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REDUCTION OF FERMIUM TO DIVALENT STATE IN CHLORIDE AQUEOUS ETHANOLIC SOLUTIONS

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There is no information in the literature confirming the preparation of Fm in the divalent state, although a standard potential of $Me^{2+} = Me^{3+} + e$ equal to -(1,2 - 1,3)v has been predicted (1,2). To reduce fermium to the divalent state it is necessary to have a system with a high reduction potential and a divalent form of fermium stabilized and identified.

This is achieved in the process of simultaneous reduction of samarium and fermium chlorides by magnesium metal in aqueous ethanolic solutions when low soluble $SmCl_2$ takes up Fm^{2+} . The true isomorphous co-crystallization which takes place in this case makes it possible both to identify and stabilize the divalent state of fermium since Fm^{2+} forms a part of the matrix of the $SmCl_2$ crystal lattice. A 310-cm heavy ion cyclotron (Nuclear Reactions Laboratory, J.I.N.R., Dubna) has been used for synthesizing fermium-252

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through the reaction

 238 U(18 O, 4n) 252 Fm

Identification of 252 Fm and detection of its activity were performed by *d*-spectrometry method using a semiconductor detector with a resolution of no less than 40 keV. During the synthesis of 252 Fm an isotope 245 Cf resulting from the accompanying reaction is produced in comparable quantities and its presence makes it difficult to measure 252 Fm. Therefore it is necessary to measure 252 Fm 8 hours after irradiation when 245 Cf activity decreased more than 10^3 times.

The extraction of fermium from the irradiated uranous-uranic oxide was carried out with the help of samarium and europium fluorides serving as fermium carriers. After the fluorides were dissolved in a mixture of nitric and boric acids the hydroxide was precipitated, washed in ethanol and dissolved in 0,5 ml of a 7M solution of hydrogen chloride in ethanol. To the obtained solution were added 1 ml of an ethanolic solution of samarium chloride $([Sm^{3+}] = 50 \text{ mg/ml})$ containing ^{85}Sr , 50 mg of magnesium metal and additional 0,5 ml of 7M HCl in ethanol. This led to the formation of a red low soluble SmCl₂ precipitate which took up ^{85}Sr and ^{252}Fm .

To measure the activity fermium was extracted from 0,6M $NH_4SCN-0,1M$ H_2SO_4 solution by a 30% methyl-trioctilammonium rhodanide solution in xylol as was recommended for the extraction of other actinides (3). After the organic

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phase was washed twice fermium was re-extracted by 1M HClO_4 . The sample that was measured represented a platinium disc on which the fermium solution in chloric acid was evaporated. After the disc was heated at 500°C the active layer did not exceed 50 μ g/cm².

Figs. 1 and 2 present spectra of samples prepared from the aliquotic part of the solution prior to reduction and from the SmCl₂ precipitate. ⁸⁵Sr activity was measured by means of a multichannel analyzer provided with a Ge(Li)detector. Aqueous phase after extraction was used to detect the ⁸⁵Sr activity.



FIG. 1

SPECTRUM OF *A*-RADIATION OF THE SAMPLE PREPARED FROM THE ALIQUOT OF THE SOLUTION PRIOR TO REDUCTION



FIG. 2

SPECTRUM OF &-RADIATION OF THE SAMPLE PREPARED FROM THE SmCl₂ PRECIPITATE

We have examined the distribution of the formium microamounts in relation to the strontium microamounts between the SmCl₂ precipitate and the solution. This distribution took place according to equation (1)

