

THE RECOVERY OF GALLIUM FROM A VIRGINIA FELDSPAR ORE

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## TABLE OF CONTENTS

	Page
I Acknowledgment -----	2
II Introduction -----	3
III Purpose -----	5
IV Theoretical -----	6
V Experimental -----	15
VI Experimental Results -----	18
VII Discussion of Procedure and Results -----	20
VIII Conclusion -----	22
Bibliography -----	23

## I ACKNOWLEDGMENT

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## II INTRODUCTION

### Gallium

Special interest attaches itself to the history of gallium because its existence, properties and compounds were predicted by Mendeleeff under the name of eka-aluminum. Within five years after Mendeleeff had made an extended list of the properties of eka-aluminum, the element gallium was discovered. The accuracy with which Mendeleeff's predictions matched the actual properties of gallium was remarkable<sup>(12)</sup>, and did much to strengthen faith in his theories.

Gallium was discovered by Lecoq de Boisbaudran<sup>(12)</sup> in 1875 while examining some zinc blende from the Pyrenees. He discovered two new lines in the violet of the spectrum,  $\lambda = 4172.2$  and  $4033.18$ , which led to the identification of the new element, for which the discoverer suggested the name gallium after the old name for France.

Gallium is one of the scarcest of the elements; however, according to Mellor<sup>(12)</sup> it occurs widely distributed in nature. Its presence has been determined spectrographically in most of the many zinc blendes, in iron ores - magnetite, pyrites, etc., and in some manganese ores. Many of the aluminum ores contain gallium; it is said<sup>(10)</sup> to be a constant constituent of bauxite whence it finds its way into commercial aluminum. The percentage of gallium in these ores, however, is extremely low. Germanite, the richest bearing ore, contains 0.57 per cent of this metal and has furnished a convenient source of supply; however, because of the scarcity and high price of germanite, no great quantity can be expected from this source.

According to Hopkins<sup>(10)</sup> the principal supply in the United States has come from the Oklahoma zinc blendes. During the First World War, the price of pure zinc permitted the redistillation of spelter. In this process a small residue was obtained which was largely lead but which was also found later to contain gallium and indium. Even though the tonnage of zinc blende is large, this does not offer a copious supply for it has been estimated that 3.5 ounces of gallium may be recovered from a ton of concentrate; this means that a maximum yield from this source cannot be expected to exceed 5 ounces of the metal from 200 tons of zinc blende.

An evidence of the scarcity of gallium is reflected in the market price for the metal. In this country at present, the price is \$3.75 per gram.<sup>(11)</sup>

Considerable interest was shown, therefore, when a Virginia feldspar ore was reported<sup>(5)</sup> to contain 2 per cent gallium. The determination was made spectrographically and was later shown to be erroneous by Professor H. D. Ussery of Virginia Polytechnic Institute. He gave the corrected value to be approximately 0.2 per cent gallium. This corrected value, however, was still relatively large enough to provoke an investigation to determine a method of separation of gallium from the feldspar ore.

### III PURPOSE

The purpose of this investigation, therefore, is to determine a method of recovery of gallium from a Virginia feldspar ore.

#### IV THEORETICAL

In a spectrographic analysis<sup>(5)</sup> of the feldspar in question, the following results were given:

SiO <sub>2</sub>	65.02%
Al <sub>2</sub> O <sub>3</sub> - Zr <sub>2</sub> O <sub>3</sub>	18.74%
Fe <sub>2</sub> O <sub>3</sub>	.01%
CaO	.08%
Na <sub>2</sub> O	2.04%
K <sub>2</sub> O	14.00%

Ti, Ga, V, Rb, and Fe are present as impurities.

From the position of gallium in the periodic table and a study of its properties, it became evident at once that the separation of gallium from the large amounts of aluminum present would be attended by considerable difficulty. The compounds of gallium resemble those of aluminum quite closely, although there is evidence of a slightly stronger basicity. Iron although present in very small amounts, however, proved to be the greatest trouble maker.

A number of methods have been given in the literature for the separation of gallium from its ores. These methods are all based on the fact that the ores have been acid soluble and that little aluminum has been present. The following are some of the methods found:

Precipitation of basic gallium by sine<sup>(12)</sup> (10)

Formation of Ga(OH)<sub>3</sub> with ammonium hydroxide and ammonium salts<sup>(10)</sup>

The sulfite method<sup>(14)</sup> (7)

Precipitation by tannin<sup>(13)</sup>

Precipitation by camphoric acid<sup>(1) (2)</sup>

Precipitation by ferrocyanide<sup>(15) (8) (10)</sup>

Precipitation by cupferron<sup>(13) (4) (20) (17)</sup>

Extraction of gallium chloride by ether<sup>(19) (9) (17) (3) (1)</sup>

Distillation of gallium chloride with hydrochloric acid<sup>(7)</sup>

Electrolytic deposition of gallium<sup>(12) (9) (16) (10) (6)</sup>

Extraction of gallium by a sodium hydroxide solution<sup>(18)</sup>

These methods will be discussed.

