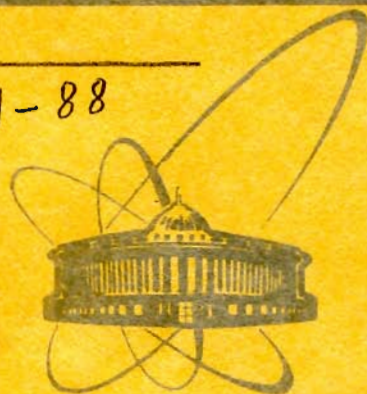


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ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ
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S.Hübener, I.Zvára

THE THERMOCHROMATOGRAPHY
OF METALLIC ELEMENTS
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Хюбенер З., Звара И.

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Термохроматография металлических элементов
в колонках из титана

Изучалась термохроматография микроколичеств Na, K, Cs, , Ba, Eu, Yb, Tm, Tl, Pb, Bi, Po, Am и Cf в элементарном состоянии в колонках из титана. Температуры осаждения показывают различные типы взаимодействия атомов адсорбата с поверхностью титана. Обсуждаются возможные аналитические и "неаналитические" применения этой техники.

Работа выполнена в Лаборатории ядерных реакций ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1979

Hübener S., Zvára I.

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The Thermochromatography of Metallic Elements
in Titanium Columns

The thermochromatography of trace amounts of Na, K, Cs, , Ba, Eu, Yb, Tm, Tl, Pb, Bi, Po, Am, and Cf in the elemental state in titanium columns has been studied. The deposition temperatures indicate different types of interaction of the adsorbate atoms with the titanium surface. Possible analytical and "non-analytical" applications of the technique are discussed.

The investigation has been performed at the Laboratory of Nuclear Reactions, JINR.

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1. INTRODUCTION

Thermochromatography is a convenient method for the separation and chemical identification of nuclear reaction products in the gaseous phase. By varying the temperature regime, the stationary and mobile phase, thermochromatography is applicable to almost all of the elements of the periodic table ^{/1,2/}. Numerous papers are devoted to volatile compounds, but only a few to the thermochromatography of elements.

We believe that it may be advantageous to separate trace amounts in the elemental state in metallic columns, because different types and energetics of bonding between metallic surfaces and adatoms could provide separation factors exceeding those attainable by distillation and sublimation of macroamounts ^{/8,9/}.

The theoretical calculation of the enthalpy of adsorption (ΔH_{ad}) on metallic surfaces is mostly incorrect ^{/8-10/}. The properties of the corresponding macroscopic metal-metal systems may not provide good estimates for ΔH_{ad} , since the bonding at the surface is not necessarily the same as in the bulk of the macroscopic system ^{/8/}. For instance, the alkali and alkaline earth metals do not react with titanium owing to their large metallic radii ^{/11/}, whereas on the surface of titanium, cesium atoms are adsorbed with ΔH_{ad} exceeding the enthalpy of sublimation of cesium, because in surface reactions the size of the adatoms is of minor importance. On the other hand, if in macroscopic systems compound formation is observed, it is also expected on surfaces ^{/8/}. This should be the case for the adsorption on titanium of the volatile elements Tl, Pb, Bi, and Po, which in macroamounts react with titanium ^{/11/}.

The experimental values of ΔH_{ad} on titanium are known only for cesium and americium. The adsorption of cesium was investigated by thermoemission ^{/12/}, and ΔH_{ad} of americium was evaluated from vacuum thermochromatography da-

ta¹³. In the present work the adsorption of trace amounts of Na, K, Cs, Ba, Eu, Yb, Tm, Tl, Pb, Bi, Po, Am, and Cf in the elemental state on the surface of polycrystalline titanium was investigated by thermochromatography in open tubular columns in order to prove the applicability of thermochromatography in titanium columns to both separation and "non-analytical" problems. The declared chemical state is of speculative character, as it cannot be determined directly. We volatilized the elements under investigation from molten lanthanum and used high-purity helium containing sodium or calcium vapours as a mobile phase. On the basis of the thermochemical data for macro-systems we believe that these conditions favor the elemental state.

