# BERYLLIUM ANALYSIS

A THESIS

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By:-

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# FOREWORD.....

Due to the large mass of material which has been published on the phases which the author at first planned to include in this work, it was found necessary to deal only with the analytical chemistry of Beryllium and its ores in this thesis. Time would not permit the collecting and arranging of all the available data on the other phases.

# ACKNOWLEDGMENT

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# INTRODUCTION

# BERYLLIUM

Beryllium, or glucium, is often listed as a rare element, though it probably is more abundant in the earth's crust (184) than many of the minor metals that are ordinarily considered rather common. According to J.H.L. Vogt (181) between 0.01 and 0.001% of the entire lithosphere is Beryllium.

There is reason to think that the alumina sometimes reported in rock analyses (10)(87) may be partly Beryllium which has not been separated from the alumina. Beryllium is a common accessory in pegmatite veins, is present (95)(108) in a great number of granite like rocks and to a small extent in clay, slate, and mica schist, in the form of aluminates, silicates, phosphates, borates, etc. Beryl is the chief source of the element and is found in nature as the only recognized beryllium ore.

The element has also been noted in some natural waters, monazite sand and aluminous schists. It is quite probable that it would have been found more frequently in rock analysis if there were some simple method of separation from Aluminium. Beryllium is very seldom looked for or determined in an igneous rock analysis. Beryllium accompanies Aluminium in the regular scheme of analysis and will be counted as this element if not detected and its amount deducted.

The quantitative determination of the Beryllium content in beryl and similar beryllium ores is usually accomplished by means of the most painstaking and at the same time most unreliable operations. The difficulties encountered in the analysis of raw beryl may be appreciated if it is considered how small a percentage of Beryllium is contained in the beryllium ore. Theoretically, beryl corresponds to the formula $3BeO.Al_2O_3.6SiO_2$. This composition corresponds theoretically to a content of 13.9% BeO; 19% $Al_2O_3$ and 67% $SiO_2$. Practically, the Beryllium content of beryl is even less. Nature does not furnish us a compound adhering to the hard and fast formula set forth. In the majority of cases, the BeO content of the mineral is between about 9 and 11% BeO. In addition to $Al_2O_3$ and $SiO_2$; FeO, or $Fe_2O_3$ are present. Frequently smaller amounts of $ZrO_2$, $Nb_2O_3$, CaO, MgO, $MnO_2$ and others are present. It is thus seen that there are present in this ore a mixture of component elements, the separation of which is very difficult analytically, and the quantitative determination of which often baffles the analytical chemist.

A few of the large number of proposed proceedures will be mentioned, and some of the better known and more promising methods will be discussed in some detail.

# Review of Literature

## I <u>Boiling KOH or NaOH</u>

In 1798, Vauquelin (1)(15)(97)(173) first Separated Beryllium from Aluminium by precipitating the Beryllium from a boiling solution of KOH. This method was also used by Gmelion (16)(28)(27)(36)(104)(175) in 1840, but shown to be inaccurate by Zimmermann (112)(139)(199)(213) in 1887, but again revived in 1911 by Wunder and Child (19)(54) and in 1921 by Britton (12)(63) and mentioned in reviews in 1863 by Joy (5)(44)(108)(121)(151)(165); and in 1931 by Travers and Schnoutka (83)(128); and in 1932 by Fresenius and Frommes (209).

Britton describes experiments which were performed (12)(63) to ascertain the best conditions for precipitating $Be(OH)_2$ by NaOH without precipitating $Al(OH)_3$ The results show that solutions containing not more than 0.3 grams of BeO and 0.4 grams of $Al_2O_3$ should be evaporated to about 25 cc, brought to room temperature and carefully treated with 6N NaOH until the precipitate just redissolves. Then, after diluting to 500 cc the Beryllium may be precipitated by boiling 40 minutes. The $Be(OH)_2$ precipitate must be filtered immediately, burned and weighed as BeO. Aluminium may be precipitated from the acidified filtrate with $NH_4OH$.

## II Boiling $NH_4OH$

Prepare a nearly neutral HCL or $HNO_3$ solution containing Beryllium as the only substance precipitable by $NH_4OH$. Slowly add $NH_4OH$ until in very slight excess. Boil 1-2 minutes, add a little macerated paper, and filter. Transfer as much of the precipitate as possible to the paper by rinsing with hot 2% solution of $NH_4NO_3$, and by thorough scrubbing. Cover the funnel and without delay dissolve any precipitate sticking to the walls of the beaker in a very little hot dilute $HNO_3$, heat to boiling and precipitate as before. Filter through the same paper and wash thoroughly with the $NH_4NO_3$ solution.

## III Use of $NH_4Cl$

The Berzelius method (which depends on the fact that the H-ion concentration to dissolve $Be(OH)_2$ is formed by boiling $NH_4Cl$ solution but not enough to dissolve ($Al(OH)_3$)) was recommended by Weeren (3)(23)(31)(106)(119)(149)(160) in 1854, considered accurate by Joy (44)(108)(121)(151)(165) in 1863, used by Klatzo (46)(110)(122)(143)(153)(162)(164)(174)(180)(194)(195)(216) in 1869, but considered inaccurate by Penfield and Harper (4)(38)(107)(111) in 1886. Britton (12)(65) in 1922, considered qualitative tests encouraging, but quantitative tests show that two hours boiling is not enough to dissolve all of the Be(OH)$_2$ suspended in 200 cc of saturated $NH_4Cl$ solution. Wunder and Wenger (55) get satisfactory results if at least 500 cc of water is used in extraction of a 5 gram melt of $Na_2CO_3$ and 0.2 grams Al$_2$)$_3$.

### IV By use of $(NH_4)_2S$

This method, discovered by Scheerer (30)(34)(35)(103)(116)(146) in 1842, has found some favor in the steel industry at the Wiesbaden laboratories (76)(90)(209) for the separation of Be and Fe, but has not been generally accepted for mineral analyses. The results are low (58)(203) when the solution is boiling, but precipitation is complete in the cold. It apparently has no advantage over the $NH_4OH$ method.

### V Use of $Na_2SO_4$

Berthier (21)(25)(117)(147) in 1843, used $(NH_4)_2SO_3$ to separate Al and Be by boiling until no more $SO_2$ fumes come off. The process depends on the fact that the H-ions of a weak solution of $H_2SO_3$ from which no more $SO_2$ can be expelled by boiling is sufficient to keep Be ions in solution, but precipitates $Al(OH)_3$. The process was not found to give good separations when tested by Bottinger (22); Weeren (3)(23)(31)(106)(119)(149)(160); and by Joy (5)(44)(108)(121)(151)(165).

## VI Use of $Na_2S_2O_3$

Glassman (40)(51) in 1907 treated a slightly acid solution of Be ~~ina~~ and Al salts with an excess of the reagent and heated to boiling. He claimed the Aluminum was precipitated completely as the hydroxide while the Beryllium remains in solution. This is the same method as proposed by Berthier (21)(25)(117)(147) in 1843, and discarded by Bottinger (22) in 1844. It was also mentioned by Joy (5)(44)(108)(121)(151)(165) and Zimmermann (112)(139)(199)(213). In 1908, Friedhem (40)(53) claimed that the precipitate described by Glassman was a mixture of $Al(OH)_3$, Sulfur, basic $Al_2(SO_4)_3$, and $Al_2(SO_3)_3$. The $Na_2S_2O_3$ method of Chancel (126) was found to give high $Al_2O_3$ and low BeO values by Britton (13)(65).

## VII Use of $(NH_4)_2HPO_4$

Rossler (48)(98)(114)(138)(154)(156)(196) in 1878, used $(NH_4)_3PO_4$ in a neutral solution buffered with $NH_4Cl$ in the presence of citric acid to remove small amounts of Aluminum.

Attempts to determine Beryllium as $Be_2P_2O_7$ as for Mg, Zn, Mn, etc were not so good, since the $Be_2P_2O_7$ is not formed as a homogeneous compound. A somewhat modified proceedure gives fair results.

To 250 cc of cold beryllium solution containing 5-10 grams of $NH_4$ salt per 0.5 grams of expected $Be_2P_2O_7$

add concentrated $NH_4OH$ until the solution is basic to Methyl Red (pH ~~613~~ 6.3) then add 1-1.3 grams of $(NH_4)_2HPO_4$ and make just acid (pH 4.2) to Methyl Red. Heat on the water bath until the amorphous precipitate of $Be(OH)_2$ has changed to crystaline $BeNH_4PO_4xH_2O$. Cool and decant through a filter and wash with 1% $NH_4NO_3$ solution made alkaline to Methyl red with $N^H{}_4OH$. Ignite and weigh.

If the solution contained $H_3PO_4$ originally, the precipitate produced by adding $NH_4OH$ at the start will be $BeNH_4PO_4$ instead of $Be(OH)_2$ and all that is necessary for the precipitation of a normal $BeNH_4PO_4$ is to produce the proper concentration of H-ions as outlined above.

## VIII Use of $K_2SO_4$ and $Na_2SO_4$

Beryllium can be separated from the cerium group by precipitation of the latter with a saturated solution of $K_2SO_4$ or $Na_2SO_4$. The elements of the cerium sub-group --Lanthanum, cerium, praseodymium, neodymium, illium and samarium--are precipitated as double sulfates (134)(136)(188) after standing at least twelve hours.

