as catalytic agent is accompanied by a glow which is distinctly characteristic of these metals. Hence this glow may be used as a qualitative test for these metals.

2. This test is sensitive to extremely small quantities of the metals, the limits being: platinum, 0.002 mg.; palladium, 0.0005 mg.; rhodium, 0.0009 mg.; and iridium, 0.005 mg.

3. The presence of other substances does not for practical purposes interfere with this test. In fact, the test may be applied directly to a solution without preliminary treatment for the separation of other substances.

4. In an analysis where all the platinum metals are to be considered, this test may serve to show the presence of the platinum group with the exception of osmium and ruthenium, and also to confirm the presence of platinum, palladium, rhodium and iridium, when the metals have been separated. In most practical work, the "glow reaction" becomes distinctly a test for platinum, the most common metal of the group. For this latter purpose the glow test recommends itself strongly, because of its sensitiveness and the rapidity with which it gives results.

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[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY OF THE COLLEGE OF THE CITY OF NEW YORK.]

# A STUDY OF THE FACTORS INFLUENCING THE SYSTEMATIC QUALITATIVE DETERMINATION OF BARIUM.[1]

BY LOUIS J. CURTMAN AND EDWARD FRANKEL.

Received March 15, 1911.

Experience with qualitative unknowns has shown that by means of a systematic qualitative analysis it is almost impossible to detect as much as 25 and in many cases 50 milligrams of barium with the group reagent $(NH_4)_2CO_3$. The failure to obtain the test at this point is due to losses which are entailed throughout the analysis. These may be accounted for under the following heads:

1. Influence of the hydrogen sulfide group;
2. Influence of the ammonium sulfide group;
3. Sensitiveness of the group and confirmatory reagent;
4. Influence of the presence of impurities (sulfates) in the various reagents employed.

1. *Hydrogen Sulfide Group.*—To determin the losses involved in the precipitation and removal of the metals of the copper group by hydrogen sulfide, a typical metal such as copper was taken. This metal furthermore possesses the advantages that its sulfide offers no difficulty in filtering and

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[1] Read at the March meeting of the New York Section of the American Chemical Society.

washing. The procedure employed to determin whether or not there is a loss involved in this part of the analysis was as follows:

A solution was prepared containing 100 mg. copper as copper nitrate,[1] and a definit quantity of barium as barium chloride accurately delivered from a buret. To this was added 2.5 cc. of hydrochloric acid (sp. gr. 1.2) and the bulk then made up to 100 cc. The solution was then heated over a low flame to about 70° and treated with a rapid stream of hydrogen sulfide until precipitation was complete. The precipitate was allowed to settle and the clear supernatant liquid filtered off. The precipitate was washed three times by decantation with water containing hydrogen sulfide, and finally on the filter until free of chlorides. The filtrate and washings were caught in a 500 cc. Erlenmeyer flask, boiled to expel the hydrogen sulfide[2] and then allowed to stand over night. An examination of the filtrate the next day showed the presence of a white finely divided precipitate which had settled to the bottom of the flask. This was then filtered off on ashless paper and the barium in the clear filtrate determined as barium sulfate. The following results were obtained:

TABLE I.—100 MG. Cu, 2.5 CC. HCl (SP. GR. 1.2) VOL. 100 CC.

| Ba taken. Mg. | Ba recovered. Mg. | Ba lost. Mg. |
|---|---|---|
| 128.7 | 127.5 | 1.2 |
| 128.7 | 126.9 | 1.8 |
| 128.7 | 127.6 | 1.1 |
| 100.0 | 98.5 | 1.5 |
| 100.0 | 98.2 | 1.8 |
| 100.0 | 98.8 | 1.2 |
| | Average loss, | 1.4 |

The presence of oxidizing agents in the solution subjected to treatment with hydrogen sulfide for the removal of the copper and tin groups will have the effect of oxidizing the hydrogen sulfide with the formation of a little sulfuric acid and a large separation of sulfur. The most common of these substances are nitric acid, permanganates, dichromates and ferric chloride. The first three of these readily reveal their presence and should be eliminated before precipitation with hydrogen sulfide. The presence of ferric chloride in appreciable amounts cannot be detected by inspection, because of the obscuring influence of other colored substances. For this reason and because its removal at this point cannot be conveniently accomplished it is generally left in solution. To determin its effect[3] in the second group precipitation a solution containing 100 mg.

