# Vacuum Chromatography with SHE

## Heavy Elements group

*Paul Scherrer Institute & University of Bern*

# Vacuum Chromatography

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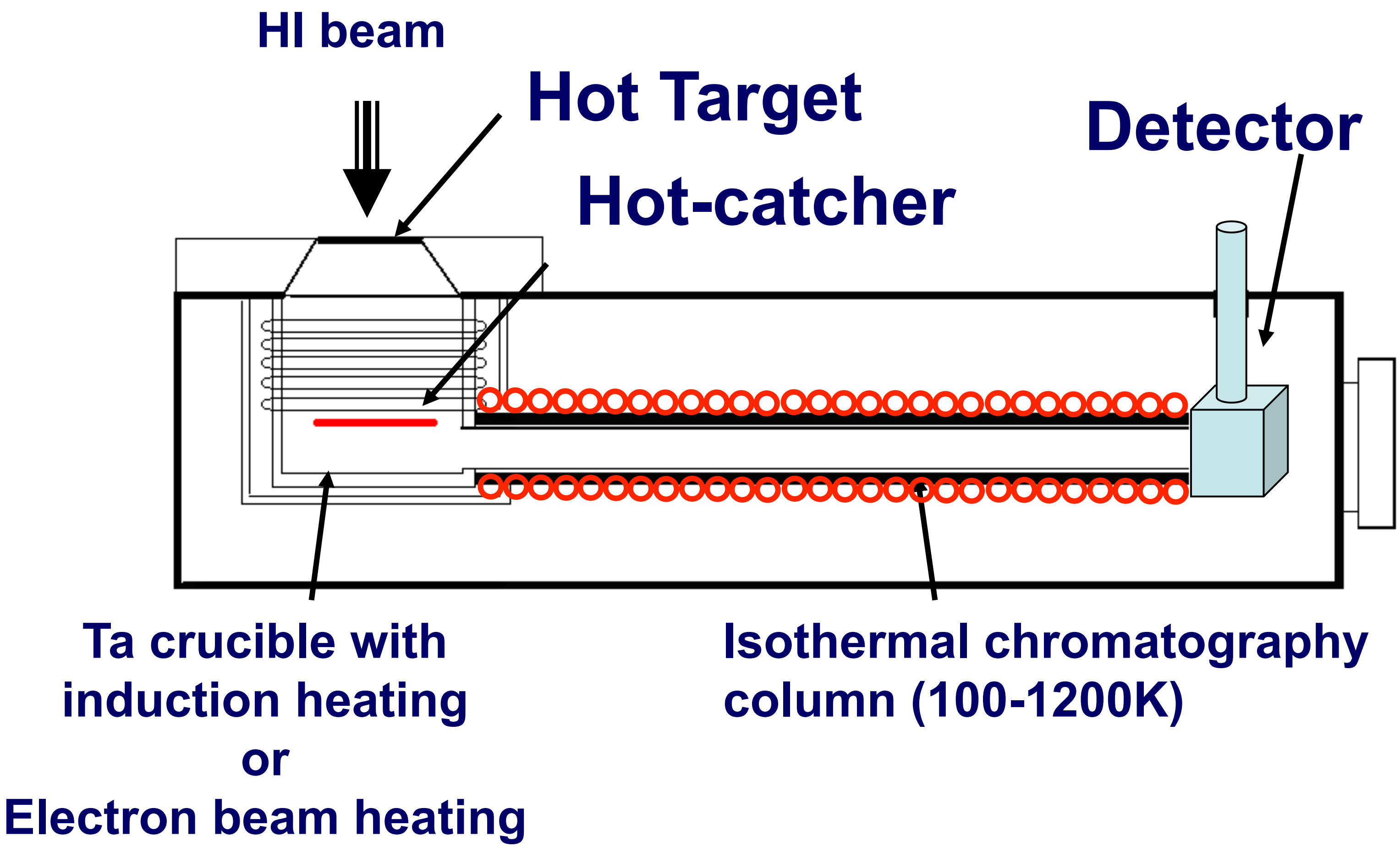
**Pros:**
- 👍 **Rapidity**
- 👍 **No aerosols**
- 👍 **Better spectroscopic resolution**
- 👍 **Less surface contamination**

**Cons:**
- 👎 **Target overheating no gas cooling**
- 👎 **Less chromatographic resolution**
- 👎 **Recoil stopping**

# Vision:
## Isothermal On-line Vacuum Chromatography



# Hot target

## Intermetallic actinide/noble metal targets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A simple idea:

<u>Electrodeposition on a noble metal backing with a subsequent reduction in $H_2$ atmosphere.</u>

- Chemical equation of a coupled reduction process :

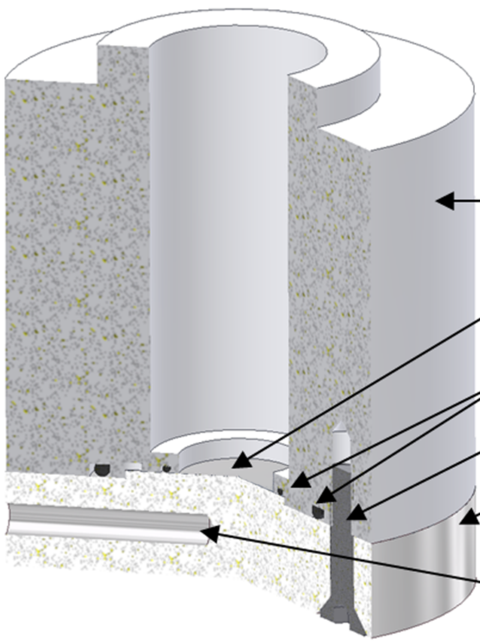
$AcxOy + yH_2 \longrightarrow xAc + yH_2O$ Does not work.

$\Delta H(AcxOy) \leq -1500$ kJ/mole

$xMe + AcxOy + yH_2 \longrightarrow xAcMe + yH_2O$ Works with a noble metal.

