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Chemical Engineering

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**THE STUDY OF THE USE OF ORGANIC COMPOUNDS
FOR THE QUANTITATIVE PRECIPITATION OF METALS**

BY

ARTHUR DECHMAN

T H E S I S

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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June 1st 1912

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Arthur Dechman

ENTITLED *The Study of The Use of Organic
Compounds for the Quantitative Precipitation
of Metals*

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF *Bachelor of Science in
Chemical Engineering*

L. L. Burgess

Instructor in Charge

APPROVED: *Geo. Parr*

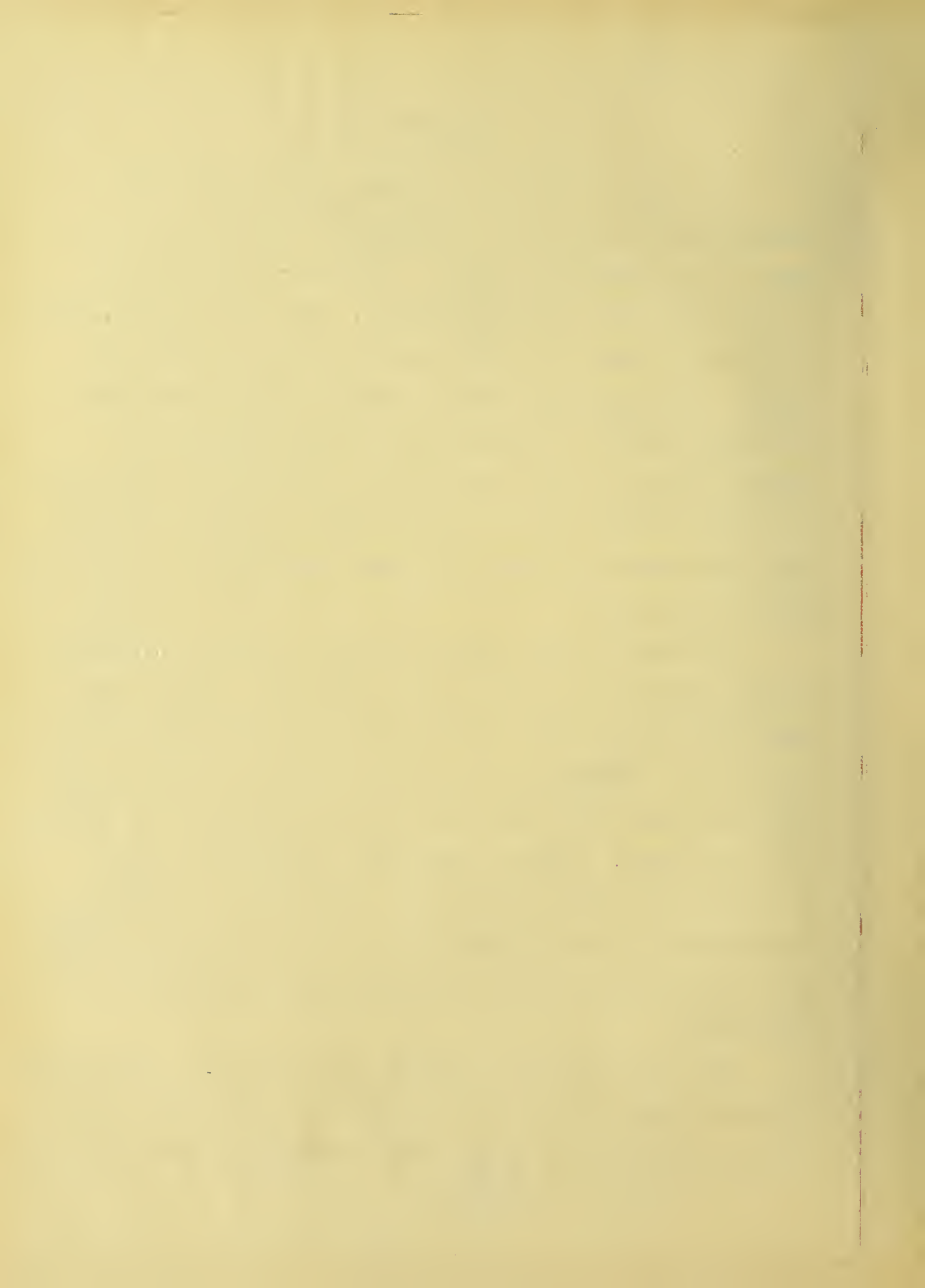
Acting HEAD OF DEPARTMENT OF *Chemistry*

INTRODUCTION.

