed by addition of definite quantities of standard base (0.1 N NaOH). A solution containing 5 c.c. of  $Al^{+++}$  solution and 4.25 c.c.  $Be^{++}$  solution contained, for example,  $\frac{9.25 \times 2.00}{1000}$  equivalents "apparent" acid. On adding 9.00 c.c. 0.1 N base, there were left  $0.01950 - 0.0009$  or  $0.0184$  equivalents "apparent" acid. On dividing this latter value by the volume of the solution and multiplying by 1000, the value of the "apparent" acidity was obtained. Different quantities of standard base were added to the solutions containing the aluminum and beryllium, and the apparent acidity calculated. These solutions were run for pH by McIlvaine's standard buffer method, excepting the one marked with an asterisk, which was determined with a glass electrode. In all cases, after addition of the tenth normal base, 5.00 ml. of 10% sodium hexametaphosphate was added, and the precipitate analyzed after washing with water.

TABLE II

Effect of Acidity on the Separation of  $\text{Be}^{++}$  and  $\text{Al}^{+++}$  with  $(\text{NaPO}_3)_6$  (0.50 g.)

$\text{Al}^{+++}$ present	$\text{Be}^{++}$ present	Final Vol.	Apparent Acidity	pH	% Al ppt.	% Be ppt.	Temp.
g.	g.	ml.					
0.0834	0.0411	122	0.140 N	3.7	23.9	5.4	Room
0.0834	0.0411	131	0.120	3.8	29.5	4.8	"
0.0845	0.0397	140	0.103	3.8	44.1	6.6	"
0.0845	0.0397	147	0.0935	3.93	59.1	5.7	"
0.0845	0.0397	153	0.0848	4.0	65.4	10.9	"
0.0845	0.0420	210	0.0631	-	67.2	18.0	"
0.0845	0.0420	215	0.0493	-	86.4	37.7	"
0.0845	0.0420	218	0.0425	-	93.6	38.1	"
0.0845	0.0420	220	0.0362	-	95.8	52.8	"

Aluminum and beryllium figures are percentages of the materials originally present in the solutions which were present in the precipitates obtained.

Keeping the aluminum and beryllium content of the solutions constant, the effect of increasing the amount of 10% sodium hexametaphosphate was studied. The following are the results:

TABLE III

Effect of Varying Amounts of  $(\text{NaPO}_3)_6$  on the Separation of  $\text{Be}^{++}$  and  $\text{Al}^{+++}$

Al present	Be present	$(\text{NaPO}_3)_6$ used	Apparent acidity	pH	% Al pptd.	% Be pptd.
0.0834	0.0411	0.50 g.	0.120 N	3.8	29.5	4.8
0.0834	"	0.55	"	"	30.0	6.4
0.0834	"	0.60	"	"	34.9	6.1
0.0834	"	0.75	"	"	56.1	18.4
0.0834	"	0.90	"	"	49.1	11.9

A maximum is reached where the beryllium accompanying the aluminum (which also reaches a maximum) is too large to be of any value. It is observed from Table II that by increasing the pH this maximum value of aluminum may be realized without at the same time increasing the beryllium appreciably, by using a smaller quantity of  $(\text{NaPO}_3)_6$  than 0.75g. and the optimum pH is 3.93, where 59% of the  $\text{Al}^{+++}$  is precipitated and the beryllium loss is but 6%. The fact that the pH should not exceed 3.93 is shown by data of Table II, where beryllium losses at apparent acidities below 0.0935 (pH = 3.93) are quite high. In Table III it is shown that a sufficiently large excess of hexametaphosphate will dissolve the precipitate.

Buffers may not be satisfactorily used in the above separations. If 10 g. ammonium nitrate be used to buffer the aluminum-beryllium solutions at a pH of 3.93, and then 5.00 ml. 10%  $(\text{NaPO}_3)_6$  added, 77.09% of the original aluminum is precipitated (which would be advantageous) but 27.4% of the beryllium accompanies it. In this connection it is interesting to note that sodium acetate and ammonium acetate allow of no precipitation at all at a pH of 3.93. Evidently if acetic acid is the acid present, a new set of desirable pH values must be worked out. Either this, or ammonium acetate and sodium acetate dissolve the precipitate.