$\Delta H(AcMe) \leq -400$ kJ/mole

# Molecular Plating

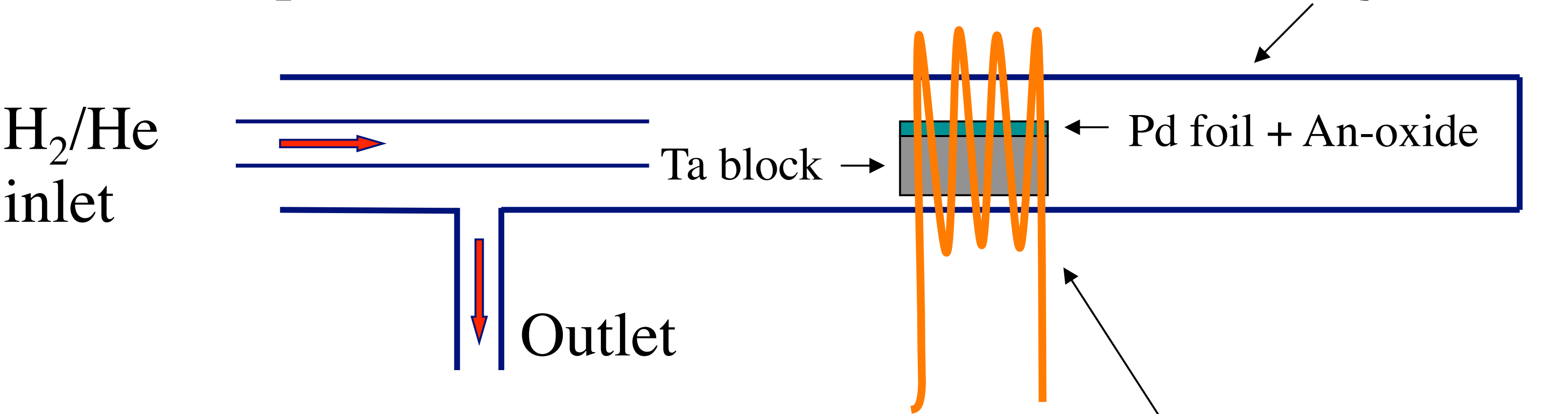



| | |
|---|---|
| Deposition thickness | 0.73 mg·cm$^{-2}$ |
| Solvent | Isopropanol |
| Backing | Pd foil |
| Area deposited | 0.38 cm$^2$ |
| Current | 0.8 – 2.1 mA·cm$^{-2}$ |
| Potential | 500 – 800 V |
| The distance between two electrodes | 1 cm |
| Overall deposition time | Performed in 5 consecutive steps. Each step 50 min long. |
| Temperature | 25$^o$C |
| Anode | Platinum spiral wire |

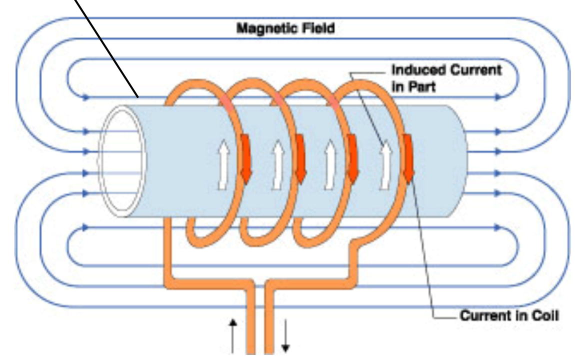
*I. Usoltsev et al. submitted NIMA 2012*

# Coupled Reduction

Reduction process:




Induction heating system:




A source of high frequency field

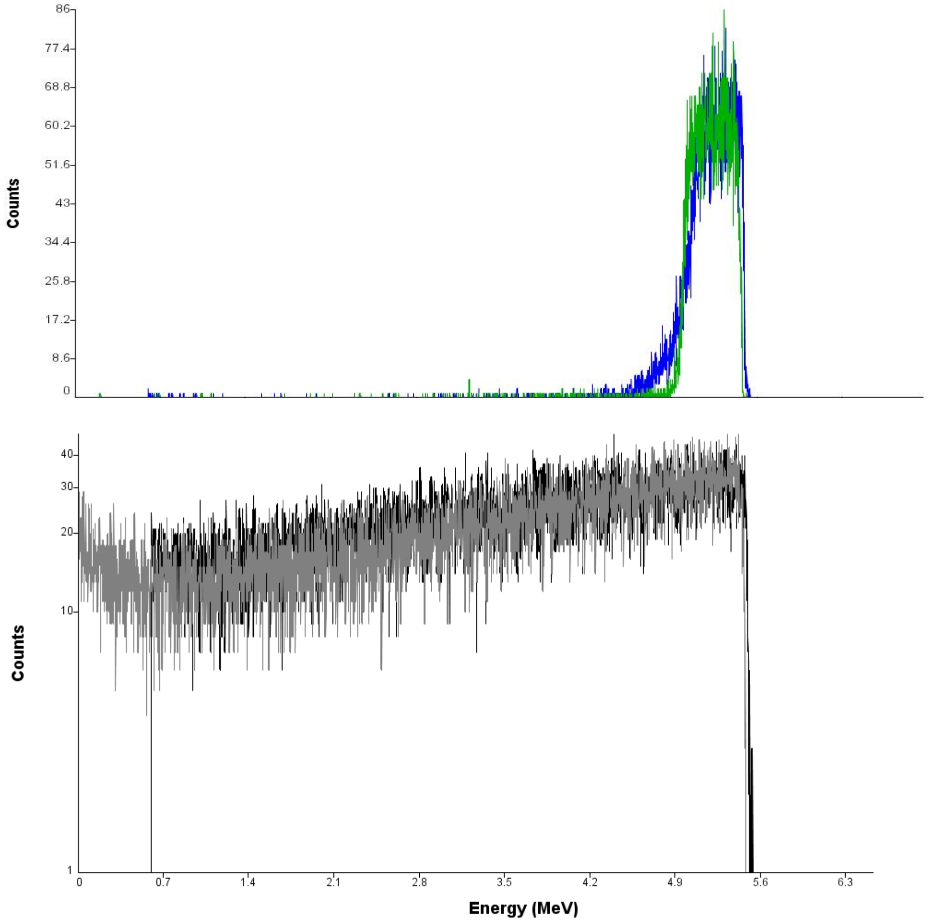
*I. Usoltsev et al. submitted NIMA 2012*

# Analysis

Alpha spectra ($^{241}Am$) before and after coupled reduction.

