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**S.Hübener**

**THE THERMOCHROMATOGRAPHY  
OF ELEMENTAL CALIFORNIUM,  
EINSTEINIUM, FERMIUM  
AND MENDELEVIUM  
IN TITANIUM COLUMNS**

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## INTRODUCTION

As metallic state studies are restricted to weighable quantities, unusual experimental approaches are to be used to characterize the elemental state properties of the heaviest actinoids available only in trace amounts. To get information about the metallic state of fermium and mendelevium Zvara and coworkers<sup>/1/</sup> compared the evaporation rates of these elements from molten lanthanum with those of Ce, Eu, Yb, Am and Cf evaporated simultaneously. The evaporation rates of Md and Fm were found to be higher than those of Eu, Yb and Cf and much higher than those of Am and Ce. From the behaviour of fermium and mendelevium their divalency in the metallic state has been concluded. Merinis et al.<sup>/2/</sup> have studied the evaporation of fermium and californium from molten uranium at  $10^{-5}$  torr and have found the same relative evaporation rates (in per cent per minute) for both californium and fermium.

As was published recently<sup>/3/</sup>, the thermochromatography of metallic elements in titanium columns is suitable for the separation of elements differing in bonding on the titanium surface. On the other hand, for the s- and f-elements a correspondence between their metallic valency and their deposition temperature has been found. Therefore besides the measurement of evaporation rates from molten metals the study of the adsorption on metallic surfaces by thermochromatography may also be a relevant method to characterize the metallic state properties of elements available only in trace amounts.

In the present work the thermochromatography of Cf, Es, Fm and Md in titanium columns was studied in comparison with the behaviour of Na, Sc, Sm, Eu, Yb and Bk in trace amounts.

## EXPERIMENTAL

### Materials

The actinoid elements were produced by bombarding <sup>249</sup>Bk with <sup>22</sup>Ne ions at the JINR 3-m cyclotron<sup>/1,4/</sup>. Up to  $3 \times 10^5$  atoms of <sup>253</sup>Es,  $10^5$  atoms of <sup>252,254</sup>Fm and  $6 \times 10^3$  atoms of <sup>256</sup>Md were produced at a time. The nuclear reaction products

were stopped in a 6  $\mu\text{m}$  aluminium foil together with  $^{249}\text{Bk}$  and  $^{249}\text{Cf}$  sputtered from the target. The decay curve measurements have shown that the spontaneous fission activity is almost exclusively due to  $^{256}\text{Fm}$  arising essentially from the decay of  $^{256}\text{Md}$ <sup>4/</sup>. From the decay curve of the  $\alpha$ -activity it is evident that  $^{253}\text{Es}$  has been produced directly in the nuclear reaction and was not accumulated as a daughter product of  $^{253}\text{Fm}$ . The trace amounts of  $^{24}\text{Na}$  and  $^{47}\text{Sc}$  were produced in the aluminium catcher during the bombardment. To obtain  $^{145}\text{Sm}$ , natural neodymium metal was bombarded with 35 MeV  $^4\text{He}$  ions at the JINR 2-m cyclotron.  $^{145}\text{Sm}$  was separated in the elemental state from a thick target by evaporation at 1400 K in a helium stream. The isotopes  $^{147}\text{Eu}$  and  $^{169}\text{Yb}$  were prepared and purified using the standard procedures described in<sup>5/</sup>.

### Procedure

The experimental procedure was very similar to that described in detail earlier<sup>3/</sup>. To obtain and stabilize the elements under investigation in the elemental state, they were evaporated from molten lanthanum simultaneously with microgram amounts of calcium - 0.5 per cent calcium were added to the lanthanum reductant - and high-purity helium was used as a mobile phase.

A nitric acid solution of the lanthanoids was evaporated in a tantalum boat. After the aluminium stopping foil containing the actinoids and the metallic lanthanum were put therein, the boat was placed into the column in the starting position. The thermochromatographic column was made from a titanium foil (30-50  $\mu\text{m}$ ), placed in a tantalum lined quartz tube 4.5 mm i.d. and was conditioned by heating in a helium stream at 1450 K. The experimental conditions were as follows: flow rate, 1.6 cm/s (NPT); starting temperature, 1425 K; average negative linear temperature gradient, 57 K/cm; separation time, 15 minutes.

Immediately after the gradient furnace had been switched off, the quartz tube was cooled by water to room temperature. Then the titanium column was removed from the quartz tube, cut alongside and contacted with a poly(ethylene-terephthalate) track detector (LAVSAN foil, 55  $\mu\text{m}$ ) to detect the  $^{256}\text{Fm}$  fissions. The registration of the spontaneous fission activity over a period of ten hours first at 20 min- and later at 120 min-intervals was followed by the spectrometric measurements of the  $\alpha$ - and  $\gamma$ -activities in one centimetre sections by Si surface barrier, Ge (Li) and Ge detectors. The statistical error ( $\sigma$ ) in determining the relative amounts of the

Thermochromatographic distribution of the trace amounts of Na, Sm, Eu, Yb, Cf, Es, Fm and Md along the titanium column.

