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Extraction of Plutonium with N-Benzoyl-Phenyl-Hydroxylamine

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With 8 figures. (Received January 31, 1965)

Summary

In this work the extraction of plutonium from aqueous solutions has been studied by means of a cupferron analog, N-benzoyl-phenyl-hydroxylamine (BPH), dissolved in chloroform.

Plutonium in the tetravalent state can be extracted from HCl-citric acid solutions in the presence of $NaNO_2$ in the studied p_H range, i. e. from 0 to 4.3. For a 0.4 BPH concentration the maximum distribution coefficient is $4 \cdot 10^3$ at a p_H of 1.2. Alpha-emitters which are not tetravalent, U(VI), Np(V) and Am(III), are not extracted under these conditions.

Pu(IV) can also be extracted from $HClO_4$-citric acid solutions with distribution coefficients higher than 250 in the range between 4.5 M acid and p_H 4.7, the maximum value being $3.5 \cdot 10^3$ at p_H 0.25.

The influence of other variables on the distribution coefficient has also been studied, such as stabilizing agents ($NaNO_2$, $K_2Cr_2O_7$), contacting time, and the concentration of BPH in the organic phase.

Zusammenfassung

Wir untersuchten die Extraktion von Plutonium aus wäßrigen Lösungen durch eine Chloroformlösung des Cupferron-Analogen N-Benzoylphenylhydroxylamin (BPH). Pu^{4+} kann im untersuchten p_H-Bereich von 0 bis 4,3 in Anwesenheit von $NaNO_2$ aus HCl/Citronensäure-Lösungen extrahiert werden. Für eine BPH-Konzentration von 0,4 m ist der maximale Verteilungskoeffizient $4 \cdot 10^3$ bei p_H 1,2. α-Strahler anderer Wertigkeit: U^{6+}, Np^{5+} und Am^{3+}, werden unter diesen Bedingungen nicht extrahiert.

Pu^{4+} kann auch im Bereich von 4,5 M Säure bis p_H 4,7 aus $HClO_4$/Citronensäure-Lösungen mit Verteilungskoeffizienten über 250 extrahiert werden, wobei das Maximum von $3,5 \cdot 10^3$ beim p_H 0,25 liegt.

Der Einfluß anderer Variabler auf den Verteilungskoeffizienten, wie Stabilisatoren ($NaNO_2$, $K_2Cr_2O_7$), Kontaktzeit und BPH-Konzentration in der organischen Phase, wurde ebenfalls untersucht.

Résumé

Nous avons étudié l'extraction du plutonium des solutions aqueuses, par un dérivé du cupferron, le N-benzoyl-phénylhydroxylamine (BPH) dissous dans le chloroforme. Pu^{4+} s'extrait des solutions HCl/acide citrique, en présence de $NaNO_2$, dans le domaine de p_H étudié: 0–4,3. Pour une concentration de 0,4 M en BPH, le coefficient de distribution maximal est de $4 \cdot 10^3$ à p_H 1,2. Les émetteurs α non-tétravalents: U^{6+}; Np^{5+}, et Am^{3+}, ne sont pas extraits dans ces conditions. Pu^{4+} peut être extrait aussi à partir de solutions de $HClO_4$/acide citrique, avec un coefficient de distribution au-dessus de 250, dans tout le domaine allant de 4,5 M acide à p_H 4,7, le maximum étant $3,5 \cdot 10^3$ à p_H 0,25.

On a étudié également l'influence d'autres variables sur le coefficient de distribution, à savoir les agents stabilisants ($NaNO_2$, $K_2Cr_2O_7$), la durée du contact, et la concentration en BPH dans la phase organique.

Introduction

Since BAMBERGER used BPH for the first time in 1919 [1], this reagent has been applied extensively in quantitative analysis for gravimetric determinations of Be [2], Mo [3], Ti [4], U [5], and Zr [6, 7]; in carrier-free radiochemical techniques [8, 9]; for separations of Nb and Ta by solvent extraction [10]; etc.

More recently, CHMUTOVA et al. have used the reagent for plutonium extraction [11]. These authors have shown the superiority of BPH over other chelating agents such as TTA, cupferron and neocupferron. In their work it is shown that Pu extractions are quantitative for very short extraction times (15 seconds) from nitric solutions between 1 and 6 M and that from hydrochloric solutions the extracted percentage decreases as the contacting time increases, probably due to the reducing action of BPH.