Wunder and Wenger (204) claimed that on protracted fusion with $Na_2CO_3$ at a high temperature and extraction of the melt with cold water the Be remains quantitatively in the residue with iron, titanium and the like, while chromium, phosphorus and most of any silica and alumina go into solution. Stock, Praetorius and Priess had no success with the method.

## X Oxalic Acid

Beryllium may be separation from the Yttrium group by precipitation with oxalic acid in a 0.5 N HCl solution of the chlorides.

## XI p-chloroaniline

This reagent is used to remove Ti from the twice precipitated Fe-Al-Ti-Be etc. hydroxide precipitate obtained in the usual manner. Fuse the precipitate with $Na_2CO_3$ and leach with water. The residue will contain Be and Ti. Dissolve in HCl and separate the bulk of the Ti from Be by the $NaHCO_3$ treatment of Parsons and Barnes. Then in view of the heavy Sodium content, precipitate with $NH_4OH$. Dissolve the precipitate in HCl and carry out the chloroaniline precipitation.

If an HCl solution of $TiCl_4$ and $BeCl_2$ (5-10 mg. neutralized with $NH_4OH$ until a turbid appearance is obtained and then treated with 1-1.5 g of p-chloroaniline, all of the Ti, and no Be will be precipitated by boiling three minutes. In 15 experiments the maximum error was 0.5 mg of $TiO_2$. Filter and precipitate $Be(OH)_2$ with $NH_4OH$ In this way excellent results were obtained in the analysis of a synthetic mixture of about 25 mg each of $Fe_2O_3$, $Al_2O_3$, $TiO_2$ and BeO. (61)

### XI Oxime

Aluminium may be rapidly separated (62) from Beryllium by use of oxime. Treat the solution of Be and Al salts (containing not more than 0.1 gram of either oxide in 100 cc) with oxime in acetic acid solution at 50-60° Add 2N acetic acid till a permanent precipitate is obtained, then add 20-25 cc in excess. Filter and wash with cold water, dry 120-140° and weigh as $(C_9H_6ON)_3Al$. In the filtrate precipitate Be by adding $NH_4OH$, filter ignite, and weigh as BeO.

### XII Amyl Alcohol

$Al(NO_3)_3$ is completely insoluble in amyl alcohol while $Be(NO_3)_2$ under the same conditions is soluble. Browning and Kuzirian (56) developed a method for pre~~cipitation~~paration of Be salts free from Al, but due to the tendency of the Al precipitate to include Be even after several treatments the method has not yet been found satisfactory for the quantitative determination of Al and Be.

### XIII Basic Acetate

Kling and Gelin (59) in 1914 used a method depending on the volatility of the basic acetate of Beryllium which can be sublimed in vacuo at 160-170° while the acetals or basic acetates of Al and Fe are nonvolatile under these conditions. Precipitate all three elements as hydroxides by $NH_4OH$, dissolve in $HNO_3$, evaporate to dryness in a boat and treat the residue with acetic acid, expelling the excess in an air bath. Heat the residue of acetals at reduced pressure (19mm) in a current of acetic acid vaper, first at 160-170° for four hours, and finally at 250° for one hour. The Be is deposited in the cool part of the tube. Dissolve it out with $HNO_3$, evaporate to dryness, and ignite the residue to constant weight.

Travers and Schnoutka (83) mention (128) a method of separation making use of the solubility of the basic acetate of Be in $CHCl_3$.

## XIV Amines

Dimethyl amine precipitates Be and Fe (49)(99) (197) from a solution of salts as a white precipitate insoluble in excess. The precipitate from Al salts is s soluble in excess reagent.

In 1903 Renz (39)(102) gave what he considered an accurate quantitative method for the separation of Be from Al by use of Methyl, Ethyl, Di-methyl, or Di-ethyl amines. The solution of Be and Al are dissolved in dilute $HNO_3$, evaporated to remove the acid, taken up in water, and shaken up with a large excess of the amine. The precipitated $Be(OH)_2$ is carefully washed and Aluminium determined in the filtrate.

## XV Guanidine Carbonate

To a solution containing not more than 0.1 grams of $Al_2O_3$ or 0.25 grams of BeO, add 50 cc of $NH_4$ tartarate soltuion, prepared by dissolving 42.5 grams of tartaric acid in water, adding enough $NH_4OH$ to make the solution neutral to methyl red and diluting to two liters. The purpose of the tartarate is to prevent the precipitation of Aluminium. If the original solution contained appreciable quantities of ammonium salt, add 5 cc of 40% formalin and enough 3N NaOH to make the solution alkaline to phenolphthalien. This serves to convert $NH_3$ to $(CH_2)_6N_4$. After this, make the solution faintly acid to methyl red and add 150 cc of 4% guanidine carbonate solution (88)(93)(123)(124)(125), stir well and dilute to 250 cc. After 12-24 hours filter and wash with a mixture of 50 cc of the tartarate solution, 150 cc of the guanidine solution and 2.5 cc of the 40% formalin. Ignite and weigh as BeO. The results are usually rather high (125).

## XVI Electrolytic method

Classen (50)(100)(159)(198) in 1881, separated

Fe, Al, and Be by electrolysis of ammonium oxalate solution. The iron was reduced, the Aluminium precipitated by use of a stronger current, as a hydroxide by the $(NH_4)_2CO_3$ produced; and the Be was left in solution. The method has not been adopted for quantitative determinations.

## XVII Microanalytical methods

Of existing microanalytical methods the potassium oxalate (recommended by Behrens (113)(200) in 1891) is probably the most satisfactory. Under certain conditions the chloroplatinig method is satisfactory. McMahon (169) says that the double salt $BeK_2(SO_4)_2.2H_2O$ is very characteristic. Boothe and Frary (95)(145) in 1932 proposed two new methods (1) the use of Potassium malonate in a similar manner to that for Potassium oxalate; (2) the use of the basic acetate, recrystalized from glacial acetic acid as a confirmatory test.

## XVIII Spectrographic Determination

The spectrographic detection (71)(190) of Be in Carbon arcs was studied with a Heiger E-1 quartz spectrograph. The relative sensitiveness of different lines was determined by examining the spectra of ammonical solution of BeO in different concentrations; and the influence of foreign materials on the sensitivety was investigated by mixing the original substances with $SiO_2$, $Al_2O_3$, CaO, and $Na_2CO_3$. The most sensitive Be line is at 2348.62 AU and the next are at 3130.42 and 3131.06 AU. It appears that 0.00001% by weight os BeO in $Al_2O_3$ may readily be detected by this method. The addition of large amounts of alkali reduces the sensitivity. It is smaller than with the original material, but not so low as with alkali addition.

The spectrographic method for detection and estimation of traces of Mn, Mg, Ca, Ba, Si, Bi, Al, Sm, Gd, Ni, La, La, and Yt have been demonstrated (73)(129) by Selwood.

## XIX <u>Nitroso-B-Napthol</u>

Schlier (101)(115)(158)(201)(211) gives details for the analysis of a mixture of Fe and Be by precipitating the Fe with nitroso-B-napthol, and says that it is the best method of removing the last traces of Fe from Be.

Copaux (62)(127) in 1919 used this reagent to separate Fe from the Be precipitaed, if much Fe was originally present in the sample.

## XX <u>Tannin</u>

The separation (67)(170) is effected when tannin is added to a dilute solution containing considerable

$NH_4OAc$. Aluminium is precipitated quantitatively but Beryllium remains in solution. For the separation and detection of Aluminium by this reaction it is necessary that both elements should be present as sulfate. To the acid solution containing about 0.1 gram ~~A~~ of Al, add hot water till the volume is about 500 cc. To the diluted solution add quickly a solution(clear) of $NH_4OAc$ and tannin which has been heated to 80° C. To prepare the reagent add 3 grams of tannin to 100 cc of cold, saturated $NH_4OAc$ solution. After the addition of the reagent, boil the solution for two minutes and filter. If less than 0.06 grams of Al is present, a paper filter is recommended but otherwise a sintered glass filtering crucible is better. Ignite the precipitate and weigh as $Al_2O_3$. In the filtrate destroy the organic matter by heating with $HNO_3$. Precipitate the $Be(OH)_2$ with $NH_4OH$ and weigh as BeO. The results are fairly good, but Be is somewhat low.

Ludwig, Moser, and Ferdinandi (70)(172) indicate that the method of the formation of the complex ion of Be with tannin may be used to separate Be from Fe, Cr, Ti, Zr, Th, and W as well as Al.

## XXI 8-hydroxyquinoline

Hilld combines (84)(131) the Parsons treatment with $NaHCO_3$ followed by precipitation of Al with 8-hydroxiquinoline for separating Al and Fe from Be. This method was first proposed by Niessner (69)(207). Thurnwald (84) (168) and Pilcher and Schneider (167) in the microanalysis of Be silicate rocks removed Al by use of this reagent.

