

## (Im-)possible ISOL beams<sup>★</sup>

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**Abstract.** Refractory elements, i.e. elements with very high melting point and low vapor pressure, cannot be released in atomic form from an ISOL target. Therefore most of these elements are presently not available as ISOL beams. However, when reactive gases are introduced into the target, they may form volatile compounds with the refractory elements, allowing for an easier transport to the ion source. Particularly useful are high-temperature stable fluorides and oxides. By these chemical evaporation methods so far ISOL beams of the refractory elements C, Zr, Hf and Ta have been produced. We discuss how ISOL beams of B, Ti, Nb, Mo, Tc, Ru, W, Re, Os and Ir could be produced in a similar way.

**PACS.** 28.60.+s Isotope separation – 29.25.Ni Ion sources – 29.25.Rm Sources of radioactive nuclei – 82.40.-g Chemical kinetics and reactions: special regimes and techniques

### 1 Introduction

The ISOL (isotope separation on-line) method allows production of very intense radioactive ion beams with good beam quality [1]. In an ISOL target the radioisotopes produced first need to diffuse to the surface of the target material and then desorb from the latter. On the way to the ion source they will collide frequently with the walls of the target and ion source unit, each time lingering a while between adsorption and desorption. For the overall efficiency slow desorption is more penalizing than slow diffusion (see detailed discussion in [2]), thus less volatile elements are generally difficult to produce as beams at thick target ISOL facilities.

### 2 Volatile versus refractory elements

The volatilization of trace amounts of an element is determined by its adsorption enthalpy on the surfaces of the target and ion source material. These adsorption enthalpies not known, but they are often<sup>1</sup> correlated to the sublimation enthalpy of macro-amounts of the element in question. The sublimation enthalpy in turn is correlated

to the vapor pressure of the element. Figure 1 shows the temperatures that are needed to exceed in elemental state a vapor pressure of  $10^{-2}$  mbar, corresponding roughly to adsorption times that provide “some” transport efficiency for radioisotopes with seconds-to-minutes half-lives. The steps of the color code are chosen arbitrarily, but it is obvious that the noble gases are most volatile. Nitrogen, oxygen and the halogens are very reactive in their atomic state, hence the effective volatility of trace amounts is far lower than suggested by the given vapor pressure of the elemental dimers. The alkali metals are also quite volatile and moreover easily surface ionized. These facts make noble gases and alkali metals the most common ISOL beams, in particular at ISOL facilities that spend little effort on target and ion source development.

For many elements with average volatility it is possible to reach a sufficiently fast release time by operating the target and ion source unit at high temperatures, typically around 2000°C. Many of these elements can be provided in an efficient and selective way by resonant laser ionization [3], a method ideally suited for use with such high temperature assemblies.

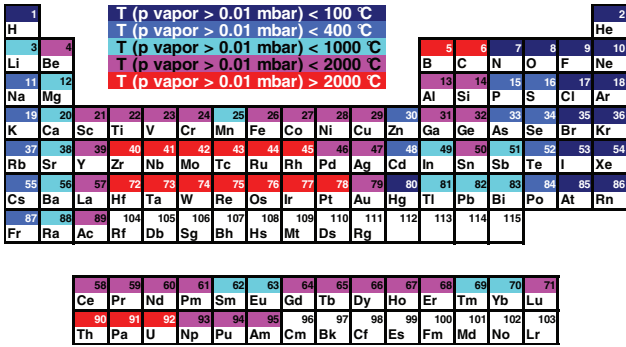
However, the least volatile elements would require temperatures far above 2000°C to reach a sufficient vapor pressure. Due to their low vapor pressure and the correlated high melting point, many of these elements are actually used as target matrix or as construction materials for the target and ion source unit. It is obvious that at temperatures where these elements reach a sufficient vapor pressure practically no material would be available

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<sup>1</sup> This is valid when the type of atom-surface bonds is similar to that in solid state and the same monomolecular species dominate desorption and sublimation.

**Table 1.** Overview of refractory elements and compounds enabling their volatilization. The data are explained in the text.