$\gamma$ -radioactive tracers did not exceed 3%. The  $\alpha$ -spectrometric measurements were continued over a period of 30 days. To determine the amounts of  $^{252,254}\text{Fm}$  their decay curves were followed, whereas the longer-lived  $^{249}\text{Cf}$  and  $^{253}\text{Es}$  were determined after the decay of the short-lived nuclides.

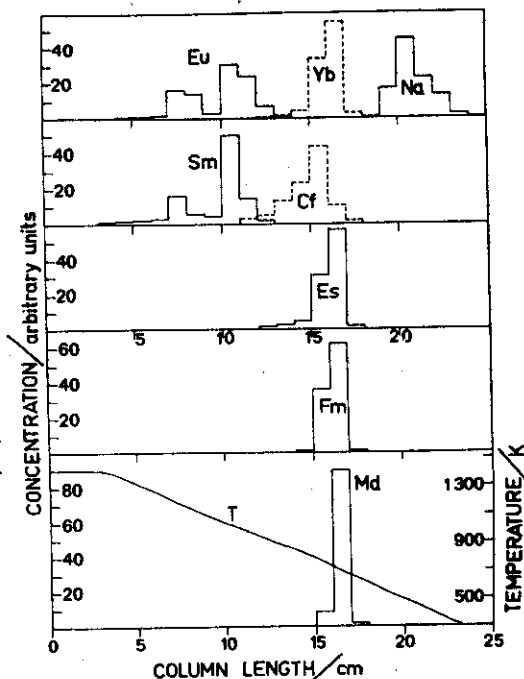
The growth-and-decay curves of the  $^{256}\text{Fm}$  spontaneous fission activity of all column sections containing fermium were

analysed by means of a computer to distinguish  $^{256}\text{Fm}$  which was present before the thermochromatographic experiments, from  $^{256}\text{Fm}$  arising from the decay of  $^{256}\text{Md}$  after the thermochromatographic process.

The error of the relative  $^{256}\text{Md}$  amounts, evaluated from the growth-and-decay curves of  $^{256}\text{Fm}$  taking into account the distribution of fermium as determined by  $\alpha$ -spectrometric measurements, is expected to lie in the range 10 to 15%, whereas the statistical error ( $\sigma$ ) in determining the relative amounts of the  $\alpha$ -radioactive tracers does not exceed 8%.

### Results and Discussion

The distribution of the elements under investigation along the column after the thermochromatographic process is shown in the Figure. The temperature gradient is also demonstrated there. The represented data were taken from two experiments under the given conditions with the exception of the mendelevium chromatogram evaluated only from one experiment. The trivalent metals scandium and berkelium remained in the lanthanum (aluminium) melt. The minor quantities of aluminium evaporated from the melt should not influence the thermochromatographic



behaviour of the studied elements, since the thermochromatograms of Sm, Eu, Yb and Cf from experiments without aluminium were the same as those presented here.

The distribution of the weighable calcium amount (500  $\mu\text{g}$ ), as determined by X-ray fluorescence analysis was almost the same as the distribution of  $^{147}\text{Eu}$  in its low temperature peak. Taking into account that the evaporation rate of calcium from the molten lanthanum (in per cent per minute) is in the range of the evaporation rates of the trace amounts of the divalent metals europium and ytterbium, it is expected that the potential oxygen impurities in the gaseous phase and on the titanium surface react preferably with calcium.

Besides such a stabilizing function for the elemental state of the trace amounts, calcium is to be considered as an internal standard for divalent metals, since the detected distribution of the studied elements along the column results from interactions of single atoms with both the titanium surface and the calcium layer on titanium and may be compared with the distribution of the calcium macroamount itself.

Bearing this in mind we conclude that the actinoids californium, einsteinium, fermium and mendelevium occur to be divalent metals in this study. The californium behaviour is shown to be intermediate between that of europium (calcium) and ytterbium, whereas einsteinium, fermium and mendelevium behave like ytterbium. The divalency of californium agrees with the results of the earlier californium studies<sup>/6/</sup>, but is inconsistent with the vapour pressure measurements done by Ward et al<sup>/7/</sup>. From the vapour pressure data, found to lie between those for samarium and europium, the trivalency of californium was concluded. Johansson<sup>/8/</sup> has given an interpretation of the discrepancies in the californium work supposing a tri-to-divalency transition on the californium surface as found in the case of samarium<sup>/9/</sup>. Therefore the divalency observed in microscale work<sup>/6/</sup> might to a large extent originate from the surface properties of californium, whereas the vapour pressure data represent its bulk properties. The difference between the surface and bulk properties can also account for the differences between our thermochromatographic results and the vapour pressure data.

However, the thermochromatographic behaviour of californium is clearly different from that of the trivalent metals such as thulium (3) and samarium which have a tendency to divalency.

The divalency of einsteinium is consistent with the results of electron diffraction measurements on nanogram metal deposits<sup>/10/</sup>.

The behaviour of fermium and mendelevium can be compared with the results of our evaporation studies mentioned above and with chemical investigations in aqueous solution, which have shown the stability of the divalent oxidation state<sup>11-18/</sup>.

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