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EXTRACTION OF CERIUM (IV) NITRATE BY BUTYL PHOSPHATE

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ABSTRACT

Cerium (IV) nitrate is readily extracted from aqueous solutions by tri-n-butyl phosphate, a solvent which is reasonably stable under the strongly oxidizing conditions. The conditions for extraction are not critical, and favorable extraction is not inhibited by perchlorates or acetates, but sulfates interfere. By oxidation with bromates and simultaneous exhaustive extraction by butyl phosphate, the cerium may be quantitatively extracted. The degree of separation of cerium from iron, zirconium, lanthanum, and praseodymium are discussed. Uranium and thorium are extracted by butyl phosphate; the first is easily removed beforehand, and the second may be separated by coprecipitation of ceric iodate. It is believed that cerium (IV) nitrate is extracted by butyl phosphate by virtue of the formation of a new complex. Some attempts were made to identify or characterize this new body, but no conclusive evidence was gained.

Introduction

In a previous report (1) on the extraction of cerium with various solvents attention was focused on the use of nitromethane, and the high solvent action of butyl phosphate was also noted. The cerium was extracted from an acid solution of ammonium hexanitratocerate (IV). The extraction method for cerium was further investigated, and is here described.

The extraction affords a method for the separation of cerium and is similar to the ether extraction technique previously employed by Imre (2).

Experimental

1. Stability of Tri-n-Butyl Phosphate toward Cerium (IV) Nitrate

Reagents: All inorganic chemicals were of reagent grade quality. The butyl phosphate, white label quality from the Eastman Kodak company, was vacuum distilled, and the portion boiling at 145-150° /8mm. was collected separately. It was saturated with water before use. Some specially treated solvent, labeled butyl phosphate-A, was prepared by extracting 10 ml. of an acid solution 0.5 M in $(NH_4)_2Ce(NO_3)_6$ with 200 ml. or ordinary butyl phosphate, allowing to stand 56 hours to destroy any oxidizable impurities, removing the cerium by re-extraction with dilute H_2O_2, and washing well with water.

To each of a series of flasks, each containing 10 ml. of an aqueous solution 0.5 M in $(NH_4)_2Ce(NO_3)_6$ and M in HNO_3, was added 5 ml. of vacuum-distilled butyl phosphate. A second series was similarly prepared, the specially treated butyl phosphate-A being employed. The solutions were titrated with standard ferrous sulfate, using ferroin indicator, after the elapse of various periods of time. In this way the per cent of the total cerium reduced by the solvent could be determined. The results are given in Table 1, and shown graphically in Figure 1.

Table 1

The Rate of Reduction of Ce (IV) by Butyl Phosphate

Vacuum-Distilled Butyl Phosphate			Butyl Phosphate-A		
Solution number	Total Time elapsed(hrs)	% Ce (IV) reduced	Solution number	Total Time elapsed(hrs)	% Ce (IV) reduced
1	1.58	0.95	1A	1.83	0.35
2	7.25	2.37	2A	7.33	1.54
3	23.6	3.49	3A	23.8	2.80
4	34.9	5.07	4A	35.1	4.00
5	54.6	5.94	5A	54.7	5.00

Table 1 con't

The Rate of Reduction of Ce (IV) by Butyl Phosphate

Vacuum-Distilled Butyl Phosphate			Butyl Phosphate-A		
Solution number	Total Time elapsed(hrs)	% Ce (IV) reduced	Solution number	Total Time elapsed(hrs)	% Ce (IV) reduced
6	120	9.94	6A	120	8.50
7	215	16.9	7A	215	15.6
8	314	21.5	8A	314	19.4
9	503	31.0	9A	503	29.0
10	816	45.1	10A	816	41.5

It was evident that while the butyl phosphate used in the second series caused the reduction of less cerium, the ordinary solvent, even without vacuum distillation, was highly satisfactory for most purposes, providing the cerium was re-extracted from the solvent within several hours.

2. Conditions for Extraction of Cerium (IV) Nitrate by Butyl Phosphate

Solutions of ceric nitrate, containing varying amounts of nitric acid and ammonium nitrate, were extracted with butyl phosphate, the layers separated, and the organic phase titrated with ferrous sulfate. In this way the per cent of the cerium extracted under a variety of conditions was determined, and representative data are presented in Table 2. In most cases the aqueous phases after extraction were colorless, and 2 to 10 per cent of the Ce (IV) had been reduced to Ce (III).

