

Behaviour of transplutonium and rare earth elements in acidic and alkaline solutions of potassium ferricyanide

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The behaviour of transplutonium (TPE) and rare earth (REE) elements has been studied and a method of americium isolation from TPE and REE is suggested using acidic and alkaline solutions containing $[\text{Fe}(\text{CN})_6]^{3-}$ ions.

The search for new complex-forming and oxidizing systems for TPE and REE has opened up new possibilities in the chemistry and technology of these elements. Ferrocyanide-ions are known to form a multitude of salts with cations of various elements and rare earths in particular.^{1,2} Formation of salts with the same cations occurs also with ferricyanide-ions³ but to a considerably lesser degree. Use of the ferri/ferrocyanide system has been described in various redox reactions, for example for oxidizing Np(V) and Pu(V) up to Np(VI) and Pu(VI), respectively,^{4,5} and for obtaining neptunium and plutonium in the heptavalent oxidation state.⁶ It is of immediate interest to study the behaviour of some TPE and REE in weakly acid and alkaline solutions containing ions of tri- and bivalent iron.

On addition of potassium ferrocyanide to an americium solution in 0.1 M nitric acid the isolation of a white precipitate occurs,⁷ just as in the case of REE.² However, on addition of potassium ferricyanide an americium species precipitates from acidic solution,⁷ contrary to REE. We have, in fact, isolated an americium ferricyanide precipitate from all the investigated solutions of mineral acids: HClO_4 , HCl , HNO_3 , H_2SO_4 , H_3PO_4 . A change in acid concentration in the range 0.01 to 1 mol dm^{-3} (at a constant concentration of 0.5 M $[\text{Fe}(\text{CN})_6]^{3-}$) and a change in ferricyanide concentration from 0.1 to 0.5 mol dm^{-3} (at constant concentration of 0.01 M HClO_4) had no pronounced effect on the completeness of americium precipitation. In all cases the remaining content of americium in the solution, determined immediately after precipitate isolation, varied from 10 to 15% of its initial amount. Curium,⁸ berkelium and californium behave, under these conditions, in the same manner as americium. Initial concentrations of TPE ranged from 1 to 3×10^{-3} mol dm^{-3} in these experiments. Curium precipitation was 82% complete while on average, 90% of the initial berkelium and californium precipitated. The remaining concentration of TPE in solution does not correspond to the value of the true solubility of ferricyanides obtained and it is conditioned by precipitate peptization similar to the peptization of REE ferrocyanides,¹ which is suppressed by the introduction of organic solvents

into the solution. We have shown that addition of EtOH (40% vol.) resulted in an increase in TPE precipitation: up to 95–98% completion.

To establish the composition of ferricyanide precipitates of the studied TPE the relationship between concentrations of metal and ferricyanide-ion was determined after dissolving these precipitates in a 0.25 M aqueous solution of potassium pyrophosphate or in a 1 M H_2SO_4 solution. The radionuclide concentration was determined radiometrically and the ferricyanide concentration was found spectrophotometrically by the magnitude of the optical density at 448 nm using the tentatively found relationship between optical density and $[\text{Fe}(\text{CN})_6]^{3-}$ -ion concentration in pyrophosphate and sulfuric acid solutions.

The metal:ferricyanide-ion ratio in isolated precipitates of studied TPE was found to be 1:1. The composition of precipitates was also studied as a function of holding time in initial solution. We have shown that a decrease in [ferricyanide-ion] and an accumulation of ferrocyanide occurred in the solid phase when the time between precipitate preparation and dissolution increased. A decrease in the optical density of the ferricyanide absorption band was determined immediately after dissolving precipitates in alkaline pyrophosphate solution. Accumulation of ferrocyanide in the solid phase was confirmed by a subsequent increase in optical density of the ferricyanide absorption band occurring after acidifying the basic pyrophosphate solution in which the precipitate was dissolved. In this case the maximum magnitude of ferricyanide-ion optical density corresponds to its concentration which is in stoichiometric ratio to TPE concentration, confirming the metal:ligand ratio as 1:1 in the precipitate. Hence a rise in optical density in the light absorption spectrum of acidic solutions occurs as a result of ferrocyanide-oxidation, the products of which accumulate in the solid phase as the precipitate is left to stand. Hydrogen peroxide formed during radiolysis, as shown in special experiments,⁷ is an oxidizer in acidic and a reductant in basic solutions. Also, we have shown that $[\text{Fe}(\text{CN})_6]^{4-}$ oxidation in acidic solutions proceeds considerably faster than $[\text{Fe}(\text{CN})_6]^{3-}$