Ammonium hydroxide, 0.1 N, if used in place of 0.1 N sodium hydroxide to adjust the solutions to a pH of 3.93 gives somewhat different results on adding sodium hexameta-

phosphate. Actual determinations showed 62.03% of the aluminum was precipitated, along with 11.1% of the beryllium. In this case, since 11.1% of the beryllium is too great a loss, a somewhat lower pH should be used. This greater precipitation of beryllium is undoubtedly due to the buffering effect of the ammonium nitrate formed.

Results thus far indicate separation of about 59% of the aluminum, accompanied by a small beryllium loss is possible at the pH 3.93, using 5.92 cc of 10%  $(\text{NaPO}_3)_6$  for each 0.1 gm. of  $\text{Al}^{3+}$  present in a volume of 140 ml., and provided that ammonium salts or other similar buffers are absent.

Having accomplished a preliminary aluminum removal by use of sodium hexametaphosphate, it was now decided to reinvestigate the processes mentioned at the beginning of this discussion, on the alkaline side. Here a preliminary aluminum removal had not been made. Four methods were described. The first used a small volume, 8 ml. 10%  $(\text{NaPO}_3)_6$  to keep 0.0496 g.  $\text{Al}^{+++}$  in solution on  $\text{NH}_4\text{OH}$  addition in the cold. The second used a rather small volume, 12 ml.  $(\text{NaPO}_3)_6$  for preventing 0.0992 g.  $\text{Al}^{+++}$  from precipitating on  $\text{NH}_4\text{OH}$  addition and heating to boiling. The third consisted in pouring  $\text{Al}^{+++}$  -  $\text{Be}^{++}$  solutions containing no free acid in a volume of 100 ml. into a solution containing 0.5-0.6 ml. 2%  $(\text{NaPO}_3)_6$  and 5 ml. conc.  $\text{NH}_4\text{OH}$  for each 0.0166 g.  $\text{Al}^{+++}$  present in the other solution. The fourth introduced  $(\text{NaPO}_3)_6$  into Gmelin's method of boiling  $\text{NaOH}$

solutions of the hydroxides.

Three of the four methods were again tried, after the preliminary aluminum removal.

Experiments using the first method will now be considered.

(1) To a solution of 100 ml volume, containing 0.0845 g.  $\text{Al}^{+++}$  and 0.0397 g.  $\text{Be}^{++}$ , 0.1 N NaOH was added to an apparent acidity of 0.0935 N. 5 ml. 10%  $(\text{NaPO}_3)_6$  were slowly added. The precipitate was filtered and washed.

To the filtrate 4 ml. 10%  $(\text{NaPO}_3)_6$  were added, and then 1 M.  $\text{NH}_4\text{OH}$  until alkaline to phenolphthalein. This gave a new precipitate which was filtered off and analyzed. It contained 33.62% of the original  $\text{Al}^{+++}$ , and 79.0% of the original beryllium.

(2) This was a duplicate of (1) but 1 M. NaOH was added to the filtrate in place of 1 M.  $\text{NH}_4\text{OH}$ . Analysis of the final precipitate gave 33.62% of the original aluminum and 79.0% of the original beryllium.

(3) To the solution containing 0.0845 g.  $\text{Al}^{+++}$  and 0.0397 g.  $\text{Be}^{++}$ , 0.1 N  $\text{NH}_4\text{OH}$  was added to an apparent acidity 0.0935 N, then 5 ml. 10%  $(\text{NaPO}_3)_6$  added. The precipitate was filtered and washed.

To the filtrate, 4 ml.  $(\text{NaPO}_3)_6$  were added, and then 1 M  $\text{NH}_4\text{OH}$  until alkaline. The precipitate obtained was filtered, washed and analyzed. It contained 33.93% of the

original aluminum and 76.2% of the original beryllium.

