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ANALYTICAL SECTION

ANALYSIS OF IRON IN THORIUM, BERYLLIUM, AND CERIUM

PROBLEM ASSIGNMENT #117

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Introduction

The colorimetric determination of iron based on the formation of the colored ferrous-1,10-phenanthroline complex has been used successfully by a number of investigators[1,2,3]. In this report, its adaptation to the routine determination of iron in cerium, thorium and beryllium metals and their compounds is described.

In the preparation of samples for the determination of iron in cerium and thorium, the use of citric acid as a complexing agent makes it possible to raise the pH of cerium and thorium solutions as high as is necessary for the complete development of the ferrous-1,10-phenanthroline color without having their hydroxides precipitate. Previously, thorium solutions were treated with ammonium acetate and the pH raised with ammonium hydroxide. This method, which was developed by Feibig[4] was limited to thorium concentrations of 0.5 g per 100 ml or less, making it difficult to determine iron in amounts of less than 20 ppm. Using citric acid, the thorium concentration can be as high as 5 g per 100 ml, making it possible to determine iron down to 1 ppm.

According to Fortune and Mellon[1], the presence of fluoride ion in amounts of 500 ppm interferes with the determination to the extent of 1.6 per cent of the iron present. This error has been eliminated in the case of beryllium fluoride, by the addition of boric acid to the acid solution, thereby removing the fluoride ion according to the following equation:

$$2BeF_2 + H_3BO_3 + 4HCl \longrightarrow 2BeCl_2 + HBF_4 + 3H_2O.$$

Apparatus and Reagents

All readings were made with 1-cm cuvettes in a Coleman Universal Spectrophotometer, Model #11, set at 515 mμ.

10% solution of hydroxylamine hydrochloride.

0.1% solution of 1,10-phenanthroline.

Iron standard solution made up from standard iron wire dissolved in hydrochloric acid and diluted until 1 ml contained 0.01 mg iron.

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Thorium nitrate solution made from reagent grade thorium nitrate and containing 0.5 g thorium per ml.

Cerous chloride solution, made by dissolving cerium metal[6] in hydrochloric acid, oxidizing the iron to ferric chloride with a few drops of nitric acid, and removing the iron by ether extraction. The solution contained 0.19 g cerium per ml.

Beryllium fluoride manufactured by Brush Beryllium Company, Cleveland, Ohio.

Boric acid, reagent grade.

Experimental – Thorium

The thorium test solutions were made up in the following manner: A measured amount of iron was pipetted into a 100-ml flask; a known amount of thorium was added followed by enough citric acid to complex it; one ml of hydroxylamine hydrochloride was then added to reduce the ferric to ferrous iron; an excess of 1,10-phenanthroline was added, 10 ml of 0.1 per cent solution being excess for quantities of iron up to one mg. The resulting solution was diluted to about 75 ml. Fifteen normal ammonium hydroxide was then added dropwise with vigorous shaking until the pH was between 4 and 6 as indicated by pH indicator paper, and finally the solution was made up to 100 ml.

It was found that 0.5 g of citric acid for every gram of thorium is sufficient to complex the thorium so that the pH may be raised to as high as ten without precipitating thorium hydroxide. Two curves were made, plotting log transmission against iron concentration. The first curve was made using solutions containing five grams of thorium per 100 ml. Both of these curves followed Beer's Law and were identical, within experimental error, to the standardization curve made using iron solutions containing no thorium. The data are shown in Table 1; the standardization curve was made from the data in the first two columns, while the "Fe Found" columns were made using the transmission obtained and taking the iron concentrations from the standardization curve. All solutions were allowed to stand one hour before measuring the transmission, as the color develops slowly in the presence of citric acid.

TABLE 1

DETERMINATION OF IRON IN THORIUM

Fe Taken, mg/100 ml	Th-Free Solution % Trans.	2 g Th per 100 ml			5 g Th per 100 ml		
		% Trans.	Fe Found mg	Deviation mg	% Trans.	Fe Found mg	Deviation mg
0.00	100	100	0.00	0.000	100		0.000
.01	97.2	97.4	.009	-.001			
.02	93.3	93.5	.020	.000			
.04	87.7	87.7	.040	.000	87.5	0.040	.000
.06	81.9	81.7	.059	-.001			
.08	75.5	76.0	.080	.000			
.10	71.2	71.C	.100	.000	71.5	.098	-.002
.12	65.7	67.0	.117	-.003			
.14	61.6	61.9	.140	.000	61.6	.141	+.001
.16	57.4	58.2	.159	-.001			
.18	53.7	54.5	.176	-.004			
.20	51.5	50.8	.197	-.003	51.3	.194	-.006
.22		47.8	.220	.000			

The citric acid concentration is not critical except that the ratio of thorium to citric acid must not exceed 2:1. Large excesses of citric acid are permissible. High concentrations of chloride added as hydrochloric acid do not affect color development; however, the dissolving of samples in hydrochloric acid is inadvisable since upon heating ferric chloride may be lost. Perchlorate ion interferes slightly with the color reaction when present in amounts of 100 ppm, according to Fortune and Mellon[1], and this error mounts rapidly with increasing perchlorate ion concentration. Sulfate ion may be present in amounts up to 1 per cent but it inhibits color development so much that the solutions should stand overnight.