Element	m.p. °C	b.p. °C	T(p <sub>vap</sub> = 1 Pa) °C	−ΔH <sub>ads</sub> on Ta kJ/mol	Diffusion matrix	Evap. compound	b.p. °C	−ΔH <sub>f</sub> <sup>298</sup> kJ/mol	S J/(mol K)	−ΔH <sub>ads</sub> on SiO <sub>2</sub> kJ/mol	Transp. temp. °C	Ion. pot. eV	Ion source	ISOL beams A	
B	2075	4000	2130	700	C, CaF <sub>2</sub> , Pt	BF <sub>3</sub>	−101	1137	254.1		RT	15.56	F, E	9–16	
C		3825	2300	962	MgO, HfO <sub>2</sub>	CO	−191	111	197.7	18	RT	14.01	F, E		
C		3825	2300	962	MgO, HfO <sub>2</sub>	CO <sub>2</sub>	−78	394	213.8	27	RT	13.77	F, E		
Ti	1670	3287	1760	525	V, Nb, Ta	TiF <sub>4</sub>		1551	314.9			11.9 <sup>D</sup>	F		
Zr	1854	4409	2370	675	Nb, Mo	ZrF <sub>4</sub>	912	1674	319.3		>600	15.3	F		82–85
Nb	2477	4744	2700	786	Mo, W	NbF <sub>5</sub>	234	1718	382.9				F		
Mo	2622	4639	2490	733	ThO <sub>2</sub> , UO <sub>2</sub>	MoO <sub>3</sub>	1155	346	283.9	280	>1000	11.8	E		
Tc	2157	4265	2820	871	ThO <sub>2</sub> , UO <sub>2</sub>	TcO <sub>3</sub>		320		156	>500		E		
Ru	2333	4150	2035	793	ThO <sub>2</sub> , UO <sub>2</sub>	RuO <sub>4</sub>	40	184	290.8	55	RT	12.15	E		
Ru	2333	4150	2035	793	ThO <sub>2</sub> , UO <sub>2</sub>	RuO <sub>3</sub>		78	276.3	≈90	>600	11.2	E		
Rh	1963	3695	2400	766	ThO <sub>2</sub> , UO <sub>2</sub>	RhO <sub>2</sub>		184				10	E		
Hf	2233	4603	2560	684	Ta, W, Ir, Os	HfF <sub>4</sub>	970	1670	263.8			15.9	F	158–185	
Ta	3007	5458	3040		W, Ir, Os	TaF <sub>5</sub>	229	1822	336.4				F	162–167	
W	3414	5555	3200	940	ThO <sub>2</sub> , UO <sub>2</sub>	WO <sub>3</sub>	1837	293	353.5	≈380	>1300	11.8	E		
W						WF <sub>6</sub>	17	1720	286.3			10.7 <sup>D</sup>	F		
Re	3186	5596	3030	967	ThO <sub>2</sub> , UO <sub>2</sub>	ReO <sub>3</sub>	750	351	341.1	190	>600		E		
Os	3033	5012	2610	980	ThO <sub>2</sub> , UO <sub>2</sub>	OsO <sub>4</sub>	135	337	288.7	40	RT	12.32	E		
Ir	2446	4428	2460	905	ThO <sub>2</sub> , UO <sub>2</sub>	IrO <sub>3</sub>		−13	293.8	87	>300	11.9	E		

**Fig. 1.** Temperature where the vapor pressure of the element reaches 10<sup>−2</sup> mbar as an indicator for the elements volatility.

to serve over long time as a target matrix or construction material.

Elements with very high melting points are called *refractory*<sup>2</sup>. Different definitions of *refractory* exist [4], including “a melting point above that of iron”, ... up to “a melting point above 2200 °C”, sometimes with the additional requirement of body-centered-cubic crystal structure. Table 1 gives a list of refractory elements with a melting point above 1900 °C (plus Ti and Zr, the lighter homologues of Hf with similar properties). This list roughly matches the least volatile elements shown in figure 1. Note however, that not all elements that are slowly released from present ISOL targets such as Al or As are necessarily *refractory* elements.

