THE EXTRACTION
OF
GALLIUM FROM ZINC ORES

Thesis

by

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THE EXTRACTION OF GALLIUM FROM ZINC ORE RESIDUES.

I. THE PURPOSE OF THE INVESTIGATION

The discovery of small amounts of gallium in zinc ores showed the possibility of its presence in a small quantity of zinc ore residues on hand at the Institute. Germanium had been previously extracted from the ore, and later, part of the zinc was recovered. During this work, the presence of gallium was shown by spectroscopic tests, and indium was at the same time shown to be absent.

In the present investigation, the reactions of different gallium compounds were studied and the action of various reagents on the residues observed, with a view toward the development of a distinctive test for gallium and finally toward the separation and purification of gallium from the residues. The residues consisted of approximately eighty liters of saturated zinc sulfate solution, containing small quantities of gallium together with various impurities.

CONTENTS

II. SUMMARY OF PREVIOUS WORK.

The discovery of germanium in certain zinc ores in this country made necessary a procedure for the extraction of germanium on an industrial scale. In 1920, Mr. P. S. Clark [1] developed such a method based upon the insolubility of the sulfide and the volatility of the chloride of germanium. Mr. J. Burkes [2], in 1921, carried out this procedure, beginning with fifty pounds of ore from the New Jersey Zinc Co. The recovery of zinc, as zinc sulfate, was worked out by Mr. Maurer [3] in 1922. This left the solution saturated with zinc sulfate and slightly acid with sulfuric acid.

A two gram sample of the original ore was analyzed by P. Clark [4], using A. A. Noyes [5] system of analysis. The results which were obtained follow:

Constituent	Amount	Constituent	Amount
Pb	20 mg.	S	10 mg.
Cd	trace.		
Al	80 mg.	SO_4	30-40 mg.
Zn	prin. constituent	Cl	trace.
K	10 mg.		
Fe	trace.		
As	3-4 mg.		
Sr	trace.		

All the lead, strontium, and arsenic were removed during the extraction of germanium. Small quantities of iron were probably introduced, however, through the use of iron containers.

A spectrogram taken during this work showed conclusively the presence of gallium and the absence of indium. Although no quantitative relation could be derived from the spectrum, it was thought that enough gallium was present to justify its recovery.

III. METHODS FOR THE SEPARATION OF GALLIUM.

From a consideration of the previous analysis of the ore, it is evident that the extraction of gallium will depend upon its separation from zinc, aluminum, and iron. Various methods were therefore studied for a separation of the individual metals. From these individual tests, a general procedure for their separation in the presence of each other could be derived.

1. SEPARATION FROM IRON. In the periodic system, gallium is found in the third group next to aluminum, and in the fifth series, following zinc. We may therefore infer that gallium closely resembles both zinc and aluminum, being less metallic than zinc and more so than aluminum. The separation from iron can, therefore, be satisfactorily accomplished by the addition of an excess of sodium hydroxide, as the remaining hydroxides are amphoteric.

As the amount of gallium which is present here is probably quite small, there is danger of a loss of gallium by occlusion. This method for the separation of iron was, however, considered complete until a distinctive test for gallium had been found. A spectrogram, taken later in the work, of the iron precipitate, confirmed this assumption.

by showing that no gallium was carried down by the iron.

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2. SEPARATION FROM ALUMINUM. The method of Dennis and Bridgman 6 was studied with a view toward using it in the extraction of gallium. Solutions of known concentrations of the sulfates of gallium and aluminum were prepared and their separation carried out as follows:

The solution containing gallium and aluminum was acidified with 25 cc. of concentrated hydrochloric acid and 25 cc. of ether were added. The mixture was saturated with hydrogen chloride and the resulting precipitate of aluminum chloride filtered on a hardened filter paper. The aluminum was determined by dissolving the chloride in water and re-precipitating it with ammonium hydroxide. A small amount of sulfuric acid was added to the filtrate and the solution was then boiled to remove the excess hydrochloric acid and ether. The gallium was then precipitated by making the solution ammoniacal and boiling it until the excess ammonia had been removed.

Separation of Gallium and Aluminum.

Number	Wt. Al_2O_3 taken	Wt. Al_2O_3 found	Wt. Ga_2O_3 taken	Wt. Ga_2O_3 found.
1	.0506 gm.	.0496 gm.	.0053 gm.	.0061 gm.
2	.1000 gm.	.0996 gm.	.0054 gm.	.0069 gm.

