

СООБЩЕНИЯ  
ОБЪЕДИНЕННОГО  
ИНСТИТУТА  
ЯДЕРНЫХ  
ИССЛЕДОВАНИЙ

Дубна

97-102

E12-97-102

I.Zvára, A.B.Yakushev, S.N.Timokhin, Xu Honggui,  
V.P.Perelygin, Yu.T.Chuburkov

CHEMICAL IDENTIFICATION OF ELEMENT 106  
(THERMOCHROMATOGRAPHY OF OXOCHLORIDES)

Submitted to «Radiochimica Acta»

1997

## 1. Introduction\*

All the isotopes of element 106 so far known have been identified exclusively on the basis of physical evidence; chemical isolation has not contributed to the discoveries because of lack of required very fast separation methods which would also ensure a high chemical yield and facilitate efficient detection of radiation. Up until recently,  $^{263}106$  has been the longest-lived known isotope of the element. It was discovered in 1974 in the reaction  $^{249}\text{Cf} (^{18}\text{O}, 4n)$  by Ghiorso *et al.* [2], who found the half-life,  $T_{1/2}$ , to be  $0.9 \pm 0.2$  s and the production cross section,  $\sigma$ , to be 0.3 nb for the  $\alpha$ -decay branch at a stated bombarding energy of 94 MeV. Later on, Druin *et al.* [3] reported  $0.63^{+0.32}_{-0.18}$  s and 0.6 nb, respectively, for the spontaneous fission (SF) branch; their bombarding energy was  $95 \pm 1.5$  MeV. Some lighter isotopes of element 106 were synthesised by the bombardments of lead with Cr projectiles [4-6]:  $^{258}106$  with  $T_{1/2} = 2.9$  ms (mostly SF);  $^{259}106$  with  $T_{1/2} = 0.5$  s, (mostly  $\alpha$ -active);  $^{260}106$  with  $T_{1/2} = 4$  ms, ( $\alpha$ /SF = 50:50); and  $^{261}106$  with  $T_{1/2} = 0.25$  s (mostly  $\alpha$ -active). Isotopes  $^{262}106$  and  $^{264}106$  are not known yet. Very recently [7],  $\alpha$ -active  $^{265}106$  and  $^{266}106$  with  $T_{1/2}$  of about 3 and 15 s, respectively, have been discovered by bombarding, again, an actinoid target,  $^{248}\text{Cm}$ , with  $^{22}\text{Ne}$ . Unfortunately, their  $\sigma$  values are several times smaller than that for  $^{263}106$ .

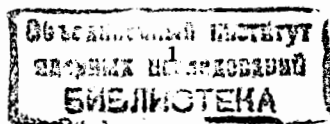
In the atoms of the heaviest elements one finds extremely dense clouds of electrons moving with relativistic velocities. This is why the studies of the chemical properties of the elements are interesting *per se*: «relativistic effects in chemical properties» [8] present the most challenging problem of experimental and calculational chemistry at the frontiers of the Mendeleev periodic table. To reveal these effects, the detailed comparative experimental studies of the heaviest elements and their lighter homologues need confronting with sophisticated relativistic calculations of atoms and molecules [9,10].

With a new element, obviously, the very first step must be its chemical identification. If the element is produced by heavy ion bombardments in a (HI,xn) reaction, the chemical identification means isolation from a number of simultaneously produced lower-Z nuclides using some characteristic chemical properties of the corresponding subgroups. The emphasis in the identification of element 106, if detecting its SF, is on the decontamination from the heavy actinoids and the transactinoid elements 104 and 105, as some of their isotopes which also exhibit SF might interfere. It is not true for lighter elements, including the expected homologues of element 106.

### *Earlier developments of prospective fast gas phase techniques for element 106*

The chemical identification of the first two transactinoids, elements 104 and 105, was first performed at Dubna [11,12]. Their isotopes undergoing SF with half-lives of

\* The work was presented at the 4<sup>th</sup> Internat. Conference on Nuclear and Radiochemistry held in St. Malo, on 8-13 September 1996. Some of the data and their preliminary evaluation were briefly reported earlier in Ref.1.



a few seconds were detected. To do this, gaseous chlorides were rapidly isolated and separated using the principles of the gas-solid isothermal frontal chromatography (IC) or thermochromatography (TC). With IC, the surviving atoms were detected at the column exit, while TC differed in that a stationary longitudinal negative temperature gradient was imposed over the column, and preparative inner chromatograms were obtained. It was found that, generally, elements 104 and 105 behaved as it was expected for EkaHf and EkaTa, respectively. So element 106 must be EkaW, a transition metal of group VI.

As early as in 1972, before element 106 was discovered, our laboratory attempted [13,14] to develop a TC isolation procedure for volatile tungsten (oxo)chlorides, ultimately aiming at the identification of EkaW. To study very rare and short-lived transactinoid nuclides, immediate «on-line» chemical processing of each created atom is needed. For that purpose (cf. also Fig. 1 below), a target thinner than the range of the recoiling products of fusion reactions is used, so that the desired nuclei be mostly ejected from it. They are let thermalise in an inert gas, which continuously flushes the target chamber. The appropriate gaseous reagents are introduced downstream, and this "carrier gas" reacting with and transporting the recoils is applied onto a TC column. A special problem with short-lived and low yield activities is how to measure the co-ordinate along the column at which a molecule resided when the decay event occurred (see below).

In the bombardments of  $^{nat}\text{Er}$  with  $^{12}\text{C}$  ions, 34-m  $^{175}\text{W}$  and 2.5-h  $^{176}\text{W}$  were produced [13,14]. The recoils were thermalised in commercial nitrogen (< 1%  $\text{O}_2$ ), while  $\text{SOCl}_2$  vapour was introduced at the exit of the target chamber to yield a partial pressure of 26 mmHg at a nitrogen flow rate of 1 l/min (STP) in an open glass column with 4-mm i.d. The tungsten activities deposited in two zones with maxima at about 260 and 145 °C. The higher the temperature of the column hot end (in the range 350 to 450 °C) was the larger percentage of the activity was found at 145 °C; the purification of the raw nitrogen from  $\text{O}_2$  by active copper also brought more activity to the lower temperature. The interpretation was that two compounds,  $\text{WO}_2\text{Cl}_2$  and  $\text{WOCl}_4$ , were formed. Elution - type experiments with raw nitrogen in an isothermal column kept well above 260°C showed that most of the W atoms reached the deposition zones in less than 0.8 s. By that time it had been learned, that elements 104 and 105, as well as their homologues, do not yield effectively volatile species under the experimental conditions with W. Thus it was shown that the identification of EkaW might be feasible provided that its half-life is not less than  $\approx 0.5$  s.

