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AROMATIC BASES AS PRECIPITANTS FOR RARE EARTH METALS.[1]

BY ALICE MACMICHAEL JEFFERSON.

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THE purpose of the present investigation was to ascertain to what degree certain well-defined aromatic bases might be applied in metal precipitations.

It seemed advisable to restrict this study to the rare earth metals. To this end salts of zirconium, thorium, cerium, lanthanum, neodymium and praseodymium were selected, and these were acted upon in succession by the bases—aniline, *o*-toluidine, xylidine, dimethyl aniline, diethyl aniline, benzylamine, pyridine, piperidine, quinoline and phenyl hydrazine. Knowing the action of the mother base—ammonia—it was of interest to discover to what degree substituted ammonias and kindred bodies might affect the salts chosen for the study. The hope was also cherished that if differences in behavior with the proposed reagents were disclosed, perhaps separations of some of the metals might possibly be realized. It will be generally admitted that the probability of discovering such results would truly warrant a study such as has been indicated in the preceding lines.

I. ZIRCONIUM.

Solutions of zirconium nitrates were prepared with great care and used in the experiments about to be described.

Zirconium and Aniline.—A definite amount of the zirconium salt solution was removed by means of a pipette, and diluted to about 50 cc. To this, aniline was added and the liquid thoroughly agitated. A beautiful white, gelatinous precipitate separated almost immediately. It was allowed to stand over night and in the morning it was filtered, washed, dried, ignited and weighed. The results indicate that the reaction took place quantitatively.

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[1] From author's thesis for Ph.D., 1901.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1382	0.0738	39.13	39.36
II.	0.0841	0.0436	39.13	38.24
III.	0.1050	0.0486	34.13	34.13
IV.	0.0908	0.0399	32.27	32.38
V.	0.3479	0.1248	26.45	26.46

Throughout the work the zirconium dioxide was ignited with a blast-lamp to constant weight.

Zirconium and o-Toluidine.—*o*-Toluidine also reacted quantitatively, giving a white gelatinous precipitate very similar to that obtained with xylidine. It was allowed to stand twelve hours before filtering.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.15084	0.0463	22.90	22.64
II.	0.15084	0.0463	22.90	22.64

Zirconium and Xylidine.—Xylidine precipitated zirconium quantitatively from its salts. About 50 cc. of the same solution were placed in a small beaker and xylidine added drop by drop with constant stirring. A white gelatinous precipitate formed which remained in suspension for some time. After twelve hours it was filtered, ignited, washed and weighed as zirconium dioxide. The precipitate was filtered with comparative readiness.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0908	0.0397	32.27	32.25
II.	0.0908	0.0401	32.27	32.58
III.	0.3479	0.1245	26.45	26.39

Zirconium and Dimethyl Aniline.—Dimethyl aniline was added to a portion of the zirconium solution with constant stirring. A yellowish white precipitate began to form slowly, and increased upon standing. After it had stood twelve hours it was filtered, washed, ignited to constant weight and the results calculated. It was found advisable to use a filter-pump in order to minimize the time factor for the excess of the precipitant filtered very slowly. The filtrate had a pink tinge.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0908	0.0394	32.27	32.00
II.	0.3479	0.1248	26.45	26.46

Zirconium and Diethyl Aniline.—The precipitation was made exactly as with dimethyl aniline. The products were very similar in appearance. The reaction took place rather slowly, and it was found advantageous to stir the liquid from time to time. After twelve hours it was filtered using a suction-pump and at times a slight violet tinge was noticed in the filtrate.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1050	0.0494	34.13	34.65
II.	0.0908	0.0401	32.27	32.58
III.	0.3479	0.1251	26.45	26.52

Zirconium and Benzylamine.—Benzylamine precipitated zirconium solutions quantitatively. The mass separated in small white floccules, which after standing a short time were easily filtered, and finally estimated as zirconium dioxide.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2158	0.0863	29.68	29.50

Zirconium and Pyridine.—A definite amount of the zirconium solution was placed in a small beaker, diluted to about 50 cc., and pyridine added with constant stirring. A very beautiful white glistening precipitate formed which settled rapidly and filtered readily after standing about an hour. After washing it was allowed to dry, and finally ignited with a blast lamp to constant weight. The results were as follows:

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0841	0.0438	39.13	38.41
II.	0.1050	0.0490	34.13	34.36
III.	0.1050	0.0486	34.13	34.13
IV.	0.0908	0.0399	32.27	32.38
V.	0.1814	0.0743	30.17	30.21