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[1] All materials used in this work were tested and found free from sulfates.

[2] A blank run to determin whether this operation involved a mechanical loss gave good results, showing the procedure to be entirely satisfactory.

[3] Noyes and Bray, THIS JOURNAL, 29, 191, call attention to the fact that the presence of 500 mg. of iron as $FeCl_3$ will have the effect of precipitating as much as 20 mg.

copper as copper nitrate, 100 mg. $Fe'''$ as ferric chloride, an accurately measured amount of barium as barium chloride and 2.5 cc. hydrochloric acid (1.2) in 100 cc. were warmed to 70° and the copper sulfide precipitated as before. The filtrate and washings from this precipitation were caught in a flask and boiled to expel the hydrogen sulfide. On standing over night a white residue settled out and was filtered off. The clear filtrates were then oxidized by boiling with 1-2 cc. of conc. nitric acid and the iron precipitated with ammonia as ferric hydroxide. The latter was filtered off and washed free of chlorides. The barium in the clear filtrate was then determined as barium sulfate.

In this procedure there are two losses to be considered: (1) The loss due to the reduction of the ferric chloride by hydrogen sulfide; and (2) the loss involved in the precipitation of the ferric hydroxide by ammonia. The latter factor will be discussed under the influences of the precipitation of the third group. The loss due to the oxidizing effect of ferric chloride on the hydrogen sulfide will be represented by the difference between the total loss sustained and those due to influences other than that of ferric chloride.

The results obtained were:

TABLE II.—100 MG. Cu, 100 MG. $Fe'''$, 2.5 cc. HCl (1.2), VOL. 100 CC.

| Ba taken. Mg. | Ba recovered. Mg. | Ba lost. Mg. | Ba lost, due to $Fe(OH)_3$ pptn. See Table IV. (Av). Mg. | Ba lost, due to $FeCl_3$. Mg. |
|---|---|---|---|---|
| 100 | 70.9 | 29.1 | 14.7 | 14.4 |
| 100 | 72.3 | 27.7 | 14.7 | 13.0 |
| 100 | 72.5 | 27.5 | 14.7 | 12.8 |
| 100 | 69.4 | 30.6 | 14.7 | 15.9 |
| | | | Average loss, | 14.0 |

If instead of Cu, whose sulfide behaves well, $Sn^{iv}$ or Cd were selected as the second group metal, it might be expected that large losses would be found, because of the well known tendency of the sulfides of these metals to pass through the filter in the colloidal state. With $Sn^{iv}$ this difficulty was surmounted by the use of a double filter,[1] a clear filtrate being readily obtained in one filtration even from a cold solution.

In the case of cadmium sulfide, however, difficulties in filtration were encountered, for even with a double filter the precipitate ran through and a clear filtrate could only be obtained by repeated filtration through the same filter. The precipitate, however, on washing, did not tend to go

of barium as sulfate in the second group precipitation with $H_2S$. As their procedure, which was somewhat different from ours, was not carried out on a strictly quantitative basis, it was thought desirable to proceed with the above work in order to obtain results which would be comparable with others obtained under parallel conditions.

[1] Schleicher and Schull, No. 595, 12½ cm.

through in a colloidal condition as is the case with zinc sulfide. After a number of preliminary trials the following procedure was adopted: A solution containing 100 mg. cadmium as cadmium nitrate, a definit amount of barium chloride and 2.5 cc. hydrochloric acid (sp. gr. 1.2) in 100 cc. was prepared. The solution was treated in the cold[1] with a rapid stream of hydrogen sulfide until precipitation was complete. The precipitate was then filtered through a double filter and the filtrate, which was cloudy, refiltered through the same filter, the funnels being covered during filtration to prevent oxidation. After two refiltrations a clear filtrate was obtained. The precipitate was then washed on the filter with a 5 per cent. solution of ammonium nitrate containing hydrogen sulfide. The filtrate and washings were caught in a 500 cc. Erlenmeyer flask, boiled to expel the hydrogen sulfide and allowed to stand over night. Contrary to expectations, no white residue settled out as in the case of copper. The clear liquid was then transferred to a beaker and the barium determined as barium sulfate.

