

INVESTIGATION OF THE BEHAVIOUR OF NUCLEAR  
REACTION PRODUCTS AT THEIR VOLATILIZATION  
FROM IRRADIATED Ag AND Au TARGETS  
IN DYNAMIC VACUUM ( $10^{-2}$ – $10^{-3}$  torr O<sub>2</sub> OR H<sub>2</sub>O)

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(Received September 27, 1979)

Volatilization of ultramicroamounts of spallogenic products (Mo, Tc, Ru, Re and Os) from the melts of irradiated Ag and Au metals under dynamic vacuum conditions at  $10^{-3}$ – $10^{-2}$  torr O<sub>2</sub> and H<sub>2</sub>O vapours and their separation in a thermochromatographic column are studied. The influence of the time of sublimation, the gas phase parameters and the materials of the crucible and the column are investigated. Possible reactions and chemical forms of volatile spallogenic products are discussed. Diffusion coefficients are defined for an Ag-melt case. The conditions of Re/Os and Mo/Tc/Ru separation are found. The possibility of using the Ag and Au melts in the ISOL-system is considered.

### Introduction

The techniques of high-temperature analysis and substance purification, based on volatility difference of the elements and their compounds, gain the utmost significance. The work with the condensed samples (solids or melts) at high temperatures (in some cases without their chemical transformations) has great perspectives for radiochemistry. In particular, the high-temperature volatility of ultramicro amounts of elements from various materials find broad application in developing the methods of fast extraction of radioactive nuclides from mixtures of nuclear reaction products.<sup>1-3</sup> Recently, great attention is paid to the development of techniques, based on vacuum evaporation of elements and their compounds due to the development of the ISOL-system (Isotope Separator On-Line<sup>4,5</sup>). By using such units there have been studied short-lived isotopes of volatile elements (noble gases, halogenides, alkali metals, Zn, Cd, Hg) the extraction of which from the target and transportation to the ion source in vacuum is easily done at temperatures up to 1000 °C. The selectivity in such cases was reached not only by means of an ion-source choice, but, mainly, by the conditions of thermochromatographic separation<sup>6,7</sup> due to temperature difference of the target, transporting system and the ion-source.

To separate short-lived isotopes of elements of low volatility (e.g. alkaline-earth and rare-earth metals) an essential increase of temperature is required that leads to a selectivity decrease. Besides, the high energy (4–6 eV) of transient element adsorption on the surface of refractory metals, which are the main constructive material for an ion-source – target system, does not allow one to be sure of the fast extraction of elements of low volatility without their transition into volatile compounds. The use of various chemical compounds as targets and reactive gases is limited because the effective work of ion-sources is possible at pressures not higher than a few millitorrs. In connection with this the investigation of production, evaporation and thermochromatographic separation of volatile compounds at the lowest pressures is of interest. These conditions allow one to unify the advantages of gas-thermochromatographic and mass-separation methods.

The present paper is dedicated to the study of volatilization of ultramicro amounts of spallation products (Mo, Tc, Ru, Re and Os) from the irradiated Ag and Au melts at low pressures of oxygen and to the determination of the conditions of their thermochromatographic separation. The influence of the material of the crucible and thermochromatographic column, of the reactive gases and of their pressures and temperatures has been investigated. On the basis of the results obtained a possible chemical form of ultramicro-amounts of volatile compounds is discussed.

### Experimental

The Ag and Au foils have been irradiated with 660 MeV protons at the JINR synchrocyclotron. A 10–15 mg sample(I) was placed into a ball joint of the apparatus (Fig. 1) when the content of radionuclides in the sample was determined by means of gamma-spectrometry. The applied thermochromatographic column (7) is a quartz or porcelain tube (about 4 mm in inner diameter and about 400 mm long). In each experiment the material of the crucible for melting the samples (10) ( $d = 2$  mm,  $h = 8$  mm) was similar to the column material. The crucible and the column were first purified in  $\text{HNO}_3$  for 24 hrs; then washed in distilled water and dried at  $500^\circ\text{C}$ . The heating was performed by the electric ovens (8, 9). Temperature distribution along the column was measured with a Pt–Pt(Rh) thermocouple. When the temperature ( $1080 \pm 20^\circ\text{C}$  for Ag and  $1330 \pm 20^\circ\text{C}$  for Au) and the pressure (about  $10^{-4}$  torr) were reached the reagent gas was let through a needle valve (the linear velocity of  $\text{O}_2$  was  $10\text{--}15\text{ m}\cdot\text{s}^{-1}$  at room temperature) till a stable dynamic vacuum in the range of  $10^{-2}\text{--}10^{-3}$  torr was set in. Then the Ag and Au foils were placed into the crucible for melting. The time required for melting the 10–15 mg samples was less than 2 s. The exposure time of the sample