The expression *refractory* is more commonly used for *refractory metals* than for *refractory elements*, but for completeness we will include in the following discussion also the non-metallic elements with very high melting point: boron and carbon.

<sup>2</sup> The addition of oxides of some of these elements (e.g. Nb or Ta) to glass increases its index of refraction.

### 3 How to volatilize refractory elements?

Despite the extremely refractory character of carbon, ISOL beams of carbon isotopes have been available at ISOLDE already for many years [5]. The beam of 126 ms <sup>9</sup>C is even sufficiently intense to permit detailed decay spectroscopy [6]. Where is the “trick”?

It is well known that solid carbon actually volatilizes very quickly when it reacts with oxygen (i.e. it burns) to CO or CO<sub>2</sub>. Both compounds are already volatile at room temperature, but remain relatively stable even at high temperatures. Indeed, to produce ISOL beams of carbon, the latter is not released in elemental state, but after oxidation to CO<sub>x</sub>. The necessary oxygen is generated in-situ by reduction of oxide targets. For a further improvement of the existing ISOL beams of carbon [7], detailed studies of the release of carbon from oxide matrices and of the adsorption of CO and CO<sub>2</sub> on different surfaces were performed in the frame of the TARGISOL project [8,9].

We can summarize that the following conditions must be met to develop a successful chemical evaporation method for the production of ISOL beams of refractory elements:

1. First the radionuclides stopped in the target matrix have to diffuse to the target surface. Hence, as for all ISOL elements a high diffusion coefficient is beneficial. This imposes a relatively high target temperature.
2. A “reactive” gas has to be introduced or generated in-situ. It should be reactive with respect to the ISOL element, but not or at least not too much with the target and ion source construction materials.
3. The introduced gas (or a dissociation product of it) should react easily with the element adsorbed on the target surface to form a volatile (i.e. more volatile than the ISOL element in atomic state) compound. The

reaction to form this compound has to be thermodynamically and kinetically favored.

4. The volatile compound should remain intact while effusing to the ion source, i.e. it should be thermodynamically stable against thermal dissociation or dissociation on the hot surfaces it encounters during effusion.<sup>3</sup>
5. Finally the compound has to be ionized whereby it either may remain intact or may dissociate partly or fully. The ionization potentials of all compounds discussed in the following are above 10 eV, requiring a plasma ion source for efficient ionization.

We may now investigate for each of the elements listed in table 1 which compounds fulfill best the given requirements. Generally a compound is most volatile if all its valences are saturated. The refractory metals being electropositive, strongly electronegative ligands allow to maximize the enthalpy of formation of the molecules and to minimize the risk of thermal dissociation. The most electronegative elements are fluorine and oxygen. Hence the best candidates are fluorides and oxides with the metal in the highest possible valence state. Table 1 shows a compilation of suitable or potentially suitable compounds. Data are from [10–20] and references therein. The given formation enthalpies of gaseous molecules are for standard conditions, i.e.  $T = 298$  K. The enthalpies at higher temperatures will be different, but normally not so much that it affects the general validity of the discussion. The entropy  $S$  allows to calculate the Gibbs free energy ( $G = \Delta H - TS$ ) at temperatures  $T \gg 298$  K and to judge if the equilibrium of compound formation and dissociation (e.g.  $\text{Os}_{(s)} + 2\text{O}_{2(g)} \rightleftharpoons \text{OsO}_{4(g)}$ ) is on the product or educt side.

Most of the given adsorption enthalpies have been measured in gas thermochromatography experiments. Therefore most data is available for oxide or hydroxide systems, less for chlorides and oxychlorides, but nothing on fluorides since the handling of fluorine is experimentally more challenging. Hydroxides or oxyhalides are often more volatile than the listed species, but also more unstable at higher temperatures and therefore not necessarily compatible with a very hot target.

Ionization energies are given where available. In some cases the energy for dissociative ionization (e.g.  $\text{WF}_6 \rightarrow \text{WF}_5^+ + \text{F}^-$ ) was derived from [12] and marked by 'D'.