From these results it appeared that aluminum is not completely separated by this procedure, but that the gallium is quite completely precipitated by ammonium hydroxide, if the excess is removed. It was found that gallium is held in solution by ammonium hydroxide until all excess ammonia is driven off and the solution becomes neutral to methyl orange. A small portion of the gallium came down immediately, but after filtering and heating the filtrate, further precipitation resulted. After being thrown down, the hydroxide of gallium showed no particular tendency to re-dissolve upon the addition of ammonium hydroxide. This was probably due to the formation of an oxychloride or similar compound. Also, if gallium hydroxide should lose its water of hydration, it would probably become insoluble in excess ammonium hydroxide. The presence of ammonium chloride caused the precipitate to be gelatinous, in contrast to the granular form obtained without ammonium chloride.

This method for the separation of aluminum and gallium has been chosen for the present work.

3. SEPARATION FROM ZINC BY THE USE OF POTASSIUM MERCURIC THIOCYANATE. Two methods have been proposed for the separation of zinc from gallium. In the method of Dennis and Bridgman [7], potassium mercuric thiocyanate was used to precipitate zinc. This method is as follows:

A solution of potassium mercuric thiocyanate is added by drops to the solution containing zinc, which is constantly stirred during the addition of the precipitant. The reagent is added until a precipitate begins to form, and from this point, 20 cc. portions of the precipitant are added for every 0.1 gram of zinc estimated to be present. After this precipitate has been removed by filtration, 10 cc. of hydrochloric acid are added to the filtrate and the mercury in the solution is precipitated by hydrogen sulfide. The mercuric sulfide is filtered off, and the gallium is then thrown down by the use of sodium sulfite.

Experiments with gallium sulfide showed that it is carried down by other sulfides in both acid and basic solutions. For this reason it was thought possible that gallium might be carried down by the mercuric sulfide in the above procedure. When tested, however, it was shown that gallium remains completely in solution in acid of this strength.

The potassium mercuric thiocyanate reagent is prepared by dissolving 27 g. of mercuric chloride and 39 g. of potassium thiocyanate in water. The solution containing the zinc should not contain more than 0.1 g. of zinc in 200 cc., and this volume of solution should contain about 2 cc. of concentrated sulfuric acid.

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4. SEPARATION OF ZINC BY THE USE OF SODIUM HYDROGEN SULFITE. The method of Porter and Browning [8] is based upon the precipitation of gallium and not zinc by sodium hydrogen sulfite. This method is:--

The neutral or slightly acid solution is boiled for two minutes with sodium hydrogen sulfite. A precipitate, indicating gallium, is filtered off after it settles. Hydrochloric acid, followed by potassium ferrocyanide, is then added to the filtrate, (~~followed by potassium ferrocyanide~~). A precipitate here shows the presence of zinc.

Both of these procedures, as stated by the authors, are of use only when the quantities of zinc which are present, are relatively small. The method of Porter and Browning was shown to be successful when 0.3 g. of zinc were present, while that of Dennis and Bridgman can be used only when the zinc which is present does not exceed 0.1 g. per 200 cc. of solution. As the original solution is saturated with zinc sulfate, neither of these procedures can be used for the initial precipitation of zinc. Two other precipitants were therefore tried.

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5. SEPARATION OF ZINC BY THE USE OF AMMONIUM CHLORIDE AND AMMONIUM HYDROXIDE. Zinc forms a soluble complexion with ammonium hydroxide, whereas gallium does not. To ascertain whether this fact could be utilized to separate zinc from gallium, it was decided to test for gallium after the separation with potassium ferrocyanide. Porter and Browning [9] have shown that gallium ferrocyanide is very insoluble in concentrated hydrochloric acid.

Fifty cc. of the original solution were diluted to 100 cc. and a large excess of ammonium hydroxide was then added. After the solution of the zinc, a mixture of a small red-brown precipitate and a small quantity of a white gelatinous precipitate remained. After this solution was filtered, the precipitate was dissolved in dilute hydrochloric acid. When this solution was made alkaline with sodium hydroxide, a red-brown precipitate, indicating iron, was thrown down. The precipitate was filtered off, and concentrated hydrochloric acid, followed by potassium ferrocyanide was added to the filtrate. As no precipitate appeared at this juncture, the absence of gallium was shown.