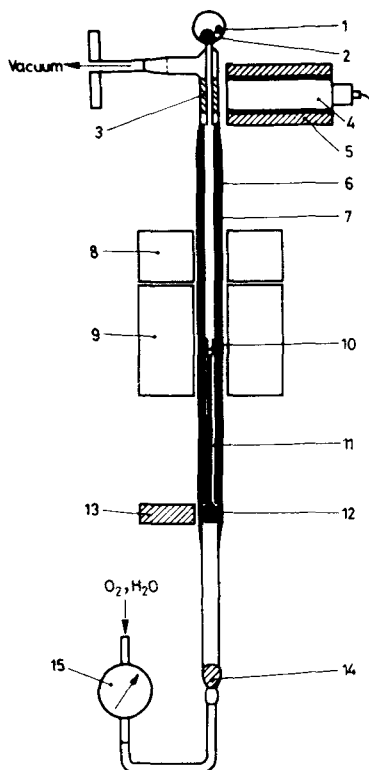


Fig. 1. Schematic drawing of the experimental arrangement. 1 – Irradiated foil; 2 – iron ball; 3 – glass wool padding; 4 – NaI(Tl) detector; 5 – lead screen; 6 – external porcelain tube; 7 – thermochromatographic column; 8, 9 – electric stoves; 10 – crucible; 11 – rod; 12 – iron stop; 13 – magnet; 14 – wool; 15 – needle valve

in melted state varied from 0.5 to 10 min. The produced volatile compounds of spallation products evaporated and passed into the column. After evaporation, the magnet (13), which kept the crucible in the heating zone by means of an iron stop (12) and a porcelain rod (11), was pushed aside and the crucible fell down into the cool part of the tube. The ovens were simultaneously switched off and withdrawn; the needle valve (15) was closed and the column was intensively cooled by ventilation to  $\sim 100^\circ\text{C}$ , so that at its withdrawal from the unit there was no drift of adsorption zones with currents of air filling. When gold was used the upper part of the tube was filled with glass wool (3) coated with vacuum lubrica-

tion for catching volatile compounds (in the case of silver they did not form and the trap was not necessary). The activity, accumulating in the trap, was measured on a scintillation detector (4), placed behind a collimator (5) and connected with a recorder.

The degree of volatility and the position of adsorption zones of volatile compounds on the column surface were determined by gamma-spectrometry. Radioactivity of separate segments of the column (each 1 cm long) and of the irradiated gold and silver samples before and after volatilization was measured on a Ge(Li)-detector. Besides, in some experiments the content of spallation products, which passed onto the crucible surface and were then extracted into the solution by the successive removing of the sample layers by etching in hydrochloric and nitric acids, was determined. The obtained gamma-spectra were analysed using the computer programme of automatic spectrum processing (EPOS-I<sup>8</sup>). Definition error of gamma-line intensity was about 15%. The obtained intensity of the corresponding lines were corrected accounting the error on the decay, self-absorption in the samples, dead time and the geometry of measurements. For each studied element the sum of its radioactivity in all measured parts of the apparatus, after the sample melt, coincided with its initial radioactivity (in the sample before melting) within 5–10% error limits.

## Results and discussion

### *Evaporation of ultramicro amounts of elements*

Fig. 2 shows the time dependences of Re and Os volatilization from the irradiated Au melt at various oxygen and water vapour pressures; and at different materials of the crucible and the column (quartz and porcelain). Fig. 3 shows similar dependences of Mo, Tc and Ru volatilization from Ag melt in an oxygen atmosphere. From these figures it can be seen that volatilization of ultramicro amounts of Re and Os from Au melt and volatilization of Ru from Ag melt practically cease in 1–2 min in O<sub>2</sub> of 10<sup>-2</sup> torr. For low oxygen pressures the transfer of Ru, Re and Os into the gas phase is 40–80% in 3–5 min and, to some extent, it depends on the material of the crucible. Technetium at 10<sup>-3</sup>–10<sup>-2</sup> torr of O<sub>2</sub> volatilizes faster than Mo, but none of them is transferred completely into the gas phase in 5 min (only 40–80%).

In dynamic vacuum at 10<sup>-3</sup>–10<sup>-2</sup> torr of H<sub>2</sub>O, Ru does not volatilize from the Ag melt while Os volatilizes from the Au melt. Here one can observe a strong dependence upon water vapour pressure. For example, Os volatilizes completely in a porcelain crucible in 2 min at 10<sup>-2</sup> torr and only 20% of Os is extracted in 10 min at 10<sup>-3</sup> torr. Rhenium is extracted completely in 3–5 min

