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New Studies in the Isolation and Properties of Curium

W. W. T. Crane and I. Perlman

August 3, 1950

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NEW STUDIES IN THE ISOLATION AND PROPERTIES OF CURIUM

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ABSTRACT

Methods of preparation and handling of pure curium compounds are described in detail. Some experimental data bearing on the stability of the tripositive oxidation state are given. The results of an investigation of the absorption spectrum of curium, using a Baird three-meter grating spectrograph are given, together with a discussion of the relation of this spectrum to that of gadolinium, the rare-earth analog of curium.

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Since the isolation of curium (element 96) was first reported[1] larger amounts have been prepared and improvements made in its separation. The currently separated curium has been used principally in the presently reported studies to attempt the oxidation above the tripositive state since the stability of this state is an important consideration in the actinide concept of heavy element structure.[2] The curium (Cm^{242}) was prepared as before by the transmutation of Am^{241} according to the following reactions and is an alpha-particle emitter with a half-life of only 162 days:

(1) L. B. Werner and I. Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 22.5 (McGraw-Hill Book Co., Inc., New York, 1949).

(2) G. T. Seaborg, Nucleonics 5, no. 5, 16 (1949).

$$Am^{241}(n,\gamma)Am^{242m}$$

$$Am^{242m} \xrightarrow[16\ hr.]{\beta^-} Cm^{242}$$

The problems of the isolation of curium are those of working with intensely radioactive materials and the chemical separation from americium and rare earth fission products which are closely allied in properties.

The methods of separating curium from macroscopic amounts of americium and from rare earth fission products have been much improved in the past two years. One of the important new methods is that of Street and Seaborg[3] for separating

(3) K. Street, Jr. and G. T. Seaborg, J. Am. Chem. Soc., 72, 2790 (1950).

actinide elements from lanthanide elements using cation exchange columns with concentrated HCl as the eluting agent. In addition, the time for separation has been cut down from the order of a week to the order of a day by using adsorption columns maintained at an elevated temperature.[4]

(4) B. B. Cunningham, E. R. Tompkins, and L. B. Asprey (unpublished April, 1947) first demonstrated the usefulness of the cation exchange column method for separating americium and curium using Dowex-50 and room temperature elutions with 0.25M ammonium citrate plus citric acid at pH of 3.05.

The few milligrams of americium, irradiated as the oxide, was dissolved in nitric acid, ten milligrams of lanthanum as the nitrate was added and the combined hydroxides precipitated with ammonia gas. The hydroxides were dissolved in 1M HNO_3 and the trifluorides of lanthanum, americium, and curium precipitated by making the solution 6M in HF. The fluorides were then put back into 0.5 ml. of 0.5M HNO_3 solution by first metathesizing to the hydroxides with 10M KOH at 85°C.

The substances in solution were added to the top of a column of Dowex-50 cation exchange resin 1 cm. in diameter and 20 cm. long. In then eluting with 12M HCl the americium and curium came off in the third column volume while the rare earths remained considerably behind. The course of the americium and curium was followed by measuring their alpha-particles. The column used in this separation was larger than needed to hold the quantities of ions involved and was used in order to dilute the band of curium as it passed through the column, otherwise the high density of alpha-particles would cause sufficient concentration of water decomposition to produce active bubbling. The amount of curium involved

was of the order of ten micrograms. Ten micrograms emit 1.2 x 109 alpha-particles per second.

The solution containing the actinide element fraction was evaporated to dryness, taken up in 0.1M HCl and placed on a similar cation exchange column. This time the column was maintained at 87°C and eluted with 0.25M citrate solution at pH 3.5 as described by Thompson, Cunningham, and Seaborg.[5] In about two

(5) S. G. Thompson, B. B. Cunningham, and G. T. Seaborg, J. Am. Chem. Soc., 72, 2798 (1950).

hours the curium and americium came off the column in the relation shown by the typical elution curve of Fig. 1. The ordinate of the curve is alpha-activity and since there is a 1000-fold difference in half-life, the americium is actually present in considerably large quantitites by weight than the curium. The activities of americium and curium were dissociated by using an alpha-particle pulse analyzer which discriminates between different energies.