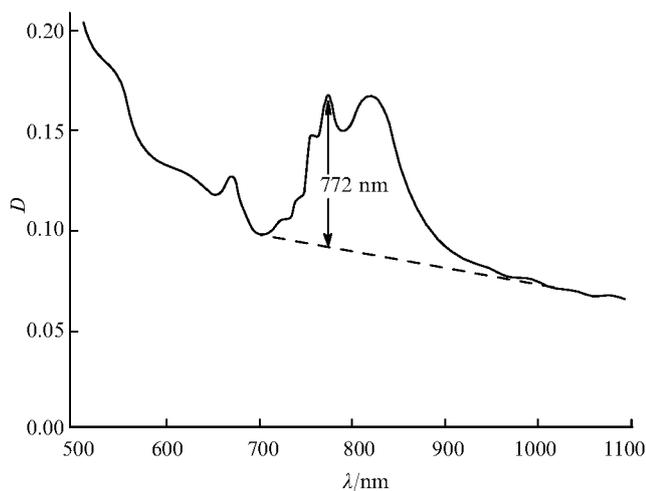


Figure 1 Absorption spectrum of the solution obtained by dissolving $\text{Am}(\text{OH})_3$ in 2–8 M NaOH containing 0.01–0.5 M $\text{K}_3[\text{Fe}(\text{CN})_6]$. $[\text{Am}] = 2.5 \times 10^{-3}$ M.

reduction in basic pyrophosphate solution. It is worth noting that although TPE ferricyanide precipitates are isolated from acidic solutions and some acidic solution is undoubtedly captured by the precipitate, nevertheless the diametrically opposite process of reducing ferricyanide to ferrocyanide proceeds in the precipitate. This would seem to be explained by the peculiarities of radiolysis in the solid phase. Hence the composition of TPE compounds formed in acidic $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution corresponds to the formula $\text{An}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ where $\text{An} = \text{TPE}$. Reduction of ferricyanide to ferrocyanide occurs gradually due to radiolysis in the precipitate solid phase. In the presence of $[\text{Fe}(\text{CN})_6]^{4-}$ in the solid phase it is evident that the composition of part of the precipitate corresponds to the formula $\text{KAn}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$.

Americium passes into the solution on treatment of americium(III), curium(III), californium(III) and berkelium(III) hydroxides precipitate with sodium hydroxide solutions containing 0.01–0.5 M potassium ferricyanide at concentrations from 2 to 8 mol dm^{-3} . Cm, Cf and Bk remain in the precipitate. A wide band in the wavelength range 700–800 nm with clearly expressed fine structure differing from the known absorption bands of americium in oxidation states +3, +4, +5 and +6 is observed in the absorption spectrum of the solutions obtained (Figure 1).

The dependence of optical density at 772 nm upon the americium concentration in the solution follows the Lambert–Beer law,⁷ suggesting the true nature of the solution. The average molar absorptivity at 772 nm is equal to $6.87 \pm 0.18 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. As the solution ages (its absorption spectrum is shown in Figure 1) americium precipitates as a grey solid. In such a manner the initial concentration of americium in solution decreases from 2.5×10^{-3} to $0.73 \times 10^{-3} \text{ mol dm}^{-3}$ after about 22 h. We have shown that americium in the precipitated compound is present in the +5 oxidation state. There are observed the only absorption bands of Am(V) at 520 and 720 nm in the absorption spectrum of the solution obtained by dissolving the precipitate in 0.1 M HNO_3 . The precipitated compound is the hydroxide of pentavalent americium, having the composition $\text{Na}_2\text{AmO}_2(\text{OH})_3 \cdot n\text{H}_2\text{O}$ because precisely this type of hydroxide precipitates at concentrations of OH^- greater than 2 mol dm^{-3} according to ref. 9. Hence the transition of americium into solution upon treatment of americium(III) hydroxide precipitate with alkaline potassium ferricyanide solution is caused by its oxidation up to the pentavalent state and by the formation with $[\text{Fe}(\text{CN})_6]^{3-}$ ions of a soluble complex having the composition $(\text{AmO}_2)_3[\text{Fe}(\text{CN})_6]$. Curium, berkelium and californium do not pass into the solution under these conditions.

Table 1 Contents of TPE and REE before and after americium isolation.

Element	Initial amount in solution ($V = 1$ ml) / μg		Amount after separation ($V = 1$ ml) / μg	
Experiment	1	2	1	2
Am	828	797	818	727
Cm	–	11.4	–	0.4
Bk	372	–	0.36	–
Cf	510	30	0.48	0.65
Eu	–	1970	–	1.5
Ce	–	1230	–	1.1

The data obtained can be used for americium isolation from the nearest TPE and REE. Group separation of TPE and REE is realized at the stage of TPE ferricyanide precipitation. In this case REE remain in acidic solution and can be easily separated from precipitated TPE. Isolation of americium from the nearest TPE is carried out at the stage of its alkaline-ferricyanide dissolving. Other TPE remain in the precipitate and can be simply separated from the americium solution. Final isolation of americium from the solution is achieved by the addition of hydrogen peroxide to this solution to reduce Am(V) to Am(III) which precipitates in the form of $\text{Am}(\text{OH})_3$. The precipitates of $\text{Am}(\text{OH})_3$ were dissolved in 1 ml of 0.5 M HNO_3 and the elemental content analysed. Quantitative results of americium isolation from TPE and REE are shown in Table 1.

It is seen from the data obtained that americium separation from milligram amounts of REE and other TPE under the conditions developed is achieved with separation factors of about 1000.

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