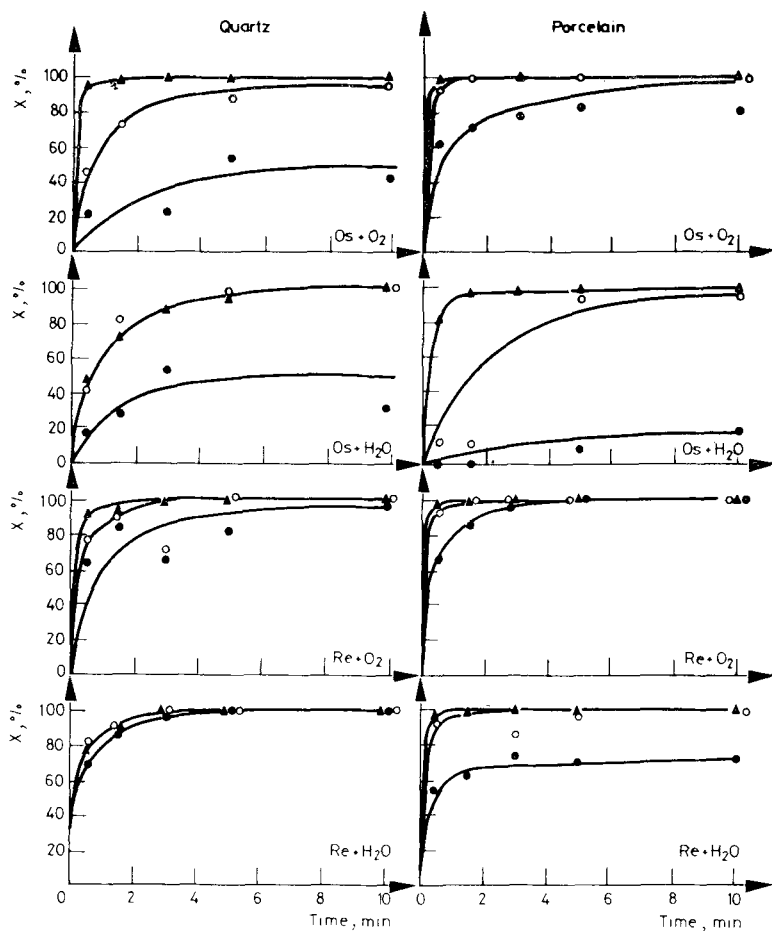


Fig. 2. Time dependences of Re and Os volatilization from the irradiated Au melt at various pressures of  $O_2$  and  $H_2O$  vapours:  $T = 1330 \pm 20^\circ C$ ;  $\blacktriangle$  -  $10^{-2}$  torr;  $\circ$  -  $3 \cdot 10^{-3}$  torr and  $\bullet$  -  $10^{-3}$  torr

under almost all conditions. Volatilization of Mo and Tc from the Ag melt at lower pressure of water vapours (Fig. 4) makes 50% in 5 min ( $10^{-2}$  torr, porcelain crucible). Contrary to  $O_2$  dynamic vacuum the extraction of Mo in water vapour is somewhat higher than the extraction of Tc.

The behaviour of some other elements (Se, Rb, Sr, Y, Zr, Nb, Pd, Rh) was investigated simultaneously. (Their ultramicro amounts were produced at irradiation of Ag with high-energy protons). The results showed, that Pd and Rh do not volatilize from Ag irrespective of the reagent gas. But Se evaporates well in both cases

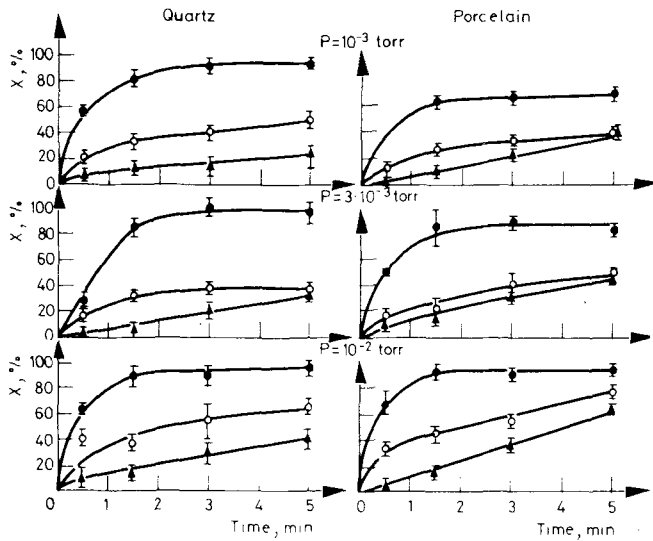


Fig. 3. Volatization of Mo, Tc and Ru from the irradiated Ag melt at various  $O_2$  pressures in the dependence on the crucible material:  $T = 1080 \pm 20^\circ C$ ;  $\blacktriangle$  – Mo,  $\circ$  – Tc and  $\bullet$  – Ru