## Targets and ion sources

Fluorides (of the alkaline earths, the rare earths, Zr and Hf) have been successfully separated from high temperature target and ion source units made from tantalum and graphite. Therefore such units could work similarly well for other fluorides provided that these do not dissociate on

or react with the Ta or C surfaces. An 'F' in the second-last column of table 1 marks the principal suitability of FEBIAD type ion sources.

On the other hand the use of volatile oxides is incompatible with hot tantalum or graphite surfaces that would act as efficient reducing agents, destroying most of the oxides at the first wall encounter. In this case oxide surfaces are promising as they are often inert against volatile oxides. The most prominent example is quartz ( $\text{SiO}_2$ ), frequently used in thermochromatography set-ups. An ISOL target unit where the target container and the transfer line were made entirely from quartz has been used before at ISOLDE [21]. For temperatures far above  $1200^\circ\text{C}$  where quartz starts to soften, a surface of alumina or other high-temperature stable oxides can be used instead.

Suitable target materials for the release of volatile oxides are also mainly oxides themselves, in particular  $\text{ThO}_2$  and  $\text{UO}_2$  that provide a wide range of products by high-energy proton induced reactions. Alternatively molten silver or gold targets [22,23] have been shown to release volatile oxides of the discussed elements. Molten gold has already been used successfully as ISOL target [24,25].

Ion sources with hot metallic cathodes have the problem that the latter acts as trap for oxides, thus reducing the release efficiency of volatile oxides, but also destroying the cathode by the oxygen partial pressure. Therefore the plasma has to be generated differently, i.e. a radio-frequency driven ion source should be used. The most common species are electron cyclotron resonance ion sources (ECRIS) that are often even operated with oxygen as support gas. An 'E' in table 1 marks the principal suitability of an ECRIS for the respective compound. A bold 'E' (or 'F' respectively) stands for beams of radioactive or stable beams that have already been produced from the given molecular compound.

In cases where the volatile molecules are not or not fully dissociated during ionization, the radioisotopes of interest will be mass-separated in a molecular sideband. For neutron-deficient isotopes produced by spallation in a closeby target, the mass of the molecular ions is often higher than the target mass. In this region little radioactive background appears and often an excellent beam purity is achieved. However, for neutron-rich isotopes efficiently produced in fission or fragmentation of heavy targets, the sideband may actually appear at a mass that has a lot of radioactive background from atomic ions. Here a two-step separation can be a remedy: mass-separation of the molecular sideband followed by a break-up of the molecules in a gas-filled device (radio-frequency quadrupole or Penning trap), by charge breeding in an ECRIS or electron beam ion source or by a stripper foil after slight acceleration, followed by a second mass separation of the remaining atomic ions.

It is likely that neighboring elements being released in the same chemical form (e.g. as trioxides) will also show up in the same molecular sidebands after ionization. Therefore the isobaric purity will be lower than in cases where the molecular sideband is rather unique

<sup>3</sup> This requirement is just opposite to the effect used in chemical vapor deposition (CVD). Therefore e.g. organic compounds working well for CVD are not an option here.

(e.g.  $\text{HfF}_3^+$  [26]). Background from less volatile oxides may however be suppressed thermochromatographically between target and ion source.

### Delay time

The flux  $\Phi$  of atoms or molecules hitting a surface is given by the Hertz-Knudsen equation:

