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THE AMALGAMATION BEHAVIOUR OF HEAVY ELEMENTS 1. OBSERVATION OP ANOMALIC AMALGAMATION OP CALIFORNIUM, EINSTEINIUM, AND FERMIUM

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Jaromír Malý

May 1967

THE AMALGAMATION BEHAVIOUR OF HEAVY ELEMENTS
1. OBSERVATION OF ANOMALIC AMALGAMATION OF CALIFORNIUM,
EINSTEINIUM, AND FERMIUM*

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The extraction of rare earths, which have somewhat stable 2+ valence (like Eu, Sm, Yb), in alkali metals amalgams is well known (1,2,3,4,5,6). Related methods which transfer these rare earth elements into the amalgams by the electrolysis of water solutions containing alkali metals, acetates and citrates, is also well described in a number of papers (1,7,8,9,10,11).

Some of these papers demonstrate methods for the purification of Yb or Sm and Eu from neighbor elements, by means of sodium amalgam extraction. Europium, Sm, and Yb may preferentially replace Na in amalgams, often with a yield of more than 50% in one extraction when the other rare earths, which have not double valences, are extracted (1,2,3,4,6,13,14) or electrolyzed (8,9,10,15,16) with \lesssim 10X less amount.

With the exception of actinium (17,18) the literature does not describe the application of these separation methods to the group of actinides. Some experiments were performed, which demonstrate the possibility of using the sodium amalgam method of separation of some transuranium elements

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from the others. The initial experiments used conditions applied to lanthanides separations (4,15,16) and may not be the optimal for the transuranium elements separation. Described below are some typical experiments, which show the possibility of high preferential extraction of Cf, E and Fm in sodium amalgam, or the possibility of electrolytic separation of Cf, E and Fm on a mercury cathode in comparison with Pu, Am, Cm, and Bk which remains mostly in the original solution.

Experimental

The extraction experiments. The "α mixture", a solution containing approximately equal α activities of ^{239}Pu , ^{241}Am , ^{244}Cm , ^{252}Cf , and eventually ^{252}Es was prepared in 0.5 M HCl at a level of about 1000 α dpm/20λ total activity (excluding ^{252}E , whose α-activity was only 10^{-3} of total α-activity). The ^{249}Bk solution and ^{169}Yb solution were prepared similarly, ^{249}Bk in 0.5 M HCl, the ^{169}Yb from natural ytterbium irradiated in the reactor and dissolved in a solution containing 1M NH_4Cl , 0.5 M HCl and $\sim 17 \mu\text{g Yb}_2\text{O}_3$ in 5λ. Both solutions contained $\sim 5,000$ dpm βγ/min per 5λ and were measured in a windowless counter. The ^{252}Fm , ^{149}Tb , and ^{151}Dy were prepared in the HILAC by irradiation of ^{248}Cm with ^{12}C , Sm with ^{12}C , and Ce with ^{16}O , respectively. The recoil of Fm, Tb, or Dy atoms were caught on a Pt disc from which they were washed with 40λ of "α mixture". The sodium amalgam contained 3.5-4.0 milliequivalents Na/ml was prepared by dissolving small pieces of freshly cut sodium metal in the mercury. For every extraction experiment 20λ to 40λ of "α mixture" were mixed in 3 ml cone with 5λ of either ^{169}Yb or ^{249}Bk solution, 5λ of 8M ammonium acetate, 150λ of 7M sodium acetate and 3λ of LaCl_3

solution, containing 300 μgm La_2O_3 . To this mixture were added by short spitzer every 1 min $\sim 50\lambda$ of sodium amalgam from a second 3 ml cone; altogether 250 λ of amalgam were added in 3-4 portions. The amalgam and tracer-containing sodium acetate solution were mixed intensively by sucking in and out of the spitzer (40-50 times during 4 minutes). Foaming and hydrogen evolution occur on introduction of the first portion of amalgam, but by the fourth the foaming usually stops and a precipitate of $\text{La}(\text{OH})_3$ appears in the solution. After 4 min of extraction the mercury was separated from the original solution and washed twice with 300 λ of 6M NH_4OH . The extracted elements were back-extracted from the mercury into 400 λ 's of 6 M HCL. After the solution was neutralized to pH⁴ (methylred indicator) the activities were plated out on a Pt disc. After washing and flaming, the Pt disc was analyzed for β -activities in a windowless counter and for α -activities in an α -grid chamber in connection with a 200 channel analyzer, which identified the amounts of ^{149}Tb , ^{151}Dy , ^{239}Pu , ^{241}Am , ^{244}Cm , ^{252}Cf , ^{255}E , and ^{252}Fm . The original amounts before extraction of the various elements were determined in a similar way using 1/10 of the original sodium acetate-tracer solution. In the case of short-lived isotopes (^{149}Tb and ^{151}Dy), these isotopes were identified by α -energy and half-life measurements and usually the sample from extraction was measured along with the original solution simultaneously on two grid α -chambers connected with two 200 channel pulse analysers.