2. EXPERIMENTAL

The arrangement for the thermochromatographic experiments is shown schematically in Fig. 1. To prepare the titanium

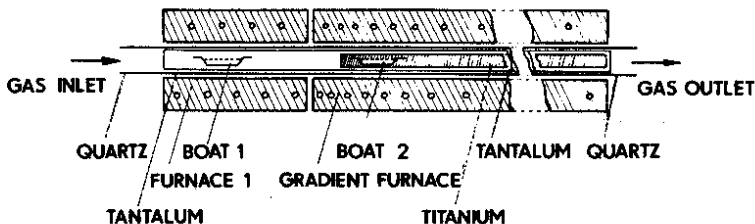


Fig. 1. Schematic picture of the experimental arrangement.

column a 50 μm tantalum foil lining was first placed into a quartz tube 4.5 mm i.d. The lining prevented reactions of titanium with silica and diffusion of oxygen from the quartz tube to the inner surface of the titanium column. Then the coiled-up titanium foil was placed inside the tube. Before starting the experiment the column was purified by heating in a helium stream at 1500K and 10^{-2} atm. The helium used was purified by molecular sieves at the liquid nitrogen temperature and a zirconium getter working at 1150-1200 K. In some experiments sodium vapours (about 10^{14} atoms/cm³) were introduced into the carrier gas, by

passing helium over molten sodium in the tantalum boat (1) heated to 560 K. The nitric acid solutions of the carrier-free radionuclides under investigation (listed in Table 1) were evaporated in the tantalum boat (2), then metallic lanthanum (99.9%) was put therein and the boat was placed into the column in the starting position (2). In the experiments with Ca vapours in the mobile phase, lanthanum containing 0.5% Ca was used. The Ca concentration in the carrier gas then varied from about 10^{17} atoms/cm³ at the beginning to about 10^{14} atoms/cm³ to the end of the experiment. After the boat has been placed, the column was evacuated twice to 10^{-2} atm and then refilled with purified helium. Simultaneously the furnaces were heated up in some side position and after having reached the temperature equilibrium, they were shifted to the working position to start the chromatographic process.

The experimental conditions were as follows:

- the flow rate was 0.7 cm/s (NTP);
- the starting temperature was 1425 K,
- the average negative temperature gradient was 57 K/cm, and
- the separation time was 30 minutes.

The distribution of the radionuclides along the column after the chromatographic process was determined by measuring the γ -activity with a Ge(Li) and the α -activity with a Si(Au) detector in one-centimeter sections. The carrier-free radionuclides used in the thermochromatographic experiments were prepared and purified by standard procedures /14-17/.

3. RESULTS AND DISCUSSION

Table 2 gives the experimental deposition temperatures (the temperatures of the peak maxima), the enthalpies of adsorption evaluated from the deposition temperatures using equations given by Eichler and Zvara /20/ and the enthalpies of sublimation of the metals /21-24/. The given uncertainties in the deposition temperature are the estimated total errors including statistical and systematic errors.

A thermochromatogram of a mixture of Pb, Tl, Eu, Yb, Cf, and Na in the He/Ca carrier gas is shown in Fig. 2, while Fig. 3 shows a thermochromatogram of Eu, Cf, Ca, and K in the He/Na atmosphere.

The elements under investigation were volatilized from the lanthanum melt with yields between 5% (Am) and 95% (Cs).

Table 1

The radioactive properties of the tracers /18,19/

Nuclide	$T_{1/2}$	γ -energy (keV)	α - energy (MeV) used for identification
^{24}Na	15.0 h	1 368.6	
^{43}K	22.0 h	616.0	
^{129}Cs	32.1 h	411.3	
^{131}Ba	11.5 d	496.3	
^{147}Eu	22.0 d	121.2	
^{168}Tm	85.0 d	815.9	
^{169}Yb	31.8 d	177.0	
^{200}Tl	26.1 h	368.0	
^{203}Pb	52.1 h	279.2	
^{205}Bi	15.3 d	703.3	
^{206}Po	8.8 d	338.4	
^{241}Am	433 yrs		5.486
^{249}Cf	352 yrs		5.810