In several later tests by PSI groups [15], the experimental conditions markedly differed. The recoiling atoms from the  $^{nat}\text{Gd} + ^{20}\text{Ne}$  interactions were thermalised in flowing He gas loaded with KCl,  $\text{MoO}_3$  or graphite aerosol and were transported several meters (through a capillary) to an IC equipment. There the aerosol particulates were destroyed by passing through a «quartz wool» filter kept at 800-900°C, while  $\text{SOCl}_2$  vapour plus  $\text{Cl}_2$  and/or  $\text{O}_2$  were introduced at the point. The gas passed through a short open chromatographic column of fused silica, and beyond it the survival yields of W isotopes versus the column temperature were measured. It was found, e.g., that at  $>150^\circ\text{C}$  the retention time for 50-s  $^{168}\text{W}$  was much shorter than its half-life. In 1995, the

PSI group started experiments with the relatively long-lived  $\alpha$ -emitters  $^{265}\text{106}$  and  $^{266}\text{106}$  at the UNILAC accelerator in GSI, Darmstadt [16]. With their OLGA III apparatus for performing on-line IC, they study the oxochloride(s) of element 106 with  $\text{SOCl}_2 + \text{O}_2$  in the carrier gas.

The PSI, Villigen - RC, Rossendorf group believe that moderately volatile hydroxides, which are characteristic of the transition elements of group VI, might also be prospective for the isolation, identification and further studies of element 106 as the hydroxides of the elements of groups III to V are much less volatile. This time [17], a  $\text{MoO}_3$  aerosol was used, the filter temperature was 1200°C, and the carrier gas was  $\text{He} + \text{O}_2 + \text{H}_2\text{O}$ . In a TC column, the W activities deposited at about 800°C or higher. The authors think that, rather than simple adsorption, a dissociative mechanism takes place:  $\text{WO}_3(\text{OH})_2(\text{g}) = \text{WO}_3(\text{a}) + \text{H}_2\text{O}(\text{g})$ . The IC studies of element 106 might be feasible using this chemical system.

In the present work, attempting the chemical identification of element 106 for the first time, we aimed at the detection of SF events due to the isotope(s) of element 106 produced in  $^{249}\text{Cf} + ^{18}\text{O}$  bombardments. This allowed us to apply the thermochromatographic approach with a chlorinating carrier gas, which proved so effective for the previous elements. Unlike Refs. 11-14, now we have used fused silica columns. This brings important advantages: the inner surface of the column can serve as the required detector of fission fragments (see below), and the chemical system is simple. The surface chemistry of silica under the action of various inorganic compounds containing chlorine seems to be rather well understood [18,19]. We first made more test experiments with isotopes of W to look for the optimum chemical system with the silica column; and then we carried out chemical identification experiments aiming at  $^{263}\text{106}$ .

## 2. Experimental

### *Bombardments and nuclear reactions*

The heavy ion bombardments were done with the extracted beams of the Dubna U-400 cyclotron at the site of the KHIPTI [20] project. Mo and W radioisotopes were produced in the following bombardments, using mostly isotopically enriched targets:  $^{24}\text{Mg} + ^{nat,70}\text{Zn} \rightarrow ^{87-90}\text{Mo}$ ;  $^{18}\text{O} + ^{nat}\text{Dy} \rightarrow ^{175-177}\text{W}$ ;  $^{20,22}\text{Ne} + ^{154,156,158}\text{Gd} \rightarrow ^{174-177}\text{W}$ ; and  $^{24}\text{Mg} + ^{144,147,149}\text{Sm} \rightarrow ^{164,167,174}\text{W}$ .  $^{48}\text{Cr}$  was a by-product created in some stainless steel parts of the target assembly. The lanthanoid targets were deposited as  $\approx 1$  mg/cm<sup>2</sup> layers of oxides on 7  $\mu\text{m}$  thick Al-foils, while the Zn target was just a 1  $\mu\text{m}$  thick metallic foil. Isotopically enriched target materials or natural mixtures of isotopes were used as indicated. The target for the production of element 106 was made of radiochemically very pure  $^{249}\text{Cf}_2\text{O}_3$ . The oxide was deposited as a 1.0 mg/cm<sup>2</sup> thick spot, 12 mm in diameter, on a 7- $\mu\text{m}$  Al foil. A little of Dy oxide was painted at the round edge of the spot to produce also W isotopes.

The U-400 cyclotron provides extracted  $^{18}\text{O}$  beams with ion energies either 180 MeV or 140 MeV. The initial particle energy was reduced to the required (optimum)

value in the upstream parts of the target assembly (cf. Fig. 1): the target backing, the special degrading foils, the gas gap, and the entrance window. Periodic accurate measurements of the actual bombarding energy were made. For that purpose, in the beam pipe, ahead of the target chamber, a thin Au foil was placed, which was seen by a spectrometric particle detector fixed in the side arm of the pipe. Thus the beam particles scattered at a certain angle could be measured. The detector was covered with some Al foils, which reduced the particle energy to nearly the same extent as the listed parts of the target assembly did.

The beam intensity reached  $2.5 \cdot 10^{12}$  pps on the target. The beam was of smaller diameter than the target, and the beam current could be taken directly from the target chamber, which was insulated from the beam pipe.