Prepare (43) a solution containing no more than 0.1 grams of $Al_2O_3$ and 1-2 drops of mineral acid per 100 cc. Warm the solution to 50-60° C. and add an equal volume of an acetic acid solution of the reagent prepared as follows;-

Dissolve enough powdered 8-hydroxiquinoline in 2N acetic acid to form a 5% solution. A solution so prepared can be kept for several weeks, lcc of which will precipitate 0.0027 grams of Al or 0.0051 grams of $Al_2O_3$. Alcoholic solutions of the reagent are undesirable because of the solubility of aluminium quinolate in alcohol.

Slowly add a 2N solution of $NH_4C2H_3O_2$ until a permanent precipitate is produced and then add 20-25 cc more in order to insure complete precipitation. Let settle, filter through asbestos, glass frit, or porous porcelain and wash the precipitate with cold water. Dry at 120-140° C. and weigh as $Al(C_9H_6ON)_3$ which ontains 11.10% of $Al_2O_3$

## XXII <u>Ether and HCl</u>

Be and Al were separated by means of the insolubility of $AlCl_3.6H_2O$ and the solubility of $BeCl_2$ in ether and water (1:1) saturated with HCl gas by Havens (2) in 1897. It was tested and found fairly accurate by Britton

(12)(63) in 1922, and used by Churchill, Bridges, and Lee (28)(130) in 1930.

To recover the last traces of Be, Fischer (75) (85)(185) found it best to dissolve the $AlCl_3.6H_2O$ precipitate in $H_2O$ and repeat the precipitation with ether and HCl.

Acetyl Chloride has been used as a sinple way of saturating a solution with HCl (acetone diminishes the violence of the reaction) to separate Be andAl as chlorides (7)(8)(60)(61). Because of the slight solubility of $BeCl_2$ the mixture of $BeCl_2$ and $AlCl_3$ should not exceed .15 grams in weight and should contain less than 1/3 $BeCl_2$. A double precipitation is required and even then $Al_2O_3$ tends to carry down BeO.

The procedure may be carried out as follows;- (32) Obtain the Al in ~~c~~ HCl solution and free from alkali salts. Evaporate the solution to as small a volume as will still keep the salts in solution, say, 5-10 cc. Cool, add enough HCl to gring the volume to 10-25 cc and saturate the solution with HCl while cooled to a temperature below 15° C. Add a volume of ether equal to the volume of liquid, and again pass in gaseous HCl into the cooled saturated solution until it is saturated. At the same time prepare a washing solution composed of equal parts of HCl and ether and saturated with HCl at 15° C. Filter on a Gooch or Monroe crucible, preferably the latter, after it has been cooled by the passage of a little of the washing liquid through it. If the precipitate is to be ignited and weighed directly use a crucible that has been tared after washing and igniting as in the method. Wash the precipitate with the cold washing solution until foreign salts are removed. If the precipitate is not to be ignited directly, dissolve the salt in dilute HCl and treat the solution as may be necessary for reprecipitation (75)(85)(185) or for precipitation with $NH_4OH$. If the precipitate is to be converted to $Al_2O_3$ and weighed, cover the chloride with a thin layer of pure (ashless) HgO to prevent mechanical loss, heat gently until hydrolysis has taken place, then raise the temperature to expel mercuric chloride and excess oxide, and finally ignite at 1000-1100° C. and weigh as $Al_2O_3$.

The BeO may be precipitated from the HCl-ether solution.

## XXIV $Na_2CO_3$ and $NaHCO_3$ method

In 1798 Vauquelin (1)(15)(97)(173) suggested the use of $(NH_4)_2CO_3$ in the separation of Be and Al. In 1859 Hofmeister (33)(150)(163)(176) proposed a number of fractional precipitations to remove all of the Al from the Be, but this method was not considered very satisfactory Joy (5)(44)(108)(121)(151)(165). Some Be was always left with the $Al(OH)_3$ and a little Al remains in solution. Hart (133) found that $Na_2CO_3$ precipitated nearly all of the $Al(OH)_3$ but Britton (12) showed that the precipitation was far from complete. On the other hand the method of separation proposed by Parsons and Barnes (52)(132)(140) (177) which is based on theuse of $NaHCO_3$ gives very good results. Hills (89)(131) considers the Parsons ad Barnes treatment with $NaHCO_3$ to be the best method for determining Beryllium in ores. This method is discussed in detail later.

## XXIV Quinalizarin

The use of quinalizarin (1-2-5-8 tetrahydroxianthraquinone) for the detection (82)(84)(92)(168)(179)(182) and determination (185) of beryllium in small amounts is quite sensitive. For a rapid test of Be in a mineral:-

1. Fuse 0.1 grams of the finely powdered substance with o gram of NaOH in an iron crucible for five minutes.
2. Cool and place in ice water and a piece of ice in the crucible.
3. Loosen the cake with a stout nickel spatula and break with a heave stirring rod.
4. Filter and dilute to 30cc.
5. By addition of acid if necessary make a portion of the solution about .33N $NaO^H$.
6. All 12 drops of 0.01% quinalizarin in 96% alcohol.

7~~1~~. Run a "blank" test also, adding only the reagents.

Beryllium causes a pure blue solution while the reagents alone give a violet-red color. Aluminium does not interfere, but phosphorus, tartarate, iron and Magnesium do. ~~A1~~ As little as 0.01% Be can be detected in a 0.1 gram sample.

Small quantities of Beryllium can be determined (66)(186) by precipitation as the water insoluble Be-dye by addition of excess of ammoniacal quinalizarin solution. The Be-dye is centrifuged off and determined colormetrically. Small amounts of Be can be titrated directly and the end point observed by the color change produced by excess quinalizarin. One mole of quinalizarin unites with 2 mols of Be.

SOME

THEORETICAL CONSIDERATIONS

dealing with

The Nature of Hydrates

of

Beryllium Oxide

as

related to its

QUANTITATIVE DETERMINATION

# Notes on the Precipitation of Be as $Be(OH)_2$ and weighing as $BeO$.

Beryllium is nearly always precipitated as the hydroxide $Be(OH)_2$ and weighed as the oxide $BeO$. The order of precipitation (65)(141) of the hydroxides was studied by gradually adding dilute alkali hydroxide and measuring the pH when precipitation took place.

$Al(OH)_3$ begins to precipitate at a pH of 4.1
$Be(OH)_2$ begins to precipitate at a pH of 5.7

Britton and German (86)(142) titrated 0.02 $BeSO_4$ with 0.045 N NaOH using a quinhydrone electrode and confirming the pH value with a $H_2$ electrode. They reported a value of pH 5.69 for the precipitation of $Be(OH)_2$.

A gelatinous precipitate of $Be(OH)_2$ formed in the presence of NaF may yeild BeO containing 23% adsorbed NaF, but by heating the suspended precipitate in the mother liquor at 80° with a reflux condensor attached, the precipitate becomes less gelatinous and more crystaline with the result that only 0.5% of NaF will be found in the ignited BeO. The gelatinous hydroxides of Fe, Al, Cr, Ti, etc can be separated more efficiently from the hydroxides of the bivalent metals if the precipitates are aged before filtering. Heating the solution produces artificial aging. However, metastable crystaline $Be(OH)_2$ is formed from the amorphous compound even on aging under cold water (74)(189)

To study farther the aging of $Be(OH)_2$ the dielectric constants and Rontgenographic measurements on the ~~di~~ hydrates of Be, in relation to time were plotted by Havenstadt and Fricke (74)(189). The increase in the dielectric constant coincides with the appearance of a crystaline structure, and this increase goes through a maximum with increasing progress of crystallization. Amorphous substances always show a decrease in dielectric constant with time. The studies show that there is a definite morphological alteration in the hydroxide particles. However, the particle sizes of BeO sols measured (91)(144) by means of the ultramicroscope, did not change with ~~thim~~ time over a period of 12-168 hours even though kept at a temperature of 80°. The rather large average mean size of 153.5 μμ for a cubic edge was obtained.

Huttig and Mytyzek (76)(192) found freshly precipitated $Be(OH)_2$ to be completely amorphous; only after long aging does it show an x-ray pattern. When reprecipitated from a NaOH solution, or by digesting with $NH_4OH$ and drying, it shows a more definite pattern of $Be(OH)_2$. By dehydration and ignition the $Be(OH)_2$ shows the pattern of BeO.

It has been found (18)(81) that $BeO.H_2O$ loses no $H_2O$ up to 190°. At 190-200° there is a short induction period, followed at 200° by a rapid decomposition and loss of 80% of the $H_2O$ present. Between 220 and 700° the rest of the $H_2O$ is removed. This is $H_2O$ of adsorption and this part of the curve is not reversible. For each maximum temperature at which the substance was heated there was obtained an adsorption curve which showed that the higher the temperature the less the adsorption for a given temperature. This can be explained only by a change in the physical state, by polymerization. BeO when heated alone does not polymerize and its state of polymerization is more advanced as the temperature is raised. Therefore $BeO.H_2O$ once dehydrated cannot be formed again.

The most suitable temperature for heating BeO in quantitative analysis was found, by means of a thermobalance (68)(137), to be above 950° C.

Double or tripple precipitations of the hydroxide must be made when non-volatile salts such as NaCl are present. The precipitate tends to stick to the walls of the vessel and must be recovered after the removal of most of the precipitate, by dissolving it in as little acid as possible and reprecipitating with $NH_4OH$.