TABLE III.—100 MG. Cd, 2.5 CC. HCl (SP. GR. 1.2), VOL. 100 CC.

| Ba taken. Mg. | Ba recovered. Mg. | Ba lost. Mg. |
|---|---|---|
| 100 | 100.1 | —0.1 |
| 100 | 99.3 | +0.7 |
| 100 | 100.0 | +0.0 |
| 100 | 100.5 | —0.5 |
| 100 | 100.5 | —0.5 |

The results obtained indicate that the losses entailed in this procedure are practically negligible.

Failure to obtain a loss with cadmium would seem to indicate that this was partly due to the fact that the beakers and funnels were covered as much as possible during the process of filtration, which was not the case with the experiments on copper. To test this point, a number of copper determinations were run under the same conditions as before except that care was taken to keep the beakers and funnels covered as much as possible in the course of filtration. The results, however, were substantially the same and the losses no lower than those already recorded. This would seem to indicate that the rate of oxidation of cadmium sulfide is smaller than that of copper.

Work is now being done in this laboratory to determin the relative rates of oxidation of sulfides, the results of which will shortly be published.

2. *The Influence of the Ammonium Sulfide Group.*—The third analytical group was studied in a manner similar to that pursued in the investigation of the second group. Here the three influences deserving prime consideration are:

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[1] Noyes and Bray, THIS JOURNAL, 29, 168, state that Cd is completely precipitated by $H_2S$ only in the cold. Some experiments made by us confirm this statement.

1. Precipitation with $NH_4OH$.
2. Precipitation with $(NH_4)_2S$.
3. Precipitation and filtration of a colloidal sulfide as zinc sulfide.

*Influence of the Precipitation with Ammonium Hydroxide.*—It is considered desirable by some chemists in the absence of phosphates,[1] etc., to precipitate the trivalent metals of the third group with ammonia rather than separate them together with the divalent elements of the third group with ammonium sulfide. Such a procedure involves losses of the alkaline earths, due to the absorption of carbon dioxide from the air by the alkaline liquid, resulting in the partial precipitation of the carbonates of the alkaline earths with the metals of this group. To determin exactly the extent of this loss, a solution, containing definit amounts of ferric chloride and barium chloride, was made up to 100 cc., boiled and treated with an excess of ammonium hydroxide and boiled. The precipitated ferric hydroxide was filtered off and washed free of chlorides, the operation taking about 40 minutes. The clear filtrates were then analyzed for barium. Contrary to expectations the loss in this operation was far greater than one might think. The results of a number of determinations made to determin this loss are:

TABLE IV.—100 MG. $Fe'''$, 2.5 CC. HCl (1.2), VOL. 100 CC.

| Ba taken. Mg. | Ba recovered. Mg. | Ba lost. Mg. |
|---|---|---|
| 100 | 84.9 | 15.1 |
| 100 | 85.5 | 14.5 |
| 100 | 84.5 | 15.5 |
| 100 | 86.2 | 13.8 |
| | Average loss, | 14.7 |

*Influence of the Precipitation with $(NH_4)_2S$.*—In the precipitation of the metals of the ammonium sulfide group losses were expected, resulting from two distinct causes, *viz.:*

1. The absorption of carbon dioxide by the alkaline liquid.
2. The oxidation of the precipitated sulfide.

To minimize the effect of the first cause the solution was kept acid until the moment of precipitation. To determin the loss due to the second cause, the metal cobalt was chosen as a typical metal of this group, because it involves no complications in precipitation and filtration. The combined effect of the precipitation of copper and cobalt was determined in the following manner:

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[1] That the presence of phosphates and oxalates may cause the alkaline earth metals to precipitate in the ammonium sulfide group is well known; but as this difficulty is successfully overcome by the use of a modified scheme, it was thought undesirable to consider this factor, particularly in view of the recent work of Noyes, Bray and Spear (THIS JOURNAL, **30,** 485, 498, 518), which provides an adequate procedure for the treatment of such cases.