### Thermochromatographic equipment

A schematic of our TC apparatus is shown in Fig. 1. The thermalised recoils were swept from the target chamber with 1-l/min argon gas into the thermochromatographic column – an open, 3.5-mm i.d. tube of fused silica, 150 cm in length. About 60% of the recoils reached the column, the rest were deposited on the walls of the target chamber. At the column inlet, the flowing argon was mixed with a smaller amount of the reactive gas. This was supplied from the end part of the apparatus through the annular channel formed by the glass jacket of the column. When, e.g., «SOCl<sub>2</sub> plus air» were used as the reagents, typically 0.2 l/min of air saturated with SOCl<sub>2</sub> vapour was supplied to yield partial pressures of 20 mmHg (or 2.6 vol%) of SOCl<sub>2</sub> and 25 mmHg (or 3.3 vol%) of O<sub>2</sub> in the resulting carrier gas. The used ambient air first passed through an efficient aerosol filter and then bubbled through liquid SOCl<sub>2</sub>.

In some experiments, a loose plug of quartz wool was placed 10 cm from the inlet, at the hottest point of the column, in the middle of the furnace, to enhance deposition of molecules of the non-volatile radioactive species.

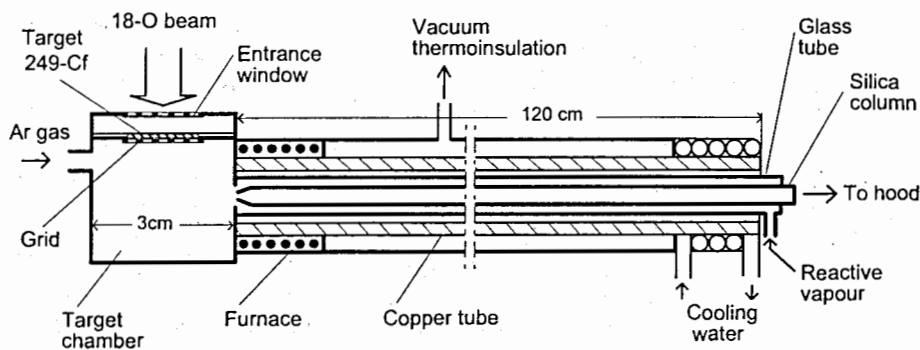


Fig. 1. A schematic view of the thermochromatographic equipment for on-line experiments.

### Measurement of chromatograms

After the bombardments, the distribution of  $\gamma$ -emitters along the column was measured by assaying its 5-cm long segments with the use of a spectrometric Ge(Li) detector. The isotopes of W with  $T_{1/2} < 30$  min could be traced by their longer-lived Ta, Hf or rare earth descendants, as these elements did not yield volatile compounds.

In the experiments with element 106, to detect long-lived  $\alpha$ -emitters like  $^{252-254}\text{Fm}$ ,  $^{253,254}\text{Es}$ , and  $^{248}\text{Cf}$ , first 20 cm of the column and the rest of it (the thermal gradient part) were separately washed with an acid, the solution was evaporated to dryness on a plate, the residue was ignited, and such sample was measured with a PIPS detector.

The inner surface of the fused silica column served as a solid state track detector of the fragments from the SF events [21]. The original latent tracks were revealed by etching the column 5-cm segments with HF and scanning the surface with an optical microscope. It proved possible to positively identify some SF events with both fragments detected, as the vector defined by the cone shaped track points to a  $\approx 1\text{-mm}^2$  spot to be searched for the opposite «coincident» track. The very low number of the observed events made random coincidences improbable. At room temperature, the detection efficiency of fission events is about 65%. It decreases at higher temperatures due to the annealing of the tracks [21]. Only after prolonged annealing at  $\geq 550$  °C the latent tracks are not etchable any more. We checked experimentally that the detection efficiency is not affected by the presence of the used chlorinating gases.

### Yields of some heavy nuclides as a function of bombarding energy

The catcher foil technique was used to measure the recoil yields from the employed Cf target versus  $^{18}\text{O}$  ion energy (91 to 104 MeV). The foils were placed on the target supporting grid (cf. Fig.1), on its side facing the target chamber. After the end of the bombardment, the SF events from the relatively long-lived  $^{256}\text{Fm}/^{256}\text{Md}$  were recorded to follow the growth-and-decay curve, and  $\alpha$ -active  $^{252}\text{Fm}$  plus  $^{255}\text{Fm}$  (the two isotopes could not be told apart) were measured by a spectrometer.

## 3. Results and discussion

### Ancillary experiments with tungsten and other elements of group VI

To look for the conditions of the selective production of the volatile compounds of W, while Hf and Ta compounds would be non-volatile, we investigated some chemical systems, in which the formation of either chlorides or oxochlorides might be expected. Different compositions of the chemically active components of the carrier gas were tried, and the temperature regime was varied. A continuous experiment usually lasted 2.5 hours. Fig. 2 shows that in the absence of air at least two deposition zones of 2.5-h  $^{176}\text{W}$  were formed. But in the presence of air, we observed a single peak of W while, indeed, Hf and Ta remained in the start zone. We selected the latter system for further

study as it had been learned in previous works of our laboratory that elements 105, 104, and actinoids do not yield volatile compounds with such a carrier gas [11,12].

Additional tests showed that an oxygen concentration of 1 to 5% plus about 2.5% of  $\text{SOCl}_2$  in argon gas makes it possible to produce volatile compounds of Cr and Mo as well, with Mo behaving very similar to W; cf. Fig. 3.

Then we performed experiments with several isotopes of W which have half-lives in a range of 5 s to 0.5 h to look whether the formation of volatile species is rapid

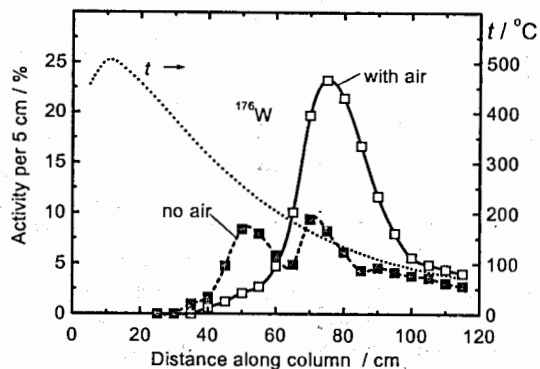


Fig. 2. Behaviour of  $^{176}\text{W}$  in the absence and presence of free oxygen. Carrier gases: argon (1.2 l/min) +  $\text{SOCl}_2$  (10 mmHg) +  $\text{TiCl}_4$  (2 mmHg), and argon (1 l/min) + air (0.2 l/min) +  $\text{SOCl}_2$  (20 mmHg).