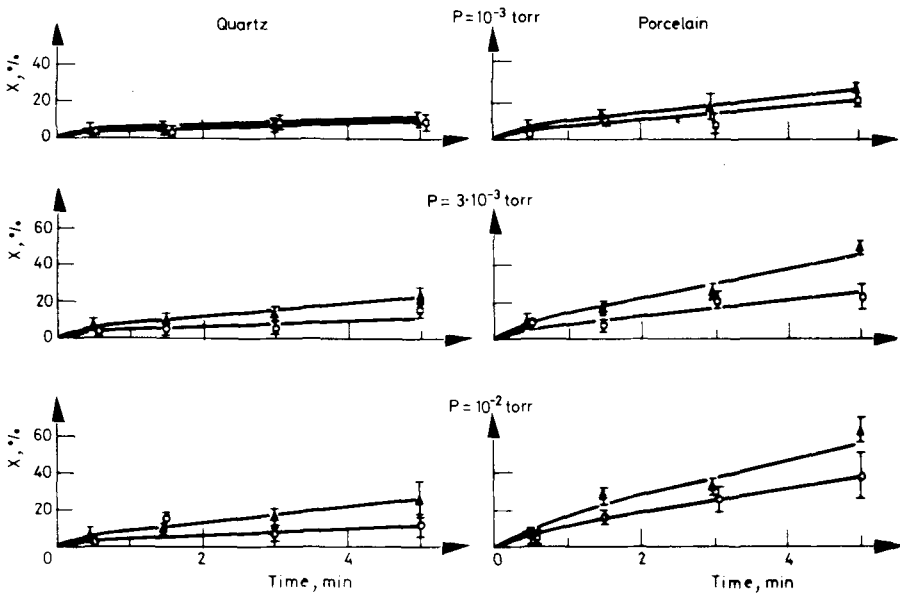


Fig. 4. Volatization of Mo and Tc from the irradiated Ag melt at various water vapour pressures in the dependence on the time and the crucible material;  $T = 1080 \pm 20^\circ C$ ;  $\blacktriangle$  – Mo and  $\circ$  – Tc

(dynamic vacuum of  $O_2$  and  $H_2O$ ). The most part of it deposited in the zone at  $T < 100^\circ C$ . Other elements (Zr, Y, Sr, Nb, Rb), having Ag in negligible quantities, do not reach the thermochromatographic column, but are transferred to the crucible surface.

Different behaviour of ultramicro amounts of element analogs [Tc(Ru) and Re(Os)] at their volatilization from Ag and Au melts, respectively, can be caused by the temperature difference of the melts and by the thermal stability of the volatile compounds.

### *Reactions and chemical forms of volatile spallation products*

In order to establish the chemical composition of the compounds one must take into account the following:

(a) Concentration of spallogenic products, produced a result of irradiation of Au and Ag, is too small. The evaluation shows, that this amount is not enough for mono-layer coating of the melt surface ( $\Theta \approx 10^{-5}$ ). Still lower surface concentrations of spallogenic products are observed on the surface of the crucible and the column. It means, that neither the reaction, resulting in the formation of polynuclear compounds (e.g.  $Tc_2O_7$ ;  $Re_2O_7$ ), nor the disproportionation reactions proceed under the studied conditions.

(b) Column sizes, temperature and gas pressure in the unit provide a molecular gas current. It can be supposed that most of reactions producing volatile oxides occur not in the gas phase, but on the surface of the melt, of the crucible and of the thermochromatographic column. Low gas pressures allow to neglect termolecular reactions and to take into account only bimolecular reactions, which proceed on various surfaces.

(c) Dynamic vacuum conditions, which lead to permanent renewal of the gas phase above the melt, make possible the realization of thermodynamically unfavourable reactions, which are characterized by large positive values of isobar-isothermal potential changes.

All these reasons allow the production and, in some cases, the long existence of simple  $MeO_x$  compounds.

The behaviour of volatile compounds in thermochromatographic column (migration rate of the adsorption zones) may be used for identification of their chemical forms.<sup>6</sup> Empirical dependences of adsorption enthalpies of ultramicro amounts (e.g. volatile chlorides or oxides<sup>19</sup>) on quartz upon sublimation enthalpies, can serve as the basis for it.

Fig. 5 shows separation of Re and Os at the column length, depending on water vapour pressure and the time of their volatilization from the Au melt. Only

