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2. DIPOSITIVE STATE OF MENDELEVIUM

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THE AMALGAMATION BEHAVIOR OF HEAVY ELEMENTS.
2. DIPOSITIVE STATE OF MENDELEVIVM*

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A previous communication (1) reported the observation of high preferential extraction of Cf, Es, and Fm, as compared to Pu, Am, Cm, and Bk by electrodeposition onto a mercury cathode amalgamated with sodium or into sodium amalgam. We report here preliminary results concerning the extraction of Md into sodium amalgam from sodium acetate solution, the possibility of a one-step electrolytic separation of mendelevium from einsteinium in citrate-acetate solutions, and observations concerning the potential of the $Md^{3+} + e = Md^{2+}$ couple.

Experimental Procedure

A. Irradiation

Mendelevium-256 was produced by irradiation with 41-MeV helium ions of an einsteinium target consisting of ~5 µg of ^{253}Es mounted on a 4 mg/cm² Be foil. Irradiation for 30 to 60 minutes at a beam current of 50 to 100 µa/cm² (10 to 20 µa through the target) yielded approximately 10^5 atoms of ^{256}Md , which were collected on a Be catcher foil, along with 10^6 to 10^7 αd/m of ^{253}Es knocked out of the target. The catcher foil was dissolved in 6 M HCl containing ~500 µg La³⁺. This precipitate, containing the isotopes of Md and Es,

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was washed with 6 M KOH and water. The washed precipitate usually was dissolved in 200 λ of 1 to 3 M HCl to form a "stock Md" solution.

B. Extraction Experiments

The extraction experiments usually were carried out from a mixture of about 1/5 of the "stock Md" solution in 1 M HCl, 100 λ of 7 M sodium acetate, 5 λ of 8 M ammonium acetate, and selected amounts of HCl, as shown in Table 1.

TABLE 1

Extraction of Md and Es by Sodium Amalgam

Exp. No.	% Es Extracted	% Md Extracted	HCl added
1	89	90-100	15 μ l 1 M
2	~100	90-100	75 μ l 1 M

The extractions were performed in a 3-ml cone, using 250 λ of sodium amalgam, containing ~3.5 milliequivalent Na/ml. The extracted actinide elements were back-extracted from the mercury phase with 6 M HCl, neutralized by NH₄OH, and then electroplated from NH₄Cl solution on a Pt disc. Details of the extraction procedure are described in reference (1). Einsteinium was determined with an α -grid chamber connected to a pulse-height analyzer; Md was determined by counting spontaneous fission events due to the fission decay of ²⁵⁶Fm, its daughter by the electron-capture process.

C. Electrolysis Experiments

The compositions of the solutions used in electrolysis were similar to those used for amalgam extractions: 150 λ "stock Md" in 1 M HCl, 600 λ of 7 M sodium acetate, 20 λ of 8 M ammonium acetate, and 100 λ of 0.5 M HCl in the first experiment, and 200 λ of "stock Md" in 3 M HCl, 25 λ of sodium citrate (0.5 M in Na), 300 λ of 7 M sodium acetate, and 50 λ of 0.5 M HCl in the second.

The electrolyses were performed in the open air using 900 λ and 300 λ of pure mercury in the first and second experiments, respectively. The anode consisted of a platinum spiral, held at the surface of the electrolyte. The Md-rich fraction from electrolysis was subsequently used for reduction experiments.

The electrolyses were carried out for 35 min, with periodic interruption at 5 min intervals for sampling the mercury phase. Current densities are given in Table 2. Following any 5-min period of electrolysis, the current was stopped, and after 1 min of mixing of both phases, 5 λ of mercury were withdrawn by pipeting. This sample was washed three times with water, transferred to a platinum disc, the mercury driven off by heating, and the residue counted for Md and Es as in the extraction experiments.

The results are summarized in Table 2.

TABLE 2

Separation of Mendeleevium from Einsteinium by Electrolysis

Exp. No.	Current Density (ma cm ⁻²)	Ratio of Spontaneous Fission Activity to Alpha Activity		Maximum Enrichment Factor ²⁵⁶ Fm + ²⁵⁶ Md Relative to Es
		Orig. Solution	In Mercury	
1	10	$\frac{1}{3150}$	$\frac{1}{100}$	31.5
2	5	$\frac{1}{9600}$	$\frac{1}{305}$	31.5

D. Evidence for Dipositive Md

Although a correlation between extractibility into sodium amalgam and the formation of a chemically stable +2 state has been established for the 4f elements (2,3,4), a similar correlation has not been demonstrated for the 5f series.

The expected analogy between Tm and Md led Seaborg (5) to predict the relatively stable Md²⁺ state in 1949.