The curium represented by the first half of its elution peak is essentially pure. By assaying the activity with a Geiger counter as well as by spectrographic analysis, this curium fraction was shown to have less than 0.1% americium by weight. Other parts of the eluate containing appreciable amounts of curium were rerun through a column obtaining more pure curium and this fractionation procedure was repeated once more.

The combined citrate solution of curium was adjusted to pH 1 and the curium was adsorbed on some fresh cation exchange resin by slurrying and this was placed on the top of another cation exchange column. The curium was again eluted with 12M HCl, evaporated to dryness, and dissolved in 0.1 ml. of 1M HNO_3. (This second "HCl column" run was made for further purification and to place the curium in a solution from which it could be concentrated by evaporation.) This solution was transferred to a fluorothane centrifuge cone and pure CmF_3 obtained by

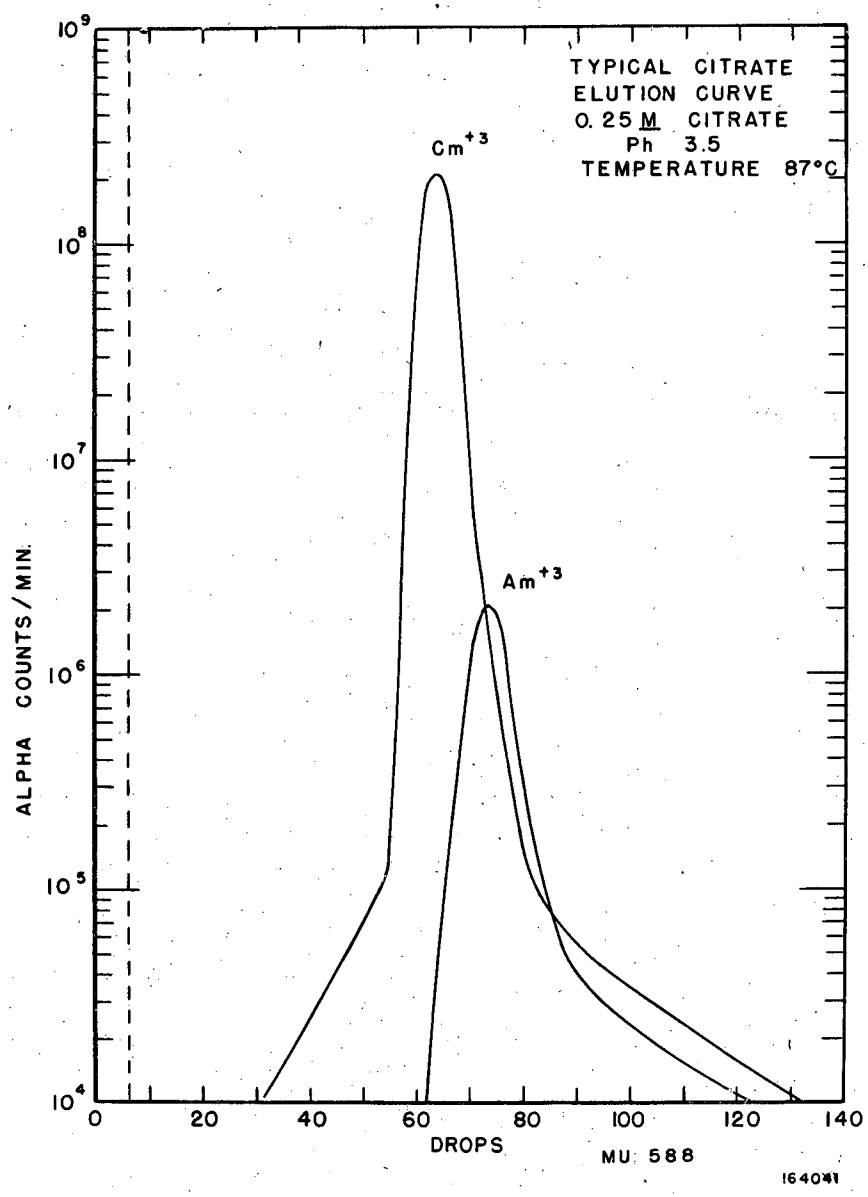
TYPICAL CITRATE
ELUTION CURVE
0.25 M CITRATE
Ph 3.5
TEMPERATURE 87°C
Cm+3
Am+3
ALPHA COUNTS / MIN.
DROPS
MU 588
164041

Fig. 1

precipitating in 6M HF. The yield of curium in this separation was 90%.