Where possible Beryllium analyses should be carried out in platinium ware.

Beryllium hydroxide is appreciably soluble in pure water, and it is therefore necessary to wash it with water containing an electrolyte, preferably $NH_4NO_3$.

The oxide is slightly hygroscopic and should be cooled then weighed in a crucible with a well fitting lid. Errors are negligible with this method if a good dissicant is used and weighings made rapidly. For example, a well covered crucible containing 0.1021 gram of ignited BeO showedno appreciable change in weight in five minutes on the balance pan, but gained 0.0012 gram in five minutes on the balance pan when uncovered.

An oxide ignited at 1200° C is less hydroscopic ~~as~~ than one ignited at 950° C.

Jelick and Kota (80)(123) claim that Hydrazine carbonate has advantages over $NH_4OH$ or $(NH_4)_2CO_3$ as a precipitant for $Be(OH)_2$ or Be-basic-carbonate, in that the precipitate is less slimey and less soluble in slight excess of the precipitant. To 100 cc of the solution containing not over 0.1 grams of Be in 100cc, add 5 grams of $NH_4NO_3$ and while boiling a slight excess (2-3) cc of hydrazine carbonate solution. Allow the precipitate to stand two hours, filter and wash with 0.1-1.0% $NH_4NO_3$ solution made neutral to Methyl Red. Ignite and weigh as BeO.

Attempts to precipitate Beryllium by means of Phenylhydrazine carbonate prepared by bubbling $CO_2$ through a mixture of water and phenyl hydrazine, were not very encouraging.

# DECOMPOSITION OF

# BERYLLIUM MINERALS..

# DECOMPOSITION OF BERYLLIUM MINERALS

Beryllium containing minerals are usually decomposed (32) by a fusion method. Sodium carbonate, or potassium (acid) sulfate are satisfactory. About 10 grams of $Na_2CO_3$ is needed for fusion of a .5 gram sample, and the full temperature of a blast lamp should be maintained until solution is complete. The cooled melt can be dissolved in dilute HCl, $HNO_3$, or $H_2SO_4$, depending on the nature of the preferred reagent. If there is evidence of incomplete decomposition of the sample, filter off the insoluble matter fuse with $KHSO_4$, and dissolve the melt in the original solution before proceeding with the analysis.

It is true that even the above described method of fusing the beryllium ore possesses a few drawbacks, such as for instance the necessity of the double fusion, first with soda, then with potassium bisulphate. It cannot be denied that the method described is time-consuming and tedious, ~~not~~ nor that the sources of possible errors are increased owing to the intricacy of the method.

The practise of the production of Beryllium salts has shown that there is still a further possibility of a rapid and quantitative decomposition of the beryllium mineral, which is vastly superior to the method described, in many respects. The transformation of the beryllium silicate contained in beryl into an easily water soluble compound, is rendered possible by means of a decomposition of the mineral with sodium-silico-fluoride. The sodium-silico-fluoride, when heated, separates out silicon fluoride, which reacts upon the beryllium oxide contained in the mineral as well as upon the aluminium oxide, by forming the corresponding fluorides or double fluorides respectively. This reaction may be rendered quantitative by using a sufficient amount of sodium-silico-fluoride for the transformation of the beryllium oxide into the fluoride. Inasmuch as both the sodium-beryllium-fluoride, and beryllium fluoride are soluble in water, while the simultaneously formed aluminium fluoride and sodium-aluminum-fluoride are fairly insoluble in water, and since, furthermore, iron is for the most part precipitated out in the form of the insoluble $Fe_2O_3$, it is possible to apply these facts to produce a method of separation suitable for purposes of separating the beryllium from aluminum and iron, by means of a simple washing out of the residue of the fusion with water. The iron oxide content of the fusion solution bears a relation to the BeO content of 1:250. Even the aluminum content, which is only determinable according to the highly sensitive method proposed by Atack (155) and by Stock, Priess, and Praetorius (42) but not however by the chloride process of Havens (212) (202), should be limited to a similar range of variability.

For this method of decomposition, 1 gram of the finely divided powdered mineral is intimeatly mixed with the same ~~ab~~ amount of sodium-silico-fluoride and the mixture maintained in a new glazed porcelain or ~~er~~ iron crucible at a temperature of between 680 and 710° C. for three hours. The residue is carefully removed from the crucible and the particles adhering to the crucible walls are removed with water. The crucibles are attacked somewhat by the material and should preferably not be used a second time, in view of the fact that the fusion residue adheres very firmly to the etched wall of the crucible after its initial use and thus renders its removal very difficult. Impurities which find their way from the ~~a~~ crucible into the the residue have no disturbing effect upon the operation, since they are present in a form insoluble in water.

The powdered residue is washed with cold water, and the solution is increased by adding as much caustic soda solution as is necessary for producing a N/4 alkalinity; this may fill a 500 or a 1000cc flask. An aliquot portion is taken for analysis.

A

very promising

method

Recently Developed

by

<u>H. Fischer</u>

using

<u>Quinalizarin</u>

We tried to obtain reagents for this method of determination, but were unable to purchase them from a number of Chemical Companies in this country; no work was attempted using this proceedure.

Recently H. Fischer (186)(206) reported on a new process fordetermining beryllium which may be carried out, in spite of the presence of aluminum, without the necessity of using tedious, time-consuming and unreliable separation methods. The quantitative determination, particularly of small amounts of Be, in accordance with this method, may be effected quickly and accurately by means of quinalizarin, by means of a so-called colorimetric titration. In testing the method he used a solution prepared to contain an average of 10.04% BeO, 20.06% $Al_2O_3$ and 1.5% $Fe_2O_3$. The solution ~~by~~ to be investigated was put into a graduated flask, and after deposition of the iron precipitate, an aliquot part was used for titrating. Instead of the beryllium oxide content of 10.04% used, the following results were obtained; 9.83% BeO, 9.84% BeO, 10.03% BeO, an average of 9.88% BeO. Percentage error 1.5%

After careful observance of the method of Parsons and Barnes, he obtained the following results:- 11.14% BeO, 10.82% BeO, 11.40% BeO, and 11.50% BeO, an average of 11.23% BeO. Percentage error 11.90%

These figures indicate a decided superiority of the colorimetric method over the sodium bicarbonate method so that the results of the titration may be considered to be considerably safer.

In view of the almost insignificant amounts of

Fe and Al in the extract from a silicofluoride decomposition the use of the quinalizarin method of determination should not therefore be affected. The powdered residue from the treatment is washed with cold water, and the solution is increased by adding as much caustic soda solution as is necessary for producing N/4 alkalinity; this may fill a 500 or 1000 cc flask. An aliquot part is taken from this solution in the usual manner for the colorimetric titration.

In order to judge this method as to its merits, let us look at a few experimental results obtained by it.

| | % BeO by colormetric silicofluoride method | % BeO by soda fusion colormetrically |
|---|---|---|
| Beryl I | 9.64 | 9.84 |
| Beryl II | 10.04 | 11.8 |
| Beryl III | 4.41 | 4.62 |

From the HCl filtrate obtained from the soda fusion method after removal of the silica, the iron, aluminum, and beryllium should be precipitated out as hydroxides, dissolved again in diluted HCl, the solution evaporated and the residue dissolved in warm water. The approximately neutral solution thus obtained should be rendered N/4 alkaline in the usual manner, and the beryllium determined colorimetrically (43).

As may be seen from the above figures, the values for BeO obtained by means of the colorimetric titration, in accordance with both methods of decomposition are in close agreement. The three beryl samples analyzed did not contain a considerable amount of iron, so that the iron content of the solution obtained colorime~~tr~~trically by the soda method which contained all three ingredients could not exert any disturbing influence. If, however the minerals had contained considerable amouats of iron, in accordance with what has been already stated, this should be sufficient reason to prefer the silico-fluoride method to the soda method.

CONCLUSION: The BeO content of raw beryl can be ascertained with sufficient accuracy by fusing the mineral with sodium-silico-fluoride, by extracting the beryllium as fluoride from the residue of the fusion, by washing with water, and then determining the beryllium in the solution by colorimetric titration by using quinalizarin.

# EXPERIMENTAL PART I

## EXPERIMENTAL PART I.

Before attempting any analytical work, standard solutions of $Al_2O_3$ and BeO were prepared as follows;-

### Standard $Al_2O_3$ solution:-

26 grams of $Al_2(SO_4)_3 \cdot 18H_2O$ (purchased from J. T. Baker Co.) was dissolved in a liter of water.

50 cc of this solution should be aproximately equivalent to a .5 gram sample of Beryl containing 40% $Al_2O_3$, or 25 cc of this solution should be aproximately equivalent to the $Al_2O_3$ in a .5 gram sample containing 20% $Al_2O_3$.

While it was not absolutely necessary, for this part of the work, the solution was standardized by precipitating an aliquot portion of the solution with $NH_4OH$; washing the precipitate well with 1% $NH_4NO_3$ solution made neutral to Methyl Red; burning; and weighing as $Al_2O_3$.

| | I | II |
|---|---|---|
| Aliquot portion | 50.1 cc | 25.0 cc |
| Wt. of residue | .2196 grams | .1099 grams |
| Titre of solution | 1 cc = 0.0043835 grams $Al_2O_3$ | 1 cc = 0.0043840 grams $Al_2O_3$ |

### Standard BeO solution:-

1.9845 grams of dry BeO (99.75% pure according to The Foote Mineral Co., from whom we purchased it) was dissolved in hot $H_2SO_4$ (1:1), then made up to 1000 cc.