The absence of gallium may be due to either of two reasons.

1. Gallium is present in such small quantities, that its extraction is impracticable.
2. Ammonium hydroxide is strong enough, as a base, to dissolve gallium hydroxide.

It was therefore decided that a separation by the use of ammonium hydroxide was impracticable.

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6. SEPARATION OF ZINC BY THE USE OF HYDROGEN SULFIDE IN SODIUM HYDROXIDE. As aluminum sulfide hydrolyzes, upon formation, to form aluminum hydroxide, it was thought that gallium might act in a similar manner. If the precipitation is carried out in an alkaline solution, the gallium hydroxide would re-dissolve.

One hundred cc. of solution were diluted with an equal volume of water, and sodium hydroxide was added until the solution was neutral. A solution of hydrogen sulfide in sodium hydroxide was next added and hydrogen sulfide was passed into the solution until the precipitation was complete. After filtering off the precipitate, the filtrate was made acid with hydrochloric acid, was boiled to remove hydrogen sulfide, and was then made alkaline with sodium hydroxide. Carbon dioxide was passed in until the solution was saturated. A small, white gelatinous precipitate was thrown down here and was filtered off and dissolved in conc. hydrochloric acid. When potassium ferrocyanide was added to this solution, no precipitate appeared. This shows that gallium sulfide is insoluble in alkaline solution, or that it is carried down by other sulfides. It has since been found that the latter conclusion is true.

From the above results it seems evident that none of the known chemical properties of gallium can be applied to separate it from zinc. Gallium chloride, however, boils at 215-220°C., while zinc chloride does not boil until 730°C. is reached. To ascertain whether this could be used to separate zinc from gallium, various salts of gallium were heated at 250°-260° C in a current of dry hydrogen chloride.

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7. SEPARATION FROM ZINC BY THE DISTILLATION OF GALLIUM CHLORIDE. A small electric furnace was constructed by winding and lagging an alundum core, 1¼"x12". The salt was placed in a boat contained in a glass tube, and this tube placed in the furnace; the distillation was carried out in this manner. Small quantities of gallium nitrate and gallium sulfate were heated with hydrogen chloride for two hours. The gas which passed through the furnace was dissolved in water. Both the distillate and the residue in the boat were tested for gallium, and with both the nitrate and the sulfate, nearly half the gallium was found to have remained in the boat. A similar test with gallium chloride showed that all the gallium was distilled over. Gallium hydroxide, however, was found to be attacked but very little by hydrogen chloride. Before treating a residue, with hydrogen chloride, ~~however~~, it must be ~~by~~ dry to prevent the hydrolysis of gallium chloride.

These results gave, therefore, a good method for the separation of gallium and zinc, if the gallium is in the form of the chloride. It was therefore necessary to convert the gallium from the sulfate to the chloride.

IV. METHOD ADOPTED.

1. THE ACID CONCENTRATION. As the actual hydrogenion concentration in the residue was not known, it was necessary to calculate its value. A sample of solution was diluted to lessen the possibility of precipitating before actual neutralization had taken place. By back-titrating with

sample, the end point was satisfactorily reached, methyl orange being used as the indicator. The hydrogenion concentration was found to be 1.17N.

2. THE SEPARATION OF THE GREATER PART OF THE ZINC. If the gallium could be precipitated, with the zinc, as the hydroxide, the solution of these hydroxides in hydrochloric acid would result in the conversion of gallium from the sulfate to the chloride. Further, if gallium hydroxide is more insoluble than zinc hydroxide, a partial separation of zinc could be obtained. A study of these hydroxides showed that this was true. To determine the amount of sodium hydroxide which was necessary to precipitate the gallium completely, various amounts were assumed and close limits were then determined from the results.