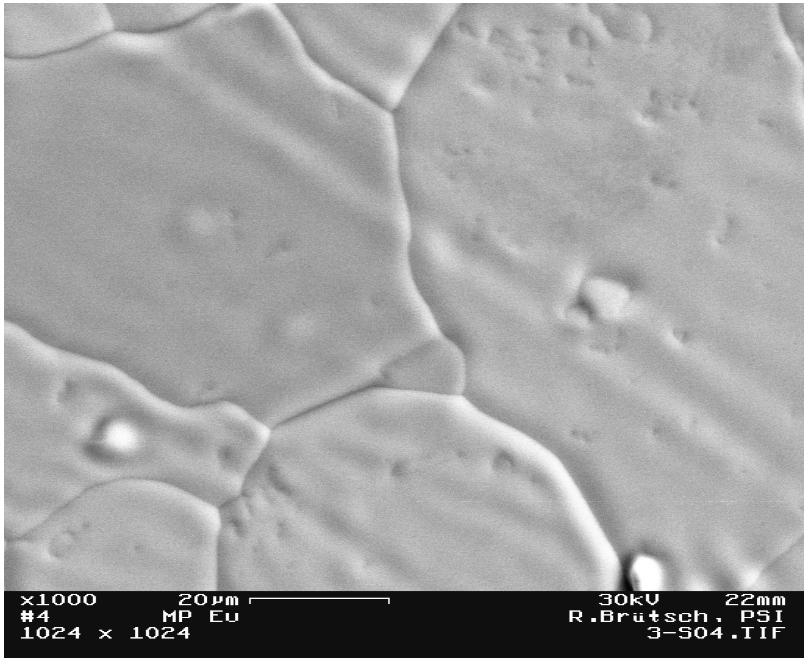
Alpha spectrum of the plated material before reduction.

After reduction. 100 ml/min $H_2$ at 1270°C (30 min).

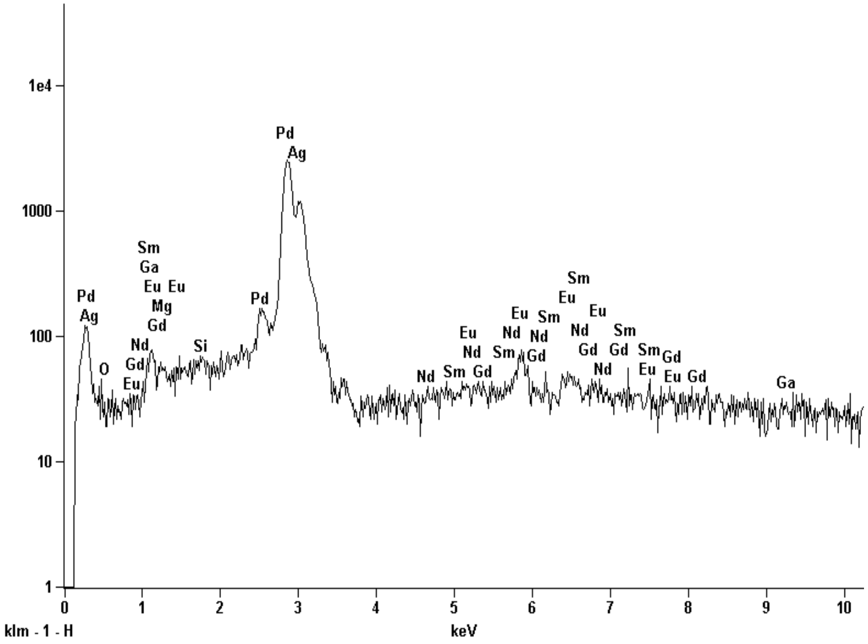



*I. Usoltsev et al. submitted NIMA 2012*

# Analysis




E.g. SEM picture of the Eu/Pd product.




EDX overview spectrum of the Eu/Pd product. Eu disapeared into the Pd below the probing depth of electrons.

# $^{243}$Am Targets on 3 μm Pd foils

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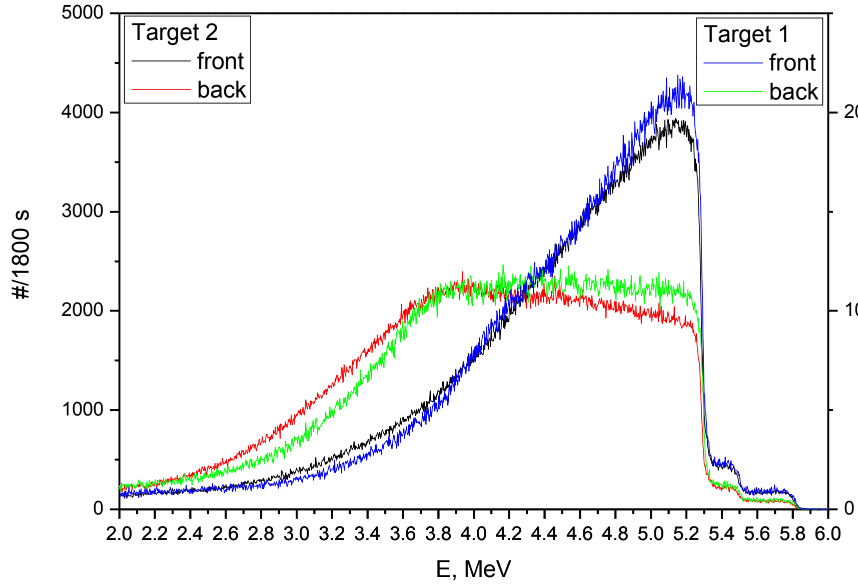
Two targets prepared with 0.7 mg/cm$^2$ and 1.4 mg/cm$^2$ $^{243}$Am