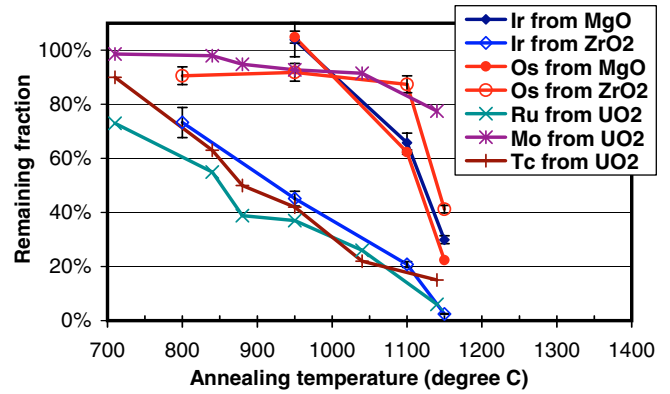
$$\Phi = p/\sqrt{2\pi mkT} \quad (1)$$

with  $p$  the (partial) gas pressure,  $m$  the mass of the particles and  $T$  the temperature. Reactive gases such as  $\text{CF}_4$  or  $\text{O}_2$  can be used with pressures of the order of  $10^{-4}$  mbar without harming the integrity of the target or disturbing the ion source operation. The gas kinetical collision cross-sections of most discussed atoms are around  $6 \cdot 10^{-16}$   $\text{cm}^2$  [27]. Thus at  $2000^\circ\text{C}$  an adsorbed atom will encounter about five reactive gas molecules per second. The reaction probability (per encounter) ranges for F and  $\text{F}_2$  from about 0.1 to 0.3 [28,29], i.e., the adsorbed refractory atom has a good chance to react to a volatile compound within about one second. A two-step process would take somewhat longer, e.g. Os needs to encounter two oxygen molecules to form  $\text{OsO}_4$ . Once formed, the volatile compound may effuse to the ion source similarly quickly as an inert gas, provided it is sufficiently stable not to dissociate at the wall collisions and sufficiently inert not to show significant adsorption times.

## 4 From theory to praxis

Much existing data on the volatility of oxides has been obtained in gas thermochromatography or isothermal gas chromatography experiments at atmospheric pressure. However, typical ISOL ion sources operate at far lower pressures and it has to be investigated if the volatilization still works under these conditions. To study this question several experiments were performed.

30 keV ISOLDE beams of  $^{185,189}\text{Hg}$  were implanted into single crystals of MgO and Y:ZrO<sub>2</sub> (yttria-stabilized zirconia). After complete decay to the daughters  $^{185}\text{Os}$  and  $^{189}\text{Ir}$  respectively, the activity of the latter was determined by gamma-ray-spectrometry. The samples were then heated in a quartz tube at ca.  $10^{-2}$  mbar air atmosphere for about one hour (13 hours respectively at  $1150^\circ\text{C}$ ). After cooling, the activity remaining in the samples was measured, see figure 2. MgO (lattice constant  $a = 2.10 \text{ \AA}$ ) and Y:ZrO<sub>2</sub> ( $a = 5.12 \text{ \AA}$ ) are not intended as ISOL target material for Os or Ir, but they have also cubic crystal structure and may thus serve as approximate surrogates to give a rough estimate of the diffusion speed in ThO<sub>2</sub> ( $a = 5.60 \text{ \AA}$ ) and UO<sub>2</sub> ( $a = 5.47 \text{ \AA}$ ). The shallow implantation (5–20 nm) leads to a very short diffusion path that does not allow one to deduce properly diffusion coefficients from the released fractions, but “real” target material would anyhow be polycrystalline, profiting from quicker grain boundary diffusion. Note that strong release



**Fig. 2.** Release of refractory elements from various oxide matrices. Data on UO<sub>2</sub> are from [11].

is observed when approaching  $1200^\circ\text{C}$ , comparable to the results obtained by Eichler and Domanov [11] for proton-irradiated UO<sub>2</sub> heated for one hour in air. ThO<sub>2</sub> and UO<sub>2</sub> can be operated at temperatures far above  $1200^\circ\text{C}$ , therefore one can expect sufficiently rapid release even for isotopes with half-lives in the minutes to seconds range.

In these experiments we did not aim for particularly dry oxygen, thus transport in form of hydroxides may play a role. However, such a partial pressure of H<sub>2</sub>O would also be acceptable for on-line use with an ECRIS.

A second series of experiments was devoted to find the minimum oxygen pressure under which Tc and Re are still volatile enough for an efficient transport. Under dry conditions an oxygen pressure of  $10^{-4}$  mbar was sufficient to achieve the maximal transport yield [30]. This is fully compatible with the typical operating pressure of an ECRIS.