Accordingly, we sought direct evidence for a dipositive state of

mendelevium, and have attempted to establish rough limits for the potential of the $Md^{3+} + e = Md^{2+}$ couple. To this end, various reducing agents were added to the "stock Md" solution, and $BaSO_4$ or $EuSO_4$ precipitated from the mixture. The distribution of Es , ^{256}Fm , and ^{256}Md activities between the precipitate and supernatant solution was then determined.

Solutions of Cr^{2+} , V^{2+} , and Ti^{3+} were prepared by reduction with amalgamated zinc. In a typical experiment, the reducing solution was obtained by adding a 0.1 M solution in 2 M HCl of the ion, later used for reduction, to ~0.5 gm of amalgamated zinc (20 mesh), contained in a 1-ml cone. The solution was heated and repeatedly mixed by pipeting for 5 min. One ml of this freshly prepared reducing solution was added to a 2-ml cone containing 50 λ of "stock Md", ~6 mg Eu^{3+} , and 300 μg of Ba^{2+} in 100 λ of 0.5 M HCl. After 1 to 2 min of reduction, $BaSO_4$ was precipitated by the addition of 25 μl of 40% H_2SO_4 . After centrifuging, the precipitate was washed with water, transferred to a platinum counting plate, dried, and counted. A sample of the stock solution was counted at the same time.

In reductions with $YbCl_2$, $EuCl_2$, and amalgamated Zn, only 400 λ of solution was used, which was 0.1 M in Eu, and pure $EuSO_4$ was precipitated in place of $BaSO_4$.

The results of these experiments are summarized in Table 3.

TABLE 3

Results of Reduction of Md

Reducing Ion	Precipitate	Reduction Potential (volts)	Corresponding Reaction	Observed Enrichment Factor $\frac{^{256}Md}{^{256}Fm}$
Yb^{2+}	$EuSO_4$	-1.15	$Yb^{3+} + e \rightarrow Yb^{2+}$	≈ 10
Zn + Eu^{3+} (Jones' Reductor)	$EuSO_4$	-0.763	$Zn^{2+} + 2e \rightarrow Zn$	≈ 10
Eu^{2+}	$EuSO_4$	-0.43	$Eu^{3+} + e \rightarrow Eu^{2+}$	≈ 10
Cr^{2+}	$BaSO_4$	-0.41	$Cr^{3+} + e \rightarrow Cr^{2+}$	≈ 10
V^{2+}	$BaSO_4$	-0.255	$V^{3+} + e \rightarrow V^{2+}$	≈ 10
Ti^{3+}	$BaSO_4$	-0.1	$TiO^{2+} + 2H^+ + e \rightarrow Ti^{3+} + H_2O$	$\approx 2-3$

The results presented in Table 1 indicated that Md is extracted by sodium amalgam somewhat more readily than is einsteinium, and on comparison with results presented previously (1), it appears that Md is extracted more readily than californium. This suggests that Md^{2+} is more stable than Cf^{2+} or Es^{2+} . The data presented in Table 2 demonstrate a very substantial separation of Md from Es by electrolysis. In both cases, the maximum ratio of spontaneous fission activity of ^{256}Fm to α activity of ^{256}Es was reached after passage of ~ 9 coulombs of electric charge. The enrichment of the mercury phase with ^{256}Fm by factor ≈ 30 is due to preferential electrodeposition of ^{256}Md and ^{256}Fm on the cathode, while Es remains mostly in solution. This result is similar to the well-known electrolytic separation of Eu and Sm from other rare earths on a lithium-amalgamated cathode (6). The observed large separation of Es from Md by electrolysis suggests that a substantial difference exists in the potentials of their $3+-2+$ couples. To prove this difference, the reduction experiments summarized in Table 3 were carried out. These data indicate that Md^{3+} can be reduced to Md^{2+} and then precipitated with $EuSO_4$ or $BaSO_4$, usually with an enrichment factor ≈ 10 , in comparison to Es, with any of the following reducing agents: $YbCl_2$, Zn (Jones' Reductor in the presence of Eu^{3+}), Eu^{2+} , Cr^{2+} , or V^{2+} 2 M in HCl solution.

It follows that the reduction potential for the $Es^{3+} - Es^{2+}$ couple must be more negative than for the $Md^{3+} - Md^{2+}$ couple by about ≈ 1 volt or more. Details of the counting data obtained in an experiment using V^{2+} as a reducing agent are given in Fig. 1.

The growth of SF activity in the $BaSO_4$ fraction from V^{2+} reduction is clearly evident and indicates enrichment of Md by a factor of 10 to 15. The deviation of the spontaneous-fission decay curve in the precipitate from the Pi^{3+} solution in comparison to the decay curve of the input solution is also evident and shows an enrichment of Md by a factor of only 2 to 3. From this last experiment it would appear that the standard reduction potential

of the $Md^{III} + e = Md^{2+}$ couple is about -0.1 volt.

