

# THE AMALGAMATION BEHAVIOR OF HEAVY ELEMENTS—IV

## THE TRACER CHEMISTRY OF DIVALENT MENDELEVIUM\*

JAROMÍR MALÝ†

Lawrence Radiation Laboratory, University of California, Berkeley, California

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**Abstract**—In this paper it is shown that the extraction of mendelevium into sodium amalgam from sodium acetate solutions results in about a ten fold enrichment relative to the lighter actinides (Pu, Am, Cm, Bk).

Separation of Md from the heavier actinides may be accomplished by either of two methods: (1) an amalgam containing Md, Fm, Es, and Cf can be decomposed in cold concentrated HCl and then the Md may be coprecipitated with  $\text{EuCl}_2$  with one order of magnitude enrichment from Fm; (2) Md can be separated by electrolysis in acetate or citrate-acetate solution on an electrode of mercury amalgamated with sodium. In the lanthanide series method (2) is used to separate Eu or Sm from the other rare earths. The sequence of electrodeposition of actinides in acetate-citrate solution is  $\text{Md} > \text{Fm} > \text{Es} > \text{Cf}$ .

These separation methods probably depend on the formation of stable  $\text{Md}^{2+}$ . The potential of the  $\text{Md}^{3+} + e \rightarrow \text{Md}^{2+}$  couple was estimated by a series of reductions, using  $\text{YbCl}_2$ , Zn,  $\text{EuCl}_2$ ,  $\text{CrCl}_2$ ,  $\text{VCl}_2$ , and  $\text{TiCl}_3$ , all in 2 M HCl. All except  $\text{TiCl}_3$  appear to reduce  $\text{Md}^{3+}$  to  $\text{Md}^{2+}$ , which can then be coprecipitated with  $\text{EuSO}_4$  or  $\text{BaSO}_4$ ; Md is thereby enriched 10–30 X in the precipitate, relative to the daughter isotope  $^{256}\text{Fm}$  in solution.

### INTRODUCTION

A PREVIOUS communication[1] reported preliminary results concerning the possible separation of Md from higher actinides by extraction into sodium amalgam from sodium acetate solutions, or by an electrolytic one step separation of Md and Fm from Es. This[1] and a subsequent publication[2] reported the first experimental evidence of the  $\text{Md}^{2+}$  state, an oxidation state which now appears to exist for other heavy actinides as well. This paper presents a more detailed study of  $\text{Md}^{2+}$ .

Because of the relatively short half life of the  $^{253}\text{Es}$  target used for Md production ( $T_{1/2} = 20$  days for  $^{253}\text{Es}$ ) experiments were limited to a period of about 1.5 months. Some experiments could not be repeated more than twice, and consequently the results are of low statistical accuracy. The present experiments on Md and other heavier actinides were done in an attempt to repeat the more

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†Permanent address: The Nuclear Research Institute of Czechoslovak Academy of Sciences, Řež u Prahy, Czechoslovakia.

1. J. Malý, B. B. Cunningham, *Inorg. nucl. Chem. Lett.* **3**, 445 (1967).

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interesting experiments on electrolysis, extraction and reduction of Eu and Sm carried out earlier by a number of workers [3–10].

### EXPERIMENTAL PROCEDURE

#### *Isotopes of Md, Fm, and Es produced by irradiation*

$^{256}\text{Md}$ , produced by irradiation with  $\approx 46\text{ MeV}$  He ions of an einsteinium target, consisting of  $\approx 5\ \mu\text{g}$   $^{253}\text{Es}$  mounted on  $4\ \mu\text{g}/\text{cm}^2$  Be foil was used for the work reported here. The Es target contained  $\approx 1\%$  of  $^{254}\text{Es}$  and  $^{255}\text{Es}$ , the latter being in equilibrium with  $^{255}\text{Fm}$ .

Irradiation for  $\approx 30\text{ min}$  with a beam current of  $50\text{--}100\ \mu\text{A}/\text{cm}^2$  ( $10\text{--}20\ \mu\text{A}$  through the target) yielded approximately  $10^5$  atoms of  $^{256}\text{Md}$  (and also some  $^{251}\text{Fm}$ ,  $^{252}\text{Fm}$ ,  $^{253}\text{Fm}$ ,  $^{254}\text{Fm}$ ,  $^{255}\text{Fm}$ , and  $^{256}\text{Fm}$  isotopes) which were collected on a Be catcher foil, along with about  $10^5\text{--}10^7$   $\alpha$   $d/m$  of  $^{253}\text{Es}$ , knocked out from the target. The catcher foil was dissolved in  $6\text{ M HCl}$ , containing  $\approx 500\ \mu\text{g La}^{3+}$ . This solution was treated with an excess of  $\text{KOH}$  to form  $\text{La}(\text{OH})_3$  which co-precipitated Md, Fm, and Es. The  $\text{La}(\text{OH})_3$  precipitate, washed with  $6\text{ M KOH}$  and water, was usually dissolved in  $200\ \lambda$  of  $2\text{ M HCl}$ , to form a "stock Md" solution.

The isotopes  $^{252}\text{Md}$ ,  $^{253}\text{Md}$ ,  $^{254}\text{Md}$  which also were produced during irradiation by  $(\text{He}, xn)$  reactions, could not be detected. They are short lived and decayed by K-capture to their Fm isotopes. A few  $7.34\text{ MeV}$   $\alpha$ -particles were observed in the  $\alpha$  spectrum due to  $^{255}\text{Md}$  ( $T_{1/2} = 30\text{ min}$ ). However this isotope was observed mainly after K-capture as  $^{255}\text{Fm}$ . A typical  $\alpha$ -spectrum of "stock Md" solution is shown in Fig. 1. A typical decay curve of  $^{256}\text{Md}$ , measured by spontaneous fission of the  $^{256}\text{Fm}$  daughter isotope is shown in Fig. 2.