Table 2
The Extraction of Ceric Nitrate by Butyl Phosphate

Conc. Ce (IV) molarity	Conc. NH_4NO_3 molarity	Conc. HNO_3, molarity	Volume aqueous phase, ml.	Volume organic phase, ml.	% Ce extracted
0.5	3	1	10	10	98
.5	1	0	10	10	95
.5	1	1	10	10	98-99
.01	0.02	1	100	10	84
.01	1	1	100	10	87
.001	1	3	100	10	60

Favorable conditions for the extraction were thus found not to be critical, although the presence of nitric acid was necessary to promote the clean separation of the phases. Solutions 0.5 M in Ce (IV), M in NH_4NO_3, and M in HNO_3 were usually employed in the remainder of the work, since they were readily prepared by dissolving ammonium hexanitratocerate and nitric acid.

3. Recovery of Cerium from the Solvent

The great affinity of cerium (IV) nitrate for butyl phosphate rendered re-extraction by water quite slow, but it was quickly and quantitatively removed by reducing agents. Hydrogen peroxide, hydroxylamine, hydrazine, ferrous sulfate, glucose, and formaldehyde were all used, the first being most practical.

Evaporation of the recovered cerous solutions to dryness and ignition yielded gray or black residues, presumably due to the presence of pyrophosphates in the oxide. This difficulty was eliminated by extracting the aqueous phase thoroughly with benzene or carbon tetrachloride before evaporation and ignition, or before precipitation of cerous oxalate. The oxide thus prepared was nearly white, having a slight cream-colored hué. Its phosphorous content was less than 1000 ppm, under the lower limit of spectrographic detection.

4. Effect of Sulfates, Perchlorates, and Acetates

Solutions were prepared 0.1 M in Ce (IV), M in NH_4NO_3, and M in HNO_3, and 0.5 in one of the following salts: $(NH_4)_2SO_4$, NH_4ClO_4 or $NH_4C_2H_3O_2$. After extraction with an equal volume of butyl phosphate, the cerium remaining in the aqueous phase was titrated with standard ferrous sulfate. This revealed that the aqueous phase from the sulfate solution retained an average of 87 per cent of the cerium, the perchlorate solution an average of 0.4 per cent, and the acetate solution 0.3 per cent. Thus only the sulfate ion introduced as serious interference with the extraction of the ceric nitrate.

5. Oxidation of Ce (III) and Exhaustive Extraction of Ce (IV)

Cerium (III) nitrate was oxidized to cerium (IV) nitrate either electrolytically or chemically. In the former the oxidation was carried out as recommended by Smith, Frank, and Kott (3), on a smaller scale; it was found advantageous to shield the cathode with a short glass tube. After three oxidation steps, each followed by a butyl phosphate extraction, over 99.5 per cent of the cerium was removed.

Chemical oxidation of cerous to ceric nitrate was effected by the action of bromates in strong nitric acid, the technique first employed by Schuman (4). Solid sodium bromate was added to the cerous nitrate solutions, 8 to 10 M in nitric acid, at room temperature. The bulk of the cerium was removed from such solutions by three extractions with butyl phosphate, but a small quantity was retained by the aqueous phase.

In order to realize complete extraction of cerium, a U-tube-stirrer extractor, described by Huzise (5), and modified in use by Cruikshank, Fitch, and Russell (6), was used. The aqueous phase, about 150 ml. in volume, was 0.2 M in Ce (III), 8-10 M in HNO_3, 3 M in $NaNO_3$, and 0.4 M in NH_4NO_3. Small quantities of solid sodium bromate were added over a period of two to three hours, using a total of 3 grams, while butyl phosphate was run in, a total of 300 ml. being employed. Qualitative tests showed that no detectable cerium remained in the water phase. The butyl phosphate extracted bromine as well as cerium; re-extraction with dilute hydrogen peroxide removed the latter. The solvent was further treated with sodium sulfite to remove bromine, and washed well with water before re-use.

