

such as color, softness, and streak, but a lower specific gravity, may perhaps be regarded as impure graphites; that is to say, mixtures of graphite with other forms of carbon."

Against the view set down in preceding paragraphs, that so-called graphite is not a simple and reproducible substance, we have the recent work of LeChatelier and Wologdine.¹ They found that the density of Acheson graphite and of five natural graphites, after purification to remove ash and compression to drive out air, was 2.255, and conclude that this property defines graphite as a simple and reproducible substance. But it should be noted that their process of purification involved fusion at a red heat with potash, a treatment which might produce profound changes in the graphite itself.

In conclusion, the wide divergence in expansion coefficient which we have noted above seems quite beyond the range of possible experimental error, and indicates some fundamental difference between these various graphites.

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A VOLUMETRIC METHOD FOR THE DETERMINATION OF THORIUM IN THE PRESENCE OF OTHER RARE EARTHS. THE ANALYSIS OF MONAZITE SAND.

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When an excess of ammonium molybdate solution is added to a solution of a thorium salt under proper conditions of temperature and acidity, thorium is quantitatively precipitated as molybdate. Other rare earths, such as cerium, lanthanum, neodymium, praseodymium, erbium, yttrium, gadolinium, etc., give no precipitation whatever under similar conditions.

The above facts, observed by one of us some years ago, forms the basis for the method described in this paper.

The thorium molybdate precipitate is somewhat gelatinous in character, pale yellow in color, and settles very slowly. In our earlier experiments an attempt was made to filter off the precipitated thorium and make the determination gravimetrically, but owing to the slimy nature of the precipitate, filtration and washing were impossible.

The usual indicators for molybdenum were tried with the hope that a direct titration of the thorium could be made, but without success.

Cazeneuve² found diphenyl carbazide to be a sensitive reagent for certain metallic salts, as those of copper, mercury, iron and also for chromates. Lecoq³ used an alcoholic solution of diphenyl carbazide as a test for molybdenum. A pink coloration is produced, and the author states that the test is more sensitive after the solution of diphenyl carbazide has been allowed to stand for some time. In order to test the applicability of this indicator, a number of titrations of pure thorium nitrate solution were made, and the results obtained were concordant. The indicator is used "outside" on a white indented tile, the end of

the titration being marked by the appearance of a pink coloration which lasts about fifteen seconds. Some experience is required to identify the end point. This is gained in standardizing the ammonium molybdate against a standard thorium nitrate solution. *It is necessary to use a solution of the indicator at least two weeks old*, as the freshly prepared solution requires a considerable excess of molybdenum to produce a pink coloration. The titration is made at room temperature, in the presence of acetic acid.

The solutions used in the experimental part of the work were as follows: *Thorium nitrate*—A solution of pure thorium nitrate accurately standardized by precipitating as oxalate, igniting and weighing as oxide. *Potassium permanganate*—An approximately 0.1 N solution standardized against specially prepared Mohr's salt; 1 cc. = 0.005835 Fe. *Ammonium molybdate*—Approximately 20 grams ammonium molybdate per liter. In order that the thorium-molybdenum ratio in the precipitate might be determined, this solution was carefully standardized by acidifying, reducing in a Jones reductor and titrating with permanganate as usual. The average of a number of titrations gave 10 cc. molybdate solution = 28.2 cc. KMnO_4 . Assuming the reduction to be $\text{MoO}_3 \rightarrow \text{Mo}_2\text{O}_3$, then 1 cc. molybdate solution = 0.0098136 Mo. *Indicator*—0.5 gram of diphenyl carbazide¹ dissolved in 200 cc. of 95 per cent. alcohol and allowed to stand at least two weeks before using. The solution when ready for use should be yellowish in color, but show no pink tinge.