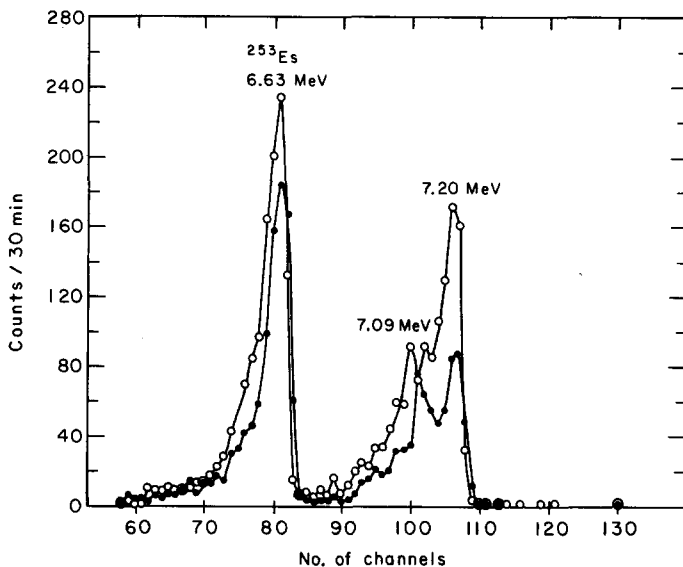


Fig. 1. Typical  $\alpha$  pulse height analysis spectra of "stock Md" solution.

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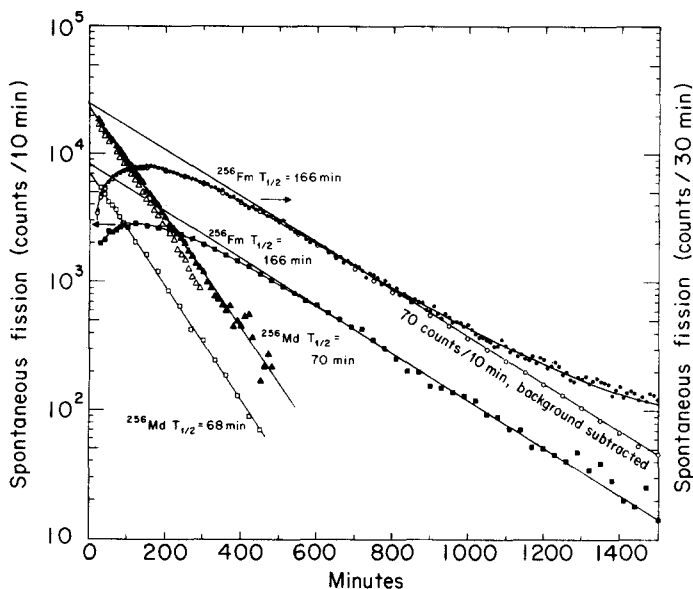


Fig. 2. Typical decay curves of  $^{256}\text{Md}$  measured by the spontaneous fission of the  $^{256}\text{Fm}$  daughter isotope [18].

#### Radioactive tracers

The tracer isotopes  $^{238}\text{U}$  (in the  $\text{U}^{4+}$  state),  $^{237}\text{Np}$  (as  $\text{Np}^{4+}$ ),  $^{239}\text{Pu}$  ( $\text{Pu}^{4+}$ ),  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ ,  $^{249}\text{Bk}$ ,  $^{252}\text{Cf}$ ,  $^{253}\text{Es}$ ,  $^{152}\text{Eu}$ , and  $^{154}\text{Eu}$  (all  $3+$ ) were used in  $\approx 0.5\text{ M HCl}$  solution.

$^{252}\text{Fm}$ ,  $^{255}\text{Fm}$ , and  $^{254}\text{Fm}$  were used for measurement of the yield of Fm in chemical operations. In the case of  $^{252}\text{Fm}$  its yield was corrected for the growth of  $^{255}\text{Fm}$  from  $^{255}\text{Es}$  (measured 40 days after bombardment and compared with the original  $^{255}\text{Es}$  present in the target) and for growth from  $^{255}\text{Md}$  (determined from the amount of  $^{255}\text{Md}$  as measured by its  $7.34\alpha$  energy and 30 min half life). A known amount of the "stock Md" solution was used for the chemical separation procedures (extraction, electrolysis, reduction, and coprecipitation), and at the end of a particular procedure a part of each separate fraction was electroplated and then counted by  $\alpha$  pulse analysis as described in references 11 and 1. The amount of  $^{256}\text{Fm}$  activity was determined for each fraction either by measuring the decay curve for spontaneous fission along with its  $\alpha$  spectrum, or by utilizing a separate  $\alpha$  chamber and a surface barrier Si-Au detector employing a discriminator for SF counts. At the same time SF and  $\alpha$  decay curves were measured for a known amount of the stock solution in order to calculate the yield of separated isotopes in each fraction.

#### Chemicals

Chemicals used were of reagent grade. The sodium amalgam was prepared by dissolving freshly cut sodium metal in hot mercury.

#### Calculation of Md Yield

(A) *Yield from decay curves.* The growth and decay curve of the SF activity (Fig. 2) is described by the formula:

$$\text{Fm}(t) = \text{Fm}_0 e^{-\lambda_{\text{Fm}} t} + \text{R}_{\text{Md}} \text{Md}_0 (e^{-\lambda_{\text{Fm}} t} - e^{-\lambda_{\text{Md}} t}) \quad (1)$$

where

$$\text{R}_{\text{Md}} = \frac{\lambda_{\text{Md}}}{\lambda_{\text{Md}} - \lambda_{\text{Fm}}} = 1.73.$$

The time  $t$  is measured from the end of bombardment, when Fm and Md are  $Fm_0$  and  $Md_0$  respectively. Because  $\lambda_{Md} > \lambda_{Fm}$ , for large values of  $t$  the curve in Fig. 2 becomes a fermium decay curve described by:

$$Fm(t) \cong [(Fm_0 + R_{Md}Md_0) e^{-\lambda_{Fm}t}]. \quad (2)$$

The yield of Md was calculated from the difference between the growth curve for Fm described by Equation (1) and the decay curve (Equation (2)), extrapolated to the time of separation. For this difference:

$$\begin{aligned} \Delta Fm(t_{sep}) &= Fm(t_{sep}) - [(Fm_0 + R_{Md}Md_0)e^{-\lambda_{Fm}t_{sep}}] \\ &= R_{Md}Md_0e^{-\lambda_{Fm}t_{sep}}. \end{aligned} \quad (3)$$

$\Delta Fm(t_{sep})$  represents the difference between total fermium after decay of Md, and fermium before Md decay. Hence the difference may be used to calculate the yield of Md.