The study of the use of organic compounds for the precipitation of metals in a quantitative way has never been taken up in a systematic manner. All of the discoveries in this line have been almost accidental. Here could be mentioned the glyoxine method for nickel and the benzidine method for sulphur. Its importance however cannot be overestimated as the routine methods of separating the metals through the regular manner are often very slow and are as often inaccurate. The authors thought that of the thousands of organic compounds known there should be some which would precipitate quantitatively some of the metals.

In taking up this study, we first referred to Beilstein for the properties of some of these compounds. Several were chosen for investigation but the most likely one seemed to be Croconic acid. $C_5H_2O_5$. This acid was mentioned as having an insoluble barium salt which was very stable and could be worked with very easily. Another reason why this acid was chosen is the fact that when oxidizing it, six molecules of oxygen are necessary for each molecule of the acid. Therefore, this would permit a large error in titration without much error in the results.

The second acid which seemed to be worthy of investigation was Lactic acid. This acid is mentioned as having an insoluble tin salt which is precipitated from a neutral stannous solution.



This compound was not investigated however because of lack of time. Dr. L. L. Burgess has precipitated this compound from a neutral stannous solution and after filtration found no trace of tin in the filtrate. A further study of this acid might prove valuable in the separation of antimony and tin as the antimonous compound is soluble.

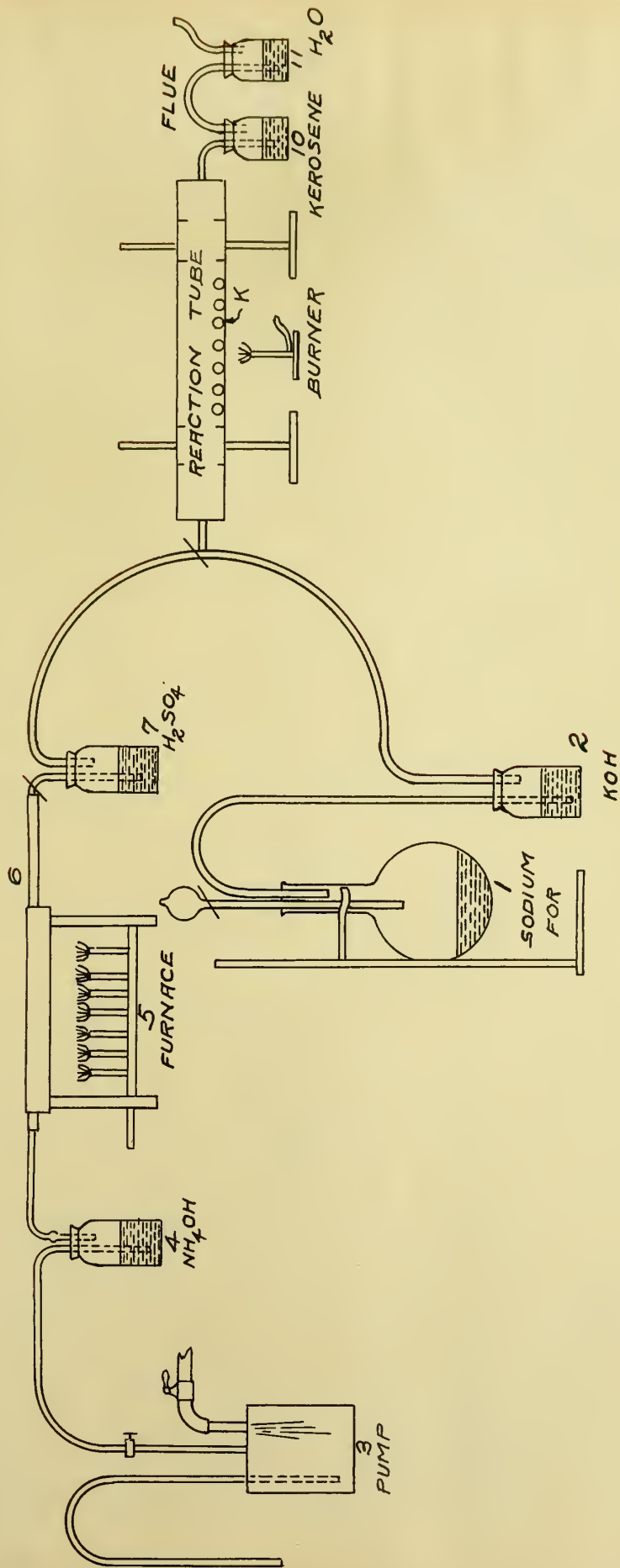
THE PREPARATION OF CROCONIC ACID.