Zirconium and Piperidine.—Piperidine also seemed to precipitate zirconium solutions quantitatively. The precipitate formed almost immediately upon agitation, and was gelatinous and beautifully white in color. As soon as it had settled it was filtered and ultimately weighed as zirconium dioxide, after being ignited with a blast-lamp to constant weight.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0691	0.0367	39.13	39.18
II.	0.1050	0.0497	34.13	34.90
III.	0.0908	0.0404	32.27	32.82
IV.	0.2436	0.0876	26.45	26.52
V.	0.3479	0.1245	26.45	26.39

Zirconium and Quinoline.—When the zirconium salt was treated with quinoline and thoroughly stirred, a white glistening rather flocculent precipitate formed, which remained suspended for some time intermingled with the excess of the precipitant without settling. It was allowed to stand over night, then was filtered and ignited as before. In this case also the results seemed to indicate that a quantitative reaction had taken place.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0841	0.0452	39.13	39.60
II.	0.1050	0.0497	34.13	34.90
III.	0.1508	0.0463	22.90	22.64
IV.	0.1508	0.0462	22.90	22.59

The action of diphenylamine—a very weak base—upon zirconium salts was not tried, and it was found that phenyl-hydrazine caused no precipitation in such solutions.

It will be observed that nine of the ten precipitants were basic enough to remove zirconium from its salts. None of the substituted anilines proved too feeble for this purpose, notwithstanding the presence in them of positive groups.

II. THORIUM.

Here as with zirconium it was found that a solution of the nitrate was best adapted for the work. It was accordingly prepared by several methods and carefully tested as to its purity.

Thorium and Aniline.—Aniline precipitates thorium salts quantitatively. The precipitate did not form at once, but after the solution had stood a short time a cloudiness appeared in the solution and gradually increased. The precipitate was always allowed to stand over night, and if by that time it had not separated out nicely after stirring, it was allowed to stand another twelve hours. The clear white gelatinous mass was then filtered, and ultimately determined as thorium dioxide. The results were as follows:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1354	0.0651	42.29	42.25
II.	0.1354	0.0662	42.29	42.96
III.	0.1083	0.0519	42.29	42.11
IV.	0.1605	0.0768	42.29	42.05

Thorium and o-Toluidine.—*o*-Toluidine, like the other reagents, at first gave no precipitate, but on standing a heavy white very gelatinous mass formed. After several days, when the precipitate appeared to have settled nicely, the liquid was filtered and the precipitate was ignited and weighed. The resulting thorium dioxide after heating to constant weight with a blast-lamp, gave the following percentages:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1212	0.0577	42.29	41.81
II.	0.3210	0.1535	42.29	42.07
III.	0.3318	0.1582	42.29	41.89

Thorium and Xylidine.—Xylidine with thorium salts also gave a heavy white gelatinous precipitate. The solution was diluted to not more than 50-75 cc. and xylidine added with constant stirring. The precipitate remained with the excess of the precipitant, but after standing several days it settled upon the bottom of the beaker, and was estimated as usual.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0541	0.0257	42.29	41.69
II.	0.1134	0.0537	42.29	41.60
III.	0.1605	0.0774	42.29	42.37
IV.	0.1605	0.0758	42.29	42.05

Thorium and Dimethyl Aniline.—Considerable time elapsed before any precipitate formed. After several days no reaction seemed to have taken place, but at the expiration of a week or ten days a precipitate was noticed which was filtered and its quantity determined. When the reaction commenced the solution seemed to separate into two layers, one whitish and opaque, and the excess of the dimethyl aniline, being lighter in specific gravity, remaining on top. On stirring, however, a white, very gelatinous precipitate formed, which filtered very slowly, one drop at a time; therefore a suction pump was found to facilitate the reaction considerably. The results are as follows:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1605	0.0774	42.29	42.37
II.	0.1605	0.0777	42.29	42.54

Thorium and Diethyl Aniline.—Diethyl aniline seemed to react quantitatively with thorium salts, but the desired result was reached with difficulty. At first no precipitation took place. After standing some time a yellowish white voluminous precipitate separated out. The product seemed more or less dependent upon conditions such as temperature, concentration, etc. The most satisfactory results were obtained from 25-50 cc. of solution, and when the beaker was permitted to stand in a rather warm place. Usually no precipitate formed until the solution had stood several days, and for one determination it stood one whole week before filtering. The mass was extremely gelatinous and at times almost transparent. The results were:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1624	0.0796	42.29	43.05
II.	0.1083	0.0517	42.29	41.92
III.	0.1512	0.0725	42.29	42.11
IV.	0.1605	0.0761	42.29	41.66
V.	0.3318	0.1579	42.29	41.82