(B) *Calculation of yield from the ratio SF of  $^{256}Fm$ :  $\alpha$  activity of  $^{253}Es$ .* In the case of electrolysis, when the SF activity was too low to give a good growth curve the activity ratio  $SF/\alpha^{253}Es$  was followed for 3–6 hr, after waiting more than 15 hr ( $t$  long =  $t_L$ ) after the end of the bombardment when essentially all  $^{256}Md$  present at  $t_{sep}$ , had decayed to  $^{256}Fm$ . From this ratio of  $SF/\alpha^{253}Es$  in the original solution and in the separated fraction and with the aid of  $^{253}Es$  yield, the yield of SF in the fraction (% SF ( $t_L$ )) was calculated. For the calculation of the yield of Md separated at  $t_{sep}$ , we used the formula:

$$\%SF(t_L) = \%^{256}Fm(t_{sep}) \frac{A}{A+1} + \%^{256}Md(t_{sep}) \frac{1}{A+1} \quad (4)$$

where

$$\frac{1}{A} = \frac{R_{Md}Md(t_{sep})}{Fm(t_{sep})}$$

and for  $\%^{256}Fm(t_{sep})$  we used the yield  $\%^{256}Fm(t_{sep})$ , measured in a given fraction and in the unseparated mixture. The value of the factor  $A$  is read from Fig. 2, a standard decay curve for the unseparated mixture, at  $t_{sep}$ .

In the above equations,  $R_{Md}Md_0e^{-\lambda_{Fm}t}$  is equal to that part of the SF activity of  $^{256}Fm$  contributed by the decay of  $^{256}Md$  at  $t_{sep}$ , while  $^{256}Fm(t_{sep})$  in Equation (4) represents that part coming from Fm present in the fraction at  $t_{sep}$ .  $1/A$  is the ratio of SF activity from Fm produced by mendelevium decay to Fm produced directly.  $A/A+1$  is the fraction of SF activity from Fm produced directly. Multiplication by 100 gives the percentage of total SF activity originating from this source.

Measurement of  $\alpha$  activity from  $^{253}Es$  permitted a check on the yield of total  $\alpha$ 's and consequently of total SF's through the chemical procedure.

#### Extraction procedure

The extraction experiments usually were carried out from a mixture of 20  $\lambda$  of the "stock Md" solution in 0.15 M HCl, 25  $\lambda$  of tracers in 1 M HCl, 9  $\lambda$  of 1 M HCl containing 120  $\mu g$  of  $Sm^{3+}$  and 150  $\mu g$  each of  $Eu^{3+}$  and  $Yb^{3+}$ , 150  $\lambda$  of 7 M sodium acetate, 5  $\lambda$  of 8 M ammonium acetate, and selected amounts of HCl, as shown later in Table 1.

The extractions were performed in a 3-ml cone using 250  $\lambda$  of sodium amalgam, containing  $\approx 3.5$  m equiv. Na/ml. The actinide elements were back-extracted from part of the amalgam with 6 M HCl, the extract neutralized by  $NH_4OH$ , and then electroplated on a Pt disc. Details of the extraction procedure are described in [11].

The remaining portion of the amalgam, after washing with  $H_2O$ , was decomposed by ice cold concentrated HCl; NaCl crystals together with  $EuCl_2$  were centrifuged out, washed with concentrated HCl, dissolved in 1 ml of  $H_2O$  and an aliquot was electroplated on a platinum plate, after neutralization with  $NH_4OH$ .

The combined HCl supernatants were diluted to 2 ml. A known fraction of this solution was neutralized and electroplated as before.

Table 1. Sodium amalgam extraction of actinides and separation with  $\text{EuCl}_2$  -  $\text{SmCl}_3$  by conc. HCl

Element	$^{237}\text{Np}$	$^{239}\text{Pu}$	$^{241}\text{Am}$	$^{246}\text{Cm}$	$^{252}\text{Cf}$	$^{253}\text{Es}$	$^{255}\text{Fm}$	$^{256}\text{Md}$
(A) 15 $\lambda$ 1 M HCl added before extraction:								
% extracted into sodium amalgam	4.0	5.3	5.65	6.8	58.1	89	$\approx 100$	$\approx 95$
% in $\text{EuCl}_{2(s)}$	0.33	0.37	0.25	0.15	1.5	1.4	3.1	$\approx 85$
% in $\text{Sm}^{3+}$ fraction	3.5	4.9	5.9	6.6	56.6	87.5	97	$\approx 10$
(B) 75 $\lambda$ 1 M HCl added before extraction:								
% extracted into sodium amalgam	18.2	19.3	20.6	12.0	96.2	$\approx 100$	$\approx 100$	$\approx 100$
% in $\text{EuCl}_{2(s)}$	1.0	0.95	4.7	0.65	5.6	2.6	4.4	97
% in $\text{Sm}^{3+}$ fraction	17.2	18.3	15.9	11.3	90.5	97.4	95.6	3

*Electrolytic procedure*

The compositions of the solutions used in electrolysis were similar to those used for amalgam extractions: 150  $\lambda$  "stock Md" in 1 M HCl, (containing  $\approx 200 \mu\text{g La}^{3+}$ ) 600  $\lambda$  of 7 M sodium acetate, 20  $\lambda$  of 8 M ammonium acetate, and 100  $\lambda$  of 0.5 M HCl in the first experiment; and 200  $\lambda$  of "stock Md" in 3 M HCl, 25  $\lambda$  of 0.5 M sodium citrate, 300  $\lambda$  of 7 M sodium acetate, and 50  $\lambda$  of 0.5 M HCl in the second. In the first experiment 110  $\lambda$  of tracer solution in 0.5 M HCl, containing  $\approx 1 \text{ mg } ^{238}\text{U}$  was also present.

The electrolyses were performed in the open air using 900 and 300  $\lambda$  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 experiments on the reduction of  $\text{Md}^{3+}$  to  $\text{Md}^{2+}$ .

The electrolyses were carried out for 35 min, with periodic interruption at 5 min intervals for sampling the mercury phase. Following any 5-min period of electrolysis, the current was stopped, and after 1 min of mixing of both phases, 5  $\lambda$  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.