In this work the Pu(IV) extractions from hydrochloric acid have been investigated in the p_H range from 0 to 4 and also from perchloric acid from 4.5 M acid to p_H 4. The drawback of working with an easily hydrolizable element such as plutonium at low acidities has been circumvented by the addition of citric acid as complexing agent. The reducing action of BPH was arrested by addition of $NaNO_2$ or $K_2Cr_2O_7$. In this way, although the extraction times required to reach equilibrium conditions are not as short as those found at acidities 1 M or higher, the destruction of the chelating agent by nitric acid is avoided. The distribution coefficients (total Pu concentration in the organic phase/total Pu concentration in the aqueous phase) are very high for Pu(IV) and at the same time very high separation factors are attained from other alpha emitters such as uranium, neptunium and americium, which may be present in the plutonium as contaminants.

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Experimental

Reagents

All reagents were of analytical grade and were used without further purification, with the exception of chloroform, which was distilled twice. The N-benzoylphenyl-hydroxylamine was obtained from T. Schuchardt (Germany).

The ^{239}Pu was obtained from Harwell as PuO_2. It was dissolved and purified from other actinides by passage through an anionic ion exchanger, then converted to the Pu(IV) state by heating with hydroxylamine at low acidity and taken twice to dryness with concentrated nitric acid. Depending on the experiments planned, the residue was then taken up in a mixture of 0.075 M citric acid with 1.5 molar mineral acid (either HCl or $HClO_4$). In no case were these solutions permitted to stand more than 5 hours before the extractions were made.

The ^{237}Np was obtained from Amersham and used without further purification. The absence of other alpha emitters was proved by alpha spectrometry using a solid state detector and the Np(V) state was obtained by the same method as described for Pu(IV). The residue was also taken up in hydrochloric – citric solutions or perchloric – citric solutions, according to the experiment to be carried out.

The ^{241}Am and the ^{233}U, both from Amersham, were analyzed by alpha spectrometry and used without further purification. Stock solutions were prepared in the same way as for plutonium and neptunium.

From a ^{95}Zr–^{95}Nb solution (Amersham) in 7 M HCl – 0.3 M HF, the ^{95}Nb was extracted with a 0.2% BPH solution in chloroform. The purity of the carrier free niobium and zirconium solutions obtained in this way was proved by β absorption curves and determination of the half-life in the case of niobium.

Equipment

The p_H control was carried out by means of a Beckman "Zeromatic" apparatus. Total alpha activity of the phases was measured with a conventional alpha scintillation counter with a ZnS(Ag) screen. Alpha spectrometry was performed with a surface barrier detector (Au-Si) and a Nuclear Data multichannel analyzer. Phase equilibrations were carried out in Pyrex tubes 10 cm high and 1 cm diameter, by inversion at a speed of 30 rev./minute. Three glass pearls were added to each tube to help contacting the phases.

Technique

Preliminary experiments showed that the plutonium extraction depends on several variables which could conveniently be studied separately in the following way:

a) The distribution coefficient (*Cd*) as a function of the $NaNO_2$ concentration and mixing time. The valency state of plutonium, the p_H value and BPH concentration were kept constant.

b) At a chosen $NaNO_2$ concentration, *Cd* was studied as function of p_H, keeping the other variables constant.

c) The variation of C_d was studied on changing the BPH concentration in the organic phase at a selected point in the curve obtained from b). The number of BPH molecules in the extracted plutonium complex can be determined in this way.

d) The plutonium extraction from a non-complexing acid such as perchloric acid was studied. The selected acidity range was from 4.5 M to p_H 4. The equilibrium times were also investigated in this case.

Case a)

To an aliquot of the Pu(IV) solution in 1.5 M HCl – 0.075 M citric acid, a sufficient amount of $NaNO_2$, NH_4OH and distilled water were added to reach the desired concentration and p_H values. The final com-

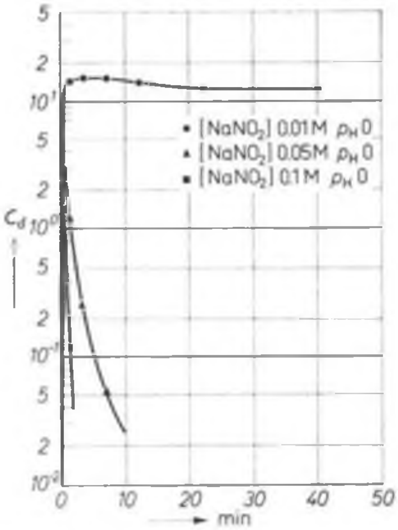

Fig. 1. Pu(IV) extraction from 1 M [Cl^-]; 0.05 M [cit.]; with 0.1 M BPH/Cl_3CH as function of time. Phase ratio: organic/aqueous = $^2/_3$