The Croconic acid used in this work was prepared in two ways. First by an inorganic preparation and second by an organic synthesis. Both methods presented many difficulties and were not very satisfactory. The following paragraphs will outline the methods used.

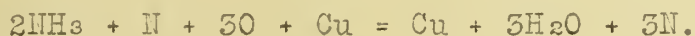
The inorganic method was first used by Justus Liebig Annalen, Vol. 11, p. 182.

The idea is to pass Carbon Monoxide over heated or melted potassium and as a final product have croconic acid.

The figure at the side shows the apparatus as it was set up. Carbon Monoxide was generated in the flask (1) by the action of sulphuric acid on sodium benzoate, and passed through a wash bottle containing potassium hydroxide, so that any carbon dioxide which may have formed in the generator would be absorbed. Through the other branch of the train, nitrogen



was being passed simultaneously with the carbon monoxide. The nitrogen was obtained in the following manner: Air was drawn in a large bottle (3) through a suction pump. The pressure caused by the incoming air would be enough to supply the air stream necessary when the stop cock above the bottle was opened. The water coming through the suction pump was siphoned off by a long glass tube. This method proved very satisfactory and gave us a steady stream of air. This air was next passed through an ammonia wash bottle (4). The purpose of the ammonia is to increase the yield of nitrogen and also so that the copper spiral will not be used up as fast. The air and ammonia gas are next passed over a heated copper spiral which is placed in a combustion tube set on the furnace. (5) The reactions involved are the following:



The air stream was then washed with sulphuric in the wash bottle (7). This removed any NH_3 which might have passed over.

The two gas streams met at the junction (8). A two way stop cock at this junction allowed us to pass either one or both gas streams through the reacting chamber.

The reacting chamber (9) was a glass tube two inches in diameter and six feet long. It was fitted with two two-holed rubber stoppers. A one-quarter inch glass tube was passed through it. The thermometer was attached to a wire so that it could be placed at any part of the tube. In this way

some idea of the temperature on the inside of the reacting tube could be obtained. About forty grams of potassium was put into the tube which was lined with thin sheet copper. The potassium was in the form of balls and could be distributed very easily over the tube. Two fish tail burners were used to heat the tube. The gases after reacting with the potassium were passed through a kerosene wash bottle (10) so that any potassium which might have come over would be stopped. They were next passed through a water wash bottle (11), which would absorb any of the vapors of the substances formed in the reaction, and then passed up the flow.

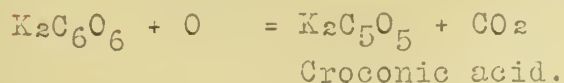
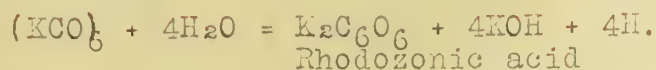
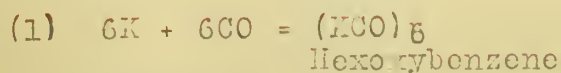
All the joints and stoppers were made air tight so that no carbon monoxide could escape.