*Reduction procedure*

The Md "stock" solution was reduced by adding 4–5 mg of  $\text{YbCl}_2$  or  $\text{EuCl}_2$ , or else with amalgamated zinc in the presence of  $\approx 5 \text{ mg EuCl}_3$ . In other experiments solutions of  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$  and  $\text{Ti}^{3+}$  were prepared by reduction with amalgamated zinc. In a typical experiment, the reducing solution was prepared by adding a 0.1 M solution of the oxidized species in 2 M HCl to  $\approx 0.5 \text{ g}$  of amalgamated zinc (20 mesh), contained in a 1-ml cone. The solution was heated and repeatedly mixed by pipeting for 5 min. The concentration of HCl after reduction to  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ , or  $\text{Ti}^{3+}$  was about 1 M, because of the Zn dissolution during reduction. One ml of this freshly prepared reducing solution was added to a 2 ml cone containing 50  $\lambda$  of "stock Md",  $\approx 6 \text{ mg Eu}^{3+}$ , and 300  $\mu\text{g}$  of  $\text{Ba}^{2+}$  in 100  $\lambda$  of 0.5 M HCl. After 1–2 min of reduction,  $\text{BaSO}_4$  was precipitated by the addition of 25  $\mu\text{l}$  of 40%

H<sub>2</sub>SO<sub>4</sub>. 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<sub>2</sub>, EuCl<sub>2</sub>, and amalgamated Zn, only 400 λ of solution was used, which was 0.1 M in Eu, and pure EuSO<sub>4</sub> was precipitated in place of BaSO<sub>4</sub>.

## RESULTS AND DISCUSSION

### *Extraction behavior of Md and evidence of MdCl<sub>2</sub>*

The results of the extraction of the tracer mixture and "stock Md" solution are shown in Table 1. The results in parts A and B of the table are equivalent to the addition of 52 λ and 276 λ of 1 M HCl, respectively, shown in graph 3 in [12]. Table 1 shows a high extraction yield for Cf<sup>3+</sup>, Es<sup>3+</sup>, Fm<sup>3+</sup>, and Md<sup>3+</sup>, whereas Cm<sup>3+</sup>, Am<sup>3+</sup>, Pu<sup>4+</sup>, and Np<sup>4+</sup> are extracted with low yield, especially when only 15 λ of 1 M HCl are present. This same method successfully separates Eu from Sm, the former showing preferential retention in the solid chloride precipitate[3-6]. The SF activities separated in the EuCl<sub>2</sub> and SmCl<sub>3</sub> fractions respectively are shown in Fig. 3. It is evident from the figure that Md appears

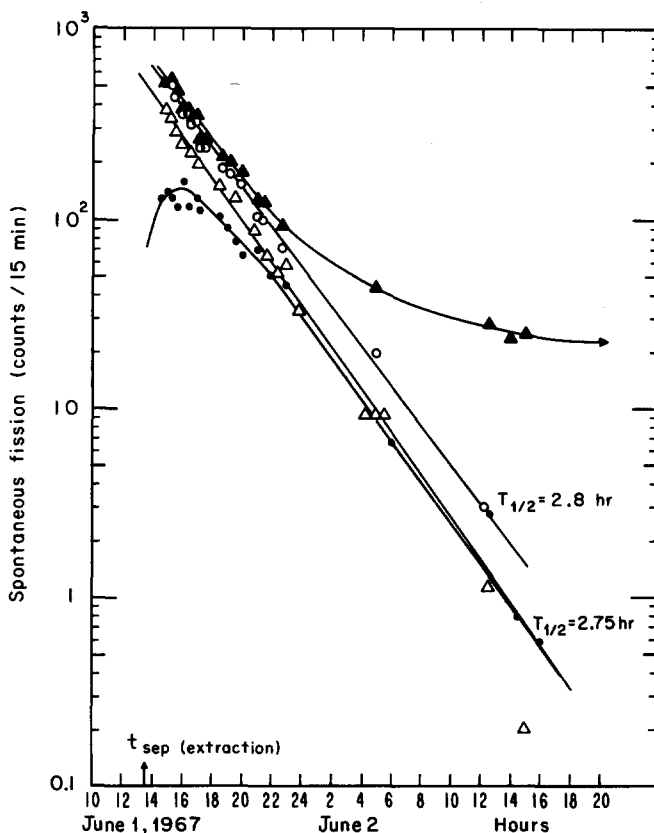


Fig. 3. Spontaneous fission activity present in the EuCl<sub>2</sub> fraction (precipitate) and the SmCl<sub>3</sub> fraction (supernatant). The SF data for the EuCl<sub>2</sub> fraction represented by ●●●; the data for the SmCl<sub>3</sub> fraction by ▲▲▲, the SmCl<sub>3</sub> data corrected for background by ○○○. A small amount of the "stock Md" solution is represented by △△△.

only in the  $\text{EuCl}_2$  fraction, (growth of SF activity) and is practically not present in the supernatant ( $\text{SmCl}_3$  fraction). The distribution of tracers shown in Table 1 indicates that other actinides are largely absent from the  $\text{EuCl}_2$  fraction, but are found instead in the  $\text{SmCl}_3$  fraction. It appears that after decomposition of the amalgam, Md was present as  $\text{MdCl}_2$ , which is carried by  $\text{EuCl}_2$ , and that  $\text{Md}^{2+}$  must be relatively stable in HCl solution, whereas the other actinides are oxidized in conc. HCl by  $\text{H}^+$  ions very rapidly to the 3+ state.