Thorium and Pyridine.—When pyridine was added to the thorium salt, for a few minutes no reaction took place, but after standing a white gelatinous mass separated out, slightly less dense than that obtained with piperidine.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1083	0.0525	42.29	42.57
II.	0.1512	0.0737	42.29	42.81
III.	0.0756	0.0366	42.29	42.52
IV.	0.1605	0.0767	42.29	41.99

Thorium and Piperidine.—Piperidine precipitated thorium salts immediately, giving a white voluminous mass which is very characteristic. It settled rapidly and was filtered almost immediately, washed, dried and ignited to white thorium dioxide, heating with the blast-lamp until a constant weight was obtained. The results were:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1083	0.0525	42.29	42.57
II.	0.1512	0.0728	42.29	42.29
III.	0.0756	0.0360	42.29	41.78
IV.	0.1605	0.0769	42.29	42.10
V.	0.4701	0.2270	42.29	42.33

Thorium and Quinoline.—Quinoline gave a glistening white semi-transparent precipitate. The reaction seemed complete after standing twenty-four hours. It filtered with much greater readiness than the substituted anilines. The determinations were as follows:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1083	0.0522	42.29	42.35
II.	0.1083	0.0510	42.29	41.37
III.	0.1605	0.0770	42.29	42.16

Benzylamine was not tried on account of lack of material.

Phenylhydrazine with thorium salts gave a canary-yellow flocculent precipitate readily soluble in excess.

Diphenylamine was not tried.

In all of the analyses of the thorium salts the volume of liquid never was greater than 100 cc. and usually not above 50 cc.

It will be observed that while thorium responds quantitatively to the same bases to which zirconium responded, and while the results are quantitative in character, the time factor in many cases is so extended that the application of these precipitants offers nothing of advantage to the analyst either in the direction of completeness of precipitation or rapidity of reaction.

Zirconium and thorium represent a rather wide range in atomic weights (90-232), and as the second has probably acquired somewhat more of the acid nature, this may account for the sluggishness of its behavior with the bases which were applied to it. This led to the introduction of cerium in the study, being a member of the same Group IV of the Periodic System with zirconium and thorium, and standing midway as it were in atomic weight (140) between them. The behavior of the chosen bases upon its salts was awaited with deep interest. Here, too, it may be added, that the precipitates in thorium solutions are from their very nature and behavior definite double salts. None of them showed the usual appearance of thorium hydroxide.

III. CERIUM.

The salt used was a ceric ammonium nitrate, orange-red in color.

Cerium and Aniline.—A definite amount of the cerium double salt was weighed and dissolved in about 50 cc. of water, and aniline added with constant stirring. A white heavy flocculent precipitate formed almost immediately, and the liquid went through various changes in color, finally becoming nearly colorless. After standing an hour or two, the solution was filtered and the precipitate was washed, dried, ignited, and weighed as cerium dioxide, yellow to reddish yellow in color. Throughout the work, the cerium dioxide was ignited to constant weight with the blast-lamp before weighing, as directed under zirconium. The following results were obtained:

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.4134	0.1281	25.13	25.22
II.	0.3554	0.1089	25.13	24.93
III.	0.3973	0.1254	25.13	25.69
IV.	0.3637	0.1113	25.13	24.91
V.	0.1996	0.0622	25.13	25.35

Cerium and o-Toluidine.—A white flocculent precipitate was formed by adding *o*-toluidine to a solution of the cerium salt and thoroughly agitating. The mass settled nicely, and after standing several hours was filtered, washed and ignited.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0785	0.0245	25.13	25.35
II.	0.1682	0.0513	25.13	24.82
III.	0.1210	0.0377	25.13	25.17

Cerium and Xylidine.—Xylidine gave a heavy white precipitate that remained suspended for some time. After stirring very thoroughly the beaker was set aside for several hours, then filtered, using a suction-pump, washed, ignited and weighed. As the results failed to show a concordance the reaction seems not to have taken place quantitatively.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2106	0.0483	25.13	18.66
II.	0.1890	0.0460	25.13	19.79
III.	0.2368	0.0447	25.13	15.36

Cerium and Dimethyl Aniline.—Cerium was precipitated with dimethyl aniline with constant stirring. A yellowish white precipitate formed and the liquid changed color rapidly, green, purple and finally nearly colorless. After standing a couple of hours it was filtered and weighed as cerium dioxide. The reaction was not quantitative, as the percentages obtained showed great variation, and the results were unsatisfactory.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1418	0.0312	25.13	17.91
II.	0.0899	0.0214	25.13	19.34
III.	0.0899	0.0151	25.13	13.66

Cerium and Diethyl Aniline.—Diethyl aniline gave a white flocculent precipitate which settled with comparative readiness, the solution becoming brown, green, purple, and finally colorless. After standing for two hours it was filtered using a suction-pump.