All the oxygen in the train was first washed out by the nitrogen stream. Then the carbon monoxide was turned on, both streams being passed at the same time. Heat was then applied to the reaction tube at the end nearest the kerosene wash bottle. The potassium soon melted. At first no reaction could be noticed but as soon as the vapors of potassium appeared the reaction began. A number of flashes were noted and later a greenish silver mass. This was the melted potassium. The large tube soon became coated with a white powder and a varied colored mass was formed in the bottom of the tube. The colors included red, green, black, white, yellow and brown. The reaction was carried on for several hours and the heat was gradually moved farther down the tube. The

absorption was very rapid and when the reaction was going at its best only a very few gas bubbles reached the last wash bottle.

After the reaction had ceased the carbon monoxide stream was turned off, but the nitrogen stream was passed through for several hours to wash out the remainder of the carbon monoxide in the train. All the potassium was not used up as we did not wish to heat the tube to close to the paraffined ends and thus cause leaks. The reaction tube was allowed to stand for several hours and then taken apart. It had broken over night which probably resulted from an explosion in the tube. As soon as the tube was stirred, violent explosions took place. The black powder which had formed on the tube was dissolved in water. It took several hours to do this as the explosions were very frequent and violent. Part of these explosions were due to the reaction of the unused potassium with water, but most of them were due to the hexoxygenbenzene (KCO_6) which was formed in the tube.

After the black mass had been all dissolved it gave a yellowish brown solution with a large amount of a black substance in suspension which was probably carbon. Air was then passed through this solution for a day and it was then filtered. The filtrate was a clear yellow solution. This was evaporated and beautiful yellow crystals of croconic acid were obtained. The reactions involved in the above are:



A yield of 1.0274 grams was obtained. This was made up to a volume of 250 c.c. after being dried on a centrifugal filter. The solution was a clear yellow.

The second method of preparing the acid is that of R. Nietzki, Berichte, Vol. 18, p. 499.

This method at the first attempt went very easily and without difficulty. After that however it was tried twelve times without success. The principal stumbling block is the nitration, but ^{at} other stages the synthesis often did not go as they were scheduled too. The reactions were very instructive and could be used to great advantage in color study. It gives a strong color as soon as the quinone structure is formed and loses it as soon as the quinone structure is broken up. Each stage has a different color.

50 gms. Hydroquinone
50 gms. Zinc Chloride
100 gms. Acetic Anhydride.

The above mixture was put into a tall beaker and cooled to -10 degrees by a freezing mixture. Next

300 gms. fuming nitric acid

were added slowly to the above and then

300 gms. concentrated sulphuric acid were added. The nitration was very violent. Heat was developed very rapidly making it difficult to keep the solution cool. At this point most of our trials were lost. It seems that if the substance gets too hot it chars and is spoiled. If it is just a trifle above zero it gives a semi liquid yellow substance which is not what we are after. However if the reaction goes on in the cold a reddish brown substance is formed. (Dinitrotetraoxybenzene). The dinitrotetraoxybenzene was then filtered through a "Büchner funnel over chipped ice using an asbestos filter. Here again some of the substance is lost as the excess sulphuric acid in reacting with the water heats up the filter and thus brings it above zero degrees.

Next a one to three solution of potassium hydroxide was poured over the dinitrotetraoxybenzene and it changed to a yellow color. The substance now remaining on the filter was potassium nitranilate. This was partially dried and weighed seventy grams.

70 gms. Potassium Nitranilate

200 gms. Stannous Chloride

1000 gms. Sulphuric Acid

1000 gms. Water

were mixed in a large beaker and allowed to stand. The above solution immediately turned to a purple color and brown violet

crystals of Nitrodiamidotetraoxybenzene separated out. The solution and precipitate were next boiled with zinc dust and zinc shavings for about three hours. The whole became colorless giving us diamidotetraoxybenzene in solution. It was then filtered and concentrated hydrochloric acid was added to the filtrate. White crystals of the hydrochloride of diamido-tetraoxybenzene were precipitated. The yield of the hydrochloride obtained was twenty grams. The filtrate was concentrated and more of the hydrochloride was obtained.