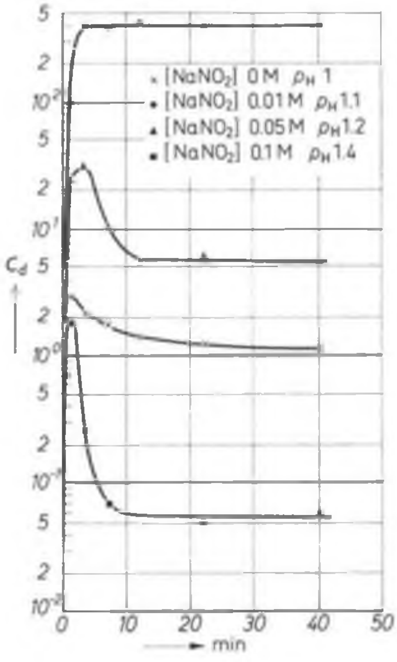

Fig. 2. Pu(IV) extraction from 1 M [Cl^-]; 0.05 M [cit.]; with 0.1 M BPH/Cl_3CH as function of time. Phase ratio: organic/aqueous = $^2/_3$

position was: Pu 2×10^{-5}M, Cl^- 1 M, citrate 0.05 M, which was kept constant for the different p_H values studied.

The organic phase, BPH in chloroform, was previously equilibrated with a plutonium free aqueous phase of the same composition as the one to be extracted, 2 ml of the organic phase being used with 3 ml of the aqueous one. Agitation by inversion was used at room temperature (about 20 °C). At the end of each investigated extraction time, 50 μl samples of each phase were taken to be dried on glass discs with an infrared lamp, flamed and counted with the alpha counter. The results of these experiments are shown in Figs. 1 to 4. It can be seen from the curves that at high nitrite concentrations and low p_H values there is a strong decrease in the distribution coefficient Cd when the mixing time is increased. A nitrite concentration of 0.01 M was selected as the suitable value for comparative runs. (A measurement with 0.005 M. $K_2Cr_2O_7$ as a stabilizing agent at p_H = 1.47 gave a Cd-value of 300, quite similar to the Cd-value found with nitrite.)

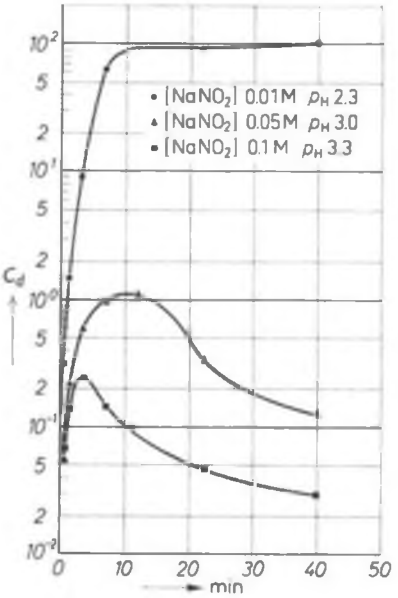

Fig. 3. Pu(IV) extraction from 1 M [Cl^-]; 0.05 M [cit.]; with 0.1 BPH/Cl_3CH as function of time. Phase ratio: organic/aqueous = $^2/_3$

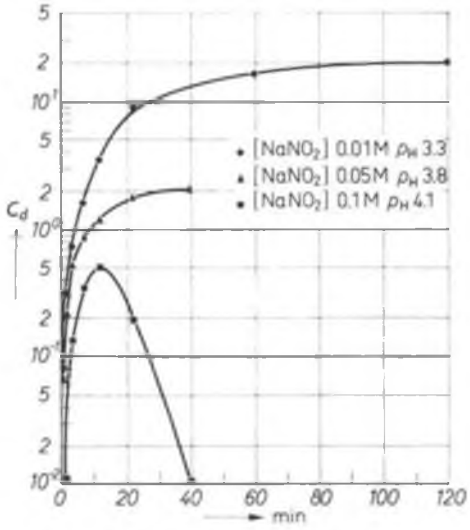

Fig. 4. Pu(IV) extraction from 1 M [Cl^-]; 0.05 M [cit.]; with 0.1 M BPH/Cl_3CH as function of time. Phase ratio: organic/aqueous = $^2/_3$

Case b)

The same technique was used as in a) with the same final composition of the aqueous phase. The p_H value was adjusted to the desired value and extractions were made from 3 ml aqueous phase with 2 ml BPH 0.1 M, previously equilibrated. The same experiment was carried out with 0.4 M BPH using an organic/aqueous ratio of 0.1. The results are shown in Fig. 5. (The points shown in these curves correspond to very pronounced plateaus in the C_d *vs.* times curves, similar to these shown for 0.01 M nitrite solutions in the preceding figures.)