#### *Electrolytic behavior of Md, Fm, and Es*

Because of time limitations, it was possible to perform only 2 electrolytic runs. In the first run (with  $\approx 1$  mg  $\text{U}^{4+}$  present) a current density of  $5 \text{ mA/cm}^2$  was used. The separation of  $^{253}\text{Es}$ ,  $^{255}\text{Fm}$ , SF activity, and  $^{256}\text{Md}$ , is shown in Fig. 4. The yield of  $^{256}\text{Md}$  was calculated according to procedure B, of the yield determination section. The second experiment was done with a current density of  $10 \text{ mA/cm}^2$  in the absence of uranium. These results are shown in Fig. 5. Figure 4 shows a yield ratio of  $\text{Es:Fm:Md} = 0.8\%:4\%:90\%$ , after

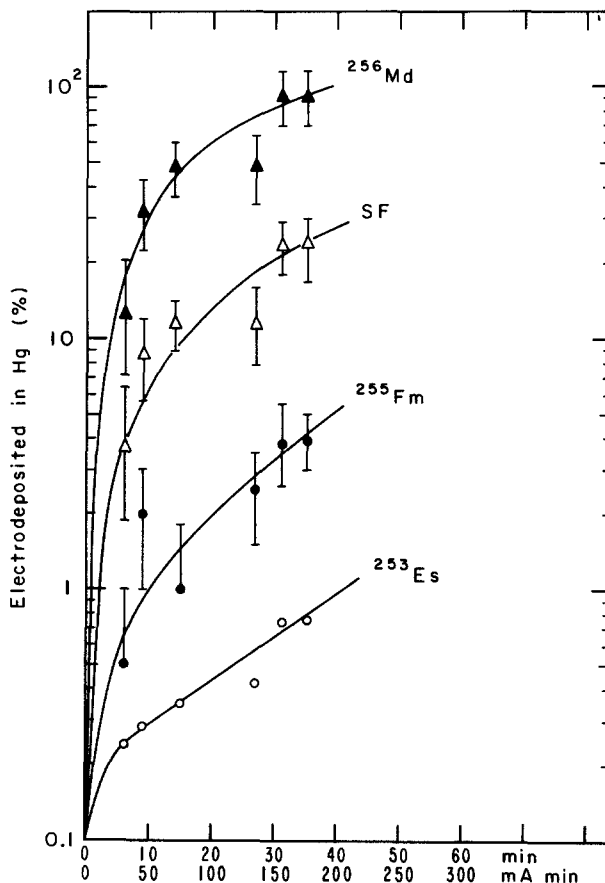


Fig. 4. Percentage of actinide tracers electrodeposited in mercury as a function of time and passed charge. Current density used in this experiment was  $5 \text{ mA/cm}^2$ .

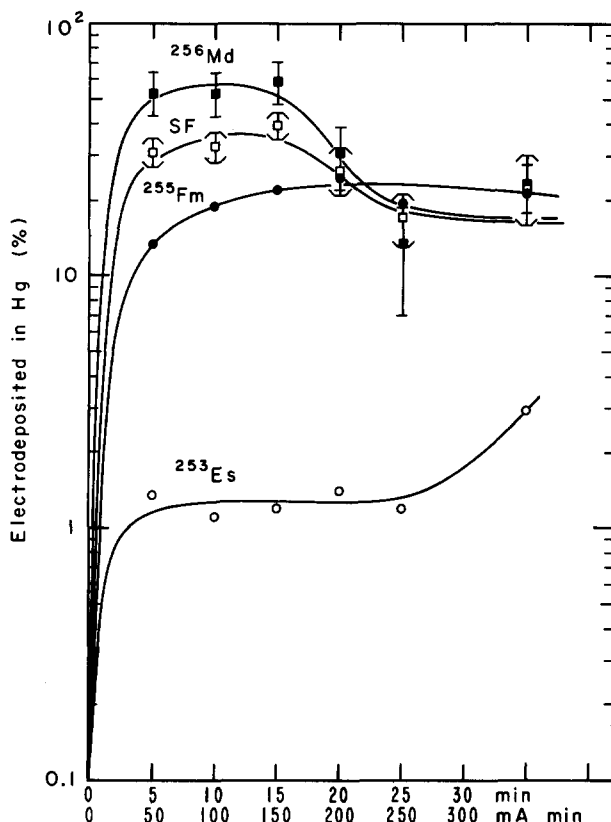


Fig. 5. Percentage of actinide tracers electrodeposited in mercury as a function of time and passed charge. Current density used in this experiment was  $10 \text{ mA/cm}^2$ .

35 min of electrolysis. In the second experiment the best relative yields are Es:Fm:Md = 1.2%:13%:52%, after 5 min of electrolysis. In the first experiment the yield of Md and Fm in mercury was increasing during the first 150 mA min of charge passed; in the second experiment ( $10 \text{ mA/cm}^2$  curr. dens.) there was observed a drop of the yield of Md in mercury, between 200–350 mA min of charge passed. It is possible that this effect might be caused by a more alkaline solution near the cathode after prolonged electrolysis, leading to re-solution of Md from the cathode. However, more work is necessary to sufficiently prove this effect and to find its explanation. In the first electrolysis there was found a much better separation of  $^{255}\text{Fm}$  from  $^{256}\text{Md}$  (with a factor  $\approx 20$ ) whereas in the second the separation was only a factor  $\approx 4$ . This fact probably cannot be explained solely by the lower current density. The reason probably lies in the effect of citrate ion in the second electrolysis and the higher pH.

For a comparison with other data reported in the literature, we recalculated the data of Fig. 4 to obtain the "amount left in solution," shown in Fig. 6. After finishing the second electrolysis we replaced the mercury phase by  $300 \lambda$  of fresh Hg and proceeded in the electrolysis of  $^{253}\text{Es}$  and  $^{255}\text{Fm}$  with  $30 \text{ mA/cm}^2$  current density, with results shown in Fig. 7. Both Fig. 6 and 7 show, in agreement with the literature[13, 14] an approximately linear relation between these



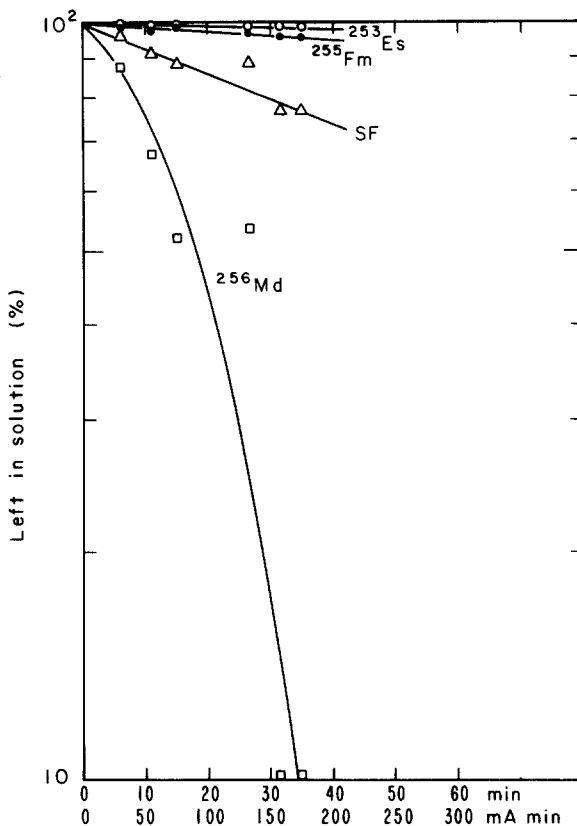


Fig. 6. Percentage of actinide tracers left in solution as a function of time and passed charge (5 mA/cm<sup>2</sup>).