#### Precipitation by Zinc

The precipitation of basic gallium salts by zinc has been used advantageously for concentrating crude gallium from its ores.<sup>(12)</sup> Basic gallium salts are precipitated from an aqua regia solution with zinc by boiling; aluminum, however, is also precipitated. It was not considered advisable to attempt any method which would involve the co-precipitation or co-separation of the gallium and the aluminum, because of the large amounts of aluminum present.

#### The Sulfite Method, Etc.

By the same reasoning as used above, the sulfite method and precipitation of gallium by either tannin, ammonium hydroxide and ammonium salts, or camphoric acid were not acceptable as methods for the separation of gallium from this feldspar ore; i.e., aluminum would also be precipitated in each case. However, these procedures, with the exception of the use of ammonium hydroxide and ammonium salts, are applicable to the purification

of crude gallium or to the separation of the metal if aluminum has first been removed. Although investigators in the past have precipitated gallium as gallium hydroxide using ammonium hydroxide and ammonium salts, Moser and Brukl<sup>(14)</sup> have shown this method to be unsuitable due to the solubility of gallium hydroxide in these reagents.

#### Precipitation by Cupferron

There has been some discussion in the literature as to the value of cupferron as a precipitating agent for gallium. Although von Bergkamp<sup>(21)</sup> states that gallium is not completely precipitated by cupferron in solutions containing as much as 5 per cent sulfuric acid by volume when tartaric acid is present and that complete precipitation is not attained in solutions having an acidity greater than 3 m.l. of sulfuric acid in 400 m.l., Sherrer<sup>(18)</sup> found that no difficulty was encountered in producing complete precipitation in solutions containing as much as 7 to 8 per cent sulfuric acid by volume provided that an excess of cupferron was added. Scherrer found that it was necessary to work with volumes of 400 m.l. for every 100 grams of aluminum present to prevent the precipitation of aluminum salts by crystallization when the necessary chilling of the solution was effected.

Since cupferron also precipitates the iron, vanadium and zirconium shown present in this ore, it did not appear feasible to use it for the preliminary separation of the gallium, but the possibilities of its use as the final precipitating agent were kept in mind.

#### Precipitation by Ferrocyanide

The separation of gallium by potassium ferrocyanide seemed to offer a

solution to the problem. The method is quantitative in nature and sensitive to the extent that it offers a qualitative means of recognizing mere traces of the metal. Vanadium (which is only present as a trace) and iron are the only interfering elements present in this ore. Porter and Browning<sup>(16)</sup> have studied this method rather fully.

Two problems appear to be involved in the application of this reaction: (1) filtration and (2) recovery of gallium from the precipitated salt free from iron and the ferrocyanide radical.

Porter and Browning<sup>(16)</sup> state that the precipitate of gallium ferrocyanide is very gelatinous. Ordinary filtration by filter paper is very slow and the precipitate is difficult to wash. They found that decantation could not be used and that none of the usual methods of coagulating a colloidal precipitate, i.e., varying the acid concentration, adding electrolytes, heating the solution, had any effect. The use of a Gooch crucible and suction proved to be of no help either.

However, according to these authors, if a mat of fine filter paper fibre, made by scratching filter paper with a knife, is washed into a funnel containing double filter paper, the precipitate is held on it providing suction is not applied too strongly.

One method given for the separation of gallium from iron was to oxidize the ferrocyanide precipitate in sodium hydroxide solution with hydrogen peroxide and then to boil with ammonium chloride to precipitate gallium hydroxide free from cyanide radicals.

Another method was to dissolve the precipitate from the filter paper with sodium hydroxide and then to treat with carbon dioxide to precipitate

gallium hydroxide. Neither of these methods appeared to be very good, for when iron is precipitated as the hydroxide it tends to absorb much of the gallium present on its surface. (22)

#### Extraction by Ether

The fact that gallium chloride is extracted from hydrochloric acid solution by di-methyl ether has been made use of by investigators for the separation of gallium. Foster, Johnson and Kraus<sup>(7)</sup> state, however, that when this method is applied to large amounts of the ore, it has the disadvantage of being both costly in time and material. Swift<sup>(20)</sup>, who discovered this method, has shown that three extractions of the solution are necessary and sufficient. Complete separation from aluminum is effected by this method; iron as ferric chloride is the only other element extracted in the case of this feldspar ore.