20 gms. Diamidotetraoxybenzene. hydrochloride

80 gms. Potassium Carbonate

120 gms. Manganese Dioxide

1200 gms. Water

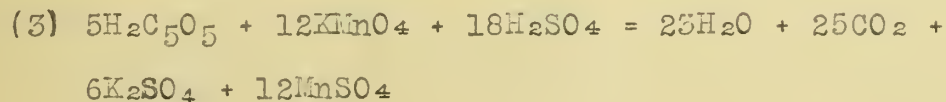
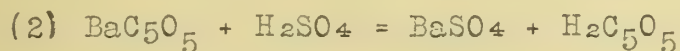
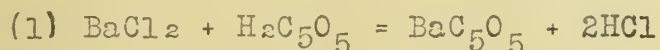
were mixed and boiled for one hour. The mixture had changed to a yellow solution by the oxidation. This was filtered and a clear yellow solution of potassium croconate was obtained. This was evaporated down and a crop of croconate crystals were obtained. These crystals were much clearer and the yield was larger than that of the first method. The yield was about 2 gms. 1.2175 grams of this were made up to 500 c.c.

THE DETERMINATION OF BARIUM AS THE CROCONATE.

Barium Croconate BaC_5O_5 is almost insoluble in water or dilute acids. We thought that by varying the conditions of the precipitation of the salt, that we might find some conditions under which it would be insoluble. The work, however, was not carried far enough to determine this.

The method used was as follows: A standard solution of Barium Chloride was made and 5 c.c. of this was precipitated by the croconic acid solution. It was then filtered and the precipitate washed free from croconate. This precipitate of barium croconate was then dissolved in sulphuric acid and the liberated croconic acid was titrated with a standard potassium permanganate solution:

The reactions involved are:



The standardization of the $BaCl_2$ solution is given below. Five c.c. of the $BaCl_2$ solution was taken and precipitated with sulphuric acid. The solution was heated on the water bath for one-half hour and then filtered, the Barium being determined gravimetrically.

Sample #1		Sample #2
5 c.c.BaCl ₂ solution taken		5 c.c.
Precipitated with H ₂ SO ₄ .		
6.8045 gms. Wt. Crucible plus BaSO ₄		7.6468 gms.
<u>6.7550</u> " Wt. Crucible		<u>7.5977</u>
.0495 " Wt. BaSO ₄		.0491 gms.
.02912 " " Barium		.02891 "
.04415 " " Barium Chloride		.04385 "

8.8 gms. Barium Chloride per liter.

The permanganate solution for the first six titrations was .12865 Normal. That used for the other determinations was .1288 Normal.

To get some idea of the strength of the croconate solutions and as to the constancy of the reaction between the croconate and the permanganate, a number of titrations were made. A little sulphuric acid was added to 5 c.c. of the croconate solution and titrated with permanganate.

First Croconic Acid Solution.

c.c. K ₂ C ₅ O ₅		c.c. KMnO ₄
5.00	6.60
5.00	6.60
5.00	6.60

Second Croconic Acid Solution.

c.c. $K_2C_5O_5$		c.c. $KMnO_4$
5.00	4.40
5.00	4.40
5.00	4.45
5.00	4.45
5.00	4.40
5.00	4.40
5.00	4.40
5.00	4.40

A number of 5 c.c. samples of the Barium Chloride solution were taken for analysis. The conditions of precipitation were varied as shown by the following table. At first the precipitate was washed with water but later it was found that the addition of a small amount of potassium chloride helped the filtration. It made the precipitate heavier and more colloidal. The precipitate of Barium Croconate when precipitated in a concentrated solution comes down as yellow crystals, but when precipitated in the presence of potassium chloride and more dilute solutions it comes down as a beautiful shiny yellow colloidal film. The first column in the table gives the amount of barium chloride solution taken for analysis, the second the amount of the potassium croconate used for precipitation, the third the special conditions of precipitation,

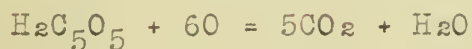
the fourth the amount of permanganate needed for the oxidation, and the last gives the error expressed in percent and in grams of Barium.