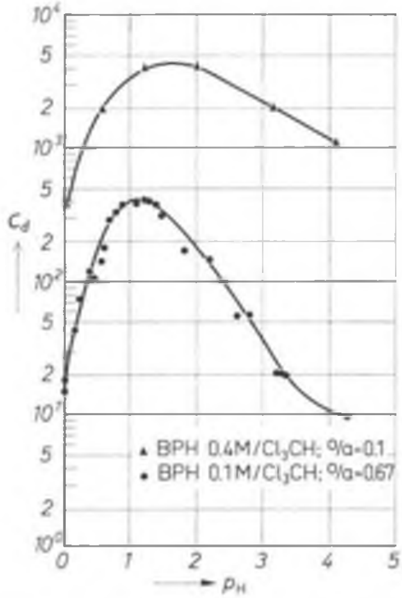

Fig. 5. Pu(IV) extraction from 1 M [Cl^-]; 0.05 M [cit.]; 0.01 M [$NaNO_2$]; with BPH/Cl_3CH as function of p_H

Case c)

The extractions were carried out on an aqueous phase of the same composition as in a) and b) with a constant p_H of 0.6. BPH concentrations ranged from 0.05 M to 0.4 M. The ratio of both phases were selected in such a way that the ratio of sodium nitrite to BPH was constant in all cases. Fig. 6 shows the variation of C_d as a function of BPH concentration in the organic phase.

Case d)

The final aqueous to be extracted was Pu(IV) 2×10^{-5}M, perchlorate 1 M, citrate 0.05 M. The p_H value was adjusted with NH_4OH and the ratio of the phase volumes was organic/aqueous = 0.1. Equilibrium extractions are reached after 5 minutes for p_H values ranging from 0 to 2. For a p_H value of 4, the equilibrium is approached very slowly. Fig. 7 shows the variation of C_d in the p_H range while Fig. 8 shows the result at perchloric acid concentrations from 1.5 M to 4.5 M. (The values at $p_H < 2.5$ indicate well-developed plateaus on the C_d *vs.* times curves, for the points at $p_H > 2$ it is, however, possible that equilibrium had not yet been reached.)

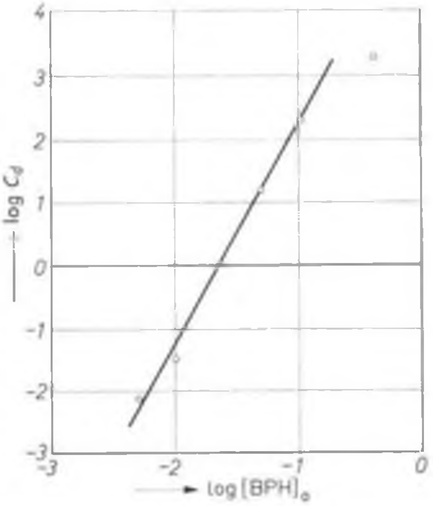

Fig. 6. Pu(IV) extraction from 1 M [Cl$^-$]; 0.05 M [cit.]; 0.01 M [NaNO$_2$]; $p_H = 0.6$; with BPH/Cl$_3$CH as function of [BPH] in the organic phase

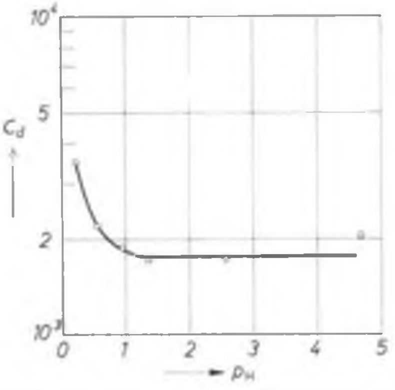

Fig. 7. Pu(IV) extraction from 1 M [Cl O$_4^-$]; 0,05 M [cit.]; 0.01 M [NaNO$_2$]; with 0.4 M BPH in Cl$_3$CH

