[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF NORTH CAROLINA.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.[1]

A STUDY OF PRASEODYMIUM: PREPARATION OF PURE MATERIAL—PRASEODYMIUM CITRATE.[2]

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We shall adopt in reporting investigations upon the rare earths the plan of succinctly stating in an introductory paragraph the facts observed and conclusions arrived at. Those desirous of familiarizing themselves with the details may peruse what follows at leisure. Perhaps others may care to pursue a similar course. No doubt a wider dissemination of the actual results arrived at wlll come about and the labors of abstractors be lessened and more accurate. Expediency influenced literary style before the twentieth century.

Synopsis. This paper contains a description of a novel method for rapidly preparing pure compounds of praseodymium. It depends essentially upon saturating a concentrated water solution of citric acid with ammonium free praseodymium hydroxide, in which the contaminating lanthanum is below 10 per cent. The solution is heated, whereby a new normal citrate is immediately precipitated and readily washed free from acid. The other procedures giving negative results were precipitations by potassium iodate, fractioning by hydrofluoric acid, gaseous hydrochloric acid, formaldehyde, fusion with potassium pyrosulphate, alkaline hydroxides, digestion in concentrated alkaline solutions, fusion with sodium peroxide, and attempts to form alums.

Fairly complete synopses of the observations leading to the breaking up of Mosander's[3] didymium into several elements have been given in an historical consideration of the rarer earths.[4] To

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[1] This and the following dozen or more papers were presented in abstracts in a lecture delivered before the New York Section under the title "The Rare Earth Crusade, what it Portends, Scientifically and Technically."

[2] Presented at the Pittsburg meeting of the American Chemical Society, 1902.

[3] *Ann. Chem.* (Liebig), **44**, 125.

[4] *Science* (N. S.), **17**, 772 (1902); see also Dennis and Dales: This Journal, **24**, 425 (1902).

Dr. Carl Auer without doubt belongs the main credit of renewing interest in and stimulating the most modern assaults upon these interesting bodies. The former grew out of his patient research, resulting in the announcement of neo- and praseodymium.[1] The latter was the outcome of his development and the extensive use of mantles composed of thorium and its co-geners for artificial illumination. The intimate relationship and the reciprocal dependence of pure and applied chemistry could not find a better illustration. The commercial demand for thorium compounds especially has caused extensive mining of and geologic investigations for the better known natural compounds, as cerite and monazite, and utilization of several others, previously regarded as rare curiosities of the mineral cabinet. In the extraction of the useful thorium oxide, there have accumulated tons of crude salt mixtures of the rarer elements biding a time of commercial extraction and utilization.

The Welsbach Lighting Company, of Gloucester City, N. J., through their late chemist, the lamented Dr. Waldron Shapleigh, and his long time associate and successor, Dr. H. S. Miner, has aided scientific men frequently in generously loaning preparations extracted and often purified to a high degree. This, and a number of other researches which follow in this series, have been facilitated and rendered possible in certain cases by Mr. Miner's gratuities, and we wish here to express profound thanks.

During the preparation of pure thorium compounds it was noted (by B)[2] that a concentrated solution of citric acid, saturated with thorium hydroxide, precipitated a pure thorium[3] citrate on heating. After destruction of the carbonaceous material and re-solution of the thorium oxide, no absorption bands were observable with a strong beam of light passing through 15 cm. of the concentrated sulphate or chloride. In the preparation of thorium tetrachloride to be used in redetermining the atomic mass of thorium, a slight red in several cases and a green deposit in others (sometimes together) was formed in the hard glass tub several centimeters beyond the boat in which the mixture of carbon and oxide was heated. While the absorption spectrum has proved a most valuable means of investigating certain of the

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[1] *Monatsh. Chem.*. **6**, 477 (1885).

[2] This Journal, **23**, 761.