3. THE SEPARATION OF GALLIUM FROM IRON, ALUMINUM, AND THE REMAINDER OF THE ZINC. The following procedure was used in all remaining determinations:

Samples of the original solution were diluted with an equal volume of water, and the sodium hydroxide was then added slowly. After filtering the solution, the precipitate was dissolved in conc. hydrochloric acid and the resulting solution evaporated to dryness. This residue was then heated for two hours at 250-260°C. in a current of dry hydrogen chloride. The exit gases were dissolved in water and this solution added to the condensate which remained in the tube. A small quantity of sulfuric acid was added to these liquors and the excess hydrogen chloride was expelled by boiling. Sodium hydroxide was added in excess to this condensed volume and the resulting precipitate of iron hydroxide filtered off. The filtrate was first neutralized with hydrochloric acid and then a slight excess of ammonium hydroxide was added. A small precipitate at this point indicated the presence of aluminum. Upon boiling the solution to remove the excess ammonia, a further precipitate resulted. Methyl orange was used to indicate the character of the solution and boiling was continued until the solution became just acid. The precipitates were filtered off and dissolved in conc. hydrochloric acid, and an equal volume of ether added to the solution. After the solution had been saturated with hydrogen chloride, a very small precipitate of aluminum chloride was filtered off and the filtrate was boiled to expel hydrogen chloride and ether. The addition, then, of a slight excess of ammonium hydroxide, and the subsequent removal of the excess by boiling, caused a very small precipitate, indicating gallium, to appear.

The quantity of sodium hydroxide which was found to cause the complete precipitation of gallium hydroxide was 4.7 gr. per 100 cc. of the original solution. As previously determined, the acid concentration of the original solution is 1.17 n, or to neutralize it, 4.68 gr. of sodium hydroxide would be required. Thus, we see that it is necessary to go only a small distance beyond the neutral point in order to precipitate gallium. After the precipitation of the hydroxides, the solution was found to be slightly acid to methyl orange. Hence, gallium hydroxide is more insoluble in slightly acid solution than is zinc hydroxide.

The precipitate which resulted as gallium hydroxide, although small, was thought to be somewhat greater than it should have been. Because of this result, tests were made for zinc and silica, both of which might act similarly to gallium under these condidions.

V. CONFIRMATION OF PROCEDURE.

1. ABSENCE OF ZINC AND SILICA. After the addition of sodium hydroxide to one liter of the original solution, and the subsequent distillation, and removal of iron, a slight excess of ammonium hydroxide was added to the solution. The excess ammonia was removed and the precipitate placed in a platinum crucible. Ten drops of nitric and five drops of hydrofluoric acid were than added. No gas bubbles, indicating the absence of silica, were evolved. After evaporating the contents of the crocible to dryness, the mercuric thiocyanate test for zinc was carried out as stated above.

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2. CONCLUSIONS. While gallium appears to have been separated by the distillation of its chloride, the presence of a relatively large quantity of other salts would make doubtful the completeness of the distillation. Because of this, the residues from the first distillation were pulverized and subjected to a second treatment with hydrogen chloride. After separating iron and aluminum, gallium was found to be present in the distillate. A third distillation, however, gave no test for gallium.

Although these results have indicated the presence of gallium, they cannot be considered as definite proof of its presence. Similarly, its complete separation cannot be considered definite because of the general character of a precipitation with ammonium hydroxide.

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3. QUANTITATIVE PROOF. A quantitative test was first considered

in order to prove its presence, but the lack of sufficient insoluble compounds of gallium made this method impracticable. Gallium forms insoluble compounds only as the hydroxide or ferrocyanide. The complete conversion of either the oxide to the ferrocyanide, or the ferrocyanide to the oxide would require a high degree of precision.

4. SPECTROSCOPIC CONFIRMATION. The two gallium lines occur at 4033 and 4172, or at the edge of the visible spectrum. Considerable doubt was expressed as to the possibility of locating the lines visually, but as Dennis and Bridgman [10] state that it is possible, the work was carried out.

In the absence of a calibrated spectroscope, the location of the gallium lines was determined by their relation to the potassium couplet at 4047--4044. The spark spectrum was employed because the gallium lines are brightest in a spark spectrum and because the flame spectrum is not suited for us with small volumes of solution. The tests were carried out first with the test solution of gallium, in order to locate accurately the position of these lines.

By the use of a direct vision, high dispersion spectroscope, no lines were visible with either the gallium solution or the potassium solution. A low dispersion instrument, however, showed the potassium lines quite distinctly, but the gallium lines were not visible.

The apparatus employed consisted of the spectroscope, an inductive coil capable of giving a spark about one inch in length, and small glass cups for holding the liquid.