Table 2

Deposition temperatures and thermodynamic functions

Element	Mobile phase He/Ca		Mobile phase He/Na		ΔH° sub 0.0 kcal/mole	ΔH° sub 298 kcal/mole
	Deposition temperature K	$-\Delta H^{\circ}$ ad kcal/mole	Deposition temperature K	$-\Delta H^{\circ}$ ad kcal/mole		
Na	495 \pm 40	24.5 \pm 2			25.66 ^a	25.92 ^b
K			395 \pm 40	19.5 \pm 2	21.54 ^a	21.42 ^b
Cs	640 \pm 40	32 \pm 2	700 \pm 50	35 \pm 2	18.54 ^a	18.72 ^b
Ba	1120 \pm 40	56 \pm 2	1150 \pm 50	57.5 \pm 2	43.7 ^a	41.7 ^b
Eu	975 \pm 50	48.5 \pm 2			42.8 ^a	42.1 ^b
	1120 \pm 40	56 \pm 2	1125 \pm 50	56 \pm 2		
Im	\approx 1425	\approx 72	\approx 1425	\approx 72	55.8 ^a	59.1 ^b
Yb	735 \pm 40	36.5 \pm 2	875 \pm 50	43.5 \pm 2	36.7 ^a	36.3 ^b
			765 \pm 50	38 \pm 2		
Tl	1350 \pm 50	67 \pm 2			43.4 ^a	42.9 ^b
Pb	\approx 1425	\approx 72			46.78 ^a	46.6 ^b
Bi	\approx 1425	\approx 72			50.2 ^a	52.83 ^b
Po	1375 \pm 50	68.5 \pm 2			34.5 ^a	34.45 ^b
Am	\approx 1425	\approx 72	\approx 1425	\approx 72	63 ^a	67.9 ^c
Cf	755 \pm 40	37 \pm 2	760 \pm 40	37 \pm 2	42 \pm 5 ^a	42 \pm 3 ^d

a - ref. /21/, b - ref. /22/, c - ref. /23/, and d - ref. /24/.

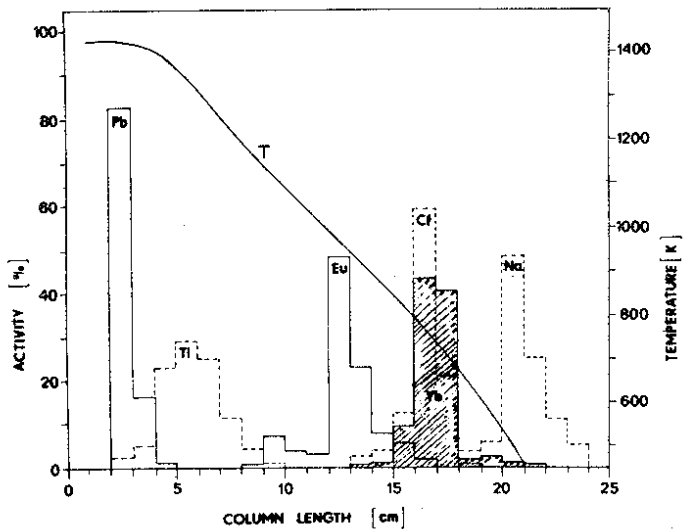


Fig. 2. Thermochromatographic distribution of the trace amounts of Pb, Tl, Eu, Yb, Cf, and Na along the titanium column (mobile phase He/Ca).

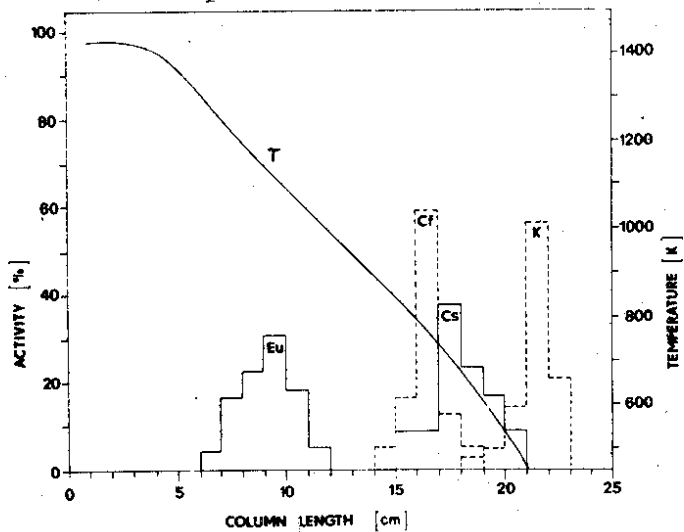


Fig. 3. Thermochromatographic distribution of the trace amounts of Eu, Cf, Cs, and K along the titanium column (mobile phase He/Na).

Only the volatilized part was considered in the description of the thermochromatographic behaviour.

