THE SEPARATION OF ALUMINUM FROM IRON BY MEANS OF ETHER

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Various methods¹ for the separation of aluminum from iron have been proposed. None of these, however, have found extensive use in analysis. As the method of separation herein proposed is based on the use of organic solvents, only such processes as have a direct bearing on this method will be discussed in this paper.

It had been noted by Gladysz² that hydrous aluminum chloride was very slightly soluble in strong hydrochloric acid, while ferric chloride was readily soluble in that medium.

Gooch and Havens³ utilized the observation of Gladysz, but introduced the use of ether to reduce the solubility of aluminum chloride. They precipitated this salt from a mixture of equal parts of concentrated hydrochloric acid and ether saturated with hydrochloric acid gas at 15° C.

It appears that the method of Gooch and Havens is the only one on record which utilizes any organic solvent (one-half aqueous hydrochloric acid and one-half ether).

Frankforter⁴ in studying the action of aluminum chloride on aliphatic ethers found that the presence of moisture caused precipitation of a compound of this salt with water and hydrochloric acid from an ether solution of the anhydrous aluminum chloride. This precipitate, however, was not constant in composition. He utilized this reaction as a qualitative test for water in ether.

The method proposed in this paper, like the Gooch and Havens method, depends on the insolubility of hydrated aluminum chloride in solvents as contrasted with that of iron, but may be more closely compared with the qualitative observation of Frankforter, as it neither uses a mixture of water and ether, nor requires saturation of the medium with hydrochloric acid gas. It is primarily the latter feature in the Gooch and Havens method which is troublesome and objectionable for ordinary laboratory procedure, as in each determination, hydrochloric acid gas must be passed through the solution at low temperature (15° C.) to saturation (a point rather difficult to determine with certainty) and the precipitate washed with ether-water mixture, itself saturated with HCl gas. In the proposed method, the medium is entirely organic solvent, except for traces of moisture introduced by the solvents.

The essentials of the method are as follows:

The dried mixed chlorides of aluminum and iron are taken up in a small amount of hydrochloric acid alcohol solution and evaporated to crystallization of the salts. The residue is then again acidified with alcoholic HCl. Ether (U. S. P.), which contains a trace of water, is gradually added, and the aluminum

is precipitated as a hydrated chloride, varying in composition, while the iron chloride remains in solution.

EXPERIMENTAL

EFFECT OF MOISTURE—It was observed in preliminary experiments that anhydrous aluminum chloride was readily soluble in absolute alcohol and absolute ether, but that the presence of a trace of moisture, introduced as such or by means of wet alcohol or wet ether, caused an immediate precipitate. An excessive amount of moisture, however, invariably caused the formation of a second layer of a viscous gelatinous mass. It was necessary, therefore, to determine the limits of water tolerance and the best means of introducing that water.

A series of experiments was performed in which water was introduced in varying amounts using, at first, strong aqueous HCl, as that acid was found necessary to keep the iron in solution. This manner of introducing the water was found impracticable as the amounts of HCl necessary caused, in many cases, an excessive amount of water to be introduced. An alcoholic solution of HCl was, therefore, prepared and water was introduced by means of the ether used. The following facts were observed:

1—When an insufficient amount of water was present as obtained by dissolving the salt in a small quantity of alcohol and using largely absolute ether, the precipitate came down in an exceedingly finely divided condition, colloidal or semi-colloidal, practically impossible of filtration. When filtered, the precipitate was exceedingly hygroscopic, behaving somewhat like finely powdered (dried) calcium chloride: the physical state of the precipitate was such that a clean separation from the iron would be impossible even if the precipitation were complete. It was, in fact, found that up to an alcoholic content of about 4 per cent, the precipitation was complete, when the suspension was filtered several times.

2—When an excessive amount of water was present, which depended on the amount of salt present to take care of it and the amount of water introduced with the ether, it was found that a gelatinous layer of the salt was formed.

EFFECT OF ALCOHOL—An excessive amount of alcohol had a tendency similar to that observed in the case of insufficient water, namely, to precipitate the aluminum chloride in a very finely divided state. In addition, the precipitation is incomplete when alcohol is present beyond certain limits, depending upon the amount of water present.

EFFECT OF HYDROCHLORIC ACID—This reagent was introduced in the form of the alcoholic solution. Aside from the fact that HCl was required to keep the iron in solution, it was found that a slight acidity was essential for two reasons: (1) to make the precipitation complete, (2) so to modify the physical state of the precipitate as to render it easy to filter. On the other hand, excessive amounts of acid seemed to tend toward formation of gelatinous salt layer as in the case of excessive water.