Scherrer<sup>(18)</sup> has shown that in the extraction of gallium trichloride by ether in the presence of aluminum it is necessary to keep the volume of the acid large to prevent the precipitation of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , the solubility of which decreases with increasing hydrochloric acid concentration and is also effected by the presence of ether.

Swift found that the concentration of gallium in the ether layer increases with increasing concentration of hydrochloric acid, attaining a maximum at approximately 7 normal hydrochloric acid, but that the proportion of gallium extracted is much less because the volume of the ether layer is reduced by its increased solubility in hydrochloric acid. From his experiments he has shown a normality of 5.5 to be the concentration of hydrochloric acid which gives optimum results in the extraction of gallium

by ether.

#### Distillation with Hydrochloric Acid

Foster, Johnson and Kraus<sup>(7)</sup> have devised a method of distilling gallium chloride with hydrochloric acid from an ore residue, gallium chloride being volatile in the neighborhood of 200° Centigrade. Aluminum chloride and, of course, iron<sup>chloride</sup>, however, are also distilled over with the hydrochloric acid. If the recovery of the gallium were placed on a commercial basis, this method would be valuable in that the gallium from a large amount of ore may be concentrated in a relatively small amount of solution. The extraction by ether from the concentrated solution might prove advantageous as an auxiliary part of this method.

#### Electrolytic Deposition

Metallie gallium in the pure state is obtained by electro-deposition from an alkaline solution. All the procedures given in the literature are based on the deposition of the metal from solutions free from large amounts of impurities. The best of these appears to be that of Hoffman<sup>(8)</sup> for the preparation of very pure gallium for use as an alloying element in a cadmium-vapor arc lamp.

#### Extraction with Sodium Hydroxide

When this investigation was undertaken, it was believed by the author that since the ore was a silicate, fusion was an essential step to bring the ore and, therefore, the gallium into solution. No other method seemed possible because of the nature of the ore; the use of hydrofluoric acid was never considered because of the danger and expense involved.

Much later after experiencing the tediousness and labor connected with fusion of the ore, the comparatively simple method of "leaching" the ore with concentrated sodium hydroxide was attempted. Although this procedure seemingly had no basis, neither was the exact manner in which gallium was "tied" in the silicate lattice known.

Sebba and Pugh<sup>(19)</sup> employed a sodium hydroxide extraction on germanite, a sulfide ore, with very satisfactory results. Germanite is an acid soluble ore and it was merely conjecture as to whether the gallium might be extracted from the silicate.

## V EXPERIMENTAL

As previously stated it was first considered necessary to fuse the feldspar ore in order to place the gallium in solution so that one of the methods of separation mentioned might be applied.

Great care was taken to insure complete fusion. The ore was ground wet in a ball mill until it would pass a 200-mesh screen, for particle size is a factor in fusion.

Sodium carbonate was used as a fluxing agent in the ratio of fourteen parts to one part ore as suggested for optimum results by the chief chemist of Consolidated Feldspar Company; later this ratio was cut to seven to one with no apparent change in completeness of fusion.

Since large platinum crucibles were unavailable, it was found necessary to use a crucible made of refractory material. The Ceramics Department of V. P. I. graciously allowed the author to use Kyanite crucibles which they had prepared. The furnace available was of the gas type; it was rather small, however, so that a crucible of <sup>500</sup>/<sub>1</sub> ml. volume had to be used. Using a sodium carbonate to ore ratio of fourteen to one, only 50 grams of ore could be fused at one time in this crucible; the ratio was later changed to seven to one so that 100 grams of the ore could be treated.

The powdered ore and sodium carbonate were intimately mixed in a mortar with a pestle, and then it was introduced into the Kyanite crucible and heat applied. The mixture melted at approximately 1850 degrees Centigrade each time fusion was attempted; of course, at this temperature the crucible was also attacked by the sodium carbonate bringing more impurities into the

solution e.g. iron and chromium. The flux was allowed to remain molten for fifteen minutes. Longer periods were not attempted, for the crucible showed signs of weakening at the top. No attempt was made to remove the flux while molten.

The crucible was allowed to cool and then by cracking the crucible carefully, it was possible to remove practically all of the fused mass. This fused mass was ground into small pieces with a mortar and pestle and added to a solution of dilute hydrochloric acid keeping an excess of acid present at all times.