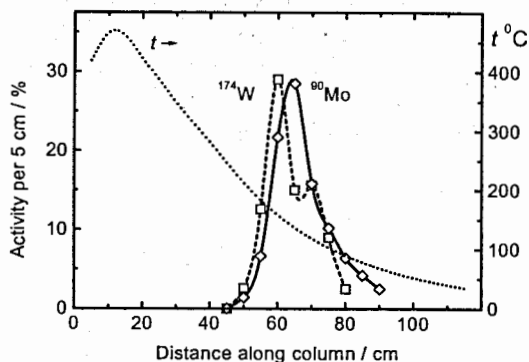


Fig. 3. Comparative TC behaviour of long-lived isotopes of W and Mo. Carrier gas: argon (1 l/min) + air (0.2 l/min) +  $\text{SOCl}_2$  (20 mmHg).

enough. Indeed, both long and the shortest-lived activities could be seen to yield adsorption peaks beyond the filter, in the thermal gradient part of the column. It means that the chlorination time of W atoms plus the retention time of the produced volatile molecules in the starting section of the column (in the absence of the quartz wool filter) did not exceed a few seconds.

#### Yields of the interfering SF activities produced in the bombardment

Simultaneously with element 106, a number of heavy nuclides can be produced without violating the laws of conservation. Some of them have an appreciable SF decay rate. So, if produced with not negligible yields, they might interfere in detecting element 106 by its SF events, and must be removed chemically to the necessary degree. While, generally, the highest cross sections occur for near - target actinoids; the pair  $^{256}\text{Md}/^{256}\text{Fm}$  seemed to be the most "dangerous". For it, based on Ref. 23, one could expect a cross section exceeding that of element 106 by at least three orders of magnitude; cf. Table 1. Using the catcher foil technique (see Experimental), we made some yield measurements for the employed target assembly. Our data and the results of another Dubna group [24] are presented in Table 1 as well. Our yields sharply drop with the energy decreasing from 97 to 91 MeV; they are lower than those ones found in Ref. 24, and much lower than in Ref. 23. But the data of the different authors cannot be directly compared. The assumption made in Ref. 23 that all the produced heavy nuclei recoil from the target is obviously wrong. Actually, unlike evaporation residues, transfer reaction products have broad angular and projected range distributions [25]; hence the yields in catcher foils must decrease in the case of a thicker target like ours. Moreover, our target supporting grid with a hole diameter to grid thickness ratio of 1:1 must also markedly reduce the recoil yields of transfer reaction products, while only slightly affecting evaporation residues [26]. Also the systematic errors in energy measurements

Table 1. Apparent «production cross sections», in  $\mu\text{b}$ , of  $^{252,255,256}\text{Fm}$  and  $^{256}\text{Md}$  in the bombardments of  $^{249}\text{Cf}$  by  $^{18}\text{O}$  obtained by the catcher foil technique.

Group	Target ( $\mu\text{g}/\text{cm}^2$ )	Nuclide(s)	Bombarding energy			
			91 MeV	94 MeV	97 MeV	104 MeV
Lee et al. [23]	$\text{CfF}_3$ (640)	$^{252}\text{Fm}$ ( $T_{1/2}=23$ h; $\alpha \approx 100\%$ )	610	--	1910	2400
Present authors	$\text{Cf}_2\text{O}_3$ (1000)	$^{252+255}\text{Fm}$	$2 \cdot 10^{-4}$	$2.1 \pm 2^a$	$43 \pm 4$	$36 \pm 4$
Lee et al. [23]	$\text{CfF}_3$ (640)	$^{256}\text{Fm}$ ( $T_{1/2}=2.7$ h; SF 90%)	0.11	--	1.2	1.5
		$^{256}\text{Md}$ ( $T_{1/2}=1.3$ h; EC 90%)	0.07	--	0.69	0.19
Sagaidak et al. [24]	$\text{Cf}_2\text{O}_3$ ( $\leq 500$ )	$^{256}\text{Fm}$	--	0.002	0.02	0.02
		$^{256}\text{Md}$	--	0.02	0.2	0.2
Present authors	$\text{Cf}_2\text{O}_3$ (1000)	$^{256}\text{Fm} + ^{256}\text{Md}$	$10^{-4}$	$10^{-4}$	0.02	0.02

<sup>a</sup> An average of Table 2 data..

and different energy spread of the beam might play a role. So the three sets of data are not necessarily inconsistent; still special quantitative evaluation would be of interest.

#### Chemical experiments with element 106.

The data characterising the conditions and results of various runs in a calendar time sequence are summarised in Table 2 and displayed in Fig. 4. In first two thermochromatographic runs (Table 2), a quartz wool filter was present in the start zone as in most ancillary tests. No fission fragment tracks were found in the column (to be discussed below). In the four other experiments, such a filter was absent. This time, the reproducible zones of the tracks of fission fragments were observed.

Table 2. Experiments with element 106 (the same target was used in all the bombardments).

No.	Date Integral dose of $^{18}\text{O}$ ions / $10^{17}$	Extracted / bombarding $^{18}\text{O}$ energy	Time of the run	Apparent $^{252,255}\text{Fm}$ yield <sup>a</sup>	Number of fission events detected
1 <sup>b</sup>	Feb. 92 0.8	180 / 94 MeV	16 h	2.0 $\mu\text{b}$	0 <sup>b</sup>
2 <sup>b</sup>	March 92 1.3	180 / 94 MeV	24 h	2.2 $\mu\text{b}$	0 <sup>b</sup>
3	April 92 1.5	180 / 94 MeV	20 h	2.3 $\mu\text{b}$	10
4	July 92 2.0	180 / 94 MeV	32 h	2.1 $\mu\text{b}$	20
5 <sup>c</sup>	Feb. 93 1.1	180 / 94 MeV	16 h	1.8 $\mu\text{b}$	18 <sup>c</sup>
6	April 95 $2.6 \cdot 10^{17}$	140 / 94 MeV	36 h	3.9 $\mu\text{b}$	11

<sup>a</sup>  $^{252,255}\text{Fm}$  activity at the end of bombardment was 0.15 to 0.35 Bq.