Because of its high specific alpha-activity, curium presents a problem in storage. It has been noted that glass vessels develop checks and cracks and plastic vessels carbonize when exposed to concentrated forms of curium. The method used so far to store curium for more than a day or two is to evaporate the solution in a small platinum boat and to store there as the solid residue.

A previous measurement of the absorption spectrum of curium in solution was made with a Beckmann spectrophotometer in which there was found no appreciable absorption in the visible region up to 10,000A but broad absorption in the ultraviolet region.[1] The absorption spectrum is among the properties desirable to compare with those of gadolinium the corresponding lanthanide element with half-filled 4f shell. In the previous measurements with the spectrophotometer, the absorption in the ultraviolet region could not be determined with satisfaction because of limitations of the instrument. As a result, with the new sample of curium, measurement was made in a special cell 1.5 mm. wide x 1 cm. deep using a 3 meter Baird 3 meter grating spectrograph. Mr. John Conway performed the spectrograph measurements. The solution was 0.0013M $Cm(ClO_4)_3$ in 0.2M $HClO_4$ and the results are shown in Fig. 2 along with measurements of gadolinium taken by Mr. D. C. Stewart with a Beckmann spectrophotometer using a hydrogen lamp. The similarity is marked in view of the fact that earlier members of both lanthanide and actinide series show prominent absorption bands in the visible region.

Attempts to oxidize curium to a state higher than the tripositive state using tracer concentrations of curium have all failed.[6] In the light of the

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(6) S. G. Thompson, L. O. Morgan, R. A. James, and I. Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 19.1 (McGraw-Hill Book Co., Inc., New York, 1949).