6. Separation from Iron, Zirconium, and Lanthanum

The degree of separation of cerium from certain other metals was determined by extractions carried out under conditions simulating those in actual cerium extractions. The aqueous phase (100 ml., M in NH_4NO_3, and M in HNO_3) contained varying amounts of iron, zirconium or lanthanum nitrates, the latter two sometimes as radioactive isotopes. The butyl phosphate layer (100 ml.) after extraction was washed four times with 25 ml. portions of solutions M in NH_4NO_3 and M in HNO_3, and re-extracted with hydrogen peroxide (100 ml., 0.5 M in HNO_3, and 1% H_2O_2). The aqueous solution was washed twice with carbon tetrachloride to remove traces of butyl phosphate, and analyzed for iron, zirconium or lanthanum. Iron analyses were carried out spectrophotometrically using 1, 10-phenanthroline (7), and zirconium and lanthanum analyses were made gravimetrically or radiometrically (Zr^{95}, half life 65 days, and La^{140}, half life 40 hours) (8). The quotient, $\frac{\text{mg. in original aqueous phase}}{\text{mg. from organic phase}}$, was taken as a "separation factor".

Table 3 gives the separation factors observed for several concentrations of the three metals.

Table 3

Separation Factors for Butyl Phosphate Extraction of Cerium (IV) Nitrate

Metal	Conc. in original aqueous solution, mg./100 Ml.	Separation factor
Fe	1	1500; 2000
Fe	5	5000; 5000
Fe	500	500000; 1000 000
Fe	5000	1 700 000
Zr	400	150; 180
Zr	4000	630
La	4	95; 95
La	400	80; 80

It is observed that while satisfactory separations from iron (III) nitrate are achieved, a little zirconium nitrate and considerable lanthanum nitrate, are extracted.

7. Behavior of Lanthanum and Praseodymium upon Exhaustive Extraction of Cerium

Experiments were made to determine the extent to which lanthanum and praseodymium nitrates were carried over in the quantitative extraction of cerium (IV) nitrate by butyl phosphate, employing the U-tube stirrer technique described above (part 5). Known amounts of the rare earths were extracted under the conditions already described, and the extracts were analyzed. In Table 4 are shown the loss of lanthanum and praseodymium incurred during quantitative extraction of cerium.

Table 4

Extraction of $La(NO_3)_3$ and $Pr(NO_3)_3$ by Butyl Phosphate

Metal Oxide	Amount taken, mg.	Amount found in extract, mg.	% Extracted
La_2O_3	240	8.6	3.6 (a)
La_2O_3	600	39.4	6.5
La_2O_3	600	42.3	7.1
Pr_6O_{11}	290	43.8	15.0
Pr_6O_{11}	194	24.8	12.7

(a) Solution extracted was 0.2 M in Ce

The rather large fraction of the praeodymium extracted suggests that some Pr (IV) compound was extracted by the butyl phosphate upon oxidation by bromates, analogous to the corresponding behavior of cerium.

8. Behavior of Uranium and Thorium

Both uranyl and thorium nitrates were observed to be readily extracted by butyl phosphate. It was found that traces of thorium could be satisfactorily removed from cerium by the following procedure: After re-extraction of cerium from the butyl phosphate, using hydrogen peroxide, the aqueous solution was washed with carbon tetrachloride to remove the small amount of solvent, and boiled to destroy the excess peroxide. Two to four per cent of the Ce (III) nitrate solution was removed, and electrolytically oxidized to Ce (IV) nitrate, which was returned to the bulk of the Ce (III) nitrate. Ceric iodate was precipitated by adding an excess of iodic acid solution, and after standing a while, the precipitate was filtered off. The ceric iodate evidently co-precipitated thorium iodate, for the thorium content of the cerium in the filtrate from the iodate treatment was less than the spectrochemical limit of detection (about 1000 ppm).

9. Nature of the Extraction

The high extraction power of butyl phosphate for cerium (IV) nitrate over a wide range of conditions suggested compound formation between solvent and solute. A possibility, for example, is the neutral body resulting from the displacement of two nitrate ions from the hexanitratocerate ion by two butyl phosphate molecules, forming the complex, $[Ce(NO_3)_4(Bu_3PO_4)_2]$. While this phase of the investigation was not pursued sufficiently to establish the identity of the extracted substance, a certain amount of information was gained.

Absorption Spectra -- Aqueous and butyl phosphate solutions 0.05 M in cerium (IV) were prepared, and the absorption spectra determined with the aid of a quartz prism Beckman spectrophotometer, using 1 cm. cells. For wave lengths below about 400mμ the solvent and nitric acid were increasingly absorbing. The curves are given in Figure 2, and are seen to be identical except for a shift toward the higher wave lengths for the non-aqueous solution. This shift in absorption band may be attributed to the change in solvent and to a change in the coordinating groups around the cerium.