Front and back side alpha measurement allows for distribution estimation of $^{243}$Am in the 3 μm Pd foil:
~30% on the top surface
~70% evenly distributed into the depth




- The targets were irradiated with 750 pnA $^{48}$Ca for several days at FLNR Dunba.
- Integral beam was 1.2*10$^{18}$ on target 1 and 0.6*10$^{18}$ on target 2.
- No considerable destruction, losses or relocation of $^{243}$Am within the targets observed.

*I. Usoltsev et al in preparation 2012*

# Hot Catcher / Release

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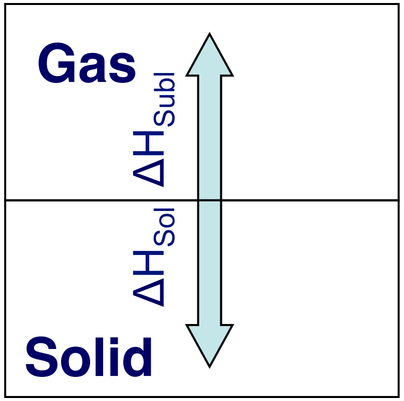
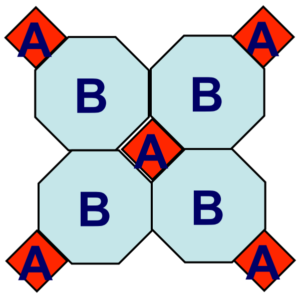
## Release Enthalpy

$$\Delta H_f = \Delta H_{Subl} - \Delta H_{Sol}$$




## Miedema model: Intermetallic solid solution




$$\Delta H_{sol} = \frac{2 \cdot V_{Asol}^{2/3}}{n_{WSA}^{-1/3} + n_{WSB}^{-1/3}} \cdot \left( Q \cdot \left( n_{WSA}^{1/3} + n_{WSB}^{1/3} \right)^2 - P\left( \Phi_A^* - \Phi_B^* \right)^2 - R_m \right)$$

$$V_{Asol} = V_A \cdot \left( 1 + a \cdot \left( \Phi_A^* - \Phi_B^* \right) \right)^{3/2}$$

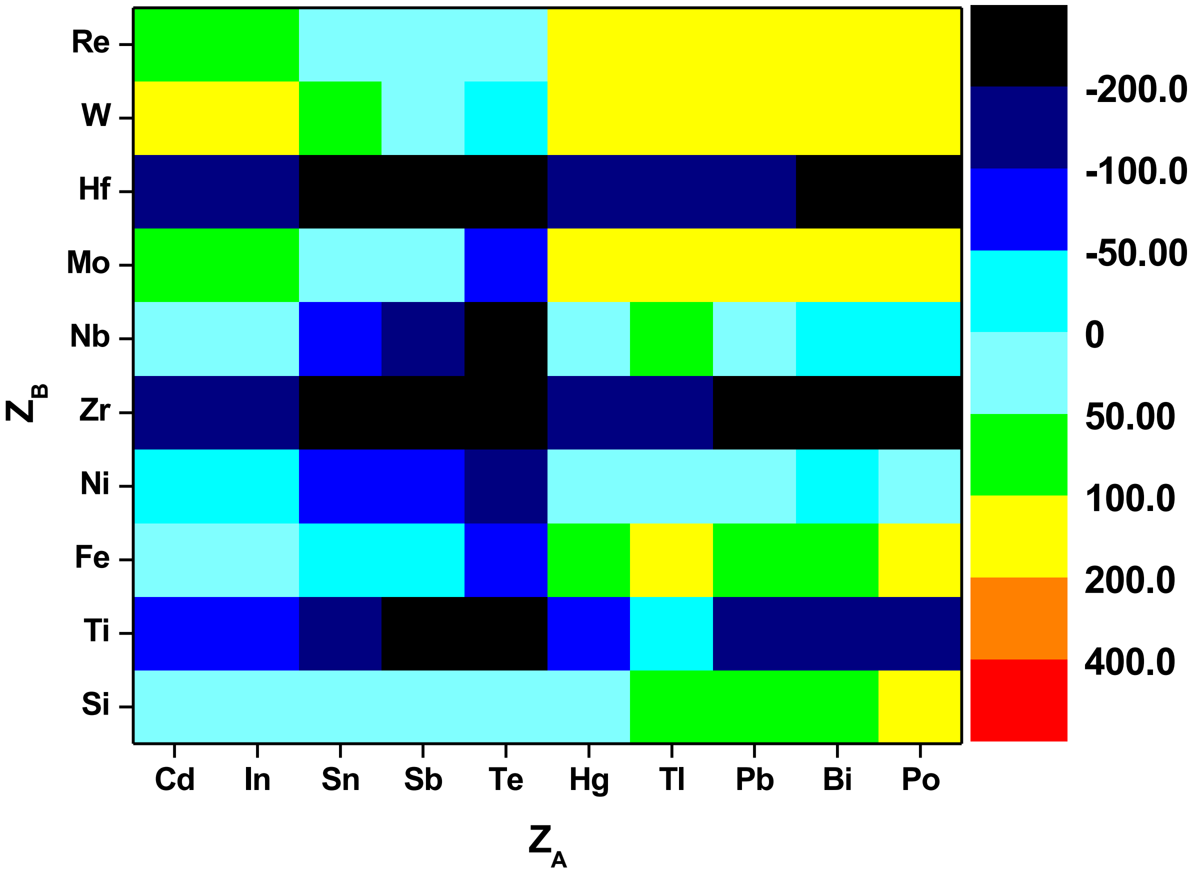
$n_{WS}$ = electron density at the boundary
$V_{Asol}$= molar volume of the species in solution
$\Phi^*$ = chemical potential of electrons
$P/Q/R_m$ = proportionality factors (empirically derived)