$$\ln \frac{a}{a - x} = \lambda \ln \frac{b}{b - y}$$
 (1) where

a and b - the amounts of fermium and strontium in the

system,

: and y - their amounts in the solid phase,

 λ - the distribution coefficient. This equation was obtained on the basis of semilogarithmic equations of co-crystallization (4) of each microcomponent with SmCl₂ as a macrocomponent. The λ value is constant when the thermodynamic parameters in the system are constant. In addition, both microelements must be in the divalent state in order to keep λ constant. If, however, Fm³⁺-which is not taken up when co-crystallization occurs - is present in the solution together with the co-crystallizing Fm²⁺ then the lower the [Fm²⁺]/[Fm³⁺] ratio, the lower the λ value. If the standard oxidation-reduction potentials of Me²⁺=Me³⁺ + e for samarium and fermium are more or less identical, a change of the [Sm²⁺]/[Sm³⁺] ratio will result in a change of the [Fm²⁺]/[Fm³⁺] ratio, i.e. in a change of the λ value. Different [Sm²⁺]/[Sm³⁺] ratios were achieved in the experiments on crystallization and recrystallization of the SmCl₂ precipitate with fermium and strontium present. In the 'orne - bace, the [Sm²⁺]/[Sm³⁺] ratio was higher than in the latter since there is a SmCl₂ supersaturated solution with SmCl₂ crystallization.

In order to prove that fermium is reduced to the divalent state in this solution it is enough to show that its co-crystallization with SmCl_2 is due to true isomorphism. For this reason the effect an admixture of LaCl_3 - the salt of an easily sorbated cation - on the λ value was examined. Besides, we have studied the co-crystallization of yttrium, europium and ytterbium with SmCl_2 precipitate. These elements were selected because yttrium is an element which is not known to exist in the divalent state, europium is quantitatively converted to the divalent state with the formation of SmCl_2 , and ytterbium has a standard oxidation-reduction potential for $\text{Me}^{2+} \Rightarrow \text{Me}^{3+} + \text{e}$ ranging between the corresponding values for samarium and europium.

Finally, we have studied the co-crystallization of Fm with EuCl₂ formed under conditions similar to those of SmCl₂ precipitation. We have found that the EuCl₂ precipitate is similar to SmCl₂as far as its structure is concerned. However, with the reduction of europium a potential which is insufficient to reduce ytterbium and samarium is created. The results of the experiments are given in Table 1.

TABLE I

Values of distribution coefficients of the microelements under study in relation to Sr microamounts with crystallization and recrystallization of SmCl_2 and $\text{EuCl}_2^{\mathbf{X}/\mathbf{I}}$

Element	SmCl ₂ precipi	tate EuCl ₂ precipitate
	crystalliza- recryst tion lizatio	al- crystallization n
y ⁸⁸	0,004 ± 0,001 -	_
Eu ¹⁵⁵	1.3 ± 0.2 1.8 ± 1.5 ± 0.3 ^{xx/}	0.5 -
¥b ¹⁷⁵	0.28 ± 0.02 0.042 0.11 ± 0.03 ^{xx/}	± 0.007 0.005 ± 0.001
Fm ²⁵²	0.95 1.20 0.72 1.10 1.30 0.71 ^{xx/} 0.72 ^x	0.015 x/

x/ 68% confidence limits.

xx/ Crystallized with LaCl₃ present, [La] - 1mg/ml

RESULTS AND DISCUSSION

From Table I it follows that Y, which is not known to exist in the divalent state, does not co-crystallize with SmCl₂. In contrast, Eu and Yb, which are reduced with the formation of SmCl₂, are taken up by the precipitate. It is significant that λ (Yb) < λ (Eu), since YbCl₂ is far more soluble than EuCl₂. Fermium also co-crystallizes with the SmCl₂ precipitate. Ytterbium and fermium do not co-crystallize with EuCl₂, although the latter's structure is similar to that of SmCl₂. The addition of La does not affect the $\lambda_{(Eu)}$ value but somewhat reduces λ for Yb and Fm. This phenomenon is due to the change of the activity coefficients ratio of Yb/Sr and Fm/Sr in the solution. These facts allow only one conclusion that Fm is converted to the divalent state, as SmCl₃ is reduced to SmCl₂.

The fact that fermium like ytterbium is taken up by the EuCl₂ precipitate in insignificant amounts makes it possible to conclude that the standard potential of $Fm^{2+} \iff Fm^{3+} + e$ is more negative than for europium. The comparison of the distribution of microelements between the solution and the SmCl₂ precipitate when the latter is crystallized and recrystallized shows that these distribution coefficients λ are constant for Fm and Eu but variable in the case of Yb. Thus, the $[Sm^{2+}]/[Sm^{3+}]$ ratio may affect the degree of Yb reduction but does not affect the degree of Eu and Fm reduction. Hence, the standard potential of Fm is more positive than that of Yb.

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