[3] By "pure thorium" is meant the "old thorium" without considering the recent researches of Schmidt, the Curies, Crookes, Rutherford, Brauner, Baskerville and others.

rarer earths, as has been and will be pointed out, it is not as extremely delicate as one might wish. Boudouard[1] has been able to separate small amounts of neodymium from quite pure yttrium preparations by repeated fractionations when the material had long since failed to show the absorption bands of the former complex. Cleve[2] has observed the same with rather pure samarium. It has been learned in this laboratory that when quite pure neodymium and praseodymium oxides are mixed with carbon and heated to a dull red in an atmosphere of chlorine they do not give rise to volatile bodies. However, we have learned that praseodymium chloride, when subjected to a temperature sufficiently high to soften combustion tubing, evolved a greenish body.[3] Matignon[4] has also observed the same in regard to neodymium, when a pink colored deposit is formed in the cooler parts of the tube. From the color of these bodies, it was immediately assumed that in spite of the prolonged and painstaking method of preparation, our pure thorium compounds[5] still retained a trace of the constituents of didymium, which hangs on in other cases. Investigations were at once begun, therefore to learn the conduct of these elements with citric acid, the only novel feature in the method of purification not previously tested.

Before giving the result of those experiments, it may be well to state that up to that time the chlorine used had been generated by the action of pure concentrated hydrochloric acid upon recrystallized and granulated potassium dichromate. Subsequently a cylinder of pure chlorine was substituted with a complete cessation of the trouble. These red and green deposits were very small, but persisted in forming as long as the chlorine was prepared by the chromate method, and finally proved to be due to chromium. This was an observation of no little interest, as the chlorine gas was thoroughly scrubbed by passing through four wash-bottles of concentrated pure sulphuric acid (98 per cent.) and two columns of beads and one tower of pumice saturated with the same desiccating agent before entering the combustion tubing. One is immediately reminded of Crookes difficulty in preventing a back flow of mercury vapor in evacuating the bulbs for his beautiful

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[1] *Compt. Rend.*, **126**, 12.

[2] *Chem. News*, **51**, 145.

[3] This will be taken up in one of the subsequent papers.

[4] *Chem. News*, **84**, 97; *Compt. Rend.*, **133**, 5, and *Chem. News*, **85**, 132.

[5] *Loc. cit.*

phosphorescence spectra examinations, when he states[1] there is "no use trusting to a solid reagent to absorb a gaseous body."

Praseodymium ammonium nitrate prepared by the method of Auer[2] was converted into the hydroxide and washed by decantation until the ammonium salts were virtually removed. Twenty-five cc. of a concentrated water solution of citric acid were saturated with the praseodymium hydroxide by shaking in a glass-stoppered bottle; the undissolved hydroxide filtered away and the green solution heated. Immediately a pale green amorphous precipitate formed, settled upon the bottom of the vessel, was easily filtered and washed with hot water.

Similar experiments were carried out with neodymium and lanthanum hydroxides. The former is about one-tenth as soluble in citric acid as praseodymium hydroxide and is not precipitated on boiling, until the solution is very concentrated.

Lanthanum hydroxide is intermediate in its solubility and not precipitated at once on boiling. It requires concentration and continued heat, although both of these substances allow tough, whitish precipitates to form, when a very strong solution is permitted to stand some days at the temperature of the room. Perhaps here we may have to do with such colloidal compounds of the rare metals as mentioned by Delafontaine.[3] This point requires investigation, however.

Numerous attempts were made to apply the observations noted to separating lanthanum from the didymiums as they occur in monazite sand and other rare earth minerals, but with little success. The lanthanum apparently causes a supersaturated solution to form, which it is difficult to precipitate by heat; further, when a precipitate forms, it contains all three of the elements[4] in all the fractions obtained.

The praseodymium ammonium nitrate contained about 10 per cent. of lanthanum. One precipitation, according to the procedure mentioned, was sufficient to give a body absolutely free from lanthanum, as shown by the arc spectrograph made with a conclave Rowland's grating, 15,000 lines to the inch and 21 feet

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[1] *Chem. News*, **54**, 29.

[2] *Monatsh. Chem.*, **6**, 477.

[3] *Chem. News*, **73**, 284.

[4] The term "element" is used advisedly here, although there is no doubt of neodymium and praeseodymium being "complexes," as will be shown in later papers. At present, however, most chemists look upon these bodies as simple.

diameter.[1] This was determined frequently with that part of the spectrum which shows the strong lanthanum lines.