Semi empirical model adjusted
to hundreds of binary compounds

A.R. Miedema, J. Less-Comm. Met. 46, 67 (1975)

# Catcher / Release

Enthalpies of release of A from B at infinite dilution [kJ/mol]




-Promising candidates:
-Si, Fe, Nb, Mo, W, and Re

-Interesting candidates due to phase changes: Ti, Zr, and Hf

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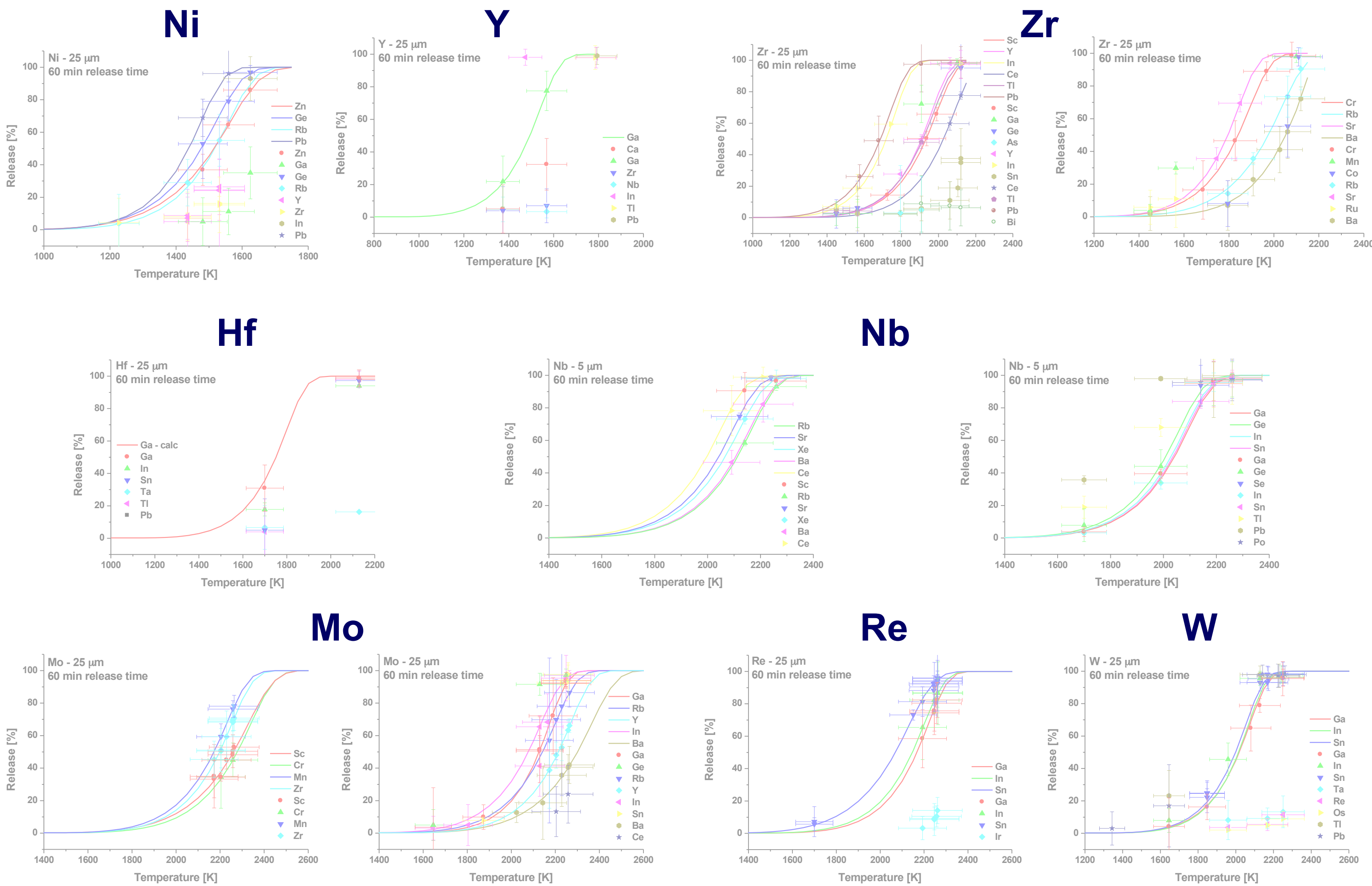
# Release:

## Experimental Results




*D. Wittwer et al. Phys. Chem.A 2012 submitted*

# Release:

## Experimental Results

- Release can be measured easily
- If the diffusion is the rate determining factor, diffusion coefficients can be calculated from the release rate

$$F = 1 - \frac{8}{\pi^2} \cdot \exp\left( - \frac{Dt\pi^2}{d^2} \right)$$

- Further the activation energy can be deduced

$$\ln\left( \frac{\left( -\ln\left( (1-F)\frac{\pi^2}{8} \right) \right) d^2}{t\pi^2} \right) = -\frac{Q}{RT} + \ln(D^0)$$