The elements Tl, Pb, Bi, and Po were deposited at quite high temperatures (e.g., deposition temperatures below 900 K were found for these elements on quartz^{/2/}). For the adsorption on titanium the $-\Delta H_{ad}$ values are larger than the ΔH_{sub} values, i.e., the force of the intermetallic adsorbent-adsorbate bonding exceeds the force of the metallic bond of the pure elements. This is in accordance with the formation of the intermetallic compounds Ti_4Pb , Ti_4Bi , Ti_3Bi ^{/25/} and of titanium polonides^{/26/}. More than 90% of the 5f -element americium was found to be adsorbed on the tantalum foil in the region of the starting temperature as a result of diffusion through the titanium foil. The 4f -elements Tm, Eu, and Yb were also found on the tantalum, but in quantities $\leq 20\%$. In contrast to the f-elements Tl, Pb, Bi, and Po were localized on the titanium probably as strong surface compounds and only 1% of them were found on the tantalum. The divalent metals europium and barium were deposited at 1150 K and 1125 K, respectively, on the titanium in the He/Na atmosphere. In the He/Ca atmosphere, barium was found almost at the same position, whereas europium was mainly deposited at lower temperatures with macroamounts of calcium serving as a carrier for europium. The high temperature peak of europium seems to correspond to the "true" adsorption on titanium. The influence of the α - β transition of titanium at 1150 K on the deposition of europium and barium cannot be excluded.

Ytterbium was deposited at 735 K in the He/Ca atmosphere and at 765 K in the He/Na atmosphere. In some experiments in He/Na atmosphere a second deposition band of ytterbium was found at 875 K.

The monovalent alkali elements were deposited at lower temperatures. The relatively high deposition temperatures of cesium may be due to the pure ionic surface bonding, because the ionization potential I of the cesium atoms is lower than the work function ϕ of the titanium^{/9,27/}. For the other alkali elements, the alkaline earth elements and the divalent lanthanoids, the relation $A < \phi < I$ is valid (A - electron affinity). This is a common criterion for the metallic character of the surface bonding, but it contains no information about the strength of bonding^{/9,27/}.

Our value of 32 ± 2 kcal/mole for the enthalpy of adsorption of cesium on titanium is in good agreement with the experimental value of 32.1 kcal/mole determined by thermo-emission^{/12/}.

A comparison of the evaluated enthalpies of adsorption with the enthalpies of sublimation shows only poor correlation. However, for the s- and f-elements there seems to exist a correspondence between the metallic valence and the deposition temperature:

- The trivalent metals with a "divalent" ground electronic state of the gaseous atoms are deposited at temperatures $T > 1400$ K with $-\Delta H_{ad} > 70$ kcal/mole (Am and Tm).

- The divalent metals possessing the same electronic structure in both the condensed and the gaseous states are deposited within the temperature range $750 \text{ K} < T < 1150 \text{ K}$ with $-\Delta H_{ad}$ in the range 35 kcal/mole $\leftarrow -\Delta H_{ad} < 60$ kcal/mole (Ba, Eu, and Yb).

- The monovalent metals are deposited within the temperature range $350 \text{ K} < T < 700 \text{ K}$ with $-\Delta H_{ad}$ in the range 17 kcal/mole $\leftarrow -\Delta H_{ad} < 35$ kcal/mole (Na, K, and Cs).

The deposition of californium in nearly the same position as ytterbium then points to a divalent form of metallic californium. This is in accordance with the investigation of the crystal structure of californium in the μg -range^{28/}. The thermochromatographic method is based on interactions of single atoms with a metallic adsorbent and does not allow a direct statement about the properties of the condensed phase. The deposition temperature gives information about the bonding energy of the adatom-adsorbent system, from which the "valence" of the adatom in the adsorbed state can be estimated, provided the surface bonding is metallic. However, the estimation of the metallic valence by comparison with the thermochromatographic behaviour of well defined elements should be suitable for the heavy actinoids fermium, mendelevium and element 102, which are available only in trace amounts.

The described thermochromatographic technique is applicable for a number of radiochemical separations, but a further study is necessary to increase the vaporization yield of some elements of interest and to avoid the losses by diffusion through the titanium. A potential application would be the separation of the hypothetical superheavy elements from the heavy actinoids, because the superheavy elements with $113 < Z < 116$ as heavier homologues of the investigated elements of the VIth period should be deposited above 1000 K, whereas the deposition of the actinoids with $99 < Z < 102$ is expected below 800 K.

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