(4) This was a duplicate of (3), but 1 M. NaOH was added in the last part. The precipitate analyzed 33.59% of the original aluminum, and 75.4% of the original beryllium.

It is seen from this that combination with the first procedure is of no value, the final precipitate not only still contains large amounts of aluminum, but large quantities of beryllium are left in solution.

The second procedure was not tried because results on previous experiments showed that it precipitated even higher amounts of aluminum along with the beryllium.

The third procedure was tried. A typical experiment and result is:

To a solution containing 0.0845 g.  $\text{Al}^{+++}$  and 0.0397 g.  $\text{Be}^{++}$  in a volume of 100 c.c., 0.1 N NaOH was added to the apparent acidity of 0.0935 N. 5 ml  $(\text{NaPO}_3)_6$  (10%) were then added slowly and with stirring. The precipitate was filtered and washed with water.

To the filtrate,  $\frac{1}{2}$  ml. 10%  $(\text{NaPO}_3)_6$  was added, then conc.  $\text{NH}_4\text{OH}$ , 10 ml. in excess (beyond litmus blue). The precipitate was filtered and analyzed; it showed 89.7% of the original beryllium and 17.69% of the original aluminum came down with it.

This procedure while giving better results than the first was of course like the first, of no value, but it

suggested that if the same quantity of sodium hexameta-phosphate were used in another run, together with an excess of sodium hydroxide, results would be considerably better, for sodium hydroxide should have a greater effect in dissolving aluminum hydroxide than would ammonium hydroxide.

The percentage of aluminum appearing in the last precipitate dropped to 13.6 on using the quantities of  $\frac{1}{2}$  ml  $(\text{NaPO}_3)_6$  (10%) and an excess of 2.00 ml. 1 M NaOH beyond phenolphthalein in the filtrate, after having made the preliminary aluminum removal. This precipitate contained 86.2% of the original beryllium. Use of 3.5 c.c. 1 M. NaOH excess dropped the aluminum to 10.4% and increased the beryllium to 89.0%, but larger amounts of 1 M. NaOH did not eliminate the aluminum and cut down the percentage of beryllium precipitated, showing that beryllium hydroxide was being dissolved. This modification of the third procedure therefore appeared to have no value as it stood.

It now appears that our preliminary separation may not be directly combined with either of the first three procedures. Next, it was combined with the fourth procedure, which is Gmelin's method of separating beryllium and aluminum, in the following manner:

To two solutions, each containing 0.0845 g.  $\text{Al}^{+++}$  and 0.0414 g.  $\text{Be}^{++}$  in a volume of 100 ml., 0.1 N NaOH was added to an apparent acidity of 0.0935 N. This requires



about 40 ml. Then 5 ml. 10%  $(\text{NaPO}_3)_6$  were slowly added with stirring. The precipitates were filtered, and washed with water.

The filtrate was now treated with 2 M NaOH until the precipitates obtained were completely peptized, and a very slightly turbid solution was obtained. Solutions were now diluted to 400 ml and boiled 2-3 minutes. Precipitates were filtered off and washed until free of sodium. Analysis of these precipitates revealed that aluminum was completely absent, and that after hydrolysis in 10% sulfuric acid, only a very slight precipitate of ammonium phosphomolybdate was obtained on treating with ammonium molybdate reagent. Beryllium determinations agreed closely and showed that 86.3% of the original beryllium was precipitated.

It is seen that the procedure may be directly combined with the Gmelin method, but yields of beryllium obtained are not entirely satisfactory.

It is obvious from the above tests that the original idea of precipitating the beryllium and holding up the aluminum with hexametaphosphate could not be applied even after 60% of the aluminum had been removed. Reference to Table II indicates that the remainder of the aluminum may be removed with hexametaphosphate if the pH is increased to 5.4. With this idea in mind, the experiments outlined in the following paragraphs, and summarized in Table IV were performed.