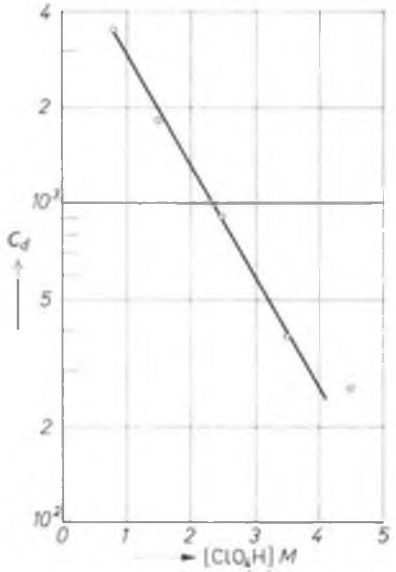

Fig. 8. Pu(IV) extraction from ClO$_4$H; 0.05 M [cit.]; 0.01 M [NaNO$_2$]; with 0.4 M BPH in Cl$_3$CH

Extraction of uranium, neptunium and americium

The extraction of these other actinides was studied at the p_H-value of maximum extraction for Pu(IV) from hydrochloric acid solutions, i.e. p_H 1–1.2. Each of these actinides was studied separately. The composition of the aqueous phases before extraction was the same as in the case of plutonium, the only difference being the actinide element itself. The original concentrations and resulting extraction coefficients with their separation factors are indicated in Table 1. The phase volume ratio was in each case aqueous/organic = 10, the p_H of the solutions being 1.2 and the BPH concentration 0.4 M in chloroform.

Table 1

Actinide μC/ml	C_d	Separation factor respective to Pu
U 1.1	0.02	2.3×10^5
Np 0.4	4.2×10^{-3}	$\sim 10^6$
Am 1.4	0.9×10^{-4}	4.4×10^7

In the same way were ^{95}Zr and ^{95}Nb contacted with BPH, both in the p_H region and at higher acidities. Both nuclides were found to extract in all cases.

Discussion

Extraction experiments from HCl solutions without addition of Na$_2$NO$_2$ or K$_2$Cr$_2$O$_7$ (Fig. 2) show that the distribution coefficients are much lower in those cases. This suggests a reduction of Pu(IV) caused by the extracting reagent. In 1 M HCl, the oxidation potential of Pu(III)-Pu(IV) is −0.970 Volt [12] while that of BPH has been estimated at −1.20 by Lutwick and Ryan [13] based on a series of oxidation reduction reactions of 1% BPH in alcoholic solution with Cr$_2$O$_7^-$, MnO$_4^-$, V^{++} and Ti^{+++}. Alimarin [14] on the other hand has found a reduction wave at 1.07 Volt using a Hg-Pt electrode in an ammonium chloride solution of BPH. We have observed the appearance of the blue colour of Pu(III) when a 10^{-2}M ^{239}Pu solution in 1 M HCl is saturated with solid BPH, and also when using alcoholic solutions of BPH. This reducing power of the reagent explains why former extractions of plutonium from hydrochloric acid solutions without the addition of stabilizing agents were not found to be satisfactory [11].

Reaction of HNO$_2$ with the chelating groups of BPH is the cause of the quick decrease of the distribution coefficient at increasing nitrite concentration (Figs. 1 to 4). This is especially noticeable at low p_H values,

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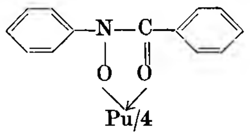
where the reactivity of HNO_2 is higher. As a result of this, the nitrite concentration should not be higher than 0.01 M when the BPH concentration is 0.1 M and the 3/2 aqueous/organic phase volume ratio is maintained.

The citric acid plays a double function: it avoids the hydrolysis and polymerization of plutonium and it increases the selectivity of the method by the formation of less extractable charged complexes of other elements. The decrease of C_d at increasing p_H values (Fig. 5) is explained by the complexing action of the citrate ion, which is more effective at higher p_H values due to the dissociation of the acid in this region.