The $\text{La}(\text{OH})_3$ which precipitated at the end of extraction and contained most of the nonextracted actinides and rare earths, was usually

analyzed similarly for its content of nonextracted isotopes, to obtain the total balance of radioactivity.

The electrolytic experiments. For electrolysis, the same mixture was used as in the sodium amalgam extraction, or else the 5λ of 8M ammonium acetate in this mixture was replaced by 5λ of tertiary sodium citrate which was 0.5M in Na⁺ as it is mentioned in the last column of Table II. This mixture was diluted before electrolysis with 200λ of H₂O and 200λ of 7M sodium acetate to 600λ of electrolyte. A glass tube with a cross section ~1 cm², with Pt contact at the bottom, covered with 600λ of pure polarographic mercury was used for electrolysis. Above the mercury was 600λ of electrolyte and a Pt anode with a single spiral of ~3 mm diam, dipping ~2 mm in the electrolyte. All electrolyses were performed on air. The electrolyzer was gently shaken during electrolysis to help mix the electrolyte. During electrolysis the electrolyzer was immersed in a beaker containing water at 15°C. The electrolysis was carried out for 30 min at a potential of 5 V and a current of 20-25 mA dc. At the end of electrolysis the steady bubbling of hydrogen from the cathode indicated the presence of sodium amalgam in the mercury. After electrolysis the mercury was separated from the supernatant solution and treated exactly the same way as the mercury after sodium extraction (i.e., washed 2X with HN₄OH, decomposed with HCl, neutralized, and electroplated).

Results and Discussion

Table I presents a summary of the sodium amalgam extraction experiments. Conditions were identical except for the addition of various amounts of HCl to the solutions just prior to adding the amalgam, as noted in the last column of Table I. The initial pH was 6.0-7.0, without any addition of HCl; with the addition of the 75 λ of 3M HCl the pH dropped only to 5.0-6.0. Larger amounts of hydrogen were evolved from the more acid solutions. In all cases the final pH was >10-11 and a clearly visible precipitate of La(OH)₃ appeared.

The data of Table I clearly show that Cf, E, and Fm are extracted with sodium amalgam very similarly to Yb (and the other lanthanides which exhibit 2+ valency). The actinide homologs of Sm and Eu - Pu and Am - are extracted poorly (< 10%), relative to Yb and Cf, but comparably to the light lanthanides, like La, Ce, Pr, and Nd (14).

Berkelium is the least extracted of the actinides tested. In this respect it resembles terbium, which shows very low extraction. However, dysprosium, the lanthanide analog of Cf shows very low extraction in the same experiment in which Cf shows high extraction, ~1000 times better than Dy, and close to Sm or Eu in the lanthanide family. Comments in the literature (14) about nonextractibility of all heavier lanthanides, starting from gadolinium (with exclusion of Yb) and the Onsott's work (10) concerning the very slow electrodeposition -long after Yb and Tb- of Dy, Ho and Er (in the same sequence), indicates that Ho and Er should be less extractable than Dy. However, the actinide analoges of Ho and Er, the elements E and Fm, are

extracted even better than Yb as shown in Table I. The results of four electrolytic experiments are shown in Table II below. Experiments 1 and 2 were performed with the addition of 5 λ of 0.5N tertiary sodium citrate; 3. and 4. were done with the addition of 50 λ of 3MHCl to the original mixture. La(OH)₃ precipitation was not observed in experiments 3 or 4.

The results in Table II are very close to those in Table I. The data are compared in Table III (mean values from Tables I and II). The yields relative to californium are observed to be the same to within less than a factor of two, when compared with the more acid extraction experiments. The main result — the preferential extraction of Cf, E, and Fm with ~10 times enrichment, relatively to Pu, Am, Cm, and Bk, in one extraction step, was observed in all experiments.

Conclusion

The results in Table I and II show that Cf, E, and Fm could be extracted or separated by electrolysis about 10-30 times more efficiently than lighter actinides.