***F*** relative release

***D*** is the diffusion coefficient or diffusivity in ***m²/s***

***D₀*** is the *preexponential* factor in ***m²/s***

***t*** is the bake out time in ***s***

***d*** thickness of the foil in ***cm meter!!!***

***Q*** activation energy in ***J/mol***

***R*** is the Boltzmann constant in ***J/mol*K⁻¹***

*J. Crank, Mathematics of Diffusion, Oxford Univ. Press London (1975)*

*D. Wittwer et al. Phys. Chem.A 2012 submitted*

# Results:

## Prediction of Diffusion Constants

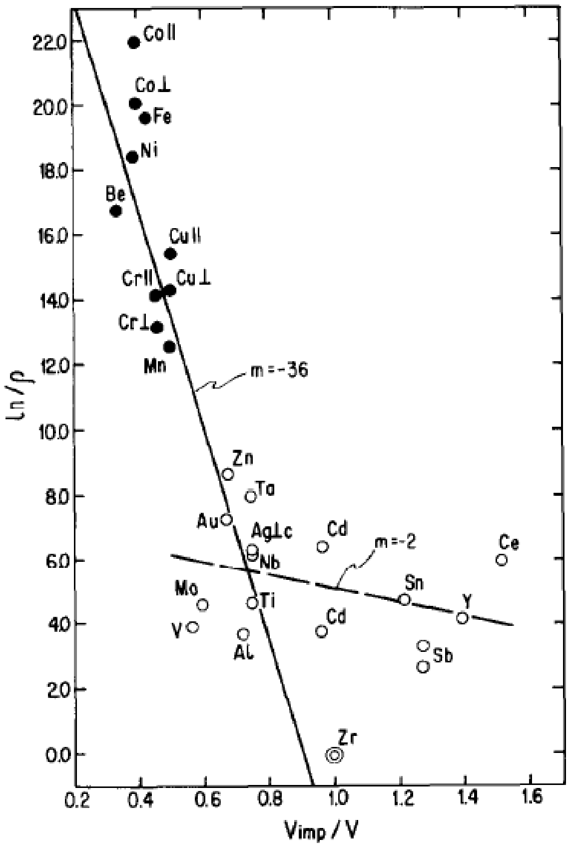
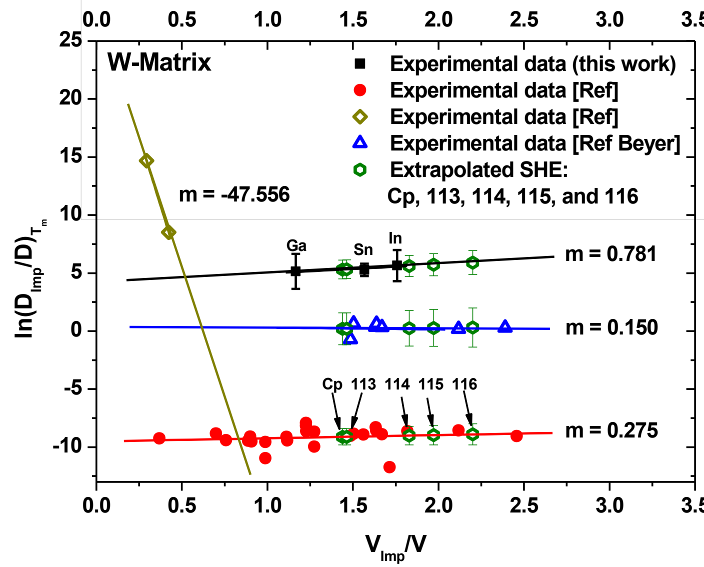



Fig. 1. ln $\rho(840\,°C)$ versus $V_{imp}/V$ for hcp-Zr. Approximation by two straight lines; $m$: slope of the lines; (●) interstitial diffusers, (○) substitutional diffusers, (◎) hcp-Zr self-diffusion.

R. Tendler et al, J. of Nucl. Mat. 150, 251 (1987)

$$\Delta V_{Imp} = \frac{P_0 V_A^{2/3}(\phi_A - \phi_B)}{(n_{WS}^A)^{-1/3} + (n_{WS}^B)^{-1/3}} \times \left[(n_{WS}^A)^{-1} - (n_{WS}^B)^{-1}\right]$$