In one example, a solution containing 0.0845 g.  $\text{Al}^{+++}$

and 0.0409 g.  $\text{Be}^{++}$  in a volume of 100 ml. was adjusted to the apparent acidity 0.0935 or pH 3.93. 5 ml. 10%  $(\text{NaPO}_3)_6$  were added. The precipitate was filtered and washed.

The filtrate was treated with 45 ml. 0.1 N NaOH, which resulted in a pH of 4.7, then 1.5 ml.  $(\text{NaPO}_3)_6$  was added. After filtration an aliquot of the filtrate was tested for aluminum.  $\text{Al}^{+++}$  was present by the Pontachrome Blue Black R Test, but in quantity less than one part in a million. The filtrate was therefore directly treated with NaOH until alkaline, and the former precipitate was saved. The new precipitate (obtained from the filtrate by NaOH addition) was dissolved in acid and an aliquot tested.  $\text{Al}^{+++}$  was present but much less than before (in the filtrate), and on analyzing the precipitate, 8-hydroxyquinoline gave no aluminum oxyquinolate precipitate. 65.8% of the beryllium free of aluminum was recovered by this procedure.

The precipitate which was saved, and which contained practically 100-59 or 41% of the original aluminum, and about 30% of the original beryllium, was dissolved in 20 ml. 3N HCl. Sodium hydroxide was now added in such concentration and volume as to approach a volume of 140 ml and a pH of 4.0. A slightly greater pH was obtained, and  $\frac{1}{2}$  c.c. of  $(\text{NaPO}_3)_6$  (10%) was added. The precipitate was filtered, washed and discarded. The filtrate was adjusted to a pH of 4.8 and a

few drops  $(\text{NaPO}_3)_6$  added. After filtration and washing, the filtrate was treated with NaOH until alkaline. The precipitate was washed and analyzed. Aluminum was absent and 21.3% of the original beryllium was recovered. The  $\text{Al}^{+++}\text{-Be}^{++}$  precipitate here (obtained at pH 4.8) was not worked up, but discarded. In the two operations 87.1% of the beryllium, free of aluminum, was recovered. Results of several determinations of this same type are summarized in Table IV.

TABLE IV

$\text{Al}^{+++}\text{-Be}^{++}$  Separations with  $(\text{NaPO}_3)_6$   
Using Successive Precipitation

No.	Initial Volume	$\text{Al}^{+++}, \text{Be}^{++}$ present	1st pH	Final pH	1st $\text{Be}^{++}$ recovery	2nd $\text{Be}^{++}$ recovery
1	140	0.0845;0.0409	3.93	4.7	65.8%	21.3%
2	140	0.0845;0.0386	"	5.4	60.7	not run
3	140	0.0845;0.0386	"	5.4	-	30.1
4	140	0.0845;0.0386	"	5.4	64.2	18.6

The first pH is the point at which the preliminary aluminum removal is made; the final pH is the point at which the filtrate was next brought for complete aluminum removal. In Runs No. 2,3 and 4 a filtration was usually made at a pH of about 4.7 in order to test the filtrate for aluminum. As mentioned in the typical example, a test for aluminum was usually obtained at this pH, although by comparison with

standards it was less than 1 part in 1,000,000. The new filtrate was then brought to the final pH noted and again filtered. More  $(\text{NaPO}_3)_6$  was added - 1.00 ml at a pH of 4.7 and 0.50 ml at the final pH - before these filtrations. The first beryllium recovery is the yield of beryllium obtained from the original solution; second, beryllium recovery is the additional yield obtained by putting the acid solution of the second aluminum beryllium precipitate through the same procedure again.

In addition to using the above procedure, the following was found successful.