quantities. One can read from these curves the “periods of amalgamation” introduced by Boussières *et al.*[13] The results are  $\approx 100$  mA min for Md, from Fig. 6 and  $\approx 300$  mA min for Fm and  $\approx 800$  mA for Es from Fig. 7. The curves for <sup>256</sup>Md in Fig. 6 and <sup>255</sup>Fm in Fig. 7 show deviations from a straight line (dropping faster when more charge is passed) as observed by Onstott in the case of rare earths electrolyses[8].

#### Potential of the $Md^{3+}-Md^{2+}$ couple

Although a correlation between the amount of extraction into sodium amalgam and the formation of a chemically stable +2 state has been established for the 4*f* elements[3, 15], a similar correlation has not been demonstrated for the 5*f* series.

The expected analogy between Tm and Md led Seaborg[16] in 1949 to predict that Md might have a +2 state.

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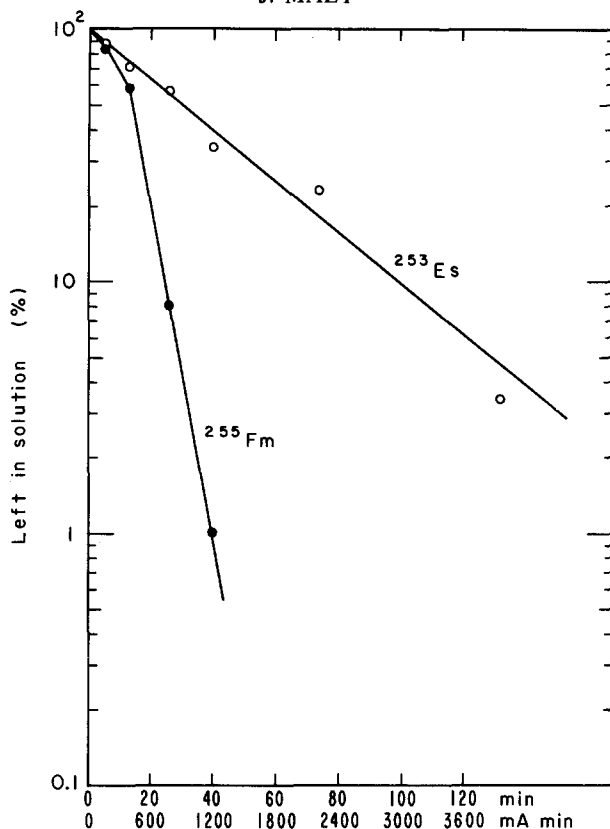


Fig. 7. Percentage of actinide tracers left in solution as a function of time and passed charge. Current density used in this experiment was 30 mA/cm<sup>2</sup>.

Accordingly, we sought direct evidence for a dipositive state of mendelevium, and have attempted to establish rough limits for the potential of the  $\text{Md}^{3+} + e = \text{Md}^{2+}$  couple. To this end, various reducing agents were added to the "stock Md" solution, and  $\text{BaSO}_4$  or  $\text{EuSO}_4$  was precipitated from the mixture. The distribution of  $^{253}\text{Es}$ ,  $^{256}\text{Fm}$  and  $^{256}\text{Md}$  activities between the precipitate and supernatant was then determined.

Typical decay curves of the original solution and the  $\text{EuSO}_4$  or  $\text{BaSO}_4$  fractions, are shown in Fig. 8 (for reduction by amalgamated zinc—in the presence of  $\text{Eu}^{2+}$ ), Fig. 9 (reduction with  $\text{Cr}^{2+}$ ), Fig. 10 (reduction with  $\text{V}^{2+}$ ), and Fig. 11 (attempt at reduction with  $\text{Ti}^{3+}$ ). The curves in Fig. 8, 9 and 10 show good evidence of growth of SF activity from  $^{256}\text{Md}$  separated in the  $\text{EuSO}_4$  or  $\text{BaSO}_4$  fractions. For the case of  $\text{Ti}^{3+}$  only slight growth of  $^{256}\text{Fm}$  was observed relative to the original solution, which indicated incomplete reduction of  $\text{Md}^{3+}$  to  $\text{Md}^{2+}$  by  $\text{Ti}^{3+}$ .

The reduction data are collected in Table 2. The enrichment factor of Md in the  $\text{EuSO}_4$  or  $\text{BaSO}_4$  fraction [defined as the ratio

$$\frac{\frac{R_{\text{MdMd}}(t_{\text{sep}})}{F_{\text{m}}(t_{\text{sep}})} \text{ ppt fraction}}{\frac{R_{\text{MdMd}}(t_{\text{sep}})}{F_{\text{m}}(t_{\text{sep}})} \text{ original solution}}$$