#### The Precipitation of Gallium by Potassium Ferrocyanide

The hydrochloric acid solution of the fused ore was evaporated on a hot plate and steam bath to dryness. Since gallium chloride is volatile at 200 degrees Centigrade high temperatures had to be avoided. Concentrated hydrochloric acid was added to dehydrate the silica and the silica removed by filtration through a Büchner funnel. The filtrate was diluted to a one part acid - three part water concentration.

A procedure found in Hillebrand and Lundel "Applied Inorganic Chemistry"<sup>(8)</sup> was followed. Potassium ferrocyanide was added in slight excess to the hydrochloric acid filtrate and the solution heated to 65 degrees Centigrade, digested at this temperature <sup>for 30 minutes</sup> and then allowed to stand for three days. By decantation and use of the centrifuge the dark blue, almost colloidal precipitate was concentrated to about 100 ml. The precipitate was very difficult to handle; however, by following the procedure suggested by Porter and Browning<sup>(16)</sup> in which a mat of filter paper fibres is prepared, filtration was finally accomplished.

The precipitate was dissolved in sodium hydroxide and the solution

acidified with sulfuric acid to a 7 per cent concentration. Excess 6 per cent solution of cupferron was added. The precipitate was ignited.

### The Ether Extraction Method

The procedure given by Scherrer<sup>(18)</sup> for the extraction of gallium chloride by ether was followed.

The ore was powdered, fused with sodium carbonate, and the flux dissolved in hydrochloric acid as before. Most of the silica was removed by continual decantation and washing with water. The volumes of the washings were reduced considerably by means of the hot plate and the resulting solution was adjusted to slightly <sup>less than</sup> six normal in hydrochloric acid.

The solution was cooled in ice water and transferred to a large separatory funnel. Chilled ether (150 m l. for every 400 m l. of solution) was added to the separatory flask. Scherrer states that both solutions are chilled to prevent the formation of the yellow color which usually appears; he does not state to what this yellow color is due. (Possibly ferric chloride)

The funnel was shaken thoroughly and chilled again by immersion in ice water. When the layers had separated, the acid was drawn off and the ether solution was placed in a 400 m l. beaker.

Two more extractions were made using 50 to 75 m l. of ether, depending on the volume of the acid solution. In the third extraction, the separatory funnel was allowed to stand at room temperature for one hour before removing the acid.

The three ether extracts were combined and allowed to stand at room temperature until the ether layer had become entirely separate from the slight amount of acid unavoidably entrained. This acid was removed and

treated with two portions of ether. The entire ether fraction was then evaporated to dryness.

#### Precipitation by Cupferron

The procedure followed in this case was also suggested by Scherrer<sup>(18)</sup>.

The residue obtained from the ether extraction was dissolved in nitric acid and 5 m l. of concentrated sulfuric acid were added and heat applied. The destruction of all organic matter was insured by adding nitric acid from time to time. Heating was continued until heavy white fumes were evolved.

The solution was diluted to 100 m l., five grams of tartaric acid added, and the solution stirred until all the crystals were dissolved. The solution was digested on the hot plate until the iron was dissolved and then diluted to 250 m.l. Ammonium hydroxide was added until the solution was nearly neutralized and hydrogen sulfide passed in for about five minutes to insure the complete reduction of the iron to the bivalent state. Ten m.l. of ammonium hydroxide were added in excess and the solution was saturated with hydrogen sulfide, filtered and the precipitate (FeS) washed four times with a two per cent solution of ammonium sulfide which also contained one per cent ammonium tartrate.

The filtrate obtained was acidified with sulfuric acid and boiled to expel hydrogen sulfide. After filtration it was then diluted to 375 m l., neutralized with ammonium hydroxide and 30 m l. of sulfuric acid added. The resulting solution was chilled in ice water and excess 6 per cent cupferron solution was added. The solution was stirred well and allowed to stand in ice water for one hour. Small pieces of filter paper were added to aid filtration.

The solution was filtered and the precipitate washed with chilled dilute sulfuric acid ( 7 parts  $H_2SO_4$  and 93 parts water), containing about 1.5 grams cupferron per liter. The filter paper (Whatman No. 40) and precipitate were placed in a platinum crucible, dried carefully, charred and ignited at 900 degrees Centigrade. The residue was weighed as gallium oxide ( $Ga_2O_3$ ).

#### Sodium Hydroxide Extraction

The powdered feldspar was slowly dusted into an iron basin containing a one to one solution of sodium hydroxide. (One-half as much sodium hydroxide as ore by weight). By being thus dusted in the ore was completely wetted. The mixture was heated over an air bath with occasional stirring until the mass became almost dry. It was then scraped into a beaker of water (one liter for one kilogram of ore). Most of the residue was removed by continual decantation and washing with water and the resulting solution filtered thru' an asbestos mat. The solution was acidified with hydrochloric acid to a six normal concentration and the silica filtered off.