ISOL beams of refractory elements produced so far are shown in the last column of table 1. In the following sections a compilation of experimental data on diffusion and volatilization is given to judge the prospects for producing other ISOL beams of various refractory elements.

### Group 4

The production of hafnium beams is discussed in a separate paper [26].

$^{82-85}\text{Zr}$  beams have been produced at ISOCELE (Orsay) in ( $^3\text{He}, xn$ ) reactions on a SrF<sub>2</sub> target [31]. The target material provided the fluorine for the formation of ZrF<sub>4</sub> that was ionized to ZrF<sub>3</sub><sup>+</sup>.

At ISOLDE the most promising target for the production of neutron-deficient Zr beams would be a Nb foil target with CF<sub>4</sub> addition. Such a combination was already successfully used for the production of SrF<sup>+</sup> and YF<sub>2</sub><sup>+</sup> [32]. The diffusion coefficient of Zr in Nb is about  $2 \cdot 10^{-9}$   $\text{cm}^2/\text{s}$  at  $2000^\circ\text{C}$  [33,34], i.e. 12% of 4.6 s  $^{80}\text{Zr}$  would diffuse out of 20  $\mu\text{m}$  thick foils before decay.

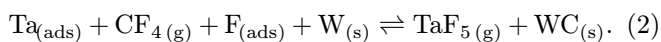
Analogously the release of TiF<sub>4</sub> is expected from a V foil target with CF<sub>4</sub> addition. At  $1600^\circ\text{C}$  the diffusion coefficient is  $2.4 \cdot 10^{-9}$   $\text{cm}^2/\text{s}$  [35], allowing for 5% diffusional release of 0.2 s  $^{42}\text{Ti}$  from 10  $\mu\text{m}$  thick foils.

Neutron-rich Ti and Zr isotopes can be produced with Ta foil targets (diffusion coefficient of Ti:  $3.6 \cdot 10^{-9} \text{ cm}^2/\text{s}$  at  $2200 \text{ }^\circ\text{C}$ ), but the  $\text{TiF}_3^+$  and  $\text{ZrF}_3^+$  sidebands will not be pure. Intense background of Ag, Cd, In, etc. appears at masses of  $\text{TiF}_3^+$  and of lanthanides at masses of  $\text{ZrF}_3^+$ .

#### Group 5

Beams of  $^{162-167}\text{Ta}$  have been produced at ISOCELE by bombarding a  $\text{LuF}_3$  target with  $280 \text{ MeV } ^3\text{He}$  ions [31, 36]. The target material provided the fluorine for the formation of  $\text{TaF}_5$  that was separated after ionization to  $\text{TaF}_4^+$ .

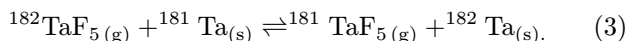
Group 5 pentafluorides are more difficult to produce than group 4 tetrafluorides. A direct reaction with the fluorination agent  $\text{CF}_4$  is no longer sufficient, but an additional fluorine atom must be found, e.g. for Ta release from W foils:



The reaction is exoenergetic ( $\Delta H^{298} = -336 \text{ kJ/mol}$ ), but might be kinetically hindered (three body reaction).  $\text{SF}_6$  is not a good alternative as fluorination agent since unwanted reactions (formation of sulphides) may occur.

In several tests with a MK5 ISOLDE type FEBIAD ion source fed with  $\text{CF}_4$  stable  $^{181}\text{Ta}$  (mainly evaporated from the hot Ta cathode) was found dominantly in the  $\text{TaF}_4^+$  sideband: 60–65% of all detected Ta containing ions. The remaining part was spread about equally over  $\text{TaF}_3^+$ ,  $\text{TaF}_2^+$ ,  $\text{TaF}^+$  and  $\text{Ta}^+$  and a small fraction appeared as  $\text{TaO}^+$ ,  $\text{TaFO}^+$ ,  $\text{TaF}_2\text{O}^+$  or as multiply charged ions.