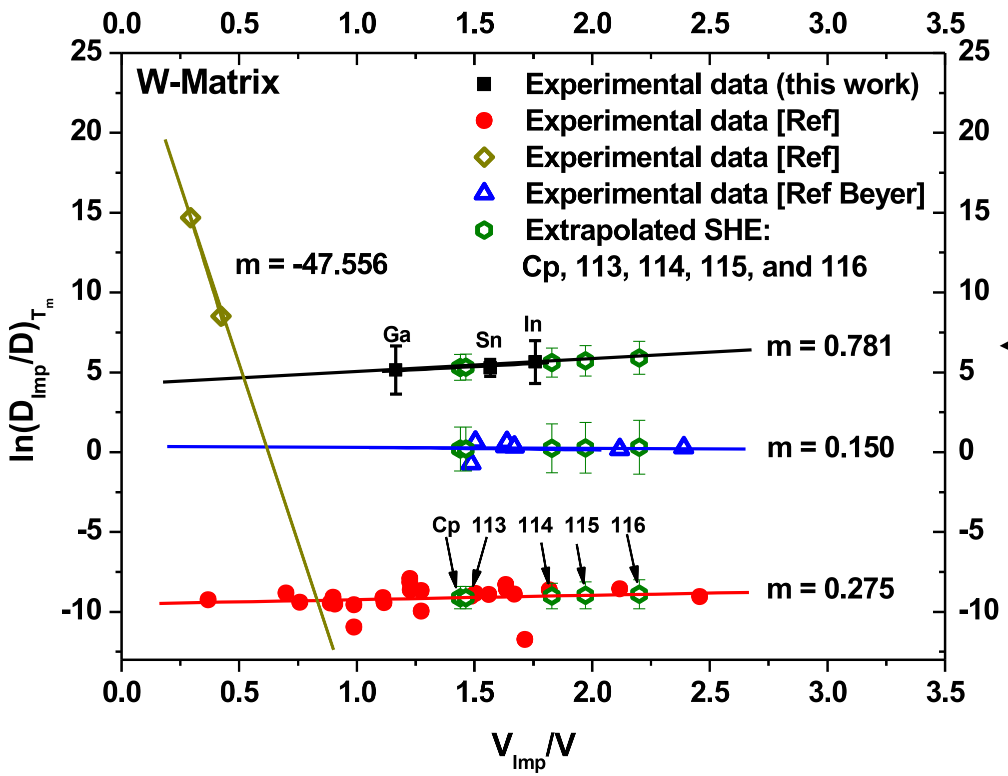

G. Neumann, Self Diffusion and Impurity Diffusion in Pure Metals, Pergamon Materials Series

G.J. Beyer et al., NIMPR B 204, 2003, 225

*D. Wittwer et al. Phys. Chem.A 2012 submitted*

# Predictions - SHE

using Tendler's atomic volume approach



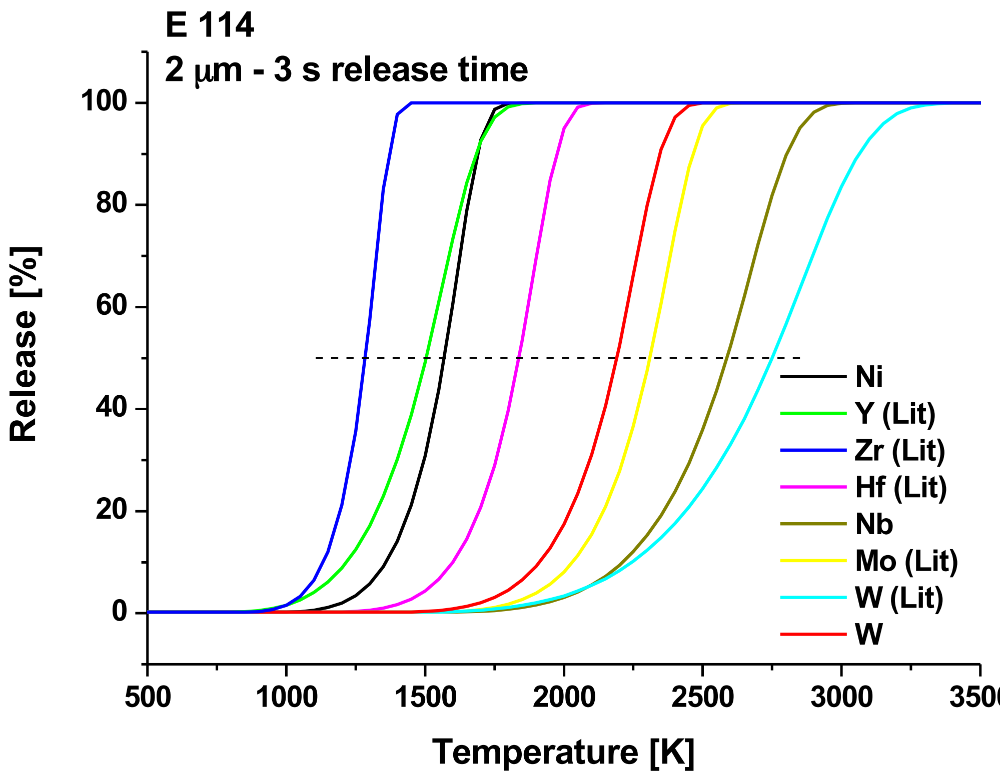

Radiation enhanced diffusion

*D. Wittwer et al. 2012 in preparation*

# Example Prediction - SHE

$$D = D^0 * exp\left(-\frac{Q}{RT}\right)$$

$$F = 1 - \frac{8}{\pi^2} \cdot \exp\left(-\frac{Dt\pi^2}{d^2}\right)$$

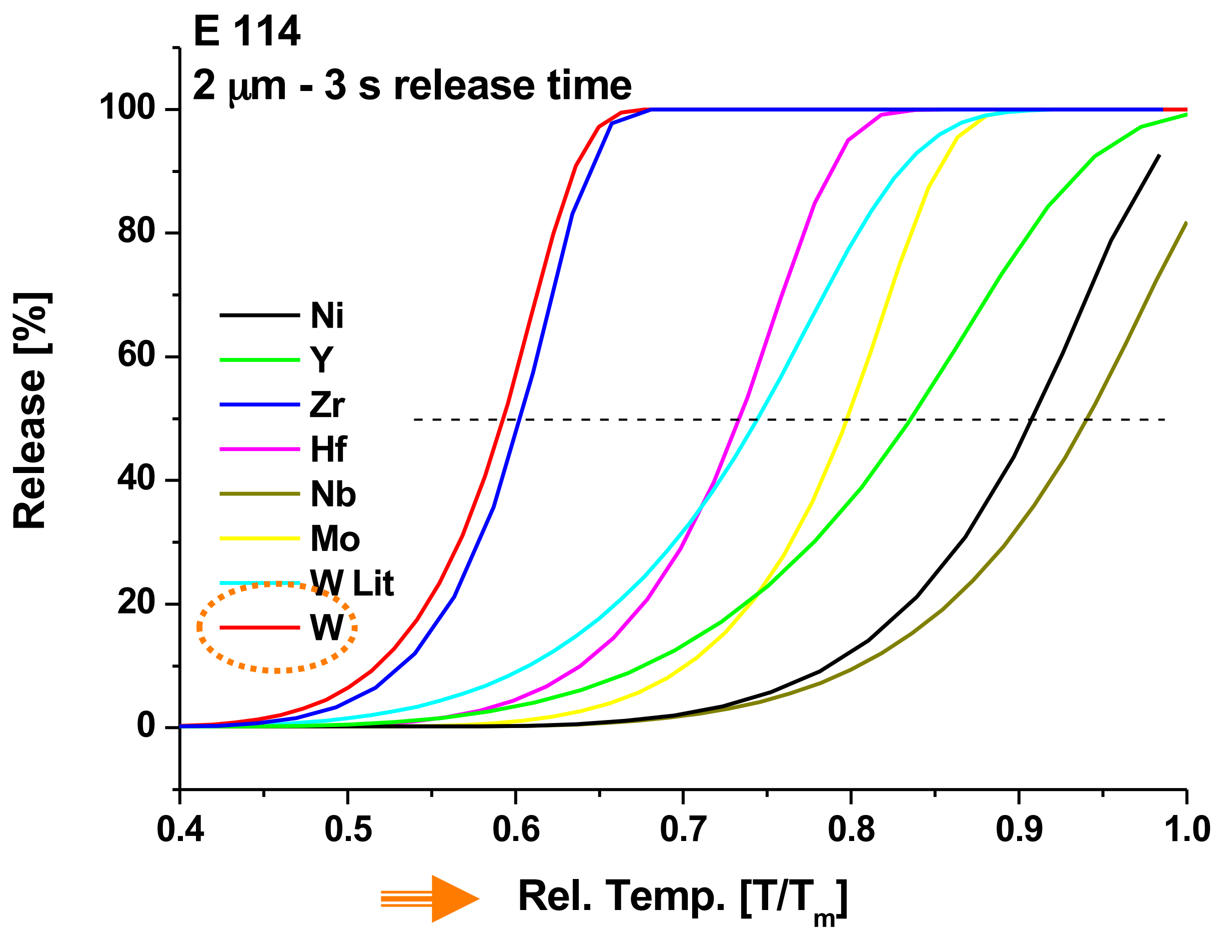