<sup>b</sup> Runs with a quartz wool filter in the start section of the column.

<sup>c</sup> A run without reagents and at ambient temperature; all the tracks were found within the starting 15 cm of the column.

The numbers of the tracks found in runs nos. 3, 4 and 6 reasonably correlate with the beam fluences if one takes into account the low statistics. Even stronger evidence of constant physical conditions is provided by the very similar apparent yields of  $\alpha$ -active Fm isotopes in runs nos. 1-5. The larger apparent yield of Fm isotopes in run no. 6 does not contradict that. The run differed from the others in the energy of the primary beam, hence, also in the thickness of the degrading foils. As shown in Table 1, around 94 MeV the Fm yield strongly depends on the bombarding energy. So the factor of two in the yield per fluence unit could well result from an error of one MeV or so in the actual bombarding energy because of the uncertainties in the accepted stopping powers.

Fig. 4 shows the distributions of the detected fission events in runs nos. 3 - 6. As can be seen, in thermochromatographic runs nos. 3, 4 and 6 very few events were recorded within the starting 20 cm of the columns where more than 99% of the  $\alpha$ -activity of various actinoid isotopes like  $^{252,254}\text{Fm}$ ,  $^{253,254}\text{Es}$ , and  $^{248}\text{Cf}$  were deposited.

The low temperature tail of the SF zone profile seems a little longer than that of the W isotope zone, yet, the last 35 cm of the column were free of tracks.

The white histogram of run no. 5, in which the column was kept at ambient temperature and reagents were absent, shows that all the 18 detected SF nuclei decayed (i.e., were deposited) within the starting 15 cm of the column, similarly with the behaviour of the non-volatile actinoid compounds in the thermochromatographic runs.

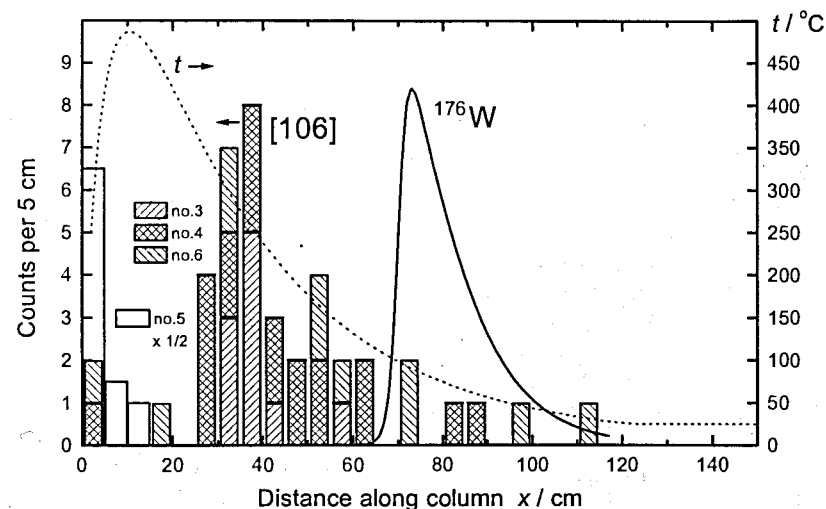


Fig.4. Experiments with element 106. Stacked hatched histograms - fission events detected in three thermochromatographic runs with the carrier gas argon (1 l/min) + air (0.2 l/min) +  $\text{SOCl}_2$  (20 mmHg); white unstacked histogram - fission events in the run with pure argon in a cold column; dashed peak - gamma activity of the W isotope in an arbitrary linear scale.

#### Assignment of the observed SF activity

A mixture of SF activities cannot be resolved by mere detecting SF events with the track detectors employed. Hence it was necessary to make certain that the tracks observed in the temperature gradient part of the column originated exclusively from element 106 in the state of a volatile compound(s). The *imaginable* sources of "background", i.e., of tracks which might stem from nuclides with  $Z < 106$ , are the following: the neutron induced fission of uranium impurities in the column material; the target material sputtered into the flowing gas by the beam (atoms, clusters or aerosol particulates); and the SF nuclei of heavy actinoid elements and of elements 104 and 105 produced in the bombardment.

We could definitely reject all these sources on the basis of the following observations: First, the special bombardments of the silica tubes by much higher

fluences of neutrons showed that even a single neutron induced fission due to the uranium impurities could not take place in the experiments with element 106; this is directly evidenced by zero counts in runs nos. 1 and 2 (cf. Table 2). Secondly,  $^{249}\text{Cf}$ , which served as a target, is mostly  $\alpha$ -active (5.81 MeV), its half-life is 350 years and the  $\alpha/\text{SF}$  ratio equals  $2.3 \times 10^8$ . So an  $\alpha$ -activity of 150 Bq is accompanied by one fission event per day. If released and deposited in the column, that much of activity could be easily noticed; but it was not the case. Also the character of the distribution of fission events along the column is inconsistent with this source. Finally, as shown in Table 2, the recoil yield of  $^{256}\text{Md}/^{256}\text{Fm}$  from our target was extremely low. Even more informative, as far as the SF bombardment products are concerned, was run no.5 in the cold column with no reactive chemicals; see Table 2 and Fig. 4. The 18 fission events detected in the column indicated a total apparent  $\sigma$  of 0.2 nb or so for all the  $Z \leq 106$  SF activities (actinoid and transactinoid) with half-lives longer than some 0.1 s (which is the time that the gas spent in the target chamber). That number itself shows that only a quite moderate degree of the separation of EkaW from the unwanted nuclides was needed to get conclusive evidence that the tracks in runs nos. 3, 4 and 6 originated from the decay of element 106. The fact (see above) that less than 1% of the actinoid atoms passed beyond the first 20 cm of the column means that the W/An separation was actually much better than required. Also dedicated experiments with Hf and Ta as well as earlier studies [11,12] of elements 104 and 105 in chemical environment very similar to that in the present work showed that these elements do not yield volatile compounds. Moreover, the calculated production cross sections [28] for the SF branch of potentially interfering isotopes of elements 104 and 105 are at least by an order of magnitude smaller than the experimental  $\sigma$ -value of SF events due to element 106. So neither actinoids nor the first two transactinoids could bear the distinct zone of the fission events displayed in Fig. 4.