A solution containing 100 mg. copper as copper nitrate, 100 mg. cobalt as cobalt nitrate, a definit amount of barium chloride and 2.5 cc. hydrochloric acid (1.2) in 100 .cc. was prepared. It was warmed to about 70°, and the copper precipitated by hydrogen sulfide. The precipitate was filtered and washed as in the previous case and the filtrate boiled to expel the hydrogen sulfide. On standing over night there invariably settled out of the filtrate a white residue which was filtered off. The clear filtrate was warmed, made alkaline with ammonia and immediately treated with hydrogen sulfide. The precipitated cobalt sulfide was filtered off and washed, first by decantation with water containing ammonium sulfide and then on the filter until free of chlorides. The combined filtrate and washings colored slightly yellow were caught in a Kjeldahl flask, acidified with hydrochloric acid and boiled to expel the hydrogen sulfide. As the bumping in this last operation was very violent, a Kjeldahl flask was used to prevent mechanical loss. The filtrates on acidification contained a large amount of finely divided sulfur which coagulated on boiling. The filtrate was allowed to stand over night, the residue filtered off and the barium in the clear filtrate determined as barium sulfate. The results obtained were:

TABLE V.—100 MG. Cu, 100 MG. Co, 2.5 CC. HCl (1.2), VOL. 100 CC.

| Ba taken. Mg. | Ba recovered. Mg. | Ba lost. Mg. | Loss due to CuS pptn. | Loss due to CoS pptn. |
|---|---|---|---|---|
| 100 | 96.2 | 3.8 | 1.4 | 2.4 |
| 100 | 96.6 | 3.4 | 1.4 | 2.0 |
| 100 | 96.6 | 3.4 | 1.4 | 2.0 |
| 100 | 96.1 | 3.9 | 1.4 | 2.5 |
| | | | Average loss, | 2.2 |

*Colloidal Sulfides.*—When nickel sulfide is precipitated by an excess of ammonium sulfide, some nickel sulfide is dissolved by the reagent to form a brown liquid, which passes through into the filtrate. In such a condition the oxidation of nickel sulfide to sulfate is probably rapid and would have the effect of throwing out some barium as barium sulfate. This difficulty may, however, be obviated by precipitating the nickel from a hot ammoniacal solution with hydrogen sulfide. This procedure was used by us successfully with solutions containing varying amounts of ammonia, the concentrated filtrates from the nickel sulfide in no case giving a test for nickel with dimethyl glyoxime, thus confirming the work of Noyes, Bray and Spear[1] on this point.

With zinc a different problem was encountered. Because of the well known tendency of zinc sulfide to pass through even a double filter, there is much trouble in obtaining a clear filtrate from the third group, if zinc is present. The presence of other sulfides tends to prevent the zinc sul-

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[1] THIS JOURNAL, 30, 536, 1908.

fides from passing through the filter, but when zinc is present alone, as frequently happens, the getting of a clear filtrate is a long and tedious process. We have found that the only method that can be applied successfully consists in repeated filtration through the same filter. It was expected that in such a procedure, requiring more than an hour to complete, the zinc sulfide would have an excellent chance to oxidize to zinc sulfate with the result that some barium would be precipitated as barium sulfate. To test this procedure, a solution containing 100 mg. zinc as zinc nitrate, a definit quantity of barium chloride and 4 grams of ammonium chloride in a bulk of 100 cc. was heated to about 90°, made alkaline with ammonia and treated with a rapid stream of hydrogen sulfide until precipitation was complete. The precipitate was allowed to settle, care being taken to keep the solution hot by wrapping the beaker in a towel. The supernatant liquid was poured off through a double filter and the precipitate washed several times by decantation with a hot solution containing 5 per cent. ammonium nitrate and 1 per cent. ammonium sulfide and then brought on the filter. The filtrate was cloudy. It was acidified, with a slight excess of acetic acid, boiled and at the same time treated with hydrogen sulfide to prevent any possible oxidation of the sulfide to sulfate. This process had the effect of coagulating the precipitate. The liquid was then filtered through the same filter. The filtrate after two such treatments with intermediate filtrations through the same filter having failed to yield a clear filtrate, the process was again repeated, a clear filtrate now being obtained, the last portions of which drained very slowly. During the process of filtration, occupying about two hours, the precipitate was protected as much as possible from the air by covering the funnel with a watch glass. The clear filtrate was caught in an Erlenmeyer flask, boiled to expel the hydrogen sulfide and allowed to stand over night. A slight white residue which settled out was filtered off and the barium in the clear filtrate determined as barium sulfate.