Two aliquot portions were used to check the BeO content of the solution. $Be(OH)_2$ was precipitated with $NH_4OH$, washed well with 1% $NH_4NO_3$ made neutral to Methyl Red, burned and weighed as BeO.

| | I | II |
|---|---|---|
| Aliquot portion | 25 cc | 25 cc |
| Wt. of BeO | .0496 g. | .0495 g. |
| Titre of solution | 1 cc = 0.0019800 g. BeO. | |

Note: According to these figures the dry BeO was 99.77% pure.

Thus 25 cc of the above sample is equivalent to a .5000 gram sample of beryl containing 10.10% BeO

## Analyses of Beryl and Topaz

These samples were ground to pass an 80 mesh seive, dried thoroughly at 120° C. before weighing, fused in Platinium cricibles with $Na_2CO_3$ and the residue fused with $KHSO_4$.

This solution was then analized according to the Parsons and Barnes method given in the ~~preceeding~~ following pages.

One sample of Beryl and two samples of Topaz were on hand for analysis. These had been obtained from the Geology Department of V. P. I. There was some question as to whether or not the topaz really contained Beryllium. State Chemists had reported 18% BeO and U. S. chemists had reported the absence of Beryllium.

Among the great number of methods used for determining the beryllium content in ores, we used the Parsons and Barnes method, not because it is the best or the most accurate method, but because it is recommended by the Bureau of Standards, Department of Chemistry, is used in numerous laboratories, such as in the laboratories of the Ledoux Co, in New York, and because the results obtained by this method are frequently recognized as being decisive in beryllium ore transactions (32)(43).

1. Fuse 0.5 grams of the finely powdered ore with 10 grams of $Na_2CO_3$.
2. Dissolve the melt with 5 cc HCl.
3. Add warm water to about 100 cc.
4. Boil until all salts are in solution.
5. Filter and fuse the residue in $KHSO_4$.
6. Dissolve in the original solution.
7. Evaporate to dryness.
8. Take up with 5 cc HCl and 100 cc of water.
9. A. Filter immediately to remove silica.

   Wash with dilute HCl (1:99)

   or

   B. Evaporate to dryness

   Remove $SiO_2$ by HF and $H_2SO_4$ evaporation.

   Take up with dilute HCl.
10. Dilute to 200 cc.
11. Saturate with $H_2S$ to remove Group II elements.

12. Allow to digest at 40-50° for some time.

13. Filter to remove Tin, Germanium, etc

14. Wash with a little water containing $H_2S$.

15. Boil filtrate to expel $H_2S$.

16. Add a little $HNO_3$ or $H_2O_2$ and ontinue boiling to oxidize the iron.

17. Reduce the volume to 25-50 cc.

18. Nearly neautralize with strong NaOH solution.

19. Heat to boiling.

20. Add enough strong NaOH solution to provide 10% solution when mixed.

21. Filter to remove Titanium, Zirconium, etc.

22. A. If phosphorus is absent.

a. acidify the filtrate with HCl

b. precipitate with slight excess $NH_4OH$.

c. Filter and wash the precipitate with hot 2% solution of $NH_4NO_3$.

d. dissolve in as little hot dilute HCl as possible.

22. B. If phosphorus is present.:-

a. Neutralize the filtrate with $HNO_3$ and dilute to 90 cc.

b. Add 10 cc concentrated $HNO_3$.

c. Add 10 grams $NH_4NO_3$.

d. Heat to 40-50° in flask.

e. add equal volume of 5% Ammonium

Molybdate reagent.

f. Let stand 1 hour.

g. filter to remove phosphorus.

h. h. boil and add slight excess of $NH_4OH$.

i. filter to remove molybdenum and excess alkali salts.

j. Dissolve in HCl.

k. reprecipitate with $NH_4OH$ and filter.

l. Dissolve in as little hot dilute HCl as possible.

23. Nearly neutralize the solution with NaOH.

24. Heat to boiling.

25. Add enough hot $NaHCO_3$ solution to provide 10% solution when mixed.

26. Quickly bring to a boil.

27. Boil 20-30 seconds.

28. Filter immediately to remove Fe and Al.

Since this does not effect a complete separation of beryllium:-

29. Dissolve the precipitate in dilute HCl.

30. Nearly neutralize solution with NaOH.

31. Heat to boiling

32. Add enough hot $NaHCO_3$ solution to provide 10% solution when mixed.

33. Quickly bring to a boil.

34. Boil 20-30 seconds.

35. Filter into the first filtrate (28)

Since this does not always effect a complete separation of the beryllium, a third repetition of the operation is recommended.

36. Combine the three filtrates.

37. Make acid with HCl, and add slight excess.

38. Boil the solution until $CO_2$ is entirely eliminated.

39. Make slightly alkaline with $NH_4OH$.

40. Filter off the $Be(OH)_2$

41. Discard the filtrate.

42. Dissolve the precipitate in the smallest possible amount of dilute HCl. into original beaker.

43. Make slightly alkaline with $NH_4OH$.

44. Let stand over night, or heat to 80° for one hour to produce artificial aging, cool.

45. Filter through best grade of quantitative paper.

46. The precipitate tends to stick to the walls of the vessel and must be recovered after the removal of most of the residue, by dissolving it in as little acid as possible and reprecipitating with $NH_4OH$.

47. Wash with 1% $NH_4NO_3$ solution made neutral to Methyl Red.

A tripple reprecipitation of the hydroxide is recommended due to the presence of non-volatile salts.

48. Ignite and weigh as BeO.

The Beryllium precipitate from the solution containing sodium salts, considerable quantities of alkali are usually contained in the hydroxide; they may be removed to a certain extent by washing. Other authorities recommend double or tripple reprecipitations. The precipitate may also contain some silica which may not have been entirely removed, or which may have come from the glassware used, therefore some authorities recommend that the solution of the hydroxide in HCl be evaporated, the residue dried at 120° and then dissolved in 5 cc concentrated HCl and 15 cc of water. The flakes of silica precipitated out are filtered off and washed on the filter in the usual manner with hot dilute HCl and the beryllium determined in the filtrate, which has been combined with the wash water, as Beryllium Oxide.

# RESULTS

# BY

# PARSONS AND BARNES METHOD

## Results by Parsons and Barnes Method.

### Topaz I

| | (1) | (2) |
|---|---|---|
| Wt of sample used | .4290 | .4418 |
| Wt of residue as BeO | .0192 | .0195 |
| % BeO indicated | 4.48% | 4.41% |

### Topaz II

| | (3) | (4) |
|---|---|---|
| Wt of sample used | .3995 | .5873 |
| Wt of residue as BeO | .0198 | .0189 |
| % BeO indicated | 5.83% | 3.22% |

### Beryl ($Be_3Al_2Si_6O_{18}$)

| | (5) | (6) |
|---|---|---|
| Wt of sample used | .4470 | .4561 |
| Wt of residue as BeO | .0632 | .0629 |
| % BeO indicated | 14.16% | 13.18% |

### Check Solutions

| | (7) | (8) |
|---|---|---|
| 25 cc Std. BeO sol. | .04955 | .04955 |
| 25 cc Std. $Al_2O_3$ sol. | .1099 | .1099 |
| Wt of residue as BeO | .0683 | .0692 |
| % BeO indicated | 13.66% | 13.84% |

# DISCUSSION OF PART I

A critical examination of the intricate procedure with its repeated precipitations gives food for thought to the analytical chemist with respect to its accuracy. Although the sodium bicarbonate separation has been designated by many authors as the most reliable method of separating beryllium from aluminum and iron, on the other hand unsatisfactory reports have also been circulated. For instance, M. Englehard (178) deems it necessary to resort to five or six precipitations to obtain satisfactory separation of Beryllium from Aluminum.

Such a process, however, apart from its intricacy and tediousness, is not apt to be conducive to the desired accuracy, if one considers that both $Al(OH)_3$ and $Fe(OH)_3$ still possess a notable solubility in hot 10% $NaHCO_3$ solution.

Thus Jander and Webber (214) have shown that considerable $Al(OH)_3$ is soluble in water ~~in~~ and in salt solutions. These factors have not always been considered in the separation of Be and Al, as well as in the quantitative determination of aluminum.

The so called "basic carbonate" of aluminum which is formed during the bicarbonate precipitation, in accord with modern views, is nothing more than a solid solution of aluminum carbonate in the excess hydroxide. Even if it is assumed that the carbonate is practically insoluble in water, the solubility of the hydroxide is still sufficient to decrease the accuracy of the process, especially in view of the great quantities of water which are unavoidable in repeated precipitation operations.

In samples (1) through (4) the gravimetric analysis showed 3.22% to 5.83% BeO while the Quartz Spectrograph showed no lines characteristic of Beryllium. Both the original mineral, and the precipitates which were burned and weighed as BeO were examined and the results in each case were negative.