Cerium dioxide ultimately obtained was ignited to constant weight with the blast-lamp.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1785	0.0566	25.13	25.80
II.	0.0899	0.0273	25.13	24.68
III.	0.0899	0.0290	25.13	26.24
IV.	0.0899	0.0285	25.13	25.78

Cerium and Benzylamine.—When benzylamine was added to a cerium salt with constant stirring, a heavy flocculent precipitate formed, which rapidly changed in color, becoming brown and finally nearly black. The precipitate settled rapidly and was filtered after standing several hours without the use of a suction-pump.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1142	0.0345	25.13	24.59
II.	0.1192	0.0375	25.13	25.59

Cerium and Pyridine.—Pyridine gave a beautiful white glistening precipitate that settled rapidly and filtered quickly and easily. It was very gelatinous. The results were quantitative.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1932	0.0609	25.13	25.65
II.	0.1192	0.0372	25.13	25.39
III.	0.2488	0.0775	25.13	25.35

Cerium and Piperidine.—Piperidine also gave a white precipitate, and its physical properties closely resembled those observed in the precipitate obtained with pyridine. The quantitative results were:

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2005	0.0631	25.13	25.62
II.	0.2248	0.0695	25.13	25.16
III.	0.1156	0.0360	25.13	25.35
IV.	0.2011	0.0635	25.13	25.70

Cerium and Quinoline.—Quinoline seemed not to give a quantitative reaction. I thought at first that the variation in results might be due to the fact that the quinoline used contained brown substances and that the excess of the precipitant clung to the sides of the beaker and was very difficult to remove, even when a glass rod with a rubber cap was used. It was thought that perhaps some of the precipitate might be lost in this way, so an alcoholic wash was used, and also chloroform, which completely removed the excess of quinoline from the beaker, but the final results were unsatisfactory.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.5027	0.1058	25.13	17.13
II.	0.2898	0.0591	25.13	16.60
III.	0.1720	0.0354	25.13	16.74
IV.	0.1364	0.0337	25.13	20.09
V.	0.2306	0.0326	25.13	11.49

In Experiment IV alcohol was used, and chloroform in Experiment V.

Both phenylhydrazine and diphenylamine failed to precipitate cerium salts.

Strangely enough, several of the bases failed to yield quantitative results. With xylidine this may be due to the presence of the additional methyl group; perhaps, too, in dimethyl aniline, the accumulation of positive substituents is the cause of the failure in reaction; if so, why should not the same occur in the use of diethyl aniline where quantitative precipitation does take place? The slight basicity of diphenylamine explains its failure, but the lack of action in quinoline is not so readily comprehended.

A glance at the arrangement of the elements in the Periodic System shows that directly opposite—preceding cerium—as a member of Group III, appears lanthanum, while following cerium in Group V, are neodymium and praseodymium. Would their conduct with the selected bases bring to light any unobserved facts? Lanthanum following in its oxide the type R_2O_3—a type readily precipitated by ammonia—might perhaps shed some light on the behavior of cerium, and account for the variations observed between it and its associates of Group IV. Therefore, it was next considered in the proposed study.

IV. LANTHANUM.

Two salts of lanthanum were used, the chloride and the double nitrate with ammonium.

Aniline *o*-toluidine and xylidine all failed to precipitate lanthanum salts. Dimethyl aniline also gave no reaction, and diethyl aniline after long standing gave a slight film at the point of contact, though no precipitate was discernible.

Lanthanum and Benzylamine.—Benzylamine gave with lanthanum salts, as with the metals previously tested, a heavy white flocculent precipitate. When the resulting oxide was ignited to constant weight, it gave the following percentages:

	Salt taken. Gram.	La_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1685	0.0741	37.94	37.50
II.	0.2051	0.0628	24.96	26.11

Lanthanum and Pyridine.—At first no precipitate formed, but after standing several days a very fine white precipitate separated. It was granular and shining in appearance, and like that obtained with praseodymium, clung very closely to the beaker, and was only removed with the greatest difficulty, and showed a tendency to run through the filter-paper.

The results were not quantitative.

Lanthanum and Piperidine.—Piperidine gave a white glistening gelatinous precipitate, similar in properties to that obtained by the same reagent with the metals already mentioned.

	Salt taken. Gram.	La_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1580	0.0705	37.94	38.04
II.	0.1713	0.0750	37.94	37.33
III.	0.2106	0.0937	37.94	37.94
IV.	0.3826	0.1141	24.96	25.43

Diphenylamine was not tried, and quinoline failed to show any reaction.

Phenylhydrazine gave a flocculent reddish brown precipitate which grew less on standing.