The filtrate from the barium sulfate was then evaporated to a small bulk and filtered. The filtrate was made alkaline with ammonia and tested for zinc with disodium phosphate. A faint cloudiness was obtained showing that a little zinc had passed into the filtrate. It was expected that such a lengthy procedure would involve a great loss, but the figures obtained show that it was surprisingly small. The results are:

TABLE VI.—100 MG. Zn, 4 G. $NH_4Cl$, VOL. 100.

| Ba taken. Mg. | Ba recovered. Mg. | Ba lost. Mg. |
|---|---|---|
| 100 | 97.8 | 2.2 |
| 100 | 96.7 | 3.3 |
| 100 | 97.1 | 2.9 |
| 100 | 97.2 | 2.8 |
| | | Average loss, 2.8 |

*3. Sensitiveness of the Group and Confirmatory Reagents.*—The failure to detect barium with ammonium carbonate may be accounted for by the fact that the solubility of barium carbonate is materially increased by the presence of ammonium salts. As these accumulate throughout the course of a systematic analysis, the test for barium in the fourth group becomes unreliable, especially for small amounts.

It may be readily seen how as much as ten grams of ammonium salts may accumulate, due to the following causes: To prevent the precipitation of 500 mg. of magnesium as magnesium hydroxide by ammonia, at least two grams of ammonium chloride must be present.[1] Ammonium salts, especially the nitrate, are added from time to time for the purpose of coagulating colloidal precipitates. The acidification of the filtrate from the third group and the subsequent neutralization give rise to still more ammonium salts. Extreme cases involving a basic acetate separation cause the amount of ammonium salts in the solution to be further increased. However, as the filtrate from the third group is generally concentrated to about 30 cc. before the alkaline earth carbonates are precipitated, the amount of ammonium salts held in solution tends to regulate itself, so that about ten grams remain.[2]

A number of experiments were made to determin the least amount of barium that could be detected under the conditions which prevail in a qualitative analysis. Solutions containing barium chloride and varying amounts of ammonium chloride in 30 cc. were heated in small (100 cc.) beakers to 60°[3] and treated with 5 cc. of reagent ammonium carbonate.[4] The solutions were then stirred vigorously and observed after two and five minutes. The results obtained were:

TABLE VII.—VOL. 30 CC., TEMP. 60° C., 5 CC. REAGENT $(NH_4)_2CO_3$.

| $NH_4Cl$ present Grams. | Least amount of Ba (mg.) detected within | |
|---|---|---|
| | 2 min. | 5 min. |
| 0 | 0.8 | 0.5 |
| 2 | 3 | 3 |
| 5 | 5 | 5 |
| 10 | 10 | 10 |

These results indicate the decided influence which varying amounts of ammonium chloride have on the precipitation of small quantities of barium. It must, however, be noted that by a procedure somewhat different from that in general use, the chief features of which are the use

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[1] Noyes, Bray and Spear, THIS JOURNAL, **30**, 533 (1908), and confirmed by us.

[2] The solubility of ammonium chloride in cold water is 33 parts in 100.

[3] Above 60° the reagent decomposes on addition to the hot liquid.

[4] Prepared by dissolving 200 grams of Merck's reagent ammonium carbonate in 200 cc. of ammonia (sp. gr. 0.9) and then diluting the whole with water to a liter. The quantity of reagent used was sufficient to precipitate over 1400 milligrams of barium.

of alcohol, and a large excess of ammonium carbonate which causes magnesium to be precipitated with the alkaline earths, Bray[1] has shown that a distinct test is obtained with 2 mg. Ba in less than five minutes.