In order to obtain uniformity in acidity of the solutions for titration and to have the conditions analogous to those obtaining in the analysis of a monazite sand, a number of determinations were made as follows:

A known amount of thorium solution, or thorium solution with the addition of other rare earths, was placed in a casserole and evaporated to dryness on a water bath. To the dry residue 4 cc. of glacial acetic acid were added, then 300 cc. of water. When the salts were dissolved, the cold solution was titrated with ammonium molybdate. The molybdate solution should be added a few tenths of a cc. at a time, with vigorous stirring after each addition, finally finishing drop by drop. The end point is reached when a drop of the solution produces the previously described pink coloration when brought in contact with a few drops of indicator on a white tile. After a little experience the end point can be determined with great accuracy. The following table shows the results obtained:

¹ A convenient and satisfactory method for the preparation of this compound is as follows: Add 23 grams of phenyl hydrazine to 7 grams of urea in a flask, and heat in an oil bath at 160–170° for six hours, using a reflux air condenser. Allow to cool, add 50 cc. ethyl ether, heat on a hot plate for one hour, decant and add 50 cc. ethyl ether, heating for two hours longer; a white precipitate is obtained, the residue of reagents going into solution in the ether. Decant the ether, dissolve the precipitate of impure diphenyl carbazide in alcohol and reprecipitate by pouring into excess of water; decant the water, redissolve the precipitate in alcohol and pour again into excess of water. Filter on a Büchner funnel, wash and dry at 105°. Yield, 14.3 grams diphenyl carbazide. M. p. 150°–151°. *The diphenyl carbazide is white when first precipitated but in time turns brownish yellow. A trace of impurity causes it to turn pink; hence all vessels, dropping tubes, etc., must be scrupulously clean. The indicator, when on the white tile, should be yellowish or brownish yellow.*

¹ *Compt. rend.*, **146**, 49–53 (1908).

² *Ibid.*, **131**, 346 (1900).

³ *Jour. Chem. Soc.*, **86**, 369 (1904).

No.	ThO ₂ , Gram.	Other earths present.	Molybdate solution, Cc.
1.....	0.0500	0	3.65
2.....	0.0500	0	3.65
3.....	0.0852	0	6.4
4.....	0.0852	0	6.4
5.....	0.0852	0	6.5
6.....	0.1000	0	7.35
7.....	0.1000	0	7.4
8.....	0.0500	0.1 Nd ₂ O ₃	3.9
9.....	0.0500	0.1 Pr ₂ O ₃	3.9
10.....	0.0500	0.1 La ₂ O ₃	3.9
11.....	0.0852	0.1 La ₂ O ₃	7.1
12.....	0.0852	0.1 La ₂ O ₃	7.1
13.....	0.0852	0.1 Pr ₂ O ₃	7.2
14.....	0.0852	0.1 CeO ₂	7.1
15.....	0.0852	0.1 gram each of Ce, La, Pr, Nd	7.1
16.....	0.0852	0.1 gram each of Ce, La, Pr, Nd	7.2
17.....	0.0852	0.1 gram each of Y, Gd, Er	7.2
18.....	0.0852	0.1 CeO ₂	7.1
19.....	0.0852	0.1 "	7.1
20.....	0.0852	0.1 "	7.1
21.....	0.0852	0.1 "	7.1
22.....	0.0852	0.2 "	7.1
23.....	0.0852	0.3 "	7.2
24.....	0.0852	0.3 "	7.1
25.....	0.0852	0.3 "	7.1
26.....	0.0852	0.6 "	7.1
27.....	0.0852	0.6 "	7.1
28.....	0.0852	0.6 "	7.2
29.....	0.0852	0.6 "	7.2
30.....	0.0852	4.26 "	7.1
31.....	0.0852	4.26 "	7.1

In titrations Nos. 11 to 31, the total dilution varied between 150 cc. and 300 cc., and one gram of sodium acetate was added to each to counteract any possible mineral acid present. These results show that although the consumption of molybdate solution was greater when other rare earths were present, the volume of molybdate was the same whether the added rare earth was small or large in amount. From this it was assumed that the concentration of acetic acid was insufficient to entirely prevent the precipitation of rare earths other than thorium.