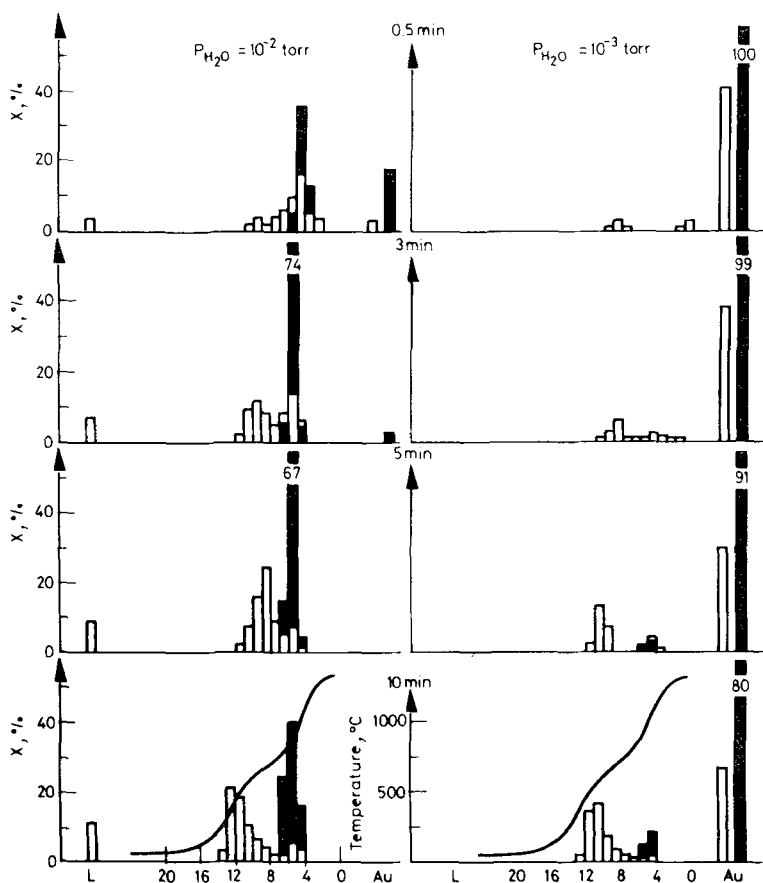


Fig. 5. Distribution of volatile Re (□) and Os (■) oxides along the column:  $T = 1330 \pm 20^\circ\text{C}$ ; L - a trap; Au - Re and Os residue in gold after volatilization; porcelain - is the material for the column and the crucible

one adsorption zone is observed for ultramicro amounts of Os. Its migration from 1150 to 900 °C in 10 min at  $10^{-2}$  torr  $\text{H}_2\text{O}$  gives the value of the adsorption enthalpy:  $\geq -50$  kcal/mol. Rhenium under such conditions produces two zones in the column. The first zone almost coincides with the Os zone. eventually it decreases along the area, while the relative value of the second zone (a low-temperature zone) increases.

Fig. 6 illustrates the existence of some volatile Re and Os compounds. Four Os zones are produced in dynamic vacuum at  $P_{\text{O}_2} = 10^{-3}$  torr where osmium oxi-



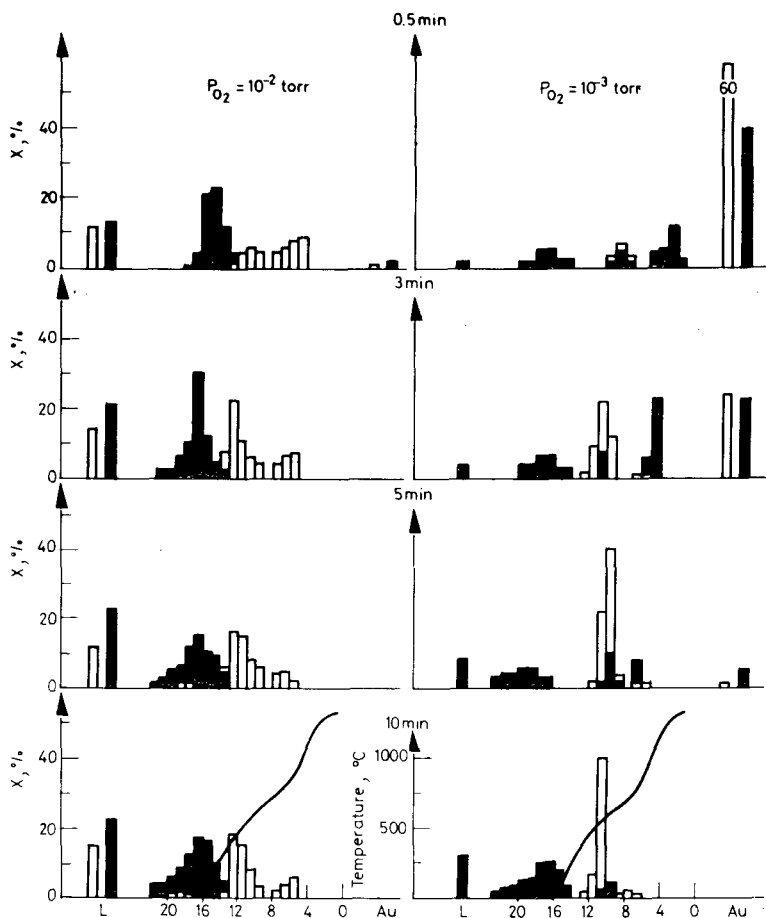


Fig. 6. Distribution of volatile Re (□) and Os (■) oxides along the column in the dependence on the time of volatilization and  $O_2$  pressure:  $T = 1330 \pm 20^\circ C$ ; L – a trap; Au is the residue of Re and Os in gold after volatilization; porcelain is the material for the column and the crucible

des, as can be supposed, are adsorbed from monoxide to tetroxide. This supposition is confirmed qualitatively by the thermodynamic evaluation of the sublimation enthalpies of simple ( $MeO_x$  type) Re and Os oxides.<sup>9-12</sup> One can explain the production of these compounds not only by the reaction of Os with  $O_2$  in the high-temperature zone of the Au melt, where the atomic oxygen concentration of the gas phase is 1%, but by the successive oxidation of OsO and  $OsO_2$  with  $O_2$  in the adsorption zone.