¹ W. W. Scott, "Standard Methods of Chemical Analysis," 1917, pp. 4-5.

² *Ber.*, 16 (1883), 447.

³ *Am. J. Sci.*, [4] 11 (1896), 416.

⁴ *J. Am. Chem. Soc.*, 37 (1915), 2560-7.

A large number of experiments were performed to observe the effect of these various factors. Table I contains a few which show in a quantitative way the results obtained.

TABLE I—PRECIPITATION OF ALUMINUM CHLORIDE FROM MIXTURES OF VARYING PROPORTION OF ALCOHOL, HCl, ETHER (U. S. P.) AND ABSOLUTE ETHER, AND IN THE PRESENCE OF FERRIC CHLORIDE

No.	Mg. USED AlCl ₃	Absolute Alcohol Cc.	Alcoholic HCl 35%	Ether U. S. P. Cc.	Ether Absolute Cc.	Condition of Filtrate	Residues as Al ₂ O ₃ Mg.
1	100	2	2 drops	50	..	Clear	0.2
2	100	2	2 drops	50	..	Clear	0.2
3	100	1.5	0.5 cc.	50	..	Clear	0.1
4	100	1	1 cc.	50	..	Clear	0.0
5	50	2	2 drops	50	..	Clear	0.1
6	50	1.5	0.5 cc.	50	..	Clear	0.1
7	10	1.5	0.5 cc.	25	25	Clear	0.3
8	500	2.5	2.5 cc.	250	..	Clear	0.3
9	10	1.5	0.5 cc.	25	25	Clear	0.2
10	500	1.5(a)	0.5 cc.	40	40	Clear	0.2(b)
11	500	1.5(a)	0.5 cc.	40	40	Clear	..
12	10	500	1 cc.	50	..	Clear	..
13	10	90	1 cc.	50	..	Clear	..
14	10	50	1 cc.	50	..	Clear	..

(a) Approximate. (b) Total residue on bath.

As indicated in the outline of the method given above, the chlorides of aluminum and iron, after driving off nearly all of the moisture in an oven, are taken up in alcoholic HCl and absolute alcohol, evaporated to a viscous semi-crystalline mass and then definite amounts of HCl, alcohol and ether are added. It was deemed advisable to see how much, approximately, HCl and alcohol remained after evaporating to a viscous mass. An experiment was performed using 0.5 g. anhydrous aluminum chloride (the maximum amount of combined salts permitted in the proposed method) adding absolute alcohol and HCl-alcohol, heating until salts completely dissolved and evaporating to viscous mass. The total was weighed before and after, and the difference found to be about 0.62 g., that is, both HCl and alcohol. In the actual method, 0.5 cc. alcoholic HCl is then added. The total volume could not exceed 1.5 cc. in that case (to which is then added the requisite quantities of ether). It is evident, as illustrated in Table I, that the amount of aluminum chloride remaining in solution is practically negligible. This fact is borne out by later experiments on actual separation of known quantities of the salts as shown in Table II.

TABLE II—RESULTS OBTAINED BY APPLICATION OF PROPOSED METHOD

No.	AlCl ₃ used Cc. solution	Amount FeCl ₃ used	GRAMS Al ₂ O ₃ Found Calculated	GRAMS Fe ₂ O ₃ Found Calculated
1....	50 A	20 mgs.	0.2068 0.2069	
2....	5 A	700 mgs.	0.0204 0.0207	
3....	25 A	350 mgs.	0.1036 0.1035	
4....	5 A	700 mgs.	0.0207 0.0207	
5....	25 A-A	300 mgs.	0.1007 0.1004	
6....	50 A-A	10 mgs.	0.2004 0.2007	
7....	5 A	50 cc. I	0.0212 0.0207	0.2029 0.2035
8....	25 A	25 cc. I	0.1041 0.1035	0.1014 0.1017
9....	50 A	5 cc. I	0.2070 0.2069	0.0208 0.0204
10....	2 A	Spilled I	0.0085 0.0083	
11....	50 A	2 cc. I	0.2071 0.2069	0.0081 0.0082
12....	50 B	10 cc. II	0.1995 0.2001	0.0478 0.0482
13....	25 B	25 cc. II	0.0999 0.1001	0.1201 0.1203
14....	25 B	2 cc. II	0.1001 0.1001	Spilled
15....	25 B	25 cc. II	0.1004 0.1001	0.1201 0.1205
16....	25 C	25 cc. III	0.1026 0.1027	0.1224 0.1227
17....	25 C	25 cc. III	0.1027 0.1027	Spilled 0.1227
18....	25 C	25 cc. III	0.1030 0.1027	0.1226 0.1227
19....	25 C	25 cc. IV	0.1029 0.1027	0.1250 0.1251
20....	2 C	25 cc. IV	0.0084 0.0082	0.0101 0.0098
21....	2 C	2 cc. IV	0.0086 0.0082	0.2501 0.2552
22....	50 D ₂	2 cc. IV	0.2010 0.2008	0.0100
23....	50 D ₂	2 cc. IV	0.2008 0.2008	0.0102 0.0100
24....	50 D ₂	2 cc. IV	0.2009 1.2008	0.0102 0.0100