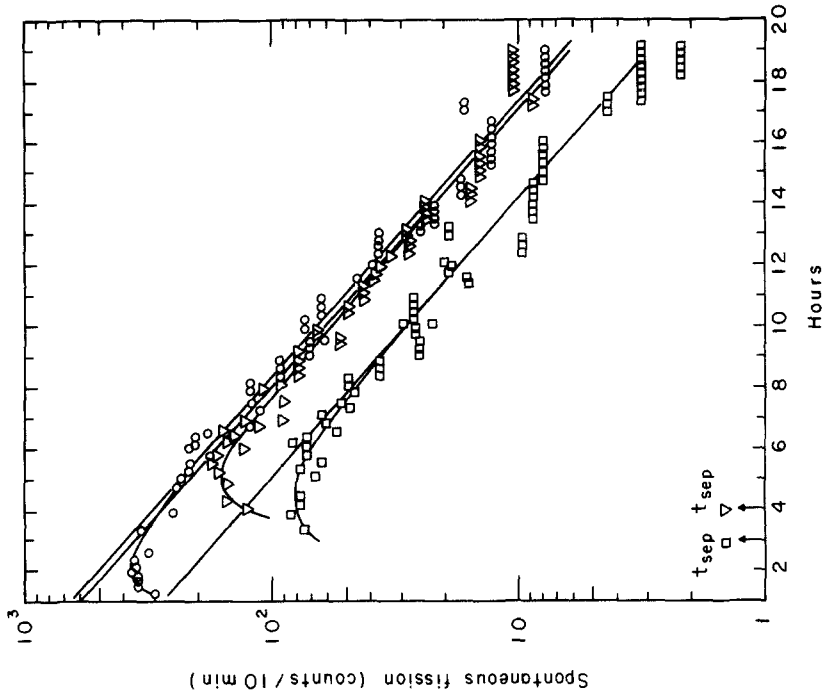


Fig. 9. Decay curves for the original solution  $\circ$  and the  $\text{BaSO}_4$  fraction  $\nabla$ ,  $\square$ . The reducing agent used was  $\text{Cr}^{2+}$ .

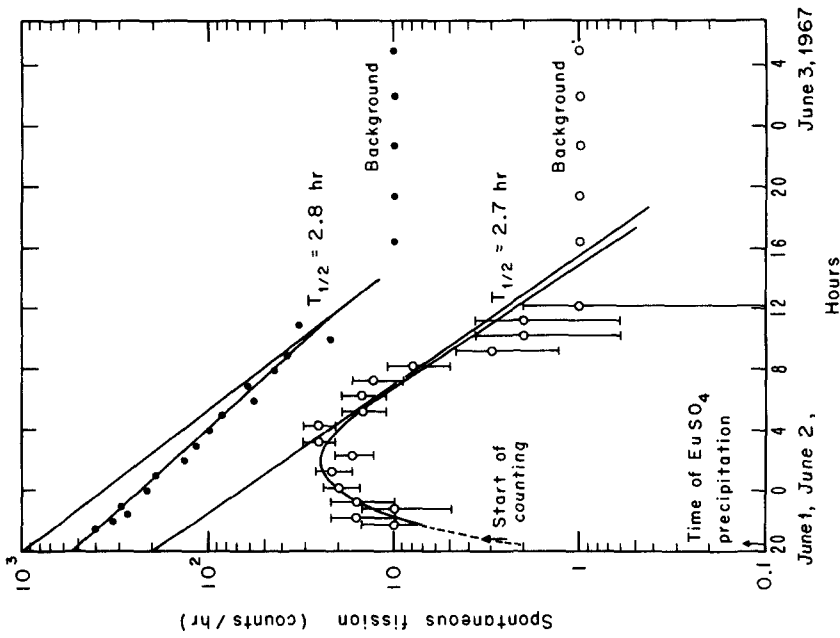


Fig. 8. Decay curves for the original solution and the  $\text{EuSO}_4$  fraction  $\circ$ . The reducing agent used was amalgamated zinc.

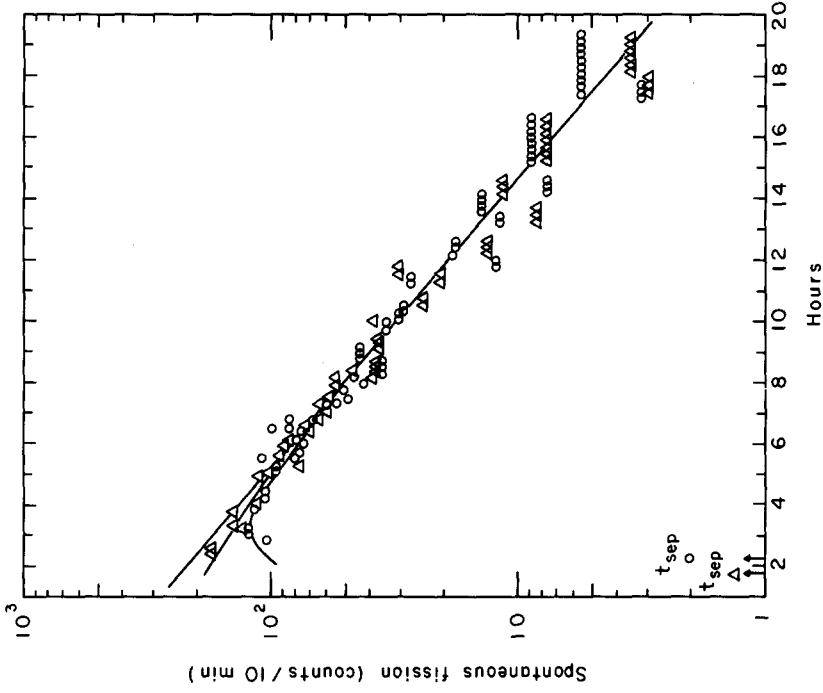


Fig. 11. Decay curves for the original solution  $\Delta$  and the BaSO<sub>4</sub> fraction  $\circ$ . The reducing agent used was Tl<sup>3+</sup>.