Our bombarding energy corresponded to the reported [2,3] experimental maximum of  $\sigma$  for the production of  $^{263}\text{106}$ . Druin *et al.* [3] expected at this energy a comparable  $\sigma$  for  $^{264}\text{106}$ , but a much smaller value for  $^{262}\text{106}$ . They assigned the SF activity to  $^{263}\text{106}$ , because their  $\sigma$ -values measured at three bombarding energies were consistent with some excitation curve calculations, and their  $T_{1/2}$  agreed with that from  $\alpha$ -measurements [2]. They did not discuss possible contribution of  $^{264}\text{106}$  to the SF counts because they lacked reliable enough theoretical calculations of  $\sigma$  and of the partial  $T_{1/2}$  for various decay modes. But according to some most recent life-time calculations [29], which are in good agreement with the experimental data for so far known nuclides, the partial  $T_{1/2}$  of  $^{264}\text{106}$  for both  $\alpha$ - and SF decay might be around a second, like  $T_{1/2}$  of  $^{263}\text{106}$ , while  $^{262}\text{106}$  must be too short-lived. The cross sections for  $^{263}\text{106}$  and  $^{264}\text{106}$  at 94 MeV are now calculated to be  $\approx 0.3$  and  $\approx 0.05$  nb, respectively [28]. So the yet unknown heavier isotope might have contributed to our tracks either directly, by its own SF, or through its  $\alpha$ -decay, which yields even shorter  $^{260}\text{104}$  with 100% SF; *i.e.*, all the decays of  $^{264}\text{106}$  finally result in SF events. On the other hand, the  $\alpha$  decay of  $^{263}\text{106}$ , produced with  $\sigma = 0.3$  nb [2], yields 4.5-s  $^{259}\text{104}$ , which has a  $\approx 9\%$  SF branching [30]. This must contribute about 0.02 nb to the total  $\sigma$  of SF activities due to element 106.

Assuming the 80% recoil yield of element 106 nuclei, 40% loss in the target chamber due to the irreversible adsorption of thermalised atoms on its walls, and the detection efficiency (see below), we found  $\sigma \approx 0.15$  nb for the  $Z = 106$  nuclei which yield SF events. This  $\sigma$  is not necessarily inconsistent with the reported 0.6 nb for  $^{263}\text{106}$  [3] because we do not know the decay losses in the starting part of the column (due to the finite chlorination and retention times), and because not very accurately known experimental values of a number of quantities are involved in evaluating  $\sigma$ .

Thus, the SF events of  $^{259}\text{104}$ , the daughter of  $^{263}\text{106}$ , must have moderately contributed to the observed tracks, and the tracks could also originate from  $^{264}\text{106}$ . But, if so, it does not affect any our conclusion concerning the chemical identification of element 106.

#### *Quantitative evaluation of the element 106 thermochromatogram.*

To further evaluate the experimental data of Fig.4, we accounted for the temperature dependant annealing of tracks. First, from the available annealing data for different temperatures and times [21] we calculated the temperature dependant fission event detection efficiencies for the 30-h experiment, relative to the efficiency at the ambient temperature (65%). We fitted these values with an empirical function and divided each value in the hatched histogram in Fig. 5 by the appropriate relative detection efficiency. This way we obtained a corrected histogram of the number of events in Fig. 5. To smooth the element 106 peak profile, we fitted the corrected histogram (omitting only the SF events within the first 5 cm of the column) by a semiempirical formula based on the theory of the peak shape in nonequilibrium thermochromatography [27]. The formula gave an accurate fit of the tungsten peak shown in Figs. 4 and 5. The maximum of the corrected peak of element 106 is only slightly shifted towards higher temperature compared with the similar fit of raw data.

The fit of element 106 data in Fig. 5 is characterised by a standard error of 2.0, and the area under the peak corresponds to ca. 60 counts. It means that about 90 atoms of element 106 yielding SF events reached the thermal gradient part of the column and were processed by the thermochromatographic system employed.

#### *Chemical state of Cr, Mo, W and element 106*

Our data provide evidence of the formation of a volatile (oxo)chloride of element 106. In the first two «unsuccessful» experiments the retention time on the quartz wool plug exceeded  $T_{1/2}$  of the particular isotope(s). A longer retention on the filters than in the open column segment was observed earlier also for the elements of groups IV and V. This takes place due to the large surface of the plug of 10- $\mu\text{m}$  thick quartz fibres (equivalent at least to several meters of an open column) and due to stronger adsorption on their active surface.

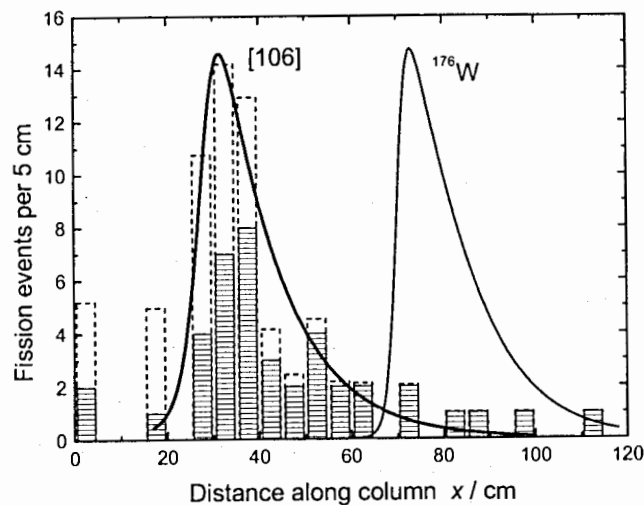


Fig.5. Treatment of the experimental thermochromatogram. Solid histogram - the data from Fig.4; dotted histogram - the data corrected for the relative detection efficiency; thick solid curve - the smoothed corrected thermochromatogram of element 106.