Off-line a release half-time of about 2 hours was measured for Ta from  $50 \mu\text{m}$  thick W foils in  $\text{CF}_4$  atmosphere at  $2050^\circ\text{C}$ , corresponding to a diffusion coefficient of  $1.7 \cdot 10^{-10} \text{ cm}^2/\text{s}$ . Thus, at least long-lived Ta isotopes should be released, but on-line no Ta beams could be observed from a mixed Ta/W foil target [26], i.e. the overall efficiency for  $^{182}\text{Ta}$  was at least a factor 20 smaller than for long-lived Hf isotopes. Probably the radioactive tantalum fluorides suffer from losses by exchange reactions on the Ta walls:



Therefore a construction material different from tantalum needs to be selected for target container, transfer line and ion source cathode if radioactive tantalum isotopes should be separated with better efficiency.

Also for the release of  $\text{NbF}_5$  tantalum surfaces should be avoided since  $\text{NbF}_5$  could get lost by giving its fluorine to  $\text{TaF}_5$  that is slightly more bound.

#### Group 6

Volatile halides exist also for groups 6 and higher, but their dissociation e.g. on Ta is thermodynamically favored [37]. Thus, the volatilization and decomposition temperatures of these halides are probably too close to permit an efficient use.

We observed no release of W radioisotopes from  $50 \mu\text{m}$  thick Re and Ir foils heated in a Ta boat for 2 hours under  $\text{CF}_4$  atmosphere to  $2050^\circ\text{C}$ . It is not excluded that thinner foils or a different environment (Re or Ir container) would show some release, but the release of short-lived W isotopes in form of fluorides is definitely challenging.

An alternative to fluorides might be oxides. As seen from table 1 tungsten trioxide is well-bound but clearly less volatile than the oxides discussed below. Still, it might be possible to release  $\text{WO}_3$  from  $\text{UO}_2$  or  $\text{ThO}_2$  heated in oxidising atmosphere to high temperatures.

The release of the lighter homologue molybdenum in form of  $\text{MoO}_3$  is indeed possible, but requires temperatures  $\gg 1200^\circ\text{C}$  to proceed quickly, see figure 2. At  $1600^\circ\text{C}$  a diffusion coefficient of  $1.5 \cdot 10^{-8} \text{ cm}^2/\text{s}$  is reached in  $\text{UO}_2$  [38]. If rapid sintering of polycrystalline  $\text{UO}_2$  powder can be prevented (e.g. by addition of another inert oxide) even the release of isotopes with seconds half-lives could become possible.

#### Group 7

Technetium and rhenium can both be volatilized in form of trioxides. The thermochromatographic separation of no-carrier-added  $\text{TcO}_3$  from macroscopic amounts of less volatile  $\text{MoO}_3$  and of  $\text{ReO}_3$  from less volatile  $\text{WO}_3$  can actually be used for the separation of  $^{94m}\text{Tc}$  from irradiated  $^{94}\text{Mo}$  targets [39], the separation of  $^{186}\text{Re}$  after (p,n) activation of  $^{186}\text{W}$  targets and for  $^{188}\text{W}/^{188}\text{Re}$  isotope generators [40] respectively. Given that the Tc and Re volatilization works even at  $10^{-4}$  mbar oxygen pressure [30], these off-line methods could certainly be adapted to produce on-line beams of longer-lived Re and Tc isotopes produced in (p,n) reactions of  $\text{WO}_x$  or  $\text{MoO}_x$  targets respectively.

Using instead  $\text{UO}_2$  or  $\text{ThO}_2$  as less volatile target material would allow to operate at even higher temperatures and release also shorter-lived radioisotopes of Tc and Re.

#### Group 8

The group 8 elements ruthenium and osmium form very volatile tetroxides. Being volatile at room temperature they could be directly used with presently available ECRIS types. In case  $\text{RuO}_4$  dissociates at higher temperatures, the resulting lower valent  $\text{RuO}_3$  is still relatively volatile.

Ru release was measured from  $\text{UO}_2$ , see figure 2 and [38, 41, 42]. The diffusion coefficients given for  $\text{UO}_2$  single crystals scatter strongly between  $2 \cdot 10^{-10}$  and  $5 \cdot 10^{-6} \text{ cm}^2/\text{s}$  at  $1600^\circ\text{C}$ . Our model experiments (see figure 2) show that also osmium should be released quickly from oxide target matrices.