No.	cc. BaCl ₂	K ₂ C ₂ O ₅	Special Conditions	KMnO ₄	Theo- retical amt. KMnO ₄	% Error	gms. Ba.
1	5	30	Titrated immediately KCl wash water	18.25	19.71	7.41	.0020
2	5	30	Allowed to stand over night	19.75	"	0.20	.00005
3	5	25	Prec. as colloid by first dil. with water.	19.00	"	3.60	.0010
4	5	25	Same as above	19.00	"	3.60	.0010
5	5	25	Same as above	18.60	"	5.63	.00160
6	5	25	Same as above	18.20	"	7.71	.0022
7	5	25	Titrated immed. prec. as colloid.	15.00	19.68	23.7	.0069
8	5	25	Same	15.00	"	23.7	.0069
9	5	25	Precipitate Boiled for one hour.	16.05	"	18.5	.0054
10	5	25	Same	16.05	"	18.5	.0054
11	5	25	Allowed to stand 1/2 hour.	16.10	"	18.2	.0053
12	5	25	1/2 hour	15.85	"	18.8	.0055

No.	cc. BaCl ₂	K ₂ C ₅ O ₅	Special Conditions	KMnO ₄	Theo- retical amt. KMnO ₄	Error %	gms. Ba.
13	5	28	3 hours	16.90	19.68	14.1	.0041
14	5	28	3 hours	16.90	"	14.1	.0041
15	5	35	3 3/4 hrs.	17.25	"	12.3	.0037
16	5	38	4 hours	17.60	"	10.5	.0029
17	5	38	4 1/2 hrs.	17.75	"	9.7	.0028
18	5	38	24 hours	17.30	"	12.0	.0035
19	5	38	24 hours	17.30	"	12.0	.0035
20	5	38	24 hours	17.65	"	10.0	.0029
21	5	38	24 hours	17.40	"	11.5	.0033

CALCULATIONS

The method of the calculations in taken from the following equations:



It is seen from the above equations that for each molecule of Ba that is furnished, six molecules of Oxygen are needed and since the normality of the permanganate solution is given, we can from this determine the theoretical amount of the permanganate solution which should be needed to oxidize the croconic acid liberated by the barium croconate.

8.8 gms. BaCl₂ per liter = .0845 Normal

KMnO₄ = .12865 Normal

1 c.c. BaCl₂ = .657 c.c. KMnO₄ solution.

But since the BaCl₂ as Barium croconate requires six times this amount of oxygen

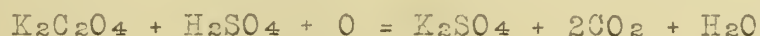
1 c.c. BaCl₂ = 6 x .657 c.c. = 3.942 c.c. KMnO₄ sol.

5 c.c. BaCl₂ = 19.71 c.c. KMnO₄ solution.
(For first six titrations)

5 c.c. BaCl₂ = 19.68 c.c. KMnO₄ solution.
(For last 15 titrations)

It is seen from the table that the results did not turn out very satisfactorily. The first six results were very much more accurate than the last ones. The reason for this we could not determine as the filtrate gave no test for barium with sulphuric acid. We suggest however that the croconic acid was not pure and some other compounds of sulphuric acid were precipitated which did not require as much of the permanganate for oxidation. The time of standing of the precipitate seems to be quite an important factor.

If this method had proved accurate it would have been very good as one could make a relatively large error in the titration without effecting the result much. The method is similar to the oxalate titration in the following equation:



but from the above equation it is seen that only one molecule of oxygen is necessary to oxidize the oxalate while in the croconate method, six molecules of oxygen are necessary.

Now if permanganate the same strength were to be used in the oxidation it would take just six times as much to oxidize the croconate, or in other words we could make an error six times as great without effecting the results anymore.

CONCLUSION.

On the whole this research did not prove very satisfactory. The preparation of the acid is very difficult. We tried several variations from that outlined by Nietzki and also tried the method which he describes in *Berichte*, Vol. 43, p. 3457 in which his main changes are to first freeze the mixture of acetic anhydride and hydroquinone and instead of the use of zinc chloride he uses a few drops of sulphuric acid. This frozen solid is then added to the nitric acid instead of adding the nitric acid to it. We however only succeeded in getting the acid once.

Even if the method had proven an accurate one for Barium it would not have been used owing to the prohibitive cost of the manufacture of the acid. The inorganic method might have been made more successful if an arrangement for dissolving the hexoxybenzene had been put into the apparatus.