As the spark spectrum was found to be inadequate for the detection of gallium, the use of the spectrograph with an arc spectrum was resorted to. This was made possible through the courtesy of Mr. Sinclair Smith of the Mt. Wilson Observatory. In as much as several exposures could be taken as readily as one, it was decided to test each step of the extraction for a possible loss of gallium.

The extraction as carried out in the previous work, may be outlined as follows:

to 100 cc. orig. solution add 100 cc. H_2O and a soln. containing 5 gr. NaOH. Filter.

A. FILTRATE. add .2 gr. NaOH. Filter.

B. Ppt. $Al(OH)_3$, $Zn(OH)_2$, $Ga(OH)_3$, $Fe(OH)_2$, $Fe(OH)_3$. Dissolve in conc. Hcl. Evaporate to dryness. Treat Residue at 250-260°C. with HCl.

H. FILTRATE

C. RESIDUE

D. Distillate. $AlCl_3$, $GaCl_3$, $FeCl_3$. Add 2cc. conc. H_2SO_4 and evaporate to 35-40cc. Add an excess of NaOH. Filter.

E. PPT. $Fe(OH)_3$

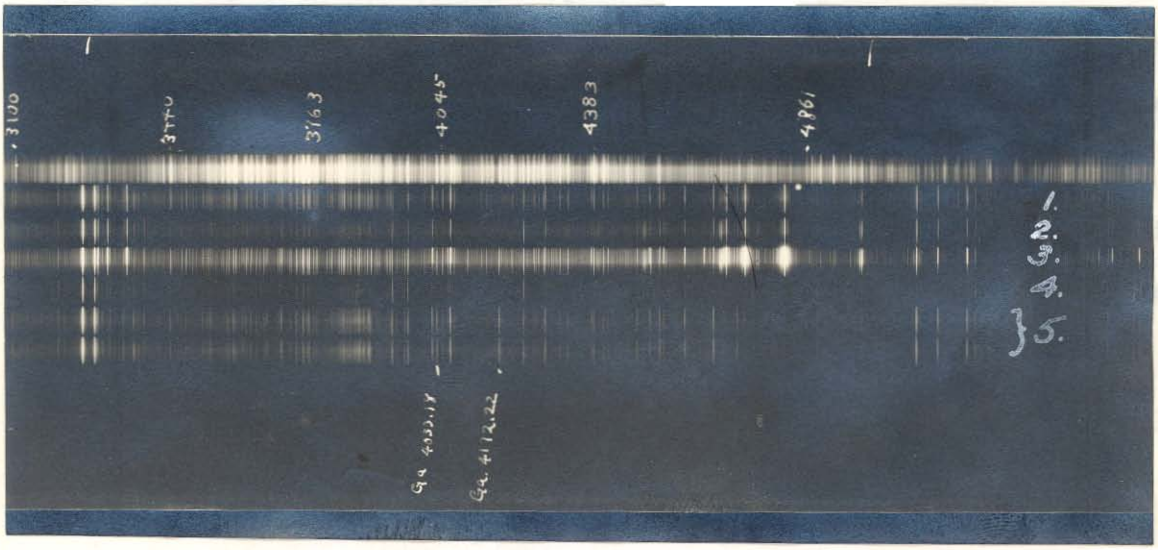
F. FILTRATE. $Al(OH)_3$ $Ga(OH)_3$ Make acid with HCl and then slightly ammonical. Boil off excess NH_3. Filter.

G. PPT. $Al(OH)_3$, $Ga(OH)_3$ Dissolve in conc. HCL and add an equal volume of ether. Saturate with dry HCL. Filter.

I. PPT $AlCl_3$

J. Filtrate. $GaCl_3$. Ppt. with NH_4OH and boil off excess NH_3. Filter.

K. PPT. $Ga(OH)_3$.


.3100
3440
3763
4045
4383
.4861
Ga 4033,18
Ga. 4172,22
1.
2.
3.
4.
}5.

In the accompanying spectrogram, the spectrums numbered 1,2,3,4, and 5, are, respectively the spectrums of divisions A, H, C, E, and G. Gallium should be found in "G" and possibly in "C", but not elsewhere. The spectrogram shows this to be the case.