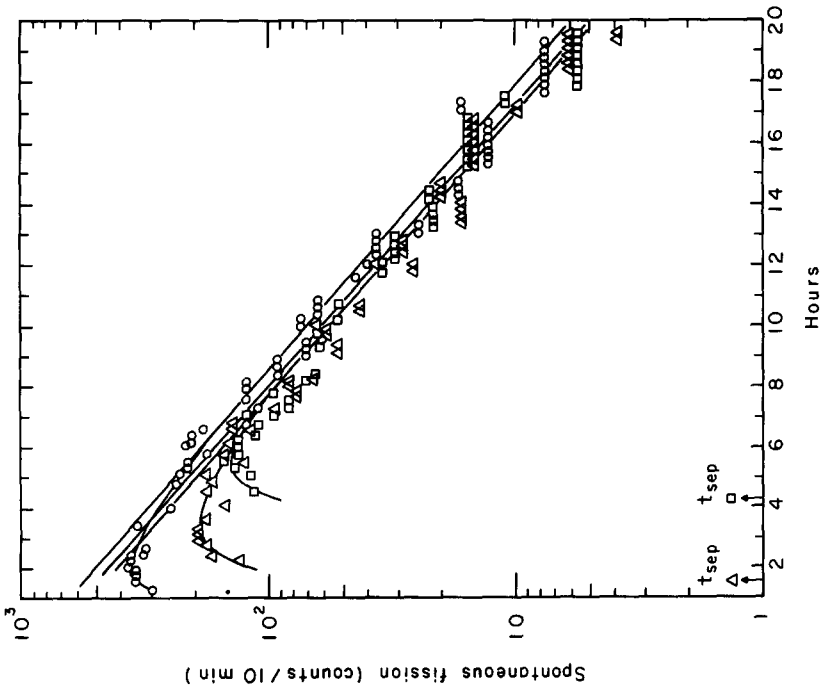


Fig. 10. Decay curves for the original solution  $\circ$  and the BaSO<sub>4</sub> fraction  $\Delta$ ,  $\square$ . The reducing agent used was V<sup>2+</sup>.

Table 2. Results of reduction of Md

Reducing ion	Precipitate	Reduction potential	Corresponding reaction	Experiment no.	$\frac{R_{Md}Md(t_{sep})}{Fm(t_{sep})}$		Enriching factor in precipitate
					of input	of reduction	
Zn + Eu <sup>3+</sup> (Jones' reductor)	EuSO <sub>4</sub>	-0.763	Zn <sup>2+</sup> + 2e → Zn	1.	0.6	19.0	31.7
				2.	0.22	4.0	18.2
				3.	1.00	90.0	90.0
Eu <sup>2+</sup>	EuSO <sub>4</sub>	-0.43	Eu <sup>3+</sup> + e → Eu <sup>2+</sup>	1.	0.21	5.25	25.0
				2.	0.25	5.0	20.0
				3.	2.00	35.0	17.5
Cr <sup>2+</sup>	BaSO <sub>4</sub>	-0.41	Cr <sup>3+</sup> + e → Cr <sup>2+</sup>	1.	0.15	1.54	10.3
				2.	0.086	3.0	34.8
V <sup>2+</sup>	BaSO <sub>4</sub>	-0.255	V <sup>3+</sup> + e → V <sup>2+</sup>	1.	0.107	2.0	18.6
				2.	0.67	9.0	13.4
				3.	0.28	5.7	20.4
Ti <sup>3+</sup>	BaSO <sub>4</sub>	-0.09	TiOCl <sup>+</sup> + 2H <sup>+</sup> + 3Cl <sup>-</sup> + e → TiCl <sub>4</sub> + H <sub>2</sub> O	1.	0.26	0.8	3.1
				2.	0.24	1.15	4.8

in all reduction runs with Zn, Eu<sup>2+</sup>, Cr<sup>2+</sup>, and V<sup>2+</sup> was between 10 and 90, as shown. The yield of Md<sup>2+</sup> coprecipitated with BaSO<sub>4</sub> was from 50–100%, but with EuSO<sub>4</sub> the yield was only ~ 5–10% when the EuSO<sub>4</sub> yield was also 5–10%. The reduction with YbCl<sub>2</sub> gave the same result as with EuCl<sub>2</sub>, with an enrichment factor ≈ 20. These results show that Md<sup>3+</sup> was reduced to Md<sup>2+</sup> by Yb<sup>2+</sup>, Zn, Eu<sup>2+</sup>, Cr<sup>2+</sup> and V<sup>2+</sup>, but with Ti<sup>3+</sup> the reduction was low. Since partial reduction occurred with Ti<sup>3+</sup> (E<sup>0</sup> = -0.09 V [17] in 1 M HCl) the Md<sup>3+</sup> + e → Md<sup>2+</sup> reduction potential apparently is about -0.1 V.

#### CONCLUSION

The results presented in Table 1 indicate 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<sup>2+</sup> is more stable than Cf<sup>2+</sup> or Es<sup>2+</sup>. Additional data in Table 1 show that in the separation of EuCl<sub>2</sub> from SmCl<sub>2</sub>, by treating these amalgams with ice cold concentrated HCl all of the Md is carried by the solid EuCl<sub>2</sub> fraction. This suggests the existence of a solid, slightly soluble MdCl<sub>2</sub> (in conc. HCl), isostructural with EuCl<sub>2</sub>.

Figures 4 and 5 demonstrate a very substantial separation of Md from Es and Fm by electrolysis. The maximum separation observed was 0.8% Es:4% Fm:90% Md by electrodeposition in mercury during the first electrolysis (Fig. 4).

The maximum ratio of spontaneous fission activity due to  $^{256}\text{Fm}$ , to  $\alpha$  activity of  $^{253}\text{Es}$  and  $^{255}\text{Fm}$  was reached after passage of  $\approx 9C$  of electric charge. The enrichment of  $^{256}\text{Fm}$  in the mercury phase by a factor  $\approx 30$  is due to preferential electrodeposition of  $^{256}\text{Md}$  on the cathode, while Es and also Fm remain 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[8–10]. 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 2 were carried out. These data indicate that  $\text{Md}^{3+}$  can be reduced to  $\text{Md}^{2+}$  and then precipitated with  $\text{EuSO}_4$  or  $\text{BaSO}_4$  usually with an enrichment factor  $> 10$  (in comparison to Es) with any of the following reducing agents:  $\text{YbCl}_2$ , Zn (Jones' Reductor in the presence of  $\text{Eu}^{3+}$ ),  $\text{Eu}^{2+}$ ,  $\text{Cr}^{2+}$ , or  $\text{V}^{2+}$ , 2 M in HCl solution.

It follows that the reduction potential for the  $\text{Es}^{3+} - \text{Es}^{2+}$  couple must be more negative than for the  $\text{Md}^{3+} - \text{Md}^{2+}$  couple by  $\approx 1\text{ V}$  or more. The oxidation potential of  $\text{Md}^{3+} \rightarrow \text{Md}^{2+}$  couple is close to the oxidation potential of  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$  in 1 M HCl, about  $-0.1\text{ V}$ .

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 experiments. The  $\text{Md}^{3+}$  can be separately reduced, for instance by zinc using a Jones' Reductor, to  $\text{Md}^{2+}$ , while Es and Fm remain in the  $3+$  state.

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