Another set of titrations with increased acidity resulted as follows:

No.	Dilu- tion. Cc.	Sodium acetate. Gram.	Acetic acid (glacial). Cc.	ThO ₂ . Gram.	Other earths.	Molyb- date. Cc.
32.....	300	1	10	0.0852	0	6.4
33.....	300	1	10	0.0852	0	6.5
34.....	300	1	20	0.0852	0	6.4
35.....	300	1	20	0.0852	0	6.4
36.....	300	1	20	0.0852	0.1 gram each of Pr, La, Nd, Gd	6.45
37.....	300	1	20	0.0852		6.4

The values here obtained are in satisfactory agreement with those obtained with thorium alone, the increased acidity preventing interference by the other rare earths.

Composition of Precipitate.—Taking the value of the KMnO₄ already given (1 cc. = 0.005835 Fe) and its equivalent in terms of molybdate solution (28.2 cc. KMnO₄ = 10 cc. molybdate) then 1 cc. molybdate = 0.0098136 Mo. The average of the eleven titrations of thorium alone (Nos. 1-7 and 32-35) gives 0.0815 ThO₂ = 6.095 cc. molybdate, or a ratio Th : Mo = 1 : 2.017. Similarly, the average of titrations 36

and 37 with impurity present gives Th : Mo = 1 : 2.03. It is therefore probable that the precipitate is a normal thorium molybdate.

Analysis of Monazite Sand.—In order to test the accuracy of the method for the determination of thorium in monazite sand, samples of North Carolina and Brazil sands which had been analyzed by the fumaric acid method, the thiosulphate-ammonium oxalate method and the metanitrobenzoic acid method¹ were analyzed.

The volumetric method is carried out as follows: To one gram of the powdered sand in a porcelain crucible is added 10-15 cc. of concentrated sulphuric acid. After several hours heating, the crucible is cooled and the contents transferred, a little at a time and with constant stirring, to about 700 cc. water which has been cooled to near 0°. After standing several hours (over night if convenient) to insure complete solution of the sulphates, the solution is filtered and the residue washed thoroughly with cold water. The filtrate is nearly neutralized with dilute ammonia, 50 cc. of a cold saturated solution of oxalic acid added, and allowed to stand over night. The oxalates are filtered and washed with a dilute oxalic acid solution. When thoroughly washed, transfer precipitate and paper to a beaker, add 20-25 cc. of strong potassium hydroxide solution and heat to boiling. Dilute, filter and wash with hot water. Dissolve the precipitate of rare earth hydroxides off the filter by means of hot, dilute nitric acid. Evaporate to dryness on a water bath. Add a few cubic centimeters of water and again evaporate to dryness to remove free acid. To the dry residue add 20 cc. glacial acetic acid, dilute with 300 cc. water, add one gram sodium acetate and stir until dissolved. Titrate at room temperature with standard ammonium molybdate solution as already described.

The following results were obtained:

Percentage ThO ₂ .			
Volumetric method.	Metanitrobenzoic acid method. ²	Fumaric acid method.	Thiosulphate ammonium oxalate method.
4.80	4.76	4.85	4.90
4.80	4.85		
4.98	4.99		
4.99			
4.99			
4.99			
5.05			
5.05			
5.05			
Average.....	4.97	4.87	4.85
			4.90
5.58	5.60	5.70	5.63
5.65	5.65		
5.65	5.67		
5.65	5.70		
5.65	5.73		
5.72			
5.72			
Average.....	5.66	5.67	5.70
			5.63

¹ For a description of these methods, the reader is referred to the original articles: F. J. Meuzger, *Jour. Amer. Chem. Soc.*, **24**, 901. A. C. Neish, *Ibid.*, **26**, 780.

² Analyses by this method were made by Dr. A. C. Neish.

Percentage ThO ₂			
	Metanitro- benzoic acid volumetric method.	Fumaric acid method.	Thiosul- phate ammon- ium oxalate method.
No. 625 Brazil.....	4.85	4.88	
	4.92	4.89	
	4.92		
	4.98		
	5.1		
	5.3 ¹		
Average (omit- ting last).....	4.95		

The following were analyzed by the volumetric method but not checked by other methods:

No. 626 North Carolina.	No. 631 North Carolina.
4.84	5.11
4.84	5.11

CONCLUSIONS.