Since the solution probably contained vanadium and titanium as well as the gallium, the ether extraction was considered necessary. The gallium was precipitated by cupferron and ignited to gallium oxide using the method previously given.

## VI EXPERIMENTAL RESULTS

### Ferrocyanide Method

Two 50-gram samples of the ore were treated by the ferrocyanide method. A spectrographic analysis of the precipitates showed the presence of gallium in each case but not as concentrated as it should have been.

The precipitates were dissolved from the filter paper by sodium hydroxide, the combined solutions acidified with sulfuric acid and the gallium precipitated with cupferron.

The ignited residue was dark brown to red, showing the presence of a great deal of iron. The residue weighing 0.2013 grams was treated with hydrochloric acid, aqua regia, but no success was obtained in dissolving it. Spectrographic analysis showed <sup>relatively</sup> ~~only~~ weak lines of gallium; therefore, the residue was abandoned.

### Ether Extraction and Cupferron Precipitation of Gallium

A 50-gram sample and a 100-gram sample of the ore were fused, extracted with ether and the gallium precipitated with cupferron.

The 50-gram sample yielded a precipitate of gallium oxide weighing 0.0303 grams. A spectrographic analysis showed the presence of iron in a very small amount (trace).

The 100-gram sample yielded a precipitate of gallium oxide weighing 0.0795 grams. The oxide in this case was also contaminated with iron, as shown by spectrographic means; it contained relatively more iron than the 50-gram sample.

Sodium Hydroxide Extraction

A 100-gram sample of ore was extracted with sodium hydroxide, acidified with  $H_2SO_4$  and the gallium precipitated by cupferron. The ignited precipitate (gallium oxide) weighed 0.0149 grams and was shown to be relatively free from iron by spectrographic means; i.e., <sup>only</sup> a trace of iron was present. The high concentration of gallium was shown by the fact that an inversion of the gallium lines occurred.

A 1000-gram sample of ore was extracted with sodium hydroxide, acidified with hydrochloric acid, extracted with ether and the gallium precipitated with cupferron. The gallium oxide residue in this case weighed 0.8978 grams. This residue was tested spectrographically and the iron content found to be less than one per cent. Traces of sodium and tin were also noted.

## VII DISCUSSION OF PROCEDURE AND RESULTS

Fusion of the feldspar in question as a preliminary step in the extraction of gallium proved laborious, costly, and unnecessary. Only small amounts of ore could be fused at one time and the large quantities of silica gel obtained were very difficult to handle. Fusion would be especially impractical from a commercial standpoint unless the other constituents of the feldspar were worth recovering.

The ferrocyanide method of separating gallium proved impractical because of the difficulty in handling the colloidal gallium ferrocyanide precipitate. This method would have no commercial possibilities unless the gallium were first concentrated.

Extraction of the feldspar by sodium hydroxide solution, although not quantitative, proved to be the simplest and most effective means of first concentrating the gallium. Large amounts of ore can be handled easily and the gallium extracted is concentrated in a small volume. The time and cost involved is very small in comparison with that of the fusion procedure, and the investigator feels that the method has commercial possibilities.

The grinding of the ore before "leaching" must be emphasized. Unless the ore is powdered very finely, it is doubtful whether this method would be applicable. The investigator feels that particle size plays an important role in the success of this procedure. The feldspar ore in this investigation was ground so that the particles would pass a 200-mesh screen.

The first extraction of the ore by sodium hydroxide was attempted to determine how the gallium was present in the silicate structure and to see if the metal might be removed from the ore without fusion. The gallium oxide residue obtained was small due probably to the fact that the sulfuric acid solution from which the gallium was precipitated with cupferron was too acid and contained no tartaric acid. Or perhaps excess cupferron solution was not present.

Extraction of the hydrochloric acid solution by ether and cupferron precipitation of the gallium seemed to yield satisfactory results when the gallium was first concentrated by the sodium hydroxide treatment.

## VIII CONCLUSION

A method of extracting gallium from a Virginia feldspar has been determined.

The steps in this method are:

1. Grinding of the ore to a very small particle size (200 mesh)
2. Extraction of gallium by "leaching" the ore with sodium hydroxide
3. Acidification of the sodium hydroxide solution with hydrochloric acid and subsequent extraction of the acid solution with ether to separate the gallium from aluminum, vanadium, and titanium, and other metals
4. Removal of iron by precipitation of ferrous sulphide with hydrogen sulphide
5. Precipitation of gallium by cupferron
6. Ignition of the cupferron precipitate to gallium oxide

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