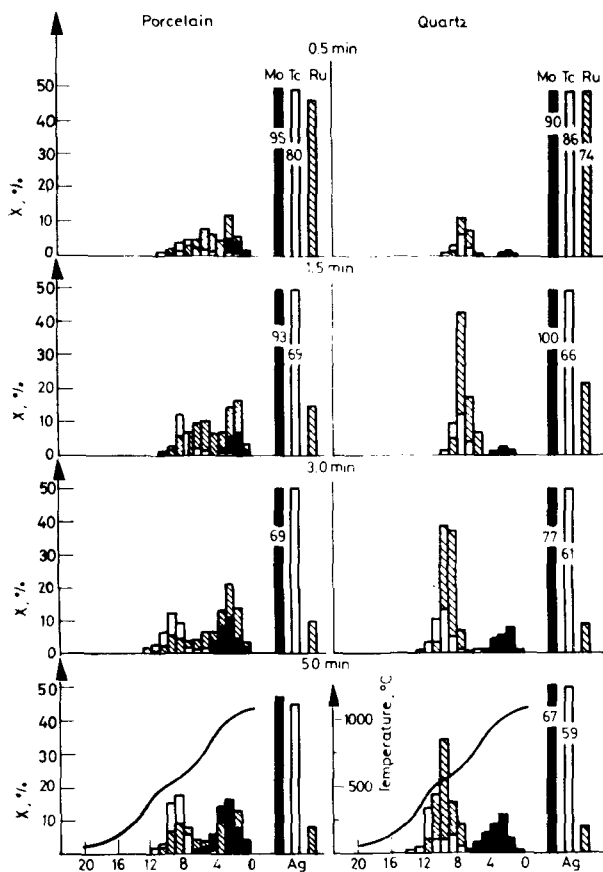


Fig. 7. Distribution of Mo, Tc and Ru along the column in the dependence on the time of volatilization and on the material of the column and the crucible:  $T = 1080 \pm 20 \text{ }^\circ\text{C}$ ; ■ - Mo; □ - Tc; ▨ - Ru; Ag is the residue of Mo, Tc and Ru in silver after volatilization;  $P_{O_2} = 3 \cdot 10^{-3} \text{ torr}$

Thermochromatographic behaviour of Mo, Tc and Ru which volatilize from the Ag melt is shown in Figs 7 and 8. The production of the highest ruthenium oxide ( $\text{RuO}_4$ ) is not observed in the studied of  $\text{O}_2$  pressure range (Fig. 7), but in  $\text{H}_2\text{O}$  vapours Ru does not volatilize at all (Fig. 8). Molybdenum forms one zone irrespective of the reagent gas. Technetium has similar behaviour but its adsorption zone is more wide.

The different behaviour of oxygen compounds of homologous transition elements of the 2nd and the 3rd rows is due, probably, to the difference in their

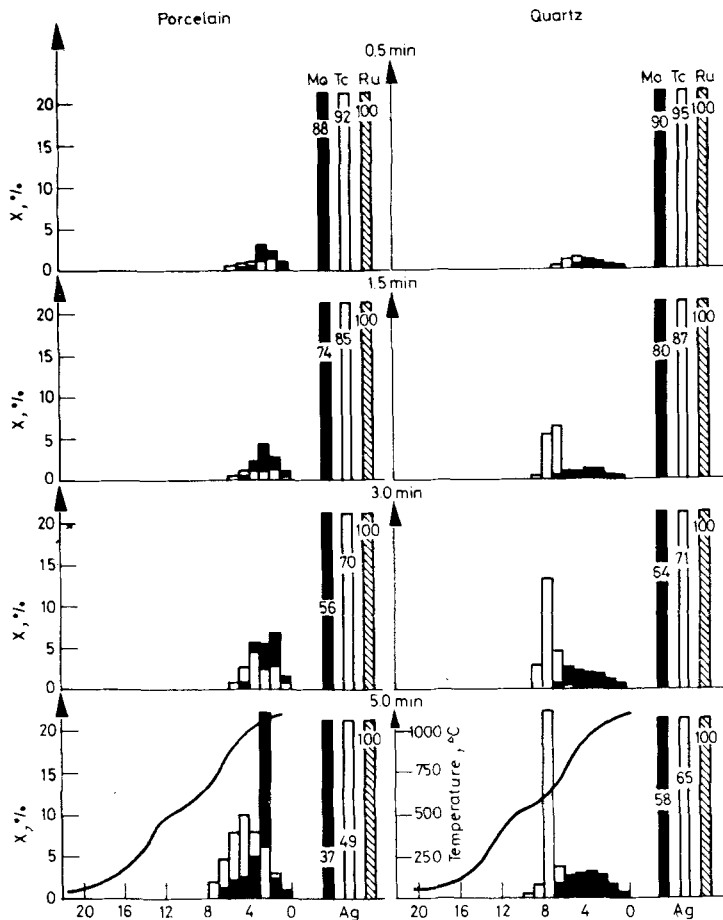


Fig. 8. Distribution of Mo and Tc along the column in the dependence on the time of volatilization and the material of the column and the crucible;  $T = 1080 \pm 20^\circ\text{C}$ ; ■ – Mo; □ – Tc; Ag is the residue of Mo and Tc in silver after volatilization;  $P_{\text{H}_2\text{O}} = 3 \cdot 10^{-3}$  torr