In the experiments for the quantitative separation of aluminum from iron, alcoholic solutions were made up of C. P. (Kahlbaum's) aluminum chloride and C. P. ferric chloride, respectively, in which 50 cc. were ap-

proximately equivalent to 0.5 g. of salt. Aliquots were pipetted at definite temperature both for determination of metal content of solution (blank) and for actual separation by the proposed method.

In the determination of iron, subsequent to the separation from aluminum by the proposed method, experiment has shown that the iron residue offers considerable difficulty of oxidation even with nitric and sulfuric acids, due to the formation of resinous condensation products of which the organic solvent is the source. Precipitation of the hydroxide is therefore not recommended. A satisfactory procedure was found in conversion of the iron chloride to sulfate and direct ignition.

The method was submitted to Messrs. C. D. Wright, H. E. Buckbinder, E. K. Nelson and W. F. Kunke, of the Bureau of Chemistry, for coöperation. Residues of mixtures of iron and aluminum chloride obtained by evaporation of definite volumes of solution were submitted to each individual. The results obtained appear in Table III.

TABLE III—COÖPERATIVE RESULTS BY BUREAU OF CHEMISTRY WORKERS

ANALYST	SOLUTION TAKEN		Grams		Grams	
	AlCl ₃ Cc.	FeCl ₃ Cc.	Found	Calc.	Found	Calc.
C. D. Wright.....	2 B	25 II	0.0078	0.0080		0.2411
	25 B	25 II	0.1007	0.1001		0.1205
	50 B	25 II	0.1998	0.2001		0.0098
H. E. Buckbinder....	25 C	25 III	0.1031	0.1027	0.1229	0.1227
E. K. Nelson.....	25 D	25 IV	0.1009	0.1014	0.1251	0.1251
W. F. Kunke.....	25 C	25 IV	0.1023	0.1027	0.1246	0.1251

PROPOSED METHOD

The chlorides of iron and aluminum (not over 0.5 g. total) are evaporated to dryness on the steam bath in a 150 cc. Erlenmeyer flask (preferably lipped). The residue is stirred occasionally with a glass rod to allow better exposure of the salts to drying. The rod is allowed to remain in the flask. The residue is then further dried in an oven at about 120° C. for one-half hour, stirring occasionally as before. When dry, the residue is moistened with 0.5 cc. to 1 cc. absolute alcoholic HCl solution¹ (25 to 35 per cent HCl), warmed on the steam bath and stirred to convert any oxides that have been formed to chlorides; about 3 or 4 cc. absolute alcohol are added and the flask is heated on the steam bath until all salts have gone into solution.²

When this has been accomplished the flask is allowed to remain on the steam bath until salts begin to crystallize out and the resulting residue is quite viscous but not solid. About 0.5 cc. alcoholic hydrochloric acid is now added, the flask again warmed and the residue stirred to have the mass uniformly impregnated with the HCl. The flask is then removed and 30 cc. U. S. P. ether (sp. gr. 713 to 716 at 25° C.) are added gradually with stirring. The hydrated aluminum chloride should come down as a uniform, granular, white precipitate, leaving the supernatant liquid clear. Forty cc. absolute ether are then added,

¹ The alcoholic HCl is prepared by passing HCl gas through absolute alcohol, the gas being conveniently generated by the action of concentrated H₂SO₄ on anhydrous calcium chloride.