Only those bases having a decidedly basic nature—benzylamine and piperidine—seem capable of throwing out lanthanum completely. Eight of them apparently fail of this end, and in this behavior is found a hint as to what cerium might be expected to do. It accordingly became still more interesting to ascertain the deportment of praseodymium and neodymium in the indicated directions.

V. PRASEODYMIUM.

Two salts were used, $Pr(NO_3)_3.6H_2O$, and the doube nitrate $Pr(NO_3)_3.2NH_4NO_3.4H_2O$, both green in color.

Aniline and praseodymium appeared not to react, although the behavior was rather confusing. Tests were made, but no precipitate formed even after long standing, but later, when the tests were repeated, it was found that when the test-tube stood in a warm place, a slight precipitate did form, which on long standing again disappeared.

Neither *o*-toluidine nor xylidine gave evidence of any reaction with praseo-salts even after long standing. Dimethyl aniline gave no precipitate and diethyl aniline behaved in a similar manner, though after standing for a long time, a very slight film was noticed at the point of contact.

Praseodymium and Benzylamine.—Benzylamine gave a white flocculent precipitate, very voluminous which, like many of the preceding precipitates, filtered rapidly, after standing several hours. The resulting brown-black oxide, after ignition with the blast-lamp, gave the following:

	Salt taken. Gram.	Pr_4O_7 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1348	0.0520	32.57	32.20

Praseodymium and Pyridine.—When pyridine was first added, no reaction seemed to take place, but on standing, a fine white granular precipitate separated on the bottom of the beaker. It was filtered and estimated as usual. The precipitate clung closely to the sides of the beaker, and it was almost impossible to thoroughly remove it. One analysis was made, and the result was unsatisfactory.

Praseodymium and Piperidine.—Piperidine gave a white, glistening, gelatinous precipitate, with a slight greenish tinge. Its properties were very similar to the neodymium-piperidine precipitate. Like the latter, it was found best to dry the product simply in the air, because when heated on a metal drying cone over a Bunsen flame, the mass melted and ran through the filter, and partly disappeared. It was a quantitative reaction.

	Salt taken. Gram.	Pr_4O_7 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2014	0.0788	32.57	32.67
II.	0.0970	0.0380	32.57	32.68
III.	0.0979	0.0378	32.57	32.22

Quinoline gave no precipitate, and the action of diphenylamine was not tried. Phenylhydrazine gave a flocculent reddish brown precipitate, which on standing partly disappeared.

Comparison with the behavior of lanthanum reveals the fact that these two elements behave almost analogously with the bases brought in contact with them and vary in about the same degree from cerium.

VI. NEODYMIUM.

Neodymium and Aniline.—When aniline was added to a neodymium solution at first no reaction seemed to take place, but after the beaker had stood some time, a slight gelatinous precipitate separated, white in color. After several hours the liquid was filtered, and the resulting blue-brown sesquioxide weighed. The reaction was not quantitative.

	Salt taken. Gram.	Nd_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.09855	0.0139	32.57	12.06
II.	0.09855	0.0109	32.57	9.44
III.	0.09855	0.0236	32.57	20.48

o-Toluidine gave no precipitate. Xylidine after long standing gave a very slight yellowish white flocculent mass. Dimethyl aniline at first failed to react, but after some time had elapsed a faint film was noticed.

Diethyl aniline showed a slight precipitate, yellowish white in color, but the result obtained was far from quantitative.

Neodymium and Benzylamine.—Benzylamine gave a voluminous white precipitate, which separated in small beautiful floccules. The result was quantitative.

	Salt taken. Gram.	Nd_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1608	0.0611	32.57	32.50

Neodymium and Pyridine.—Pyridine after standing a short time gave a slight yellowish white precipitate. The reaction was incomplete.

Neodymium and Piperidine.—The neodymium salt was immediately precipitated, giving a glistening white product, with a faint violet tinge. It was very gelatinous, but readily filtered, and gave results closely corresponding to the theoretical. It was dried simply in the air, for when I attempted to dry it upon a stove-plate, using a metal cone, the precipitate melted and ran through the filter-paper.

	Salt taken. Gram.	Nd_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I	0.2912	0.1135	32.57	33.44
II.	0.0985	0.0378	32.57	32.78
III	0.1471	0.0436	25.36	25.35
IV.	0.1869	0.0557	25.36	25.47

Quinoline failed to react. No attempt was made to precipitate neodymium salts with diphenylamine. Phenylhydrazine gave a fine orange-red flocculent mass, which on standing appreciably decreased in bulk, finally disappearing almost entirely.