thermal stability (e.g.  $\text{RuO}_4$  and  $\text{OsO}_4$ ) and to the different temperature of the target melts. It should be taken into account that atomic oxygen concentrations at  $1330^\circ\text{C}$  and  $1080^\circ\text{C}$  are equal to 1.257 and 0.033%, respectively, for  $P_{\text{O}_2} = 10^{-3}$  torr. The fact that Ru begins to volatilize from the Ag melt already at  $1140^\circ\text{C}$  and  $10^{-2}$  torr of water vapour pressure, confirms the essential influence of temperature. The latter influences not only the probability of the flow of the

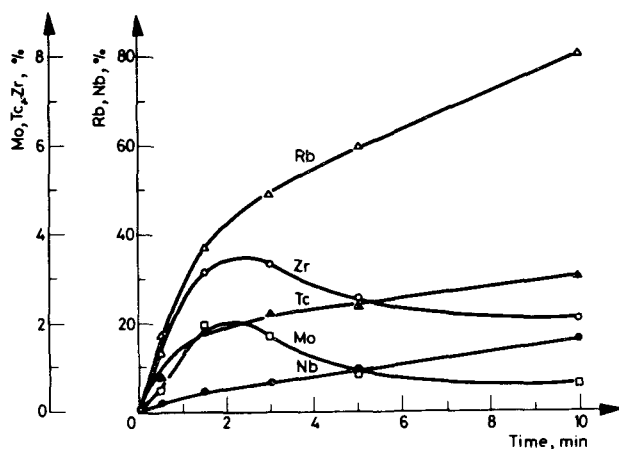


Fig. 9. Time dependences of some spallation products content in quartz crucible at melting the irradiated silver;  $T = 1080 \pm 20$  °C;  $P_{O_2} = 10^{-3}$  torr

oxidation reaction but also the desorption velocity of the products of these reactions from the melt and the crucible surfaces.

Fig. 9 shows the accumulation of ultramicro amounts of some elements on the crucible in the dependence on the hold-up-time of melted silver in it. Sr and Y (from Ag) which are not shown in this figure, and rare-earth elements (from Au) which are easily oxidized under the studied conditions, are accumulated on the crucible surface similarly to Rb forming probably stable silicates.

Oxidation of spallogenic products which are homogeneously distributed in the target (Ag and Au) can proceed differently. For example, one can give two limited, but not alternative, cases:

- (a) oxidation of metals in the melt by means of a gas diffusing into it;
- (b) oxidation of metals diffusing from the bulk of the melt on its surface.

#### *Diffusion of spallogenic products in Ag melt*

Fig. 10 shows the distribution of some spallation products along the depth of the cooled Ag mass after its melting in oxygen atmosphere. "O" is a silver surface level, the absciss is the distance of the centre of gravity of pickled silver layer from the surface; the ordinate is the ratio of element concentrations in the strip-ped layer and in silver sample before sublimation. According to their volatilization and adsorption the elements can be ordered into four groups.

Pd belongs to group (a); Mo, Ru and Rb to group (c); Nb, Y and Sr to group (d) besides the elements shown in the figure.