Praseodymium Citrate.—The body was prepared on different scales, using from a few grams of praseodymium ammonium nitrate to as much as 4 kilograms, in one place. The cold citrate solution (as much as 5 liters of the solution being used in certain experiments) was placed in a tall cylindrical precipitating jar and stirred by a water motor while the hydroxide was added to complete saturation, the agitation being continued from two to four hours. The temperature was kept down by placing the jar in running water. The turbid liquid was then quickly filtered by upward suction through an unglazed porcelain pear-shaped bomb. The beautiful, clear, leek-green solution was heated in large Jena glass beakers submerged in baths of boiling water, and filtered through a hot funnel, suction being applied at times, by means of the biscuit-ware mentioned, a most useful piece of apparatus when working on the large scale in the laboratory. The precipitate was readily and quickly washed by boiling water, in which it is insoluble (the washings being kept separate), until the fitrate was no longer acid to litmus.

The precipitate, when dried, was a loose powder, amorphous, of a beautiful pale green color. On analysis the following results were obtained:

					Calculated for (Pr 140.5)	
	Found.				$Pr(C_6H_5O_7)$.	$Pr(C_6H_5O_7).H_2O$.
Oxide (black) .	48.83	48.70			as PrO_2, 52.35	49.64
					or	or
					as Pr_4O_7, 49.90	48.49
Carbon........	....	....	21.05	21.18	21.85	20.72
Hydrogen.....	....	....	1.46	1.86	1.52	1.44

REMARKS AND PRECAUTIONS.

Ammonia prevented the formation of this normal citrate in this manner; hence the necessity for thoroughly washing the hydroxide. The citrate is soluble in ammonium citrate. So far, we have not sought to separate the double salt which is evidently formed.

As is well known, lanthanum hydroxide and in fact most of these so-called trivalent rare earth hydroxides combine with the carbon dioxide of the air, whereby a partial solution results and

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[1] Dr. W. J. Humphreys, of the Rouss Physical Laboratory, University of Virginia, kindly prepared these plates, a discussion of which he will publish in due time.

an increasing turbidity of the wash-water that is decanted, is observed, depending upon the poverty of ammonia and its salts. We avoided this by rapid working, making use of the largest unglazed porcelain suction filter made.

The filtrate from the citrate precipitate was concentrated by heat, and successive precipitates formed and were separated. They were mealy precipitates, which, on drying, formed light but tough masses, each succeeding mass being tougher than the preceding and more difficult to disintegrate into a powder. The fifth appeared in the solution as flocculent agglomerations like paper pulp and, on drying, became hard and leathery. The followng precipitates presented the same appearance and were almost white in color. The change in form and the disappearance of the green color were progressive throughout each series that was carried out. The percentage of oxide in the bodies correspondingly decreased from 48.83 per cent. to 35.77. The third precipitate gave strong lanthanum lines in the arc spectrum. They were not further investigated and are hardly worthy of the time necessary in view of the following facts.

In attempting to purify praseodymium on the large scale by this method, we observed that when the percentage of lanthanum rose above twenty no success attended our efforts. By the method of Auer[1] a large proportion of the lanthanum is first crystallized out as double ammonium nitrate. It has been observed by Dennis,[2] Bettendorff[3] and others that didymium breaks up the more readily, accompanied with less frequent formation of supersaturated solutions, difficult to handle, when lanthanum is present in notable amounts. By this modified Welsbach method, praseodymium may be readily separated from neodymium, but it is a more difficult proposition to secure the latter devoid of the former. To separate pure neodymium, Boudouard[4] and Muthmann[5] advocate crystallizing the double potassium sulphate, but this does not leave either one free from lanthanum, unless the material is subjected to a prolonged series of fractional crystallization, almost exasperating in their consumption of time, as all who have worked with these rare earths know.[6] With

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[1] *Loc. cit.*

[2] This Journal, **19**, 800 (1897).

[3] *Ann. Chem.* (Liebig), **256**, 163.

[4] *Compt. Rend.*, **126**, 12; *Chem. News*, **77**, 193.

[5] *Ber. d. chem. Ges.*, **31**, 1731.