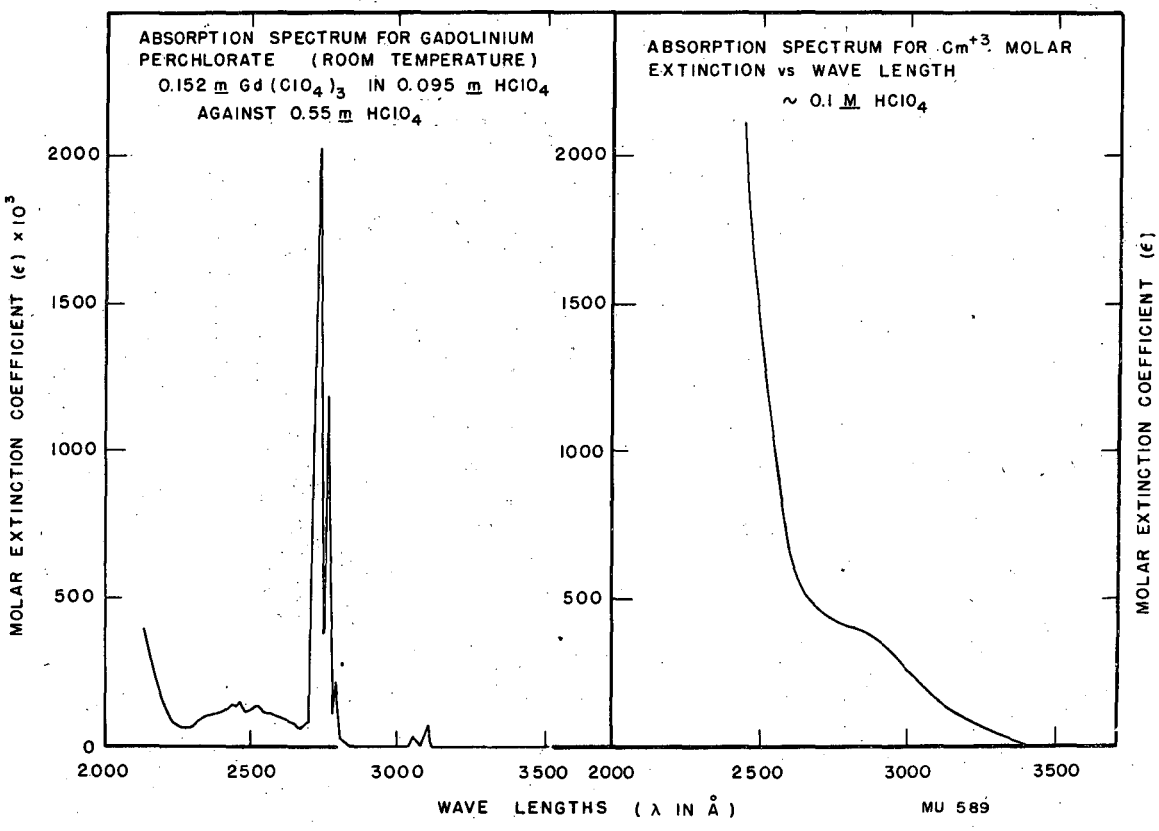
ABSORPTION SPECTRUM FOR GADOLINIUM PERCHLORATE (ROOM TEMPERATURE)
0.152 m Gd(ClO4)3 IN 0.095 m HClO4
AGAINST 0.55 m HClO4
ABSORPTION SPECTRUM FOR Cm+3 MOLAR EXTINCTION vs WAVE LENGTH
~ 0.1 M HClO4
MOLAR EXTINCTION COEFFICIENT (ε) x 10^3
MOLAR EXTINCTION COEFFICIENT (ε)
2000
1500
1000
500
0
2000
2500
3000
3500
WAVE LENGTHS (λ IN Å)
MU 589

Fig. 2

recent success in oxidizing Am(III) to Am(VI) using macro-concentrations of americium[7] attempts were made to oxidize Cm(III) under similar conditions. A

(7) L. B. Asprey, S. E. Stephanou, and R. A. Penneman, J. Am. Chem. Soc., 72, 1425 (1950).

solution of 0.1M HNO_3 containing 0.004M Am(III), 0.007M La(III) and 0.00015M Cm(III) was treated with ammonium peroxydisulfate for two hours at 85°C. The lanthanum was then precipitated as the fluoride as a means of removing all of the actinide ions that had not been oxidized to the hexapositive (fluoride soluble) state. Essentially all of the curium and americium were found in the precipitate showing that neither the curium nor the americium were oxidized. When the curium concentration was reduced 20 fold, other ions remaining the same, the americium became oxidized while the curium remained unaffected. The inability to maintain a strong oxidizing potential in solutions ~10^{-4} molar in curium must be related to reducing substances formed by the intense alpha-radioactivity, probably hydrogen peroxide.

Similar attempts were made to produce Cm(IV) and Cm(V) without success. Oxidation was carried out with peroxydisulfate in phosphate solution to make use of the complexing action of phosphate for tetrapositive actinide ions in decreasing the (III)-(IV) potential. Zirconium phosphate was then precipitated to remove any tetrapositive curium. Over a range of acidities and curium concentrations, no oxidation could be detected. The oxidation to the pentapositive state was attempted using a method found applicable to americium and plutonium. If either of these actinide elements is treated with NaOCl in carbonate solution (40% K_2CO_3), oxidation takes place and an insoluble compound is found which can be proved to be the pentapositive state.[8] Under none of the conditions tried was

(8) L. B. Werner and I. Perlman, J. Am. Chem. Soc., to be published.

there evidence for curium oxidation.

From these attempted oxidations it may be concluded that all of the potentials from Cm(III) to higher oxidation states are either more negative than about -2 volts or that the rates are too slow for concentrations of curium that will allow an oxidizing medium to persist.

This work was performed under the auspices of the U. S. Atomic Energy Commission.