Extraction of Ammonium Salts. -- An acid solution of ammonium hexanitratocerate was extracted with butyl phosphate, and the organic phase washed with dilute nitric acid; this phase was then analyzed for ammonium nitrogen by the Kjeldahl method. Entirely negligible amounts of ammonia were evolved, demonstrating that the ammonium ion plays no role in the extraction.

Butyl Phosphate-Cerium Ratio. -- Aqueous solutions containing $(NH_4)_2Ce(NO_3)_6$ and HNO_3 were treated with small, known quantities of butyl phosphate, and the mixture shaken well. The organic phase was then extracted with carbon tetrachloride, and the Ce (IV) content established by titration with ferrous sulfate. This permitted the determination of the Bu_3PO_4/Ce ratio under conditions where the Ce (IV) was in great excess. The results are expressed in Table 5.

Table 5

Removal of Ce (IV) by Limited Quantities of Butyl Phosphate

Aqueous Solution				Bu_3PO_4	Bu_3PO_4/Ce
Vol., ml.	Ce (IV) conc., M	NH_4NO_3 conc., M	HNO_3 conc., M	g.	ratio
20	0.5	1	3	0.194	2.55
"	"	"	"	.194	2.64
"	"	"	"	.835	2.52
"	"	"	"	.969	2.48
"	"	"	"	1.561	2.40

The formula $[Ce(NO_3)_4(Bu_3PO_4)_2]$ would demand a ratio of two, but there was no assurance that all of the butyl phosphate entered the complex.

Nitrate-Cerium Ratio. -- Ammonium hexanitratocerate solutions were prepared without the use of nitric acid, and aliquots extracted with various volumes of butyl phosphate. The organic phases were washed twice with water, and filtered through papers wetted with butyl phosphate. Portions of these solutions were weighed out, and half were titrated with ferrous sulfate to determine the cerium content. The remaining butyl phosphate solutions were made very weakly acid with sulfuric acid, and dilute hydrogen peroxide added until the orange Ce (IV) color disappeared. The organic phases were washed repeatedly with water, and the aqueous phases, containing the nitrate and cerium (III), were extracted with petroleum ether to remove traces of butyl phosphate. The solutions were boiled a few minutes, and analyzed for nitrate by the nitron method (9), with the results given in Table 6.

Table 6

Nitrate-Cerium Ratios of Butyl Phosphate-Extracted $(NH_4)_2Ce(NO_3)_6$

Conc. $(NH_4)_2Ce(NO_3)_6$, M	Vol. $(NH_4)_2Ce(NO_3)_6$, ml.	Vol. Bu_3PO_4, ml.	NO_3/Ce ratios
0.2	10	15	3.44; 3.40
.5	10	25	3.18; 3.26
1.0	20	20	3.22; 3.28
1.0	10	20	3.30; 3.22

The above ratios are distinctly less than four, required by the formula $[Ce(NO_3)_4(Bu_3PO_4)_2]$, but a number of possible errors were not entirely eliminated. No substantial evidence was gained which supported the above formula.

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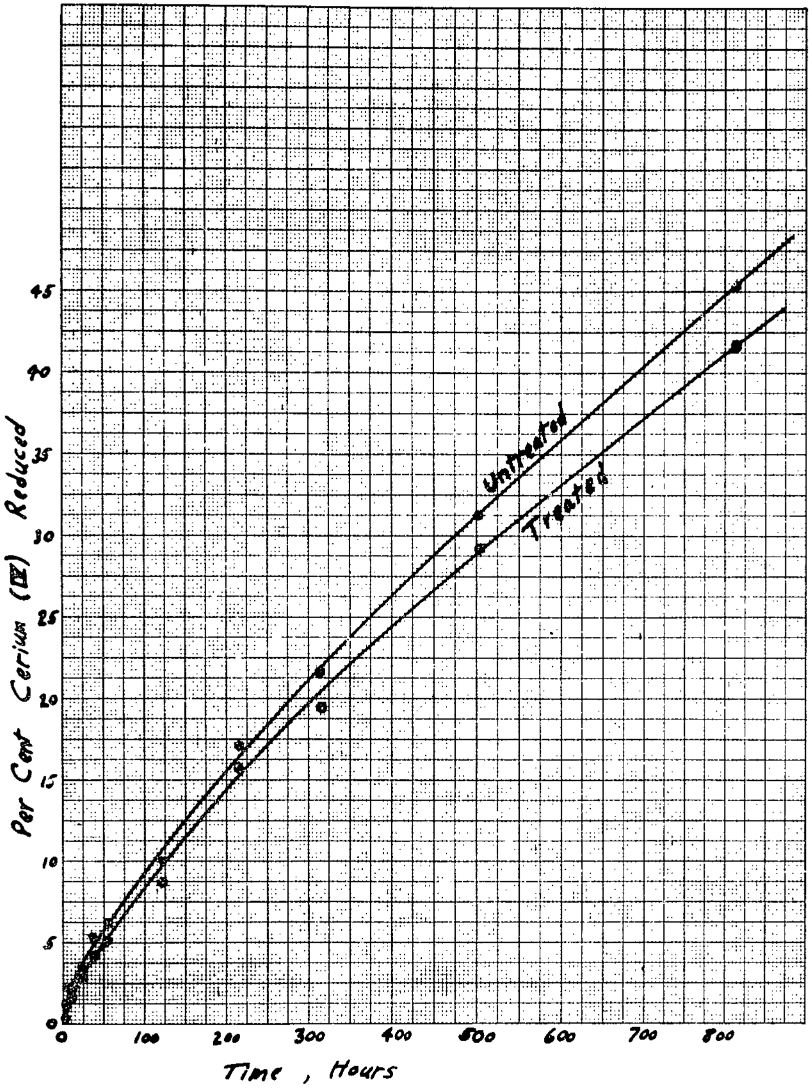