Carbon electrodes were first used for the arc, but they gave dark bands in the spectrum at the position gallium was expected. Because of this difficulty, copper electrodes were substituted for the carbon ones. The lower electrode was a copper rod, $\frac{1}{2}$ inch diameter, and was fitted to hold the solid by boring a hole 1/8"x1/8" in the center of one end. The upper electrode was a copper rod, round on one end, and $\frac{1}{4}$ inch in diameter. The exposure which was found to show the lines most clearly was one ranging from five to seven seconds.

These results show, therefore, that the above procedure is efficient if the distillation is carried out for a longer period of time. Grinding the furnace residues and redistilling them is also necessary.

VI. METHOD OF TREATING RESIDUES.

In carrying out the extraction from the large volume of residues, several modifications were necessary. In order to prevent local concentration in the addition of sodium hydroxide, the use of an electric stirrer, with feed mechanism in the drive shaft, was found to be advantageous. The precipitates formed were quite gelatinous and of a somewhat colloidal nature. Filtration was therefore not advisable if it could be prevented. By allowing the mixtures to settle from forty-eight to sixty hours, however, it was found that it was possible to decant and filter the supernatant layer rapidly and completely. In the evaporation of the hydrochloric acid solution, the temperature was not allowed to go above 85°C., in order to eliminate rapid evaporation, and thereby preventing a possible loss of gallium chloride. It would have been advisable to perform this evaporation with an industrial evaporator, but as they were not set up, large evaporating dishes were used. As evaporation directly to dryness in the dishes would cause their breakage, the solutions were evaporated to supersaturation, allowed to cool and filtered. After filteration, this process was repeated. As these residues contained a large amount of mother liquor, they were dried at 100°C. in a gas oven. The subsequent distillation of the chloride was carried out in a current of chlorine gas, in a two-stage electric furnace. The use of chlorine eliminated the subsequent boiling to remove HCL. From this point, the process was carried out similarly to the preliminary work.

VII. PURIFICATION OF THE PRODUCT.

Three methods are known to effect the purification of gallium; namely, fractional distillation of gallium chloride, fractional electrolysis, and fractional crystallization. A combination of the latter two methods should prove successful in this case, as the fractional distillation has already been carried out.

L. FRACTIONAL ELECTROLYSIS. Richards and Craig[11] have completed a very efficient method for purifying gallium by electrolysis. Ammonium sulfate is added to the neutral solution of the metals and electrolysis carried out, the cathode being a rod of platinum wire and the anode consisting of platinum foil. Any zinc which is present is deposited first. The solution is boiled throughout the electrolysis, and this boiling causes an insoluble basic gallium ammonium sulfate to be deposited on the bottom of the container. This basic salt is dissolved in a slight excess of potassium hydroxide and the resulting solution electrolyzed. A large excess of potassium hydroxide causes the formation of a potassium gallium alloy which acts but very slightly upon water and acid. The ~~original~~ initial deposit must be re-electrolyzed, as it contains some gallium.

2. FRACTIONAL CRYSTALLIZATION. As gallium metal solidifies at 29.75°C., the purified metal may be obtained by fractional crystallization. If we put the metal, obtained from the electrolysis, on a watch glass and suspend a small fragment of solid gallium in it, the gallium will grow out as large crystal. These crystals can be cleaned with dilute nitric and sulfuric acids, washed with distilled water, and solidified in droplets.

VIII. SUMMARY.

1. A method for the separation of gallium from zinc ores has been developed.

2. Gallium hydroxide may be completely precipitated by ammonium hydroxide, if the excess ammonia is removed.

3. Gallium hydroxide is more insoluble than zinc hydroxide in acid solution.

4. Gallium chloride may be completely distilled at $250-260^{\circ}$C. in a current of dry hydrogen chloride.

1. Thesis by P. S. Clark.

2. Thesis by J. Burkes.

3. Thesis by F. Maurer.

4. Thesis by P. S. Clark.

5. A. A. Noyes' "Qualitative Analysis".

6. Jn. Am. Ch. Soc. Vol 40 -- Page 1531.

7. " " " " " " -- " "

8. " " " " " 43 -- " 126.

9. Chem. Abstracts " 11 -- " 3005. Am. J. Sc. Vol. 44 -- Page 0221-4

10. Jn. Am Ch. Soc. " 40 -- " 1531.

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Jn. Am. Ch. Soc. -- Vol 43 -- Page 111-114

Fogg and James --

Jn. Am. Ch. Soc. -- Vol 41 -- Page 947-949.