#### Group 9

Volatile rhodium trioxide has been reported once [43], but not much is known about its thermal stability. Rhodium

dioxide is only volatile at higher temperatures [44]. No data for diffusion in potential target materials are available.

Iridium can be volatilized as trioxide. Our model experiments with Y:ZrO<sub>2</sub> indicate that Ir should show a sufficiently rapid release from oxide targets at temperatures  $\gg 1200$  °C.

### Group 13: Boron

Boron has not only a low vapor pressure, but is also forming strong bonds with carbon, oxygen, nitrogen and many metals (refractory borides). Thus, atomic boron will adsorb strongly on practically all surfaces typically present in ISOL target and ion source units. At 2200 °C atomic boron is slowly released from graphite [45], but chemical evaporation is needed to give the short-lived <sup>8</sup>B ( $T_{1/2} = 0.77$  s) a chance to be released. The obvious compound for volatilization is BF<sub>3</sub> that is already gaseous at room temperature. At higher temperatures BF<sub>3</sub> may decompose to lower fluorides BF<sub>2</sub> and BF, but these are also volatile. The efficient ionization of BF<sub>3</sub> in existing ECR ion source types is straightforward [46,47].

Boron diffuses in many materials interstitially with very high diffusion coefficients. The diffusion coefficient in polycrystalline graphite at 2200 °C is  $(2.2\text{--}2.7)\cdot 10^{-5}$  cm<sup>2</sup>/s [48,49], thus diffusion delays will be negligible even for coarse grained graphite. The rate-determining step will be the chemical evaporation. Boron diffusion data in other refractory materials compatible with fluorination are scarce. Therefore we launched a program to measure boron diffusion by neutron depth profiling to follow the depth profile of <sup>10</sup>B implanted samples after stepwise annealing, compare [50]. Detailed measurements are still ongoing, but so far we identified as most promising target materials apart from graphite also Pt and CaF<sub>2</sub>.

### Other elements

What about the lighter homologues (3d transition metals) that are not shown in table 1, but that are also known to be slowly released? The discussed chemical evaporation methods cannot be necessarily applied for all these elements, since the stability of the discussed compounds decreases for lighter homologues [16].

Experiments were performed to volatilize V as vanadium oxide from heated TiO<sub>2</sub> matrices [51]. When heated for many hours, a very slow release of vanadium was observed, still in principle sufficiently quick to produce at least beams of the long-lived isotopes <sup>47–49</sup>V. However, the temperature range where V is released while the vapor pressure of the TiO<sub>2</sub> matrix remains acceptable is extremely narrow, making an on-line operation very difficult.<sup>4</sup>

<sup>4</sup> Using instead chlorine for the chemical evaporation indeed an ISOL beam of <sup>48</sup>V could be produced at HRIBF, though with low overall efficiency [51].

On the other hand an extension to the heavier homologues, the transactinide elements Rf to Hs, is promising. In particular the method could be used to identify uniquely the mass of the long-lived Db daughter of element 115 [52]. To optimize the separation efficiency for DbF<sub>4</sub><sup>+</sup>, test experiments with NbF<sub>4</sub><sup>+</sup> and TaF<sub>4</sub><sup>+</sup> are presently under way [53] at the MASHA ISOL separator [54].

## 5 Conclusion and outlook

It has been shown that the chemical evaporation technique can help to extend the ISOL method to refractory elements, presently not available as ISOL beams. For few elements (Zr, Ti, may be Nb and B) the realization is relatively straightforward by combining a suitable target material with an existing type of target container and ion source. Elements volatilized as oxides require a radio-frequency driven ion source, e.g. an ECRIS. Only few elements (Os, Ru) are compatible with presently available cold-body ECRIS models, but many more could be produced with an ECRIS with hot plasma chamber. The availability of such an ion source type should therefore lead to a similar breakthrough in ISOL beam development as the application of resonant laser ionization did.

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