Fig. 1. Reduction of Ce (IV) Nitrate by Butyl Phosphate

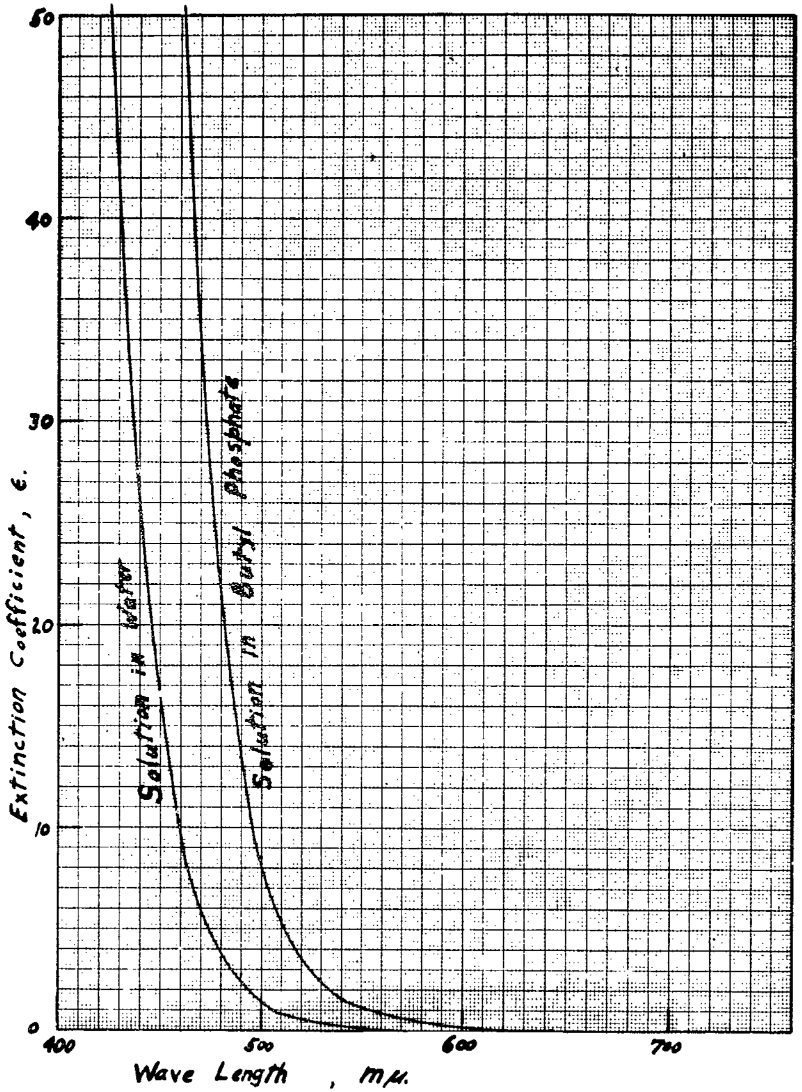

Fig. 2. Absorption Spectra of Cerium (IV) Nitrate Solutions