In Part I, the author exercised special care to follow the procedure for analysis carefully, to wash well, to use the same conditions of temperature and volume of solutions, for each sample, to use C.P. reagents, and to remove all traces of precipitates. The $NaHCO_3$ separations were made in 200 cc of solution (plus or minus 10 cc); and four separations were made on each sample. The combined filtrates were acidified, concentrated, and $Be(OH)_2$ precipitated with $NH_4OH$, with care not to add excess. The Beryllium precipitates were reprecipitated three times and washed well each time with 25 cc (plus or minus 3 cc) of warm 1% $NH_4NO_3$ solution (made neutral to Methyl Red) to insure the complete removal of all non-volatile sodium and potassium salts.

Referring to the weights of the BeO precipitates obtained from samples (1) through (4) we note that they fall in a range of 0.0139 to 0.0198 grams.

If we consider the difference between the BeO actually present (0.04955 grams) in (7) and (8) and the amount indicated (0.0683 - 0.0692 grams) by the analysis we get 0.0192 - 0.0197 grams.

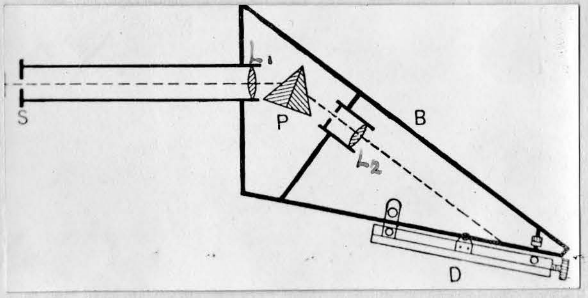
Since the conditions of the analyses, especially the temperatures and volumes were kept as constant as possible, and since each of the samples gave 0.0189 to 0.0198 grams of residue which is not due to BeO as is shown by the above results, and since we are dealing with a saturated solution of $Al(OH)_3$ the amount that goes into solution will be very nearly constant and will account ~~of~~ for the deviations from actual Beryllium content.

To bear out the above, and to explain the differences in the results obtained in Part I and Part II, and to explain the deviation of the results in the check solutions, a new series of analyses were devised.

# EXPERIMENTAL

## PART II

## Diagramatic representation of the Quartz Spectrograph



B. Camera

D. Photographic plate.

P. Quartz Pris~~o~~m

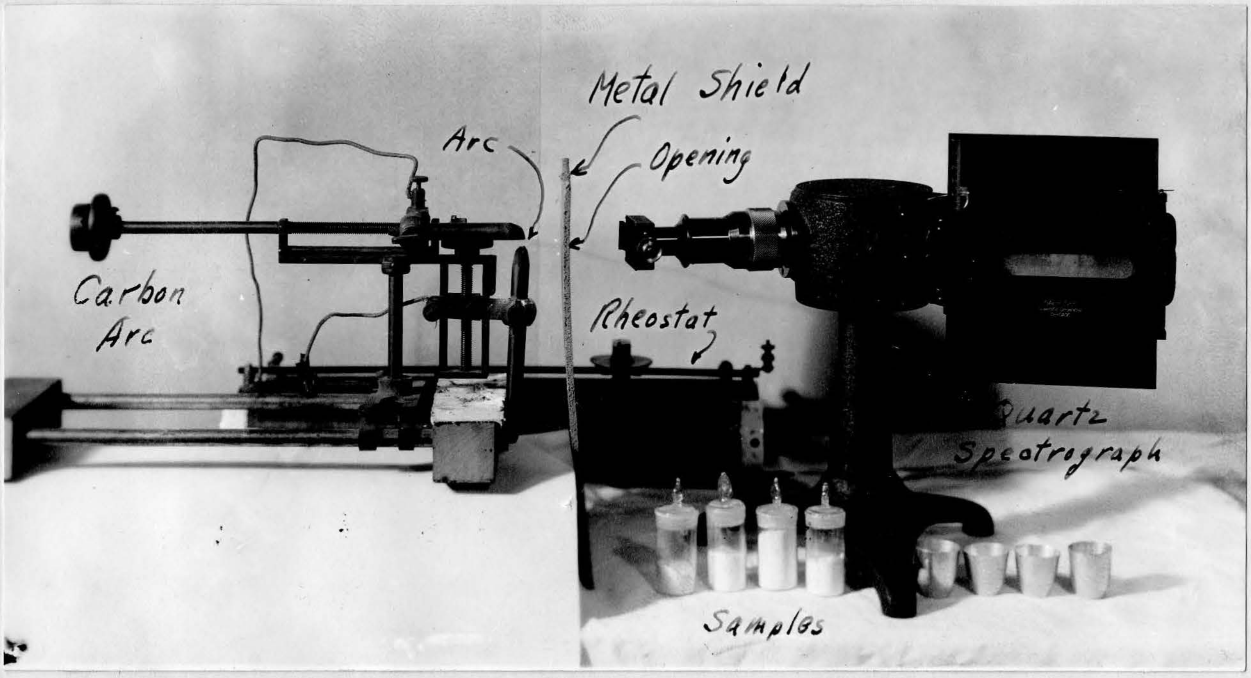
S. Polished Metal Slit.

Since the most important Beryllium lines occur in the ultraviolet region at 3131 and 2651 A. U. the quartz spectroscope (see diagram) had to be used instead of an ordinary glass spectroscope.

Light from a suitable source is cast upon the slit S of the spectroscope. By means of a quartz lens $L_1$, the beams are rendered parallel before striking the quartz prism P. The latter consists of two 30° half-prisms placed face to face, one prism being cut from a right-handed, and the other from a left-handed, crystal of quartz in such a manner as to bring the optic axis parallel to the base of each half-prism. This type of prism was devised by Corner in order to eliminate the doubling effect due to the polarizing action of quartz on the emergent beam. The refracted and dispersed rays then enter the camera B via the quartz lens $L_2$ where the spectra is focused on the photographic plate D.

The plate holder is fitted with a rise and falling motion by means of which the plate may be raised or lowered through measured distances in a vertical plane, thus enabling the operator to photograph a number of spectra on the same plate.

The plate holder is also fitted with a rack and pinion by means of which the angle the plate makes with the desired rays may be varied. The lines are so close together

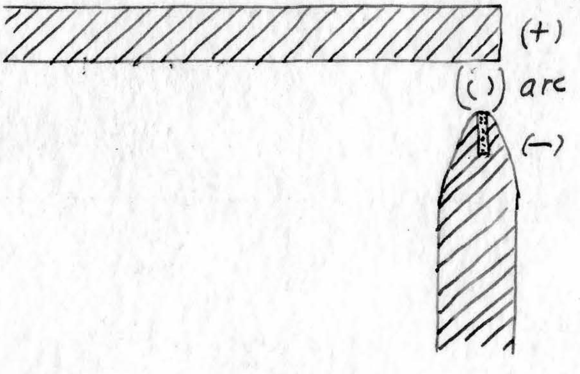


Apparatus used to photograph the Spectra of Minerals that they could not be measured with any degree of accuracy if the plate were placed perpendicular to the rays, as it is placed in ordinary cameras. The greater the slant, the greater will be the separation of the lines, however, another factor enters, and the greater the slant, the narrower will be the range in which the lines are in sharp focus.

A very good arbritration was obtained by setting the slant of the plate at 4.9, setting the focusing barrel at 9. and using the narrowest possible slit (open about ¼ of a turn of the adjusting screw from the closed position). This brought the lines between 2300 and 4300 A. U. into sharp focus.

A carbon arc lamp from an old projection machine was placed in series with about 15 ohms resistance and attached to the 110 D. C. generator.

The negative rod was ground to a point, and with a 1/16 inch drill a hole sunk to a depth of about 1/4 of an inch, so that the sample could be packed into this hollow to be sure of obtaining a spectra of the mineral in question.

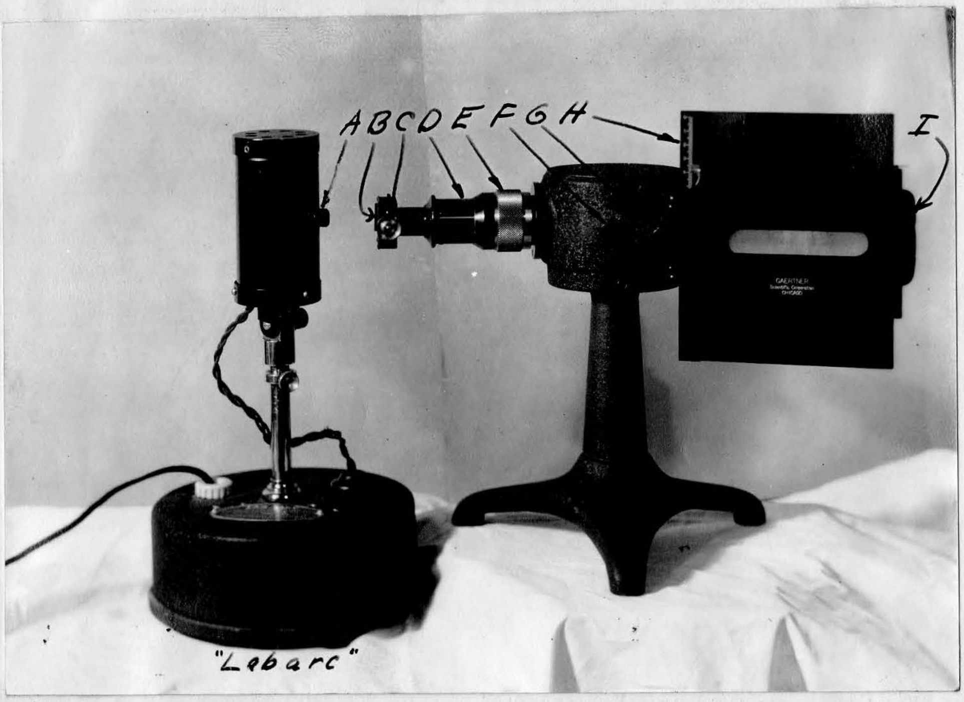


The positive carbon rod was not pointed, but was cut off even.