One can see a marked difference between the deposition temperatures of element 106 and  $^{176}\text{W}$  (Figs. 4 and 5). There would be a shift even if the properties of the elements were identical because the particular nuclides have very different half-lives, so also migration times [31]. But this factor can hardly account for so large a difference. This points to nonidentical chemical states of the two homologues or to quite different volatilities of the compounds of similar stoichiometry. To solve the problem of the chemical state, we performed some detailed studies of the comparative TC behaviour of Mo and W activities with half-lives in a range from seconds to hours. We, generally, observed two zones of adsorption, at fixed temperatures, while the percentage deposited in the lower temperature zone increased with increasing  $T_{1/2}$  of the nuclides. The isotopes with half-lives of a few second were deposited in the «high temperature» zone to  $> 50\%$ . This obviously gives evidence for more than one compound being involved; the less volatile species reacts relatively slowly to form more volatile one. To make an assignment of these chemical states, we have analysed the results taking into account the volatility of known (oxo)halides of W, Mo and Cr, the expected thermodynamic equilibria in the system, and some considerations about the kinetics of the reactions involved. This analysis goes beyond the scope of the present paper and will be published in detail elsewhere with supporting experimental data. We came to the conclusion that the dioxodichlorides and more volatile oxotetrachlorides of

W and element 106 are responsible for the observed behaviour of the two elements. In the case of tungsten,  $\text{WO}_2\text{Cl}_2$  is first rather quickly formed and is deposited in its proper temperature range; the compound then reacts in a few dozens of seconds to yield more volatile  $\text{WOCl}_4$ . In the experiments with element 106, the long lived  $^{176}\text{W}$  was completely converted into the more volatile compound (Fig.4). By analogy, most probably element 106 was deposited on quartz surface as  $[\text{106}]\text{O}_2\text{Cl}_2$ , but its nuclei decayed «long» before the compound could be transformed into  $[\text{106}]\text{OCl}_4$ .

#### Acknowledgements

The authors are grateful to Professor Yu. Ts. Oganessian for his support for the study, and to the U-400 staff for the operation of the cyclotron. We thank Dr V. A. Lebedev, Mr V. I. Vakatov and Mr G. V. Buklanov for their help with the experiments.

#### References:

1. Timokhin, S. N., *et al.*: Rep. at the NRC-4 Internat. Conf., Vienna, September 1992 - J. Radioanal. Nucl. Chem. Lett, **212**, 31 (1996); Timokhin, S. N. *et al.*: JINR Rapid Commun. **4**[61]-93, 60 (1993); Timokhin, S. N. *et al.*: In Internat. School-Seminar on Heavy Ion Phys., Dubna, May 1993, Yu.Ts. Oganessian Editor, Vol.1. Dubna, 1993; p.204; Yakushev, A. B. *et al.*: J. Radioanal. Nucl. Chem. Art. **205**, 63 (1996).
2. Ghiorso, A., Nitschke, J. M., Alonso, J. R., Alonso, C. T., Nurmia, M., Seaborg, G. T.: Phys. Rev. Lett. **33**, 1490 (1974).
3. Druin, V. A., Bochev, B., Lobanov, Yu. V., Sagaidak, R. N., Kharitonov, Yu. P., Tretyakova, S. P., Gulbekian, G. G., Buklanov, G. V., Yerin, E. A., Kosyakov, V. N., Rykov, A. G.: Sov. J. Nucl. Phys. **29**, 591 (1979).
4. Oganessian, Yu. Ts., Hussonnois, M., Demin, A. G., Kharitonov, Yu. P., Bruchertseifer, H., Constantinescu, O., Korotkin, Yu. S., Tretyakova, S. P., Utyonkov, V. K., Shirokovsky, I. V., Estevez, J.: Radiochim. Acta **37**, 113 (1984).
5. Ambruster, P.: Ann. Rev. Nucl. Part. Sci. **36**, 135 (1985).
6. Muenzenberg, G., Hoffman, S., Folger, H., Hessberger, F. P., Keller, J., Poppensieker, K., Quint, B., Reidorf, W., Schmidt, K.-H., Schoett, H. J., Armbruster, P.: Z. Phys. A **322**, 227 (1985).
7. Lazarev, Yu. A., Lobanov, Yu. V., Oganessian, Yu. Ts., Utyonkov, V. K., Abdullin, Sh., Buklanov, G. V., Gikal, B. N., Iliev, S., Mezentssev, A. N., Polyakov, A. N., Sedykh, I. M., Shirokovsky, I. V., Subbotin, V. G., Sukhov, A. M., Tsyganov, Yu. S., Zhuchko, V. E., Loughheed, R. W., Moody, K. J., Wild, J. F., Hulet, E. K., McQuaid, J. H.: Phys. Rev. Lett. **73**, 624 (1994).
8. Keller, O. L.: Radiochim. Acta **37**, 169 (1983).
9. Zhuikov, B. L., Glebov, V. A., Nefedov, V. S., Zvara, I.: J. Radioanal. Nucl. Chem. Art. **143**, 103 (1990).
10. Pershina, V.: Chem. Rev. **96**, 1977 (1996).
11. Zvara, I., Chuburkov, Yu. T., Belov, V. Z., Buklanov, G. V., Zakhvataev, B. B., Zvarova, T. S., Maslov, O. D., Caletka, R., Shalaevski, M. R.: Radiokhimiya **12**, 565 (1970); Sov. Radiochemistry **12**, 560 (1970); J. Inorg. Nucl. Chem. **32**, 1885 (1970).
12. Zvara, I.: In: XXIVth Int. Congress Pure Appl. Chem., Hamburg 1973. Vol.6. Radiochemistry. Butterworths, London, 1974; p.73.
13. Lazarev, Yu. A., Zvara, I., Korotkin, Yu. S., Shalayeviski, M. R., Schegolev, V. A., Domanov, V. P.: JINR Report R6-6685 (in Russian), Dubna, 1972.
14. Zvara, I., Eichler, B., Belov, V. Z., Zvarova, T. S., Korotkin, Yu. S., Shalayeviski, M. R., Shchegolev, V. A., Hussonnois, M.: Radiokhimiya **16**, 720 (1974); Sov. Radiochemistry **16**, 709 (1974).