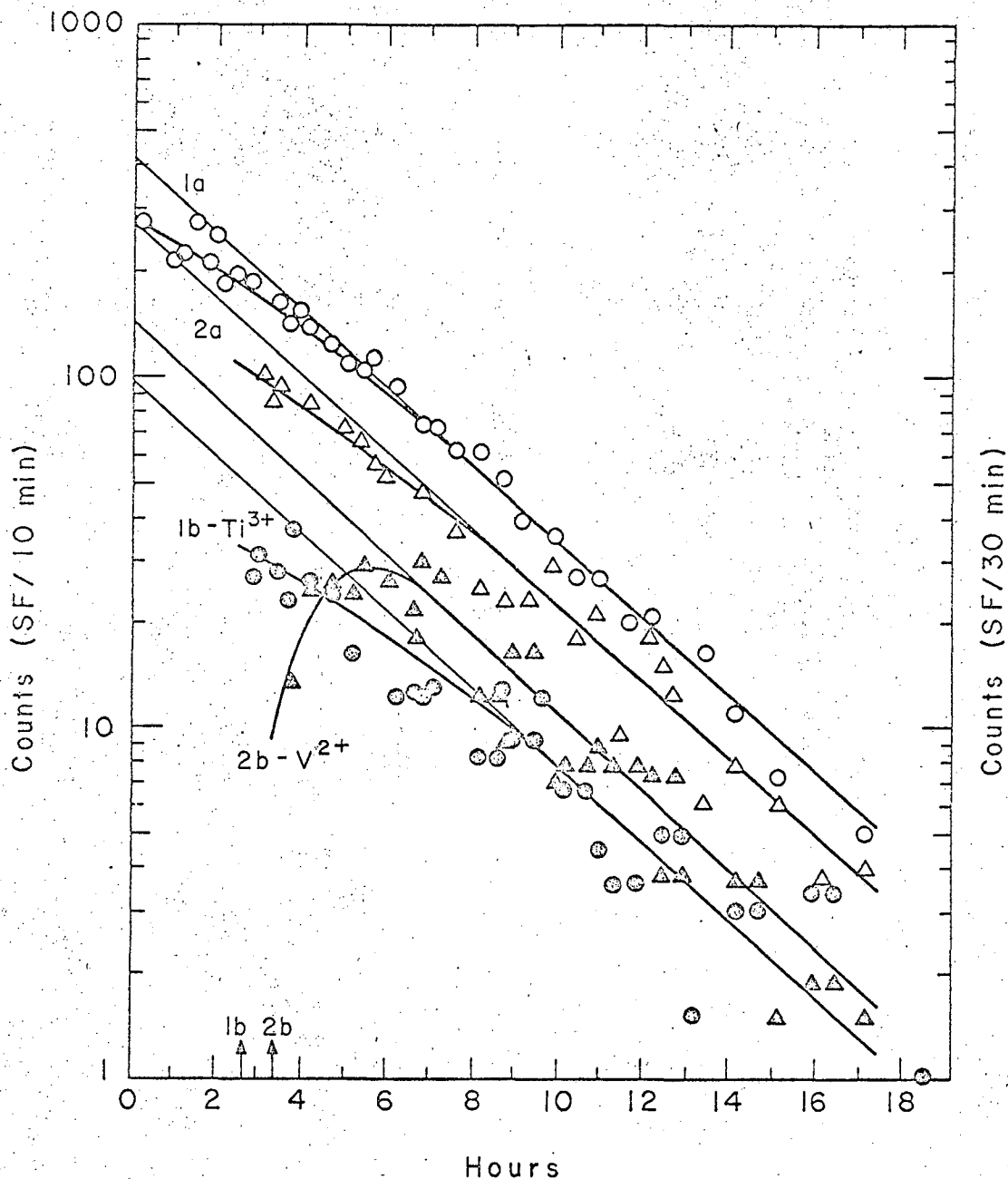


Fig. 1

Spontaneous-fission decay of $BaSO_4$ fractions after reduction with Ti^{3+} and V^{2+} .
 1a and 1b- decay curves of "stock Md" solutions (left scale, SF/30') used to reduction with Ti^{3+} (1a, 22% of input) and V^{3+} (2a, 34% of input).
 2a and 2b- decay curves of $BaSO_4$ fraction after reduction (right scale, SF/10') with Ti^{3+} (1b) and V^{2+} (2b). The arrows 1b and 2b show the separation time (precipitation of $BaSO_4$) in the case of V^{2+} or Ti^{3+} reduction.

The results suggest that the +2 state of mendelevium is more stable than the dipositive state of ytterbium, and even of europium. The substantially greater ease of reduction of Md as compared to Es affords a basis for a rapid and efficient separation of the elements as shown by the reduction experiment. The Md^{3+} can be separately reduced, for instance by zinc in Jones' Reductor, to Md^{2+} , while Es and Fm remain in the 3+ state.

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