For each determination a freshly ground and drilled set of carbon rods were used.

It was found necessary to place a metal shield between the acr and the slit of the spectroscope to act as a heat insulator and to eliminate the glow from the hot carbon electrodes, which gives such an intense and continuous spectra that many important lines are obscured.

# Apparatus used to photograph the Ultraviolet- Spectra of Mercury



A. Window, through which Ultraviolet Rays pass.

B. Polished metal slit.

C. Screw, to vary width of slit.

D. Focusing scale.

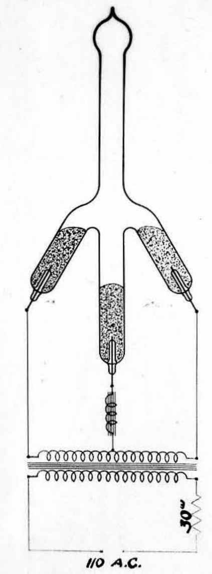
E. Focusing barrel.

F. Screw, to adjust slant of plate--scale not shown.

G. Screw, to adjust Height of plate--to obtain more than one exposure on a plate--

H. Scale, to show position of spectra on plate.

I. Photographic plate inserted here.



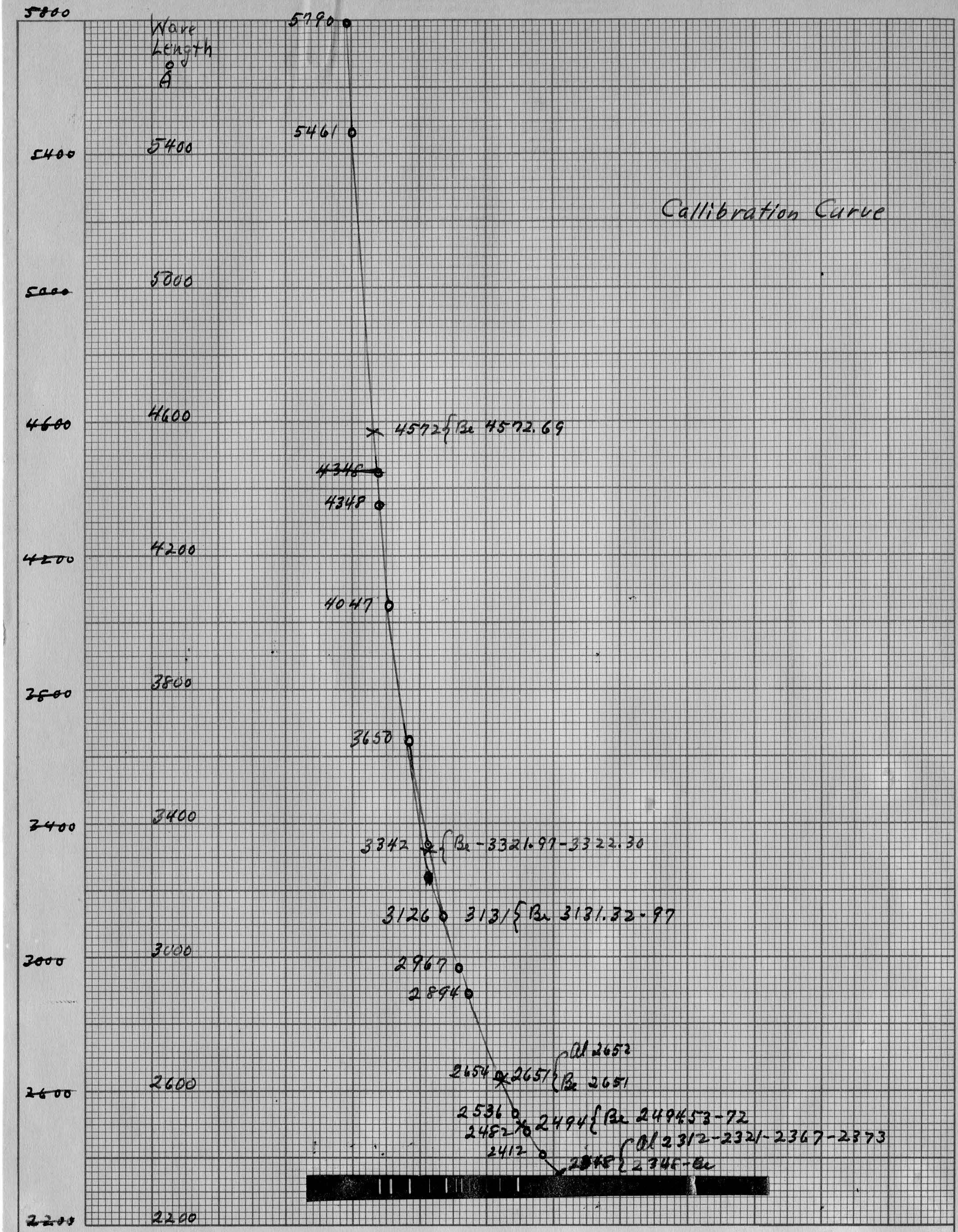
Quartz tube
(highly evacuated)
Arc

Mercury

Neutral Arm

Sealed in Electrodes

Diagramatic representation of the Mercury Arc Lamp



Callibration Curve

EVERETT WADDEY CO. RICHMOND, VA.

In order to identify the Beryllium lines, the spectra produced by a Cooper Hewett "Labarc" was photographed on the same plate with a carbon and a mineral spectra. The manufacturers of the "Labarc" supply a spectrogram with the lamp, on which the lines are identified and their wave lengths given. Using these values a callibration curve was plotted for the spectroscope. It was found more accurate however to use a special microscope attached to a microvernier screw by means of which a reading for the position of the line in question, with respect to a known line on each side of it could be taken, and by interpolation a very accurate value may be assigned to the line.

Eastman Par Speed Portrait Film was found to give very good rendering of lines in the Ultra-violet region and was used to make the spectral photographs. An exposure of five seconds to the Carbon arc, and ten seconds to the Mercury "Labarc" were found, after several trials, to give the best results.

The films were developed in a special "contrast" bath, made according to the Eastman formula D-9:-

Stock Solution A

| | |
|---|---|
| Sodium Bisulphite | 22.5 grams |
| Hydroquinone | 22.5 grams |
| Potassium Bromide | 22.5 grams |
| Water | 1.0 liter |

### Stock Solution B

| | |
|---|---|
| Sodium Hydroxide | 52.5 grams |
| Water | 1.0 liter |

For use, mix equal parts of A and B and one part of water. Good clean contrasty negatives are produced if the films are developed for one minute at 24° C.

Due to the high caustic content of the bath it is well to use a slightly stronger than usual acetic acid short stop bath and a fixing bath containing twice the usual amount of hardening solution.