[6] A paper follows, giving a new method for freeing neodymium of lanthanum.

these facts in mind, it becomes evident at once that a quick method for the separation of 5 to 10 per cent. of lanthanum is worth while, and one that separated the praseodymium absolutely pure is most desirable. In fact, one phase most engrossing rare earth work at present has to do with finding such means for the separation of pure compounds.

Our last work was with 7 kilograms of praseodymium ammonium nitrate free from neodymium, but containing more than 20 per cent. of lanthanum. The material had undergone 300 crystallizations and came from about 100 tons of monazite. A water solution was precipitated by ammonium hydroxide in large glazed earthenware vessels (100-liter capacity), provided with spiral outlets by which, on removing rubber stoppers, the supernatant liquid might be drawn from different heights. The excess of ammonium nitrate was thus removed by two washings to prevent the attack of platinum (by its decomposition) in which the entire precipitate was ignited in portions. To decrease the percentage of lanthanum present, the method of Auer[1] proved satisfactory, and is not expensive, *viz.*, the mixed oxides were added to dilute nitric acid until almost saturated, an account being kept of the weight, and then as much more oxide added. The more basic lanthanum forms the nitrate and remains in solution, taking a part of the praseodymium, as might be expected, while the major portion of the latter oxide is undissolved. Lanthanum, of course, is still present in the undissolved portion, but in much smaller percentage. The difference in the affinity, at least towards nitric acid, is not sufficient to serve as a method for bringing about a rapid separation of these bodies in the pure state. The solution was separated by filtration, washed once or twice and the respective fractions converted into hydroxides of the earths free from ammonia. Citric acid saturated with the hydroxide from the nitrate solution gave no precipitate on boiling, while that from the undissolved oxides immediately gave an excellent separation of the citrate, yielding over a kilogram of pure praseodymium oxide on ignition. The material is absolutely free from lanthanum and as pure as that used by Jones[2] in his atomic weight determination. It may be well to state that Dr. Humphreys made the spectrographs for Dr. Jones and had the plates for comparison.

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[1] *Monatsh. Chem.*, **5**, 508.

[2] *Am. Chem. J.*, **20**, 5. 345 (1898).

Although chemically pure citric acid free from lead, ammonia free from silica and sulphuric acid, and nitric acid giving no residue on evaporation, and redistilled water were used, the preparation contains such impurities as would be gathered from the containers used in the process, but they are in such small amounts as not to vitiate the results reported in several of the following papers, and of such a character that they may be readily removed at the stage it is deemed necessary.

This material as a neutral nitrate, examined at various dilutions and different thicknesses, showed an absorption spectrum that is given for the normal so-called elementary praseodymium (bands 569, 482, 469 and 443) and was used in the other work reported in this series. The absorption spectrum was examined and photographed with a Steinheil grating (14,438 lines to the inch) spectroscope, as described by Dennis.[1] The instrument is essentially the same, except that it is a size larger and has a quartz slit. The source of light used at first was a 100-candle power Edison incandescent light with a helexoid filament. Latterly we have substituted a 600-candle power arc light enclosed in a projection lantern which serves to focus the rays upon the slit. The bright lines of carbon and its impurities, once noted, do not interfere with the observations of the bands. The instrument was purchased with a grant from the Bache Fund of the National Academy.

During the progress of this work, the application of other methods for accomplishing the same object were attempted. Separating by potassium iodate, hydrofluoric acid, crystallizing a concentrated chloride solution by saturating with gaseous hydrochloric acid, formaldehyde, fusion with potassium pyrosulphate, alkaline hydroxides, digestion of rare earth[2] hydroxides in concentrated alkaline solutions, fusion with sodium peroxide, and endeavoring to form alums, were tried and they either gave negative results or such as did not warrant pursuit.

Conclusion.—Pure praseodymium compounds may be prepared by heating a saturated citric acid solution from which praseodymium citrate separates when the percentage of lanthanum is below 10, in a few hours, while by the former methods weeks or even months were required.

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[1] This Journal, **24**, 415.

[2] See papers on "Lanthanates," "Neodidymates," "Double Sulphates," etc., following.