To solutions containing in all cases 0.0845 g.  $\text{Al}^{+++}$  and 0.0414 g.  $\text{Be}^{++}$  in a final volume of 140 ml., after adjusting to the pH 3.93, 5 ml. 10%  $(\text{NaPO}_3)_6$  were added and the precipitate filtered, washed and discarded. The filtrates were now treated with varying amounts of 0.1 N sodium hydroxide (as shown in the table below) and the new precipitates filtered through Number One Whatman and washed. New filtrates were then treated with  $\frac{1}{2}$  ml. 10%  $(\text{NaPO}_3)_6$  and 1 M NaOH added until phenolphthalein changed color, then 2.0 ml excess. Precipitates were washed and analyzed.

TABLE V  
 Separations by Incomplete Aluminum  
 Removal

0.1N NaOH added	pH	% original Al <sup>+++</sup> in last ppt.	% original Be <sup>++</sup> in last ppt.
10.00 ml.	-	13.98	86.1
20.00 "	-	7.58	87.3
25.00 "	-	4.82	79.5
30.00 "	-	3.06	81.5
35.00 "	4.35	absent	70.6

It is obvious that this procedure may also be used to produce Al<sup>+++</sup> free beryllium. If the precipitate obtained at a pH of 4.35 is thrown back in the original, there is no loss of beryllium.

It should be noted here that final beryllium precipitates, of Tables IV and V, while free of aluminum contained metaphosphate in appreciable quantities.

In concluding the experimental part of this dissertation it should be mentioned that what we have termed the "preliminary aluminum removal" is a process entirely comparable with the alum process which is extensively practiced today in beryllium - aluminum separations. This is confirmed by the following experiment:

In a duplicate run, with 0.0845 g. Al<sup>+++</sup> and 0.0397 g. Be<sup>++</sup> in a volume of 50 ml., acidity of H<sub>2</sub>SO<sub>4</sub> was adjusted to

5 N; the solutions were saturated with potassium sulfate, heated to boiling, and set to crystallize at 0°. 63.8% of the aluminum crystallized out as potassium alum,  $KAl(SO_4)_2 \cdot 12H_2O$ , but 3.6% of the beryllium crystallized with it. The hexametaphosphate process which uses only a small quantity of a cheap chemical, and requires no heat, or time consumption is quite comparable in aluminum removal, and what is far more important, it results in an immediate recovery of 65% of the beryllium free from aluminum.

## VI. CONCLUSIONS

1. Sodium hexametaphosphate may be used to effect a complete separation of beryllium and aluminum by the following process:

Solution containing  $\text{Al}^{+++}$ ,  $\text{Be}^{++}$ . Adjust to pH 3.93. Add 5.92 ml 10%  $(\text{NaPO}_3)_6$  for each 0.1 g.  $\text{Al}^{+++}$  present, slowly with stirring. Filter the precipitate, wash with water.

<p><u>Precipitate</u> 59.1% of <math>\text{Al}^{+++}</math> as slightly basic metaphosphate. Small <math>\text{Be}^{++}</math> loss. Discard</p>	<p><u>Filtrate</u>. Contains 94-5% of the <math>\text{Be}^{++}</math>. 40-41% of the <math>\text{Al}^{+++}</math>. Add 0.1 N NaOH to pH 4.7. Add 1.18 ml. 10% <math>(\text{NaPO}_3)_6</math>. Filter. Test filtrate for <math>\text{Al}^{+++}</math>.</p>	
<p><u>Ppt (1)</u> Contains both <math>\text{Al}^{+++}</math> and <math>\text{Be}^{++}</math>; dissolve in acid, and repeat the procedure.</p>	<p><u>Filtrate</u> If <math>\text{Al}^{+++}</math> present, add more 0.1 N NaOH to pH about 5.4. Add 0.59 ml 10% <math>(\text{NaPO}_3)_6</math>. Filter, test filtrate for <math>\text{Al}^{+++}</math>.</p>	
	<p><u>Ppt. (2)</u> Al and Be as basic metaphosphates combine with (1).</p>	<p><u>Filtrate</u> <math>\text{Al}^{+++}</math> is now absent. Add NaOH or <math>\text{NH}_4\text{OH}</math> until alkaline. Ppt. is <math>\text{Be}(\text{OH})_2 + \text{Be}(\text{PO}_3)_2</math></p>

Advantages of the process are that a cheap reagent is used, and beryllium recovery of over 87% is possible. In addition, methods are simple - involving only addition of reagent, obtaining a precipitate, and immediately filtering. No external heat is required in the process.