15. Gaggeler, H. *et al.*: In: PSI Annual Rep., Annex IIIA, Wuerligen und Villigen, 1991, p.74; Tuerler, A. *et al.*: ibidem, 1993, p.98; Dressler, R. *et al.*: ibidem, 1994, p.87; Gaertner M. *et al.*: ibidem, 1995, p.67. Gaertner M. *et al.*: In: 4<sup>th</sup> Internat. Conf. on Nuclear and Radiochemistry (St. Malo, September 1996) Extended Abstracts. IPN Orsay, 1996, vol.1, A-P10.
16. Tuerler A. *et al.*: In: PSI Annual Rep., Annex IIIA, Wuerligen und Villigen, 1995, p.65; Tuerler A. *et al.*: In: 4<sup>th</sup> Internat. Conf. on Nuclear and Radiochemistry (St. Malo, September 1996) Extended Abstracts. IPN Orsay, 1996, vol.1, A-05.
17. Huebener, S. *et al.*: In: PSI Annual Rep., Annex IIIA, Wuerligen und Villigen, 1991, p.73; Huebener, S. *et al.*: ibidem, 1992, p.102; Ross, A.: ibidem, 1993, p.99, 101; Huebener, S. *et al.*: ibidem, 1994, p.88; Vahle, A., Huebener, S., Eichler, B.: *Radiochim. Acta* **69**, 233 (1995).
18. Sorbents Based on Silica Gels in Radiochemistry (in Russian). B. N. Laskorin Ed. Atomizdat, Moscow, 1977
19. Iler, R. K.: *The Chemistry of Silica*. Wiley-Intersci., N.Y., 1979.
20. Zvara, I., Timokhin, S. N., Yakushev, A. B., Kasztura, L.: In *JINR FLNR Sci.Rep.* 1991-92, Heavy Ion Physics. *JINR E7-93-57*, Dubna, 1993; p.155.
21. Gangrskii, Yu. P., Markov, B. N., Perelygin, V. P.: *Registration and Spectrometry of Fission Fragments (in Russian)*. Moscow, Energoizdat, 1981.
22. Timokhin, S. N., Yakushev, A. B., Fedoseev, E. V., Lebedev, V. Ya., Xu, Honggui, Zvara, I.: In *JINR FLNR Sci.Rep.* 1991-92, Heavy Ion Physics. *JINR E7-93-57*, Dubna, 1993; p.164.
23. Lee, D., Moody, K. J., Nurmia, M. J., Seaborg, G. T.: *Phys. Rev. C* **27**, 2656. (1983).
24. Sagaidak, R. N., Demin, A. G., Druin, V. A., Lobanov, Yu. V., Utyonkov, V. K., Huebener, S.: *JINR Commun.* R7-82-890, Dubna, 1982.
25. Oganessian, Yu. Ts.: In: *Proc. R.A. Welch Found. Conf. On Chem. Res. XXXIV Fifty Years with Transuranium Elements*, Houston, Oct. 22-23, 1990; p.159.
26. Oganessian, Yu. Ts., Lobanov, Yu. V., Tretiakova, S. P., Lazarev, Yu. A., Kolesov, I. V., Gavrilov, K. A., Plotko, V. M., Poluboyarinov, Yu. V.: *Atomnaya Energiya* **28**, 393 (1970).
27. Zvara, I.: *Isotopenpraxis* **26**, 251 (1990).
28. Smolancuk, J., Skalski, J., Sobiczewski, A.: *Phys. Rev. C* **52**, 1871 (1995).
29. Muzychka, Yu. A., Pustyl'nik, B. I.: *JINR Rapid Commun.* 4[61]93, 54 (1993); private communication (1996).
30. Somerville, L. P., Nurmia, M. J., Nitschke, J. M., Ghiorso, A., Hulet, E. K., Loughheed, R. W.: *Phys. Rev. C* **31**, 1801 (1985).
31. Zvara, I.: *Radiochim. Acta* **38**, 95 (1985).

Received by Publishing Department  
on March 26, 1997.

Звара И. и др.

E12-97-102

Химическая идентификация элемента 106  
(термохроматография оксохлоридов)

Элемент 106 (предположительно изотоп с массовым номером 263), детектируемый по актам спонтанного деления, был химически выделен из продуктов облучения  $^{249}\text{Cf}$  ускоренными ионами  $^{18}\text{O}$  с помощью термохроматографии оксохлоридов. В частности, он был отделен от элементов 104 и 105, а также от тяжелых актиноидов. Наблюдаемое поведение элемента 106, по-видимому, обусловлено образованием диоксидхлорида. Зарегистрировано около 40 атомов элемента.

Работа выполнена в Лаборатории ядерных реакций им.Г.Н.Флерова ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна, 1997

Zvára I. et al.

E12-97-102

Chemical Identification of Element 106  
(Thermochromatography of Oxochlorides)

Element 106, isotope mass number presumably 263, detected by its spontaneous fission, has been isolated chemically from the products of the bombardment of  $^{249}\text{Cf}$  with  $^{18}\text{O}$  and separated specifically from elements 105, 104 and heavy actinoids by the thermochromatography of oxochlorides. Dioxodichloride seems to be responsible for the observed behaviour of element 106. Some 40 atoms of the element have been registered.

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

Preprint of the Joint Institute for Nuclear Research. Dubna, 1997