Recommended Procedure for Thorium

The weight of the metal sample taken should be consistent with the iron believed to be present. If the iron content is not known at all, a 5 g sample may be taken and if it gives less than 50 per cent transmittancy upon development of the ferrous-1,10-phenanthroline color, it can easily be diluted further. The weighed sample is heated with

100 ml nitric acid in a 400 ml beaker. When it boils, a pinch (5 mg)
of sodium fluosilicate is added to facilitate solution. When the solu-
tion is clear and is less than 15 ml in volume, it is transferred to a
100-ml volumetric flask and 1 g of citric acid added for each gram of
thorium. Then 1 ml of 10 per cent hydroxylamine hydrochloride and 10 ml
of 0.1 per cent 1,10-phenanthroline are added and the pH adjusted to
4-6 (pH indicator paper) by adding ammonium hydroxide dropwise with
vigorous shaking. If the solution contains a precipitate at a pH of 6,
more citric acid may be added and the pH readjusted. The solution is
now made up to 100 ml and allowed to stand for one hour. The transmit-
tancy is then measured at 515 mμ using distilled water for a reference
solution. From a previously prepared standardization curve, the iron
content of the solution is readily found.

This method may be used to determine iron not only in thorium metal
but also in the chloride, oxide and nitrate of thorium, since these
materials contain no ions which interfere with the full color development
of the ferrous-1,10-phenanthroline complex.

Experimental - Cerium

It was found that cerium could also be complexed with citric acid
to prevent its precipitation as a hydroxide at high pH. The full color
development of the ferrous-1,10-phenanthroline complex was found to re-
quire a pH range of 7.5 to 9. Within this range a cerous chloride solu-
tion of 0.5 g of cerium per 100 ml is usually colored a slight yellow by
impurities and has a transmittancy of about 98 per cent as compared to
pure water at 515 mμ. This fact requires the reference solution, in the
determination of iron in cerium, to have the same concentration of cerium
as the solutions being tested.

The cerium test solutions were made up in the following manner: A
measured amount of iron was pipetted into a 100-ml volumetric flask fol-
lowed by a known amount of cerium. Citric acid was added to complex the
cerium in the proportion of 1 g of citric acid to 0.5 g cerium, followed
by 2 ml of 10 per cent hydroxylamine hydrochloride and 10 ml of 0.1 per
cent 1,10-phenanthroline. The pH was adjusted to 7.5-9.0 with ammonium

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hydroxide, the solution made up to 100 ml, and allowed to stand for one hour. The transmittancy of the solution was measured at 515 mμ and the log transmittancy plotted against the iron concentration. The curve obtained was identical, within experimental error, to the standard iron curve. The data are in Table 2.

TABLE 2

DETERMINATION OF IRON IN CERIUM

Fe Taken, mg/100 ml	Ce-Free Solutions % Trans.	Solutions Containing 0.5 g Ce/100 ml		
		% Trans.	Fe Found mg	Deviation mg
0.000	100	100	0.000	0.000
0.050	83.2	83.2	.050	0.00
0.100	68.7	68.5	.101	0.001
0.150	56.5	56.4	.152	0.002

With this curve it is possible to determine iron in amounts as low as 20 ppm in 0.58 samples of cerium. Since the cerium now being produced at this laboratory contains a few hundred ppm of iron, it was not thought necessary to determine iron in smaller amounts by making new curves with higher concentrations of cerium.

Recommended Procedure for Cerium

Two equal samples containing approximately 0.5 g of cerium are taken. If the samples are in the metallic state they can be dissolved easily in hydrochloric acid and heated until a clear solution results. If they are in the form of chloride, nitrates, or oxides, they may be heated with nitric acid, and a pinch (5 mg) of sodium fluosilicate added when the acid boils, to facilitate solution. When the solutions are evaporated to less than 15 ml they are transferred to 100 ml volumetric flasks and treated with 1 g of citric acid. To one flask 4 ml of 10 per cent hydroxylamine hydrochloride and 10 ml of 0.1 per cent 1,10-phenanthroline are added. To the other only the 4 ml of 10 per cent hydroxylamine hydrochloride are added. Both solutions are adjusted to a pH of 7.5-9.0 with ammonium hydroxide and made up to 100 ml. The transmittancy of the solution

containing the 1,10-phenanthroline is measured at 515 mμ with the other solution as the reference. Should the transmittancy be less than 50 per cent, both solutions should be further diluted in the same manner until the transmittancy is greater than 50 per cent.