1. At room temperature thorium is precipitated quantitatively from a cold acetic acid solution (20 cc. glacial acetic acid and 300 cc. water) by means of ammonium molybdate.

2. Other rare earths found in monazite sand are not precipitated under the conditions defined in "1."

3. The ratio of thorium to molybdenum (1 : 2.017 and 1 : 203) indicates that the precipitate is a normal thorium molybdate.

4. By observing proper conditions of acidity, thorium may be accurately titrated by means of ammonium molybdate. Other rare earths have no effect on this titration.

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THE RESENES OF RESINS AND OLEORESINS.

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The oleoresinous exudate of pine trees, commonly called "crude turpentine," consists of a mixture of a volatile oil, acids and unsaponifiable matter. On distillation with steam the volatile oil, "spirits of turpentine," passes off; the residual resin, freed from excess of water by heating, solidifies on cooling and constitutes commercial "rosin." The name "resene" has been applied by Tschirch² to the non-volatile, unsaponifiable constituent of such resins and oleo-resins.

Though the composition of crude turpentine varies considerably in different specimens, an average analysis of specimens collected by the usual commercial methods would show approximately:

	Per cent.
Spirits of turpentine.....	20
Acids.....	74
Resene.....	6

Resenes, according to their origin, show varying physical states, some being colorless solids while many are very viscous liquids, extremely sticky and non-crystallizable. They are composed of carbon, hydrogen and oxygen, but the per cent. of oxygen is usually smaller than in the accompanying acids. Toward reagents they are very resistant, especially

toward alkalis. Although containing oxygen, they show, according to Tschirch,¹ none of the usual reactions indicating the presence of hydroxyl, carboxyl, aldehyde or ketone oxygen, nor are they ethereal salts or lactones. Tschirch inclines to the view that they belong to the class of oxyterpenes or oxypolyterpenes.

While much work has been done upon the volatile oils and the acids of oleoresins, little attention has been paid to the resenes, except ultimate analyses and approximate statements of the proportion present in isolated specimens studied. In connection with an investigation carried out in this laboratory in collaboration with the United States Forest Service, there remained a large number of specimens of resin from well identified individual trees growing in Florida. It seemed desirable, therefore, to study more closely the question of the proportions of resene in these specimens. The investigation was extended to the resins of conifers growing near this laboratory, and to specimens collected in other countries. Finally the amount of resene was determined in several oleoresins obtained in perfectly fresh condition from individual trees in Florida. These specimens were collected from the two species of pines from which crude turpentine is commercially obtained in this country, *Pinus Palustris*, (Longleaf Pine) and *Pinus Heterophylla* (Cuban or Slash Pine).

The resins were prepared by distilling the oleoresins in a current of steam slightly superheated, the temperature being raised to 140° C. toward the end of the distillation. After complete removal of the volatile oil, the residue was kept at 140° C. in the oil bath surrounding the distillation flask until all water was driven off. The molten resin was then filtered through absorbent cotton and cooled to solidification in glass or iron molds.

The determination of resene in the resins was carried out in the usual manner. The weighed specimen, about two grams, was dissolved in a considerable excess of *N/2* alcoholic potassium hydroxide, allowed to stand at room temperature eighteen hours, diluted with water until separation of the resene began and the solution cleared by the addition of a small quantity of ninety-five per cent. alcohol. This solution was then extracted three times with petroleum ether, boiling below 40°. The combined extracts were shaken out with fifty per cent. alcohol to remove slight amounts of dissolved potassium salts of resin acids. After drawing off the petroleum ether extract into a weighed glass evaporating dish, it was allowed to evaporate spontaneously to constant weight.

In the case of the oleoresins, after spontaneous evaporation of most of the petroleum ether the residue was heated for five hours on a steam bath in order to remove completely the petroleum ether and the volatile oil. Considerable difficulty was experienced at the outset in these evaporations due to the tendency of the material to "crawl" over the rim of the vessel.

¹ The authors are unable to account for this high result.

² Tschirch, "Die Harze und die Harzbehälter," Second edition, p. 1079.

¹ *Loc. cit.*