Both kinds of experiments presented above are very similar to the known results with preferential extraction in sodium amalgam (2,3,4,5) or preferential electrolytic separation on mercury cathode of double valent rare earths, Sm, Eu, and Yb (15,16).

Several authors (15, 16) explain this preference in electrolysis by a mechanism in which they suppose that probably first the Yb, Eu, and Sm are reduced in 2+ state, before the preferential electrolysis occurs. It seems logical to expect therefore that in the family of actinides Fm, E,

or Cf may form a +2 valence. It will be most interesting to extend the above presented extraction and electrolysis experiments to Mv and No, or to the lower actinides, to know more about the amalgamation, eventually about the tendency to 2+ state in whole actinide family. The experiments in this direction are now in progress.

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TABLE I
Sodium Amalgam Extraction
of Lanthanide and Actinide Elements

Element	¹⁴⁹ Tb	¹⁵¹ Dy	¹⁶⁹ Yb	²³⁹ Pu	²⁴¹ Am	²⁴⁴ Cm	²⁴⁹ Bk	²⁵² Cf	²⁵² E	²⁵² Fm	HCl added
% Extracted and ratio to Cf extracted in Exp. No.											
1. %	---	---	29	4.9	3.3	1.5	---	40	---	---	---
Ratio to Cf			0.725	0.125	0.082	0.037		1.000			---
2. %	---	---	33	2.3	2.1	1.8	---	45	---	90	---
Ratio to Cf	---	---	0.732	0.051	0.047	0.040		1.00		2.00	---
3. %	---	---	---	2.7	2.3	2.2	0.5	39	---	57	---
Ratio to Cf				0.047	0.040	0.039	0.013	1.00		1.46	---
4. %	---	---	---	5.6	3.3	3.3	0.9	51	50	---	50λ of 3M HCl
Ratio to Cf				0.11	0.065	0.065	0.018	1.00	0.98		
5. %	---	---	---	6.7	5.4	4.1	1.4	60	61	---	50λ of 3M HCl
Ratio to Cf				0.112	0.090	0.068	0.023	1.00	0.98		
6. %	0.15	---	62	5.1	3.0	2.6	---	68	---	---	75λ of 2M HCl
Ratio to Cf	0.0022		0.912	0.075	0.044	0.038		1.00			
7. %	0.14	---	53	2.7	1.5	2.3	---	50	---	---	75λ of 2M HCl
Ratio to Cf	0.0028		1.06	0.054	0.030	0.046		1.00			
8. %	---	0.06	50	16.9	7.9	5.7	---	95	---	---	75λ of 3M HCl
Ratio to Cf		0.0006	0.526	0.179	0.083	0.060		1.000			
9. %	---	0.06	53	16.3	7.7	5.3	---	~100	---	---	75λ of 3M HCl
Ratio to Cf		0.0006	0.530	0.163	0.077	0.053		1.000			

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TABLE II

Electrolysis of Lanthanide and Actinide Elements

Element Yield of electro- lysed elements in Exp. No.	¹⁶⁹ Yb	²³⁹ Pu	²⁴¹ Am	²⁴⁴ Cm	²⁴⁹ Bk	²⁵² Cf	²⁵² E	²⁵² Fm	Added in electro- lyser
1. % Ratio to Cf	27 0.55	4.7 0.096	2.2 0.045	2.1 0.043	-	49 1.00	-	80 1.63	5λ 0.5N Nacitrate
2. % Ratio to Cf	-	3.6 0.095	1.8 0.097	4.8 0.126	0.3 0.008	38 1.00	-	67 1.76	5λ 0.5N Nacitrate
3. % Ratio to Cf	-	5.1 0.072	3.2 0.045	5.2 0.073	1.6 0.022	71 1.00	75 1.056	-	5λ 3MHCl
4. % Ratio to Cf	-	5.3 0.096	2.8 0.051	4.8 0.087	0.6 0.011	55 1.00	60 1.091	-	5λ 3MHCl

TABLE III

Comparison of Sodium Amalgam Extraction and Electrolysis of Lanthanide and Actinide Elements

Element	Tb	Dy	Yb	Pu	Am	Cm	Bk	Cf	E	Fm
Yield of extracted elements										
mean value from extraction	0.0025	0.0006	0.748	0.102	0.062	0.050	0.018	1.000	0.98	1.73
mean value from electrolysis			~0.55	0.090	0.047	0.082	0.014	1.000	1.072	1.695

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