The behavior of praseodymium is here repeated. In almost every particular the representatives of Group V conduct themselves similarly, and manifest a decided relationship, from the present point of study, to lanthanum, whereas they differ markedly from cerium. May not the obvious conduct of cerium with the different precipitants enumerated in the preceding paragraphs, be safely regarded as decided evidence of the true position of cerium in the periodic classification. Is not its deportment with these bases more in harmony with that of zirconium and thorium than with that of lanthanum, neodymium, and praseodymium? Its juxtaposition to the latter unquestionably explains why it is not precipitated by xylidine, dimethyl aniline and quinoline, with all of which its natural associates gave quantitative precipitations.

SEPARATIONS.

Having made the observation that many of the precipitations described were quantitative, and that other salts with the same reagents failed to react at all, the thought arose that probably separations could be made, and accordingly investigations along these lines were begun. The results of these attempts are given in the following pages. The field seems to be a large one, by no means exhausted, and the possibilities appear great.

I. Separation of Thorium and Neodymium by Quinoline.—A known amount of the thorium solution diluted to approximately 50 cc. was placed in a beaker, and a weighed quantity of the neodymium salt added. Quinoline was then added with constant stirring and the beaker set aside for twenty-four hours. It was then carefully filtered and washed thoroughly, the beaker containing the neodymium filtrate removed, and a fresh vessel substituted. The precipitate while still moist was dissolved in dilute hydrochloric acid or preferably dilute nitric acid, and the filter-paper washed thoroughly with water to remove the last traces of the acid solution. It was found advisable to use as little acid as possible to prevent the final dilution from being unnecessarily great.

The acid solution was next neutralized as nearly as possible with ammonia water. A little nicety in manipulation was required, because if too great an amount of ammonia were added, the metals would be precipitated, while, on the other hand, too large an excess of acid would retard the reprecipitation by quinoline, making the final results too low. Leaving the solution very slightly acid, quinoline was again added, and the liquid agitated. The reaction commenced almost immediately, and in every case it was noticed that the reprecipitation gave a mass much more flocculent than that obtained by simply precipitating once.

After twenty-four hours, the solution was filtered, adding this filtrate to the first one, and the precipitate washed, dried, ignited with the blast lamp to constant weight, and determined as thorium dioxide. The reprecipitation was found necessary, because when the thorium was only precipitated once, the resulting oxide showed a very faint color of neodymium, whereas the thorium dioxide obtained by dissolving and reprecipitating was in every case pure and white without the slightest trace of the blue-brown oxide of neodymium.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.15466	0.0751	42.29	42.67
II.	0.15466	0.0746	42.29	42.38
III.	0.1206	0.0581	42.29	42.33
IV.	0.15157	0.0734	42.29	42.55
V.	0.15157	0.0724	42.29	41.96
VI.	0.15157	0.0728	42.29	42.20
VII.	0.15157	0.0740	42.29	42.88

II. Separation of Zirconium and Neodymium by Quinoline.—The separation was carried out exactly as directed under thorium, but in each case the precipitate stood twelve hours instead of twenty-four hours. The same precautions were observed. The results are appended.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.14406	0.0595	30.30	30.47
II.	0.14406	0.0590	30.30	30.20
III.	0.14406	0.0582	30.30	29.78
IV.	0.10948	0.0448	30.30	30.14
V.	0.15084	0.0462	22.90	22.59
VI.	0.15084	0.0471	22.90	23.00

Here also, the resulting zirconium dioxide was white, not the slightest trace of the color of the neodymium oxide being perceptible, but the neodymium percentages were too high when determined by ammonia in the filtrate. In each of the separations described the resulting filtrates were precipitated with pure ammonia, but in every case the resulting percentages were found to be somewhat too high when compared with the theoretical.

	Salt taken. Gram.	Nd_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2092	0.0624	25.36	25.51
II.	0.1433	0.0435	25.36	25.96
III.	0.1291			
	Taken together	0.0837	25.36	26.19
IV.	0.1442			

Zirconium and ammonia, the resulting mean, used as the unit of comparison:

	Salt taken. Gram.	ZrO_2 found. Gram.	Found. Per cent.	Mean. Per cent.
I.	0.14406	0.0587	30.06	
II.	0.14406	0.0597	30.54	30.30
I.	0.15084	0.0468	22.87	
II.	0.15084	0.0469	22.93	22.90

III. Separation of Thorium and Lanthanum by Aniline.—The procedure was exactly as directed under quinoline, and both times the precipitate stood twenty-four hours before filtering. It was advantageous to allow the excess of the precipitant to filter through, and then wash the precipitate with water before dissolving in dilute nitric acid, because otherwise the organic material in solution rendered it darker in color, and it was more difficult to decide when the point of neutralization was being approached. As the oxides of thorium and lanthanum are both white, it was, of course, not possible to tell whether the final thorium dioxide contained a slight amount of lanthanum by the color, as was done with the blue-brown neodymium oxide. Therefore, endeavoring to make the results as accurate as possible, the weighed thorium dioxide, was in each case treated in the crucible with concentrated hydrochloric acid or nitric acid, and allowed to stand several hours.