Experimental - Beryllium

A beryllium solution was made by dissolving nearly iron-free beryllium oxide, prepared from the basic acetate in sulfuric acid and diluting until 1 ml contained 7 mg of beryllium.

In studying the effect of the presence of beryllium on the colored ferrous complex of 1,10-phenanthroline, the reference solution was made up containing 70 mg of beryllium, 1 ml of 10 per cent hydroxylamino hydrochloride and 10 ml of 0.1 per cent 1,10-phenanthroline. The best solutions contained in addition, measured amounts of iron and all solutions were adjusted to pH 4-5 and made up to 100 ml. The transmittancies of these solutions were measured in the spectrophotometer at 515 mμ. This procedure was duplicated with solutions containing 350 mg of beryllium per 100 ml. For each concentration, the curve obtained followed Beer's Law and was identical to the standardization curve for iron. The data are shown in Table 3.

TABLE 3

THE DETERMINATION OF IRON IN BERYLLIUM

Fe Taken, mg/100 ml	Solutions Containing 70 mg Be/100 ml			Solutions Containing 350 mg Be/100 ml		
	% Trans.	Fe Found mg	Deviation mg	% Trans.	Fe Found mg	Deviation mg
0.010	96.30	0.010	0			
.050	83.10	.049	−0.001	83.2	0.050	0
.100	68.80	.100	0			
.150	57.17	.149	−0.001			
.200	47.65	.197	−0.003	47.47	0.199	−0.001
.250	39.90	.242	−0.008			

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The determination of iron in beryllium fluoride required a different method than that described on the preceding page because of the fluoride ion. Five grams of beryllium fluoride and 3.5 grams of boric acid were dissolved in hydrochloric acid (approximately 1 N). Continued heating was required to effect solution of the fluoride. This, upon dilution to 500 ml, gave a solution containing the equivalent of 2 mg of beryllium per ml. A series of test solutions was prepared, each containing 50 ml of the stock solution and known amounts of added iron. One, the reference, contained no added iron and was used to compensate for the iron already present when readings were made by the null method. The color was developed in each case by treating with 1 ml of 10 per cent hydroxylamine hydrochloride and 10 ml of 0.1 per cent 1,10-phenanthroline followed by adjustment to pH 3-5 (pH indicating paper) and dilution to 100 ml. Table 4 lists the results thus obtained.

TABLE 4

DETERMINATION OF IRON IN BeF_2

mg Fe Added/100 ml	mg Fe Found	Deviation mg
0.010	0.010	0.000
.050	.048	.002
.100	.097	.003
.150	.148	.002
.200	.196	.004
.250	.242	.008
.300	.287	.013
.350	.330	.020

The curves obtained from the above data follow the standardization curve for iron and is a straight line for concentrations up to 0.20 mg of iron after which Beer's Law no longer holds.

Recommended Procedure for Beryllium

The weight of sample taken should be consistent with the iron believed to be present. If the material is beryllium fluoride the weighed sample should be treated in a 400 ml beaker with 2-4 g of boric acid, depending on the amount of fluorine to be complexed, and 200 ml of 1 N

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hydrochloric acid. Beryllium oxide must be dissolved in hydrofluoric acid in a platinum dish and then treated with boric and hydrochloric acids. The chlorides and nitrates may simply be dissolved in HCl with no boric acid treatment. The solutions should be evaporated to less than 15 ml and transferred to a 100 ml volumetric flask. One ml of 10 per cent hydroxylamine hydrochloride solution and 10 ml of 0.1 per cent 1,10-phenanthroline are added and the pH adjusted to 3-5, followed by dilution to 100 ml. The transmittancy of the solution is measured at 515 mµ with distilled water as a reference. From a previously prepared standardization curve, the iron content is readily found.

Should the transmittancy of any solution be less than 50 per cent, the solution should be further diluted until its transmittancy is greater than that value.

Conclusion

From the data obtained it can be seen that the use of citric acid as a complexing agent for thorium and cerium offers no appreciable hindrance to the full development of the ferrous-1,10-phenanthroline color. This is also true of the use of boric acid to complex fluorine. The intensity of the ferrous-1,10-phenanthroline color, therefore, offers a convenient method of determining iron in ppm amounts in thorium, cerium, beryllium and certain of their compounds.

The use of boric acid in the solution of UF_4 has been mentioned in the literature[5] and in this laboratory has been found to give excellent results in the colorimetric procedure for iron. The extension of this method to other metal fluorides is now in progress.

Acknowledgements

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