Tests with short-lived isotopes needed!

*D. Wittwer et al. 2012 in preparation*

# Example Prediction - SHE

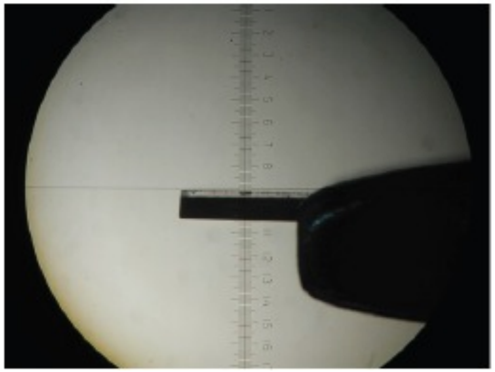
Relative temperature $T/T_{m(catcher)}$

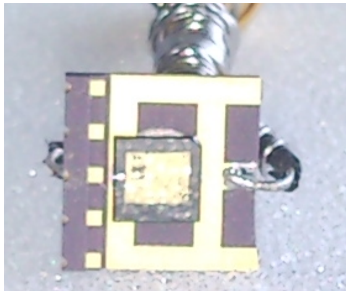


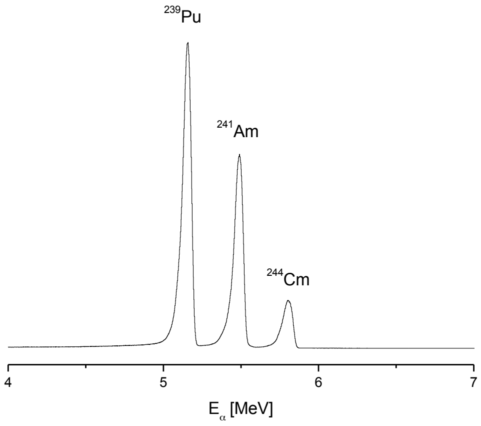

Tests with short-lived isotopes needed!

*D. Wittwer et al. 2012 in preparation*

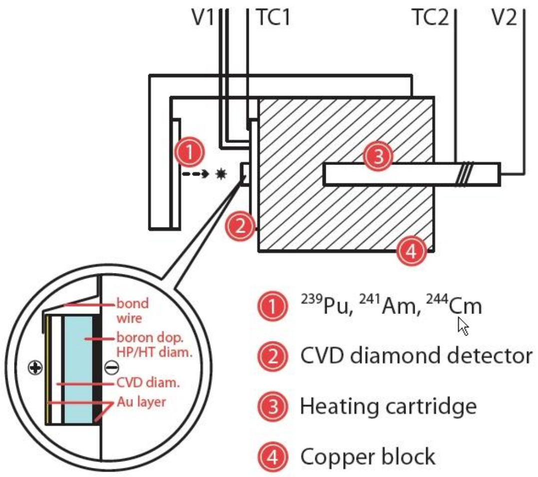
# Detectors: CVD Diamond








Heating setup ready for high temperature tests:



# Test experiments
## with CVD Diamond detectors

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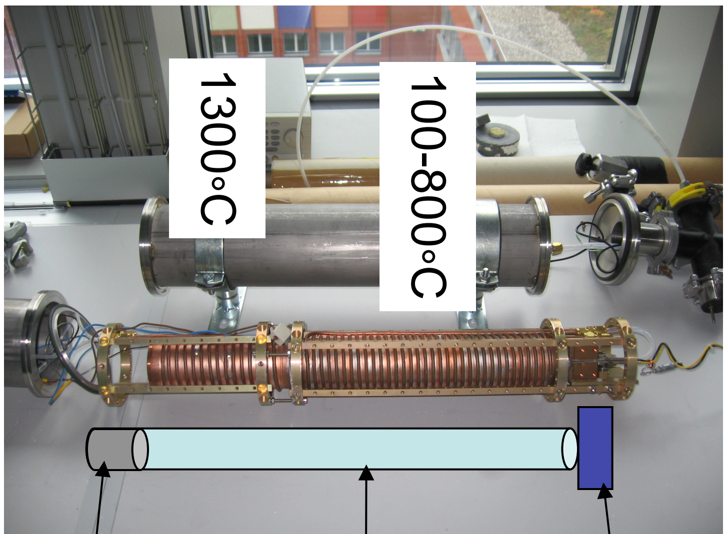