As the lanthanum sesquioxide is soluble in acids, it should dissolve leaving the thorium dioxide. The acid solution was poured quickly into a small beaker and the precipitate of thorium dioxide washed into the beaker with water. If care be taken, no milkiness will be noticed. The liquid was then filtered, the precipitate ignited to constant weight, and finally weighed as thorium dioxide. The filtrate which would contain the trace of lanthanum if present, was added to the first filtrate known to contain the lanthanum from the separation. The final results were as follows:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.3210	0.1550	42.29	42.43
II.	0.3210	0.1552	42.29	42.49
III.	0.3210	0.1550	42.29	42.43
IV.	0.3210	0.1552	42.29	42.49
V.	0.3210	0.1554	42.29	42.54

IV. Separation of Zirconium and Lanthanum by Aniline.—The reaction was carried out exactly as directed under the separation of thorium and lanthanum by aniline, except that in each case the time factor was twelve hours instead of twenty-four. The resulting zirconium dioxide was treated with concentrated hydrochloric or nitric acid to dissolve out any trace of lanthanum.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.13458	0.0576	31.96	31.57
II.	0.2539	0.1034	30.13	30.04
III.	0.2539	0.1036	30.13	30.09
IV.	0.2539	0.1043	30.13	30.29

Zirconium and Ammonium Hydroxide.

	Salt taken. Gram.	ZrO_2 found. Gram.	Found. Per cent.	Mean. Per cent.
I.	0.2539	0.1040	30.21	
II.	0.2539	0.1034	30.04	30.13
I.	0.1345	0.0586	32.10	
II.	0.2045	0.0883	31.82	31.96

V. Separation of Thorium and Lanthanum by Quinoline.—A known number of cubic centimeters of the thorium solution, and a weighed quantity of the lanthanum salt, were placed in a small beaker, diluted to about 50-75 cc. and quinoline added, stirring the liquid very thoroughly. The subsequent operations were carried out in a manner quite similar to that described in the preceding experiments. The precipitate was allowed to stand twenty-four hours each time. The final thorium dioxide obtained was treated with concentrated acid, to remove any lanthanum that might have been carried down by the thorium.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.3318	0.1577	42.29	41.77
II.	0.3318	0.1592	42.29	42.16
III.	0.3318	0.1581	42.29	41.86
IV.	0,3318	0.1585	42.29	41.98
V.	0.3318	0.1582	42.29	41.89

VI. Separation of Cerium and Praseodymium by o-Toluidine.—After ascertaining the fact that *o*-toluidine precipitated cerium salts quantitatively, and with the salts of neodymium gave no reaction, I endeavored to separate the two, using this means. It was found by experiment that if the precipitate of cerium were dissolved in acid, it refused to be reprecipitated when, after neutralizing, an excess of the precipitant was again added. Consequently, *o*-toluidine was added only once, and no attempt was made to dissolve and reprecipitate.

The experiment was made, using from 50-75 cc. of solution, and allowing the precipitate to stand over night before filtering. The resulting cerium dioxide seemed rather darker in color than usual, which may have been due to a trace of praseodymium oxide, notwithstanding the fact that the weight of the cerium dioxide found agreed with the theoretical within the limit of experimental error.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1750	0.0543	25.13	25.25

VII. Separation of Thorium and Praseodymium by Aniline.—The confusing behavior of praseodymium with aniline has already been mentioned. I am inclined to think that possibly conditions such as temperature, concentration, etc., influence it, because when a test-tube containing the two stood in a warm place, a slight precipitate formed, which was quite perceptible, but after standing for some time in the cold, it entirely disappeared. At another time aniline and praseodymium stood in contact for months, without any precipitate separating out. Another thought is that perhaps even if the conditions were such as to allow a precipitate to form, possibly the small amount of acid present in the solution after dissolving the thorium precipitate in acid and almost neutralizing, would be sufficient to prevent any reaction between the two.