A disadvantage is that one must determine, in particular, the first pH of 3.93 quite accurately. Small differences in pH affect the results markedly.

2. Sodium hexametaphosphate may be used as a preliminary means of removing a large part of the aluminum, and then the filtrate treated by the Gmelin method of boiling the sodium hydroxide solution of the hydroxides.

3. Other methods of using sodium hexametaphosphate for a complete beryllium-aluminum separation are discussed.



## VII. LITERATURE CITED

1. Vauquelin, Ann. Chim. Phys. 1798, 26, 155.
2. Gmelin, Pogg. Annalen, 1840, 50, 175.
3. Berzelius, vide H. Rose Handbuch der Analytischen Chemie, 1851, II, 61.
4. Berthier, Ann. Chim. Phys., 1843 (iii) 7,74.
5. Hart, J. Am. Chem. Soc., 1895, 17, 604.
6. Debray, Ann. Chim. Phys. 1855 (iii) 44,1.
7. Gibbs, Sill. Am. J. Sci., 37, 356.
8. Rossler, Z. Anal. Chem., 1878, 17, 148.
9. Vincent, Bull. Soc. Chim., 1880, 33, 157.
10. Renz, Ber., 1903, 36, 275.
11. Havens, Chem. News, 1897, 76, 111.
12. Haber, Z. anorg. Chem. 1903, 40, 465.
13. Parsons and Barnes, J. Am. Chem. Soc., 1906, 28, 1589.
14. Britton, Analyst, 46, 359, 437.
15. Wunder and Wenger, Z. Anal. Chem. 1912, 51, 470-3.
16. Hills, Ind. Eng. Chem. Anal. Ed., 4, 31-2.
17. Kling and Gelin, Bull. Soc. Chim. 1914, 15, 205.
18. Kolthoff and Sandell, J. Am. Chem. Soc. 50, 1900, 1928.
19. Knowles, Nat. Bur. Stds. J. Res., 15, 87, 1935.
20. Churchill and Bridges, Ind. Eng. Chem., Anal. Ed. 2, 405-7, 1930.
21. Adami, Ann. Chim. Applicata, 23, 428, 1933.
22. Willard and Fowler, J. Am. Chem. Soc. 54, 496, 1932.
23. Jilek and Kota, Collection Czechoslov. Chem. Comm. 3,336,1931.

## LITERATURE CITED (CONT'D.)

24. Fogg and Coughlin, *Ind. Eng. Chem.*, 23, 318, 1931.
25. Lebeau, *Compte Rendus*, 121, 641-4, 1895; 126, 1202, 1898.
26. Engle and Hopkins, *Eng. & Min. J. Press.*, 118, 49, 1924.
27. Sloman, *J. Soc. Chem. Ind. (London)* 48, 309, 1929.
28. Eritton, *J. Soc. Chem. Ind. (Trans.)* 349-52, 1922.
29. Dyson, *Can. Min. J.* 52, 359.
30. Negru, *Chem. & Met. Eng.* 21, 353, 1919.
31. Pascal, *Compte Rendu*, 196, 828, 1933.
32. Travers and Chu, *Compte Rendu*. 198, 2100, 1934.
33. Mellor's *Comprehensive Treatise on Inorganic Chemistry*,  
Vol. 8, London, Longmans.
34. Boullé, *Compte rend.*, 200, 658, 1935.
35. Boullé, *Compte rend.*, 200, 832, 1935.
36. Lowe, C.S., *Master's Thesis*, U. of Md., 1937.
37. Parent, P.A., *Master's Thesis*, U. of Md., 1935.