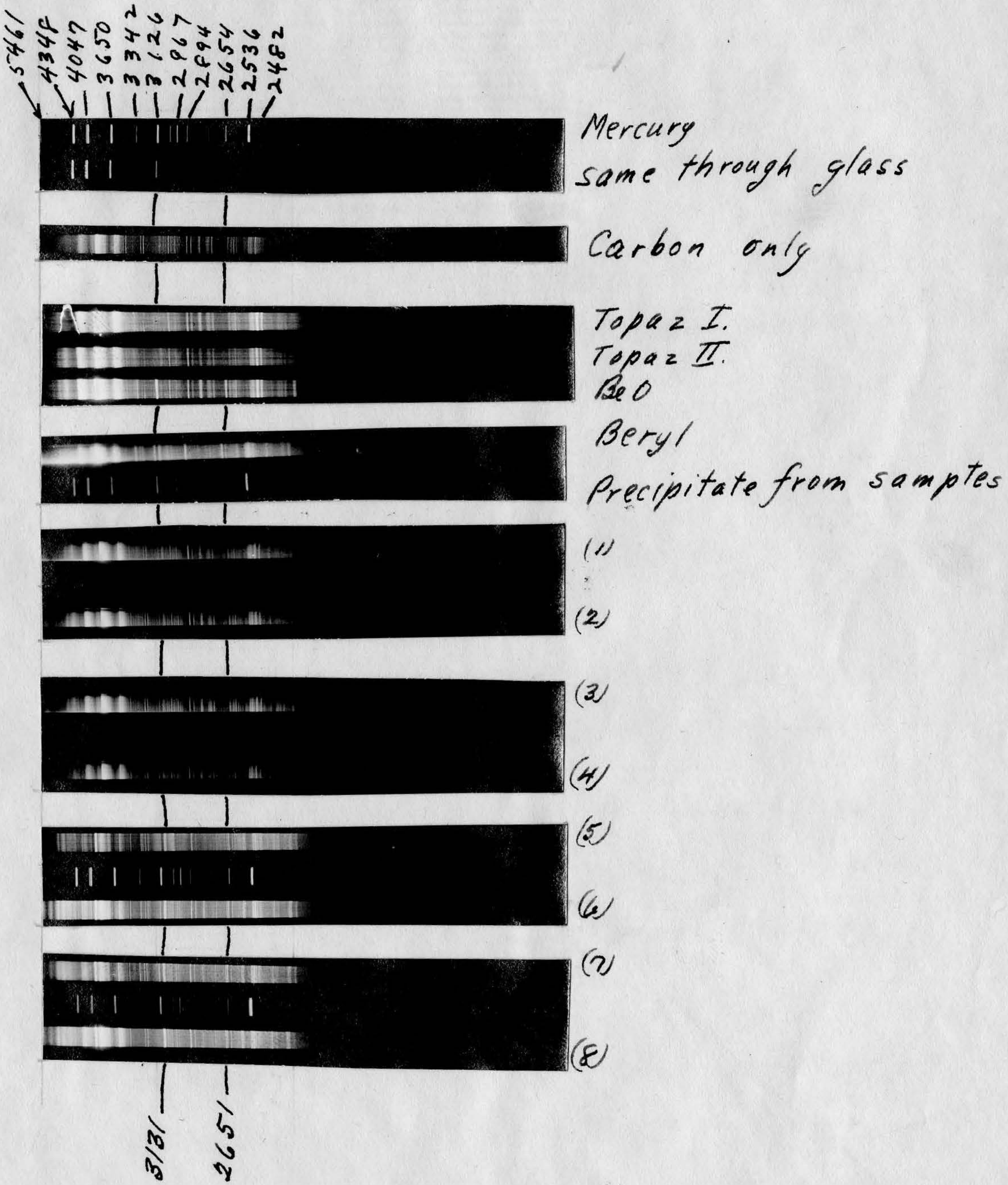
# DISCUSSION

# of

# the

# SPECTRAL PHOTOGRAPHS

The following prints of the negatives of the various spectra fail to show some of the more delicate lines, due to the fact that no paper has a tone range great enough to correctly render the long range of tones that a negative will produce. The paper used was Single Weight Azo E 2. All line determinations were made directly from the negatives, since the paper prints will often stretch out of shape in the process of developing and finishing, resulting in gross errors.


5461
4348
4047
3650
3342
3126
2967
2894
2654
2536
2482
Mercury
same through glass
Carbon only
Topaz I.
Topaz II.
BeO
Beryl
Precipitate from samples
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
3131
2651

Two very characteristic Mercury arc lines occur at 3126 and 2536 A. U. The former may most readily be ascertained by making two spectra photographs as shown in 1 and 2; the first is a photograph of the Mercury arc spectra transmitted through Quartz glass (which does not absorb ultraviolet light) and the second is made through a glass plate (which absorbs light having wave lengths below 3000 A. U.---this does not hold ~~absolut/ely~~ absolutely true, as we can on longer exposures get weak lines below this wave length---).

The 2536 line is by far the most intense line in the true ultra-violet region (below 3000 A. U.).

Having identified the above two lines, then with the aid of the spectrograph furnished by the makers of the "Labarc", the other Mercury lines may be identified.

<u>Note</u>: Due to the lack of space, all of the lines are not identified on the preceeding pabe; further, two lines 5970 and 5461 which are visible on the negatives but not in the prints were not included.

On each film before putting the powdered mineral in the arc, a photograph was made with the carbon rods only, to act as a check to make sure the rods were cleaned thoroughly, and were free from Beryllium contamination. Such a spectra is shown in 3.

4 and 5 show lines characteristic of Aluminum and other metals, but do not show Beryllium lines. These spectra were of Topaz I and Topaz II respectively.

6 shows the strongest Beryllium lines of any of the graphs, and it should, since pure (99.77%) BeO was used.

Powdered Beryl was used to produce spectra 7, which shows strongly characteristic Beryllium lines.

It was feared that the ground Topaz may have contained traces of Beryllium in such a form that it would not ionize in the arc, and consequently give no lines. From experimental Part I, the precipitates which had been burned and weighed <u>as</u> BeO were next used. Since the pure BeO gave such good lines (spectra 6)--the precipitates (if they are BeO) should also give good lines.

The precipitates from Samples (1) and (2)--Topaz I--spectra 9 and 10--~~and~~ and Samples (3) and (4)---Topaz II ---spectra 11 and 12--- show no Beryllium lines, but show Aluminum lines fairly strongly, supporting the author's assumption that the precipitate was $Al_2O_3$ instead of BeO.

Samples (5) and (6)--from Beryl--spectrae 13 and 15-- and samples (7) and (8) from standard Al and Be solutions--spectrae 16 and 18 show both Al and Be lines, further supporting the author's assumption that the Parsons and Barnes method of separation is not quantitative, and that $Al(OH)_3$ is quite appreciably soluble in boiling 10% $NaHCO_3$, solution.

# RESULTS

# of

# SPECTRAL ANALYSIS

## Results of Spectral Analysis

|  | Presence of Beryllium | Spectra |
|---|---|---|
| Topaz I | - | (4) |
| Topaz II | - | (5) |
| BeO | + | (6) |
| Beryl | + | (7) |

Precipitates from above mineral analyses reported as BeO in Part I

|  | Sample |  |  |
|---|---|---|---|
| Topaz I | (1) | - | (9) |
|  | (2) | - | (10) |
| Topaz II | (3) | - | (11) |
|  | (4) | - | (12) |
| Beryl | (5) | + | (13) |
|  | (6) | + | (15) |
| Al and Be Solutions | (7) | + | (16) |
|  | (8) | + | (18) |

# Experimental Part III

To explain the differences in the results obtained in Part I and Part II, and the deviation of the results obtained in the check solutions, a new series of analyses were devised. Six solutions were prepared:-

(1) 25 cc BeO solution (Standardized Part I)
(2) 25 cc BeO solution
(3) 25 cc $Al_2O_3$ solution
4 25 cc $Al_2O_3$ solution
(5) 25 cc $Al_2O_3$ solution
(6) 25 cc $Al_2O_3$ solution

NaOH solution was added to each of the above until the solution was neutral; then each solution was diluted to 200 cc, heated to boiling, 22 grams $NaHCO_3$ added, stirred well till dissolved, boiled for 30 seconds, and finally filtered.

(1) and (2) had no visible precipitate and after filtering, washing thoroughly with 50 cc 1% $NH_4NO_3$ solution, and burning, the following results were obtained.

| | (1) | (2) |
|---|---|---|
| Crucible and residue | 9.6119 | 9.8276 |
| Crucible | 9.6118 | 9.8271 |
| Residue as $Al_2O_3$ | .0001 | .0005 |

which goes to show that no BeO was precipitated from the $NaHCO_3$, so that phase of the separation was very good. However we did not and will not take into account the

Beryllium that is adsorbed by $Al(OH)_3$ in the actual analytical procedure.

The precipitate from (4) was dissolved in dilute $HCl$ and reprecipitated from 200 cc (plus or minus 10 cc) of boiling $NaHCO_3$ solution, and the two filtrates combined.

(5) was twice reprecipitated, each time from 200 cc of boiling 10% $NaHCO_3$ solution and the filtrates combined.

(6) was three times reprecipitated and the filtrates combined.

The final combined filtrates of these samples were acidified with $HCl$, boiled to expel $CO_2$, concentrated, and precipitated with $NH_4OH$, washed ~~twice~~, and twice reprecipitated to remove the non-volatile salts. The $Al(OH)_3$ which was precipitated was burned and weighed.

| (3) | (4) | (5) | (6) |
|---|---|---|---|
| 10.1170 | 9.9302 | 10.5746 | 9.8893 |
| 10.1110 | 9.9205 | 10.5615 | 9.8712 |
| .0060 | .0097 | .0131 | .0181 |
| 200 cc used | 400 cc | 600 cc | 800 cc |

The above shows that $Al(OH)_3$ is quite appreciably soluble in boiling 10% $NaHCO_3$ solution to about 2.3 mg per 100 cc according to the results below:-

From Sample

(3) the solubility as $Al_2O_3$ is .00300 gms. per 100 cc

(4) the solubility as $Al_2O_3$ is .00242 gma. per 100 cc

(5) the solubility as $Al_2O_3$ is .00218 gms. per 100 cc

(6) the solubility as $\underline{Al_3O_2}$ is .00226 gms per 100 cc

Average .00228 gms per 100 cc.

# CONCLUSIONS

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The two Topaz samples do not contain Be, as was shown by the absence of characteristic Beryllium lines in the ultraviolet spectra of these minerals.

The sample of Beryl probably contains 10% or less BeO, instead of the 14% as indicated by the Parsons and Barnes method of analysis.

$Al(OH)_3$ is appreciably soluble in boiling $NaHCO_3$ and the repeated represipitations produce a very questionable degree of accuracy in the separations.

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