The composition of the BPH-Pu(IV) complex can be investigated by studying the variation of C_d on changing the concentration of the complexing agent in the organic phase, at a fixed p_H value. The slope of the line of log C_d versus log (BPH), which represents the number of BPH molecules associated to the central plutonium atom, is found to be equal to 4 from Fig. 6, corresponding to a structure of the type



Die Verbindungen des dreiwertigen Plutoniums, Americiums und Curiums mit 8-Hydroxychinolin und einigen seiner Derivate

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Mit 2 Abbildungen. (Eingegangen am 29. Oktober 1965)

Zusammenfassung Chelatverbindungen der dreiwertigen Actinidenelemente Plutonium und Americium mit 8-Hydroxychinolin der Zusammensetzung Me(Ligand)$_3$ lassen sich durch Fällungsreaktion aus wäßriger Lösung darstellen. Die Plutoniumverbindung ist jedoch nur bei völligem Ausschluß von Sauerstoff zu erhalten, da sehr leicht Oxydation zu Pu(IV) erfolgt. In ihren Eigenschaften gleichen die Actiniden(III)-Oxinate weitgehend den analogen Verbindungen der Seltenen Erden. Bei der Extraktion mittels einer Lösung der Chelatbildner in Chloroform gehen die Verbindungen Am(Oxin)$_2$Y, Cm(Oxin)$_2$Y und Am(5,7-Dichloroxin)$_3$ in die organische Phase über, wahrscheinlich ist $Y = OH^-$. Die Bruttostabilitätskonstante des Am(5,7-Dichloroxin)$_3$ ist $\lg \beta_3 = 21{,}93$ bei $T = 25{,}0 \pm 0{,}5$ °C und $\mu = 0{,}1$.

Summary Chelates Me (ligand)$_3$ of trivalent plutonium and americium with 8-hydroxyquinoline are obtained by precipitation from aqueous solutions. As the plutonium compound is very easily oxydized to Pu(IV), it can only be prepared in a completely oxygen-free medium. The properties of the oxinato-complexes of trivalent actinides are much alike those of the analogous rare earth compounds. Solutions of the chelating agent in chloroform extract the compounds Am(oxine)$_2$Y, Cm(oxine)$_2$Y and Am(5,7-dichloro-oxine)$_3$ into the organic phase, Y probably being OH^-. The overall stability constant of Am(5,7-dichloro-oxine)$_3$ is $\log \beta_3 = 21.93$ at $T = 25.0 \pm 0.5$ °C and $\mu = 0.1$.

Résumé On prépare les complexes chelatés Me (ligande)$_3$ des ions trivalents du plutonium et de l'américium avec la 8-hydroxy-quinoléïne par précipitation en solution aqueuse. Le complexe du Pu^{3+} ne s'obtient qu'en absence totale d'oxygène, puisqu'il est facilement oxydable en Pu^{4+}. Les propriétés des oxinates des actinides trivalents sont analogues à celles des composés correspondants de terres rares. Les solutions des agents chelatants dans le chloroforme extraient les composés Am(oxine)$_2$Y, Cm(oxine)$_2$Y et Am(5,7-dichloro-oxine)$_3$ dans la phase organique, Y étant probablement OH^-. La constante de stabilité totale de Am (5,7-dichloro-oxine)$_3$ est $\log \beta_3 = 21{,}93$ à $T = 25{,}0 \pm 0{,}5$ °C et $\mu = 0{,}1$.

1. Einleitung

Dreiwertige Actiniden und Lanthaniden besitzen weitgehend die gleichen chemischen Eigenschaften, der Hauptunterschied ist die etwas größere Tendenz der Actiniden zur Bildung von Koordinationsverbindungen. Eine Trennung der beiden Elementgruppen ist daher ziemlich schwierig, sie erfolgt zumeist durch Ausnützung der unterschiedlichen Komplex- oder Chelatbildung. 8-Hydroxychinolin (kurz Oxin genannt) und seine Derivate sind viel verwandte Reagenzien zur Trennung und Bestimmung von Metallen, deren Verhalten gegenüber den Lanthaniden in zahlreichen Veröffentlichungen beschrieben ist [1]. Über Actiniden (III)-Oxinate gibt es nur kurze Hinweise [2, 3]. Daher schien es interessant, die Verbindungen des Oxins mit den dreiwertigen Transuranen darzustellen und zu untersuchen, ob sie zur Trennung der Transurane untereinander oder von anderen Elementen benützt werden können. Als Chelatbildner fanden neben dem einfachen 8-Hydroxychinolin einige seiner in 5- und 7-Stellung substituierten Derivate Verwendung.

2. Experimenteller Teil

a) Ausgangssubstanzen

Die Ausgangslösungen der dreiwertigen Transurane wurden durch Auflösen der Dioxide (AmO_2, CmO_2) oder des Metalls (^{239}Pu) in HCl oder $HClO_4$ erhalten. Die chemische Reinheit war nach Angaben der Lieferanten besser als 99%, die Abwesenheit radioaktiver Verunreinigungen ließ sich α-spektroskopisch nachweisen.

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