² When AlCl₃ is present to the extent of nearly 1/4 g., and very little iron is present, it is sometimes very difficult to get all salts in solution. With small amounts of iron present the last traces of AlCl₃ need not pass into solution.

with stirring, and the flask allowed to stand. The solution, when the precipitate has settled, is filtered through a Gooch crucible, using a bell jar arrangement, into a 250 to 300 cc. Erlenmeyer flask. The crucible is fitted preferably with a small circular filter paper (cut to size) instead of asbestos. The flask should be washed with wash-ether (100 parts absolute ether and 2 parts alcoholic HCl) while filtering so as not to allow any ferric chloride to dry on the white precipitate or on the crucible. The usual precautions of washing the flask, crucible and funnel are taken to insure complete transfer of iron. It is not necessary, however, to transfer all of the aluminum chloride precipitate to the Gooch crucible. The aluminum precipitate is removed with the paper from the crucible by tapping it into a 25 cc. beaker and then washing with water to remove adhering particles. The original flask is also washed to transfer completely any adhering aluminum precipitate. The aluminum chloride solution is diluted to approximately 100 cc., about 5 g. ammonium nitrate are dissolved in it, and made just alkaline¹ with ammonia (using methyl red as indicator, preferably), boiled, filtered and the precipitate is washed in the usual way. The precipitate is ignited in a covered crucible² and weighed as Al_2O_3 . The ether solution of iron is distilled or evaporated to remove the ether. The residue is transferred with a little water and HCl to a weighed platinum dish, using as little water as possible, and evaporated to dryness on the steam bath, moistened with 1 cc. concentrated H_2SO_4 , warmed on the steam bath gently to expel most of the HCl, and then slowly over a flame by placing the dish on a triangle which in turn is put on an asbestos gauze (to prevent too rapid heating), and heated until all the ferric chloride is converted to sulfate and no further fuming of sulfuric acid takes place. The dish is then heated over a free flame and finally over a blast to entirely convert the sulfate to ferric oxide. This is then cooled and weighed as oxide in the usual manner.

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A METHOD FOR THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF ANILINE

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In the sanitary examination of air in industrial establishments where aniline is employed, the detection and estimation of aniline vapors is quite important. A method for this purpose has been worked out by Hebert and Heim.³ According to these authors, the aniline vapors are collected by bubbling 10 liters of the air through a suitable absorption bulb containing 10 cc. of water acidified with sulfuric acid. For

¹ W. Blum, "Determination of Aluminum as Oxide," Scientific Papers of the Bureau of Standards No. 286.

² The difficulties involved in the accurate determination of alumina are not generally known and the reader is referred to the exhaustive work by Doctor Blum on this subject.

³ *Res. chim. ind.*, 21, 338-340; from *Chem. Abs.*, 5 (1911), 791.

ascertaining the presence of aniline, the calcium hypochlorite test is employed. The quantitative determination is carried out by precipitating the aniline as tribromoaniline with bromine water. The precipitate is caught on a tared filter paper, dried *in vacuo*, and weighed.

In this connection, it occurred to the writer that it might be possible to work out, for estimating the aniline, a colorimetric method based on the qualitative test with hypochlorite. If this were possible, it certainly would be desirable, for not only would considerable time and effort be saved but probably a considerably smaller sample than 10 liters would be sufficient and quantitative measurements could also be applied in cases where the amount of aniline in the samples available, or that can be conveniently collected, is too small for the gravimetric determination. A detailed study of the hypochlorite test for aniline was therefore undertaken.

THE HYPOCHLORITE TEST FOR ANILINE

The hypochlorite test for aniline is described by various authors in rather indefinite language. Thus Blyth¹ in describing this test simply states that an aqueous solution of aniline or its salts is colored blue by "a little" chloride of lime or hypochlorite of soda. Heffter,² although stating that an excess of the reagent should be avoided, does not give any information as to the proper strength of the hypochlorite solution or what amount of it to use for a given volume of the solution to be tested. All the information given is contained in the statement that on adding to the aqueous solution of aniline, chloride of lime or sodium hypochlorite solution, a purplish violet coloration appears which later changes to a dirty red. That the proportion of hypochlorite to aniline and the degree of their concentration are, however, important factors and hence should be taken into consideration in applying this test, appears conclusively proven by the following results:

EFFECT OF VARYING THE PROPORTION OF HYPOCHLORITE

That the proportion of hypochlorite used for a given amount of aniline is an important factor in the test, even when the concentration of the aniline remains the same, and that in certain cases it may even cause a change in the result from negative to positive, is shown by the results obtained in the following experiment. To each of two small tubes there was added 0.5 cc. of a 0.02 per cent aqueous solution of aniline. No. 1 was then mixed with 0.5 cc. of a calcium hypochlorite solution, the available chlorine of which was about 1 per cent; No. 2 was similarly treated with 0.5 cc. of a calcium hypochlorite solution, the available chlorine of which was only about 0.1 per cent. Immediately after mixing, No. 1 developed the characteristic purplish color but No. 2 appeared³ practically colorless.

¹ "Poisons: Their Effects and Detection," 4th Ed., p. 285.

² Neuberger, "Der Harn," 1 (1911), 831.

³ On standing a little while, however, a slight yellowish color developed.