A study of the potassium chromate test for barium was made under the conditions proposed by Bray[2] with the exception that the solutions were not filtered, but directly compared with a blank run under the same conditions. Our results showed that 0.4 mg. gave a distinct test while with smaller amounts no difference from the blank was noted.

4. *Influence of the Presence of Impurities in the Reagents Employed throughout the Analysis*.—The factor which perhaps deserves as much attention as the others is the presence of sulfates in the reagents. Many of the so-called "highest purity" reagents sold by prominent manufacturers often contains enough sulfates to make the test for barium in the fourth group a practical impossibility even though appreciable amounts of the element are present. The group reagent, ammonium carbonate, generally contains enough sulfates to cause the precipitate obtained with this reagent to be partially insoluble in acetic acid with the result that a negative test is obtained for barium with the confirmatory reagent, potassium chromate. This would account for the fact that even though an indication of the presence of the group is obtained, no test for its individual members can be gotten.

## Conclusion.

A consideration of the factors studied above shows that they are typical of the conditions prevailing in actual qualitative work. In order to get a definit idea of the extent of the losses entailed by these factors they were studied from a quantitative standpoint. However, as the na ure of the work in qualitative analysis is such that the chances for mechanical losses are many, we may confidently expect that the several losses enumerated above will be greatly magnified under ordinary qualitative laboratory conditions. To test this point a number of test analyses were run. The substances analyzed were all unknown mixtures containing varying amounts of barium together with other components in proper proportions. In no case was a significant amount of barium found with ammonium carbonate although as much as 50 milligrams of the element was present in a number of the samples analyzed. With some of the substances, tests with dilute sulfuric acid were obtained where the ammonium carbonate test failed. As this reagent is capable of detecting exceedingly small[3]

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[1] THIS JOURNAL, 31, 625.

[2] *Ibid.*, 31, 616 (1909).

[3] The smallest amount of barium that could be detected within 5 minutes was 0.02 mg. in the absence of ammonium salts and 0.05 mg. in a saturated solution of ammonium chloride. The tests were made on 5 cc. of solution to which 1 cc. 20 per cent. $H_2SO_4$ was added and the mixture boiled. The solutions were then compared with a blank run under the same conditions.

quantities of barium the test obtained can hardly be considered conclusive except for traces.

In the light of these facts it is clear that by means of a systematic qualitative analysis it is not possible to detect barium when it occurs to the extent of 5 per cent., if a gram sample be used. This fact has led us to the task of working out another method for the systematic detection of the alkaline earth metals, which will be reported in another communication.

## Summary.

It has been shown as a result of a quantitative study that in the ordinary systematic qualitative scheme the test for barium with ammonium carbonate is unreliable in consequence of losses which have been accounted for under the following heads:

1. Loss involved in the precipitation of a typical metal of the copper group, 1.4 mg. Ba.
2. Loss due to the action of ferric chloride on hydrogen sulfide, 14.0 mg. Ba.
3. Loss due to the absorption of carbon dioxide in the precipitation of the iron group with ammonia, 14.7 mg. Ba.
4. Loss involved in the precipitation of a typical metal of the ammonium sulfide group, 2.2 mg. Ba.
5. Loss involved in the precipitation and filtration of zinc sulfide, 2.8 mg. Ba.
6. Failure of the reagent ammonium carbonate to detect as much as 10 mg. barium in the presence of ammonium salts.
7. Presence of sulfates in the reagents employed.

These figures represent the minimum losses, but that they are larger in actual qualitative work is shown by the results of a number of test analyses which failed to disclose the presence of as much as 25 and in some cases 50 milligrams of barium.

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# METHYLENEDISALICYLIC ACID AND ITS REACTION WITH BROMINE AND IODINE.

BY ERIK CLEMMENSEN AND ARNOLD H. C. HEITMAN.

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This work was undertaken to study the interaction between methylenedisalicylic acid and iodine, and as the results were of a complicated and unexpected nature, we also included the action of bromine to see if similar or more normal conditions would prevail.

Methylenedisalicylic acid was first prepared by Geigy,[1] who obtained it by heating a mixture of salicylic acid and formaldehyde solutions with strong hydrochloric acid.

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[1] D. R. P. 49970.