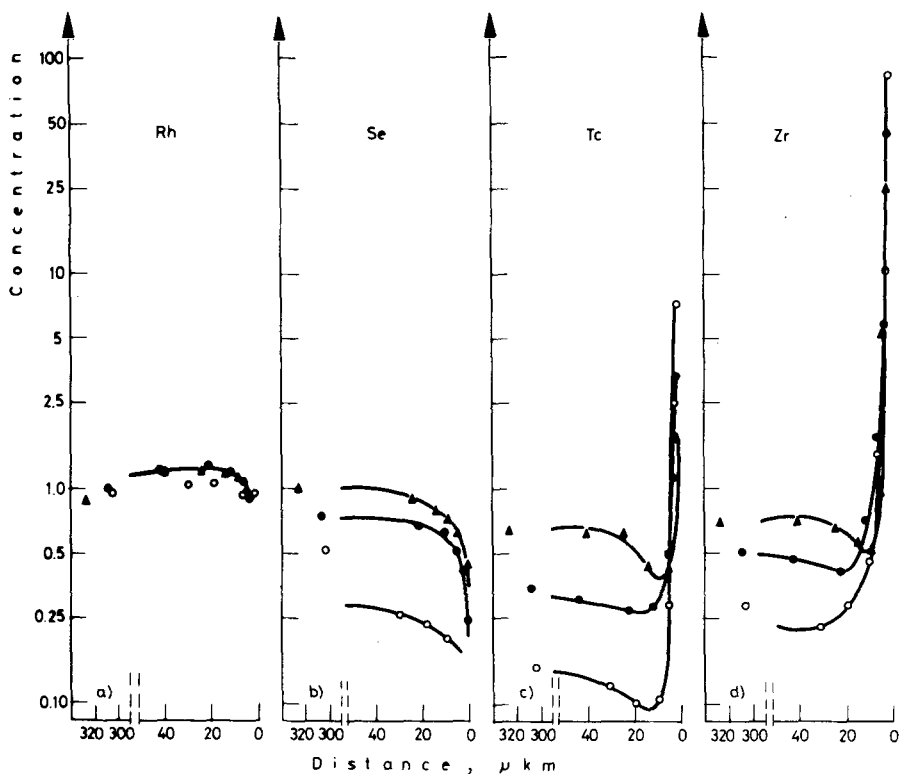


Fig. 10. Change of concentration of spallogenic products in a ball of irradiated Ag in the dependence on the time of volatilization and the distance from the surface:  
 $T = 1080 \pm 20^\circ\text{C}$ ;  $P_{\text{O}_2} = 10^{-3}$  torr;  $\Delta$  - 1.5 min;  $\bullet$  - 5 min; and  $\circ$  - 10 min

An attempt has been made to determine the diffusion coefficients by using these data and by proceeding from the supposition that the elements which are homogeneously distributed in silver before melting are oxidized on the melt surface (the shape of a 10–15 mg Ag has been taken spherical).

The behaviour of Se, concentration of which on the melt surface is too small (it tends to zero) because of its fast evaporation, is a more simple case. For the elements of group (c) and group (d) the data of their distribution in silver was used in calculations, eliminating a  $\sim 20 \mu\text{m}$  thick surface layer, where, as can be assumed, the back diffusion takes place into the melt of the products oxidized on the surface. Table 1 illustrates the diffusion coefficients for some elements, diffusing in silver melt at  $1080 \pm 20^\circ\text{C}$ .

Table 1  
Diffusion coefficients  
of the elements diffusing in silver

Element	$D \times 10^6, \text{cm}^2 \cdot \text{s}^{-1}$
Se	$0.3 \pm 0.1$
Rb	$1.7 \pm 0.1$
Tc	$1.0 \pm 0.1$
Ru	$2.7 \pm 0.2$
Y	$0.7 \pm 0.1$
Zr	$0.7 \pm 0.1$
Nb	$0.7 \pm 0.1$

The calculated values of diffusion coefficients of spallogenic products are under studied conditions, in average an order of magnitude lower than of the known values (from Refs<sup>1 3-1 5</sup>) for the diffusion of the indicated metals in elementary form. Data on oxide diffusion of the studied metals in the Ag melt, which could be compared to the calculated ones, are not known at present.

The results obtained confirm the complexity of the processes of oxidation, adsorption and volatilization. The similar processes has been marked out earlier, e.g. in investigations of admixture concentration by the zone melting technique.<sup>1 6</sup>

#### *The use of Ag and Au melts in the ISOL-facility*

The analysis of the results obtained allows one to draw a conclusion on the possibility of using Ag and Au as targets in the ISOL-system. In this case the thermochromatographic column with necessary thermal gradient will be put between the ion sources and the target.

Fig. 5 shows the possibility of the "on-line" extraction of ultramicro amounts of Re (the yield of Re in the column zone with temperature lower 750 °C is rather high, and the impurities with Os are insignificant). Fig. 6 shows the possibility of the "on-line" extraction of ultramicro amounts of Os (the yield of Os in the column zone at temperatures lower than 250 °C reaches 50%, and Re impurities are insignificant and make only 0.1%).

Using the results obtained, it is possible to choose the conditions for the complete separation of two elements from a third one: separation of Tc and Mo from Ru in water vapours; separation of Ru and Tc from Mo in oxygen atmosphere; and it is possible to extract Tc which possesses insignificant Ru impurities in admixture of these gases.

Thus, it can be assumed that the targets of Ag and Au melts can be combined with a plasma source of the mass separator for selective extraction of short-lived isotopes: Mo, Tc and Ru or Re and Os.

When using the Ag and Au melts, as targets, for the ISOL-systems one should take into account the evaporation of these metals.

The velocity of Ag evaporation at  $T = 1080\text{ }^{\circ}\text{C}$  appeared to be independent of the dynamic vacuum range ( $10^{-4} - 10^{-2}$  torr) and is equal to  $\sim 10^{-4}\text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  which coincides with the values determined earlier for  $10^{-6}$  torr.<sup>17</sup> Evaporation rates of Au, measured at  $1200\text{ }^{\circ}\text{C}$  and  $1250\text{ }^{\circ}\text{C}$ , also correspond to the values given in DASHMAN's monograph.<sup>18</sup> It should be emphasized that at the temperatures, which are  $100\text{ }^{\circ}\text{C}$  higher than the melting temperatures, the rate of Au evaporation is 100 times smaller than the velocity of Ag evaporation ( $\sim 10^{-6}$  and  $10^{-4}\text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ , respectively). The significant rate of Ag evaporation must not, however, complicate essentially the construction of the joint (target – thermo-chromatographic column – ion-source).

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