Accordingly, an attempt was made to separate thorium from praseodymium using aniline as the precipitant. The method was quite similar to that pursued in the foregoing separations, the precipitate being allowed to stand each time for twenty-four hours. The mass first obtained was dissolved in dilute nitric acid. carefully neutralized and reprecipitated. The thorium dioxide ultimately obtained was treated in the cold with concentrated nitric acid, allowing it to remain undisturbed for two hours, hoping in this way to remove the slight trace of color noticed. After filtering, washing and igniting, a *very* faint brownish tinge was always noticed. The weights corresponded quite well with the theoretical but at no time was the resulting thorium dioxide absolutely white. Even after treatment with nitric acid, the thorium dioxide showed a slight tinge of color, upon close examination.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.3318	0.1600	42.29	42.37
II.	0.3318	0.1592	42.29	42.16
III.	0.3318	0.1600	42.29	42.37
IV.	0.3318	0.1602	42.29	42.43

An attempt was made to separate zirconium and praseodymium using *o*-toluidine. Only one analysis was attempted, and the result was rather low, but near enough to indicate the probability of such a separation being made under proper conditions. The zirconium dioxide obtained was perfectly white in color.

VIII. Separation of Zirconium and Lanthanum by Xylidine.—As previousy stated, xylidine precipitates zirconium quantitatively, so an attempt was made to separate zirconium from lanthanum using it as the medium. Xylidine was added to the solution containing the two salts, with constant agitation. The precipitate formed almost immediately, but as a matter of precaution it was allowed to stand over night. In the morning it was filtered, allowing the excess of xylidine to run through the filter, washing thoroughly with water, and then with 95 per cent. alcohol, till the brown color of the xylidine had disappeared and the precipitate and filter were clean and white. It was then again washed with water, dissolved in dilute nitric acid and almost neutralized with ammonium hydroxide, leaving the solution very slightly acid. After reprecipitating with xylidine it was allowed to stand twelve hours, and again filtered, finally estimating as zirconium dioxide. The resulting oxide was treated for two hours in the cold with concentrated nitric acid, then filtered and determined as usual.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2158	0.0864	29.69	29.52

Zirconium and Ammonia:

	Salt taken. Gram.	ZrO_2 found. Gram.	Found. Per cent.	Mean. Per cent.
I.	0.2158	0.0863	29.50	
II.	0.2158	0.0874	29.87	29.69

If nitric acid were added to dissolve the precipitate in the separation of lanthanum and zirconium by xylidine, without previously washing with alcohol, the excess of xylidine would combine with the nitric acid, giving an organic precipitate so dense that it would prevent one from seeing when the point of neutralization was approaching in the subsequent treatment with ammonium hydroxide, hence the advisability of using an alcoholic wash.

IX. Separation of Zirconium and Praseodymium by Xylidine.— An attempt was made to separate these two in a manner perfectly analogous to that just described. The resulting zirconium dioxide was light yellow in color, though the weight corresponded with that required.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2158	0.0867	29.69	29.63

SUMMARY.

Six metals were acted upon by characteristic aromatic bases, when it was found that zirconium is precipitated quantitatively by nearly all of them. Thorium is precipitated by aniline, *o*-toluidine, xylidine, diethyl aniline, dimethyl aniline, pyridine, piperidine and quinoline. Aniline *o*-toluidine, diethyl aniline, benzylamine, pyridine and piperidine are the only precipitants of cerium, while with lanthanum, neodymium and praseodymium, the precipitants are benzylamine and piperidine.

Quinoline will separate thorium from neodymium and zirconium from the latter, while aniline separates thorium and also zirconium from lanthanum. The latter and thorium are also separated by quinoline. With *o*-toluidine cerium may be separated from praseodymium, and the latter and thorium may be separated by aniline. Finally, xylidine will separate zirconium from lanthanum, as well as from praseodymium.

UNIVERSITY OF PENNSYLVANIA.

A NEW METHOD FOR THE APPROXIMATE DETERMINATION OF URIC ACID IN URINE.

BY JULIUS RUDISCH AND LEOPOLD BOROSCHEK.

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SEVERAL of the most important methods for the quantitative determination of uric acid in urine, depend on the practically complete precipitation of the uric acid, as a magnesia silver urate, by the addition of an ammoniacal silver solution and a magnesia solution to the urine.

This method of precipitation is open to several objections:

First, the ammoniacal magnesia solution causes a voluminous precipitate of triple phosphate to separate from the urine. This precipitate, if not previously removed, contaminates the silver urate precipitate, rendering filtration and washing difficult owing to its large bulk. In Ludwig's method[1] the phosphates are thrown down together with the uric acid. Salkowski[2] recommends the removal of the phosphates by means of an ammoniacal magnesia solution and filtering the urine, previous to the addition of the ammoniacal silver solution. Folin and Shaffer found[3] that if this

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[1] *Ztschr. anal. Chem.*, **21**, 148 (1882).

[2] *Ztschr. physiol. Chem.*, **14**, 50 (1890).

[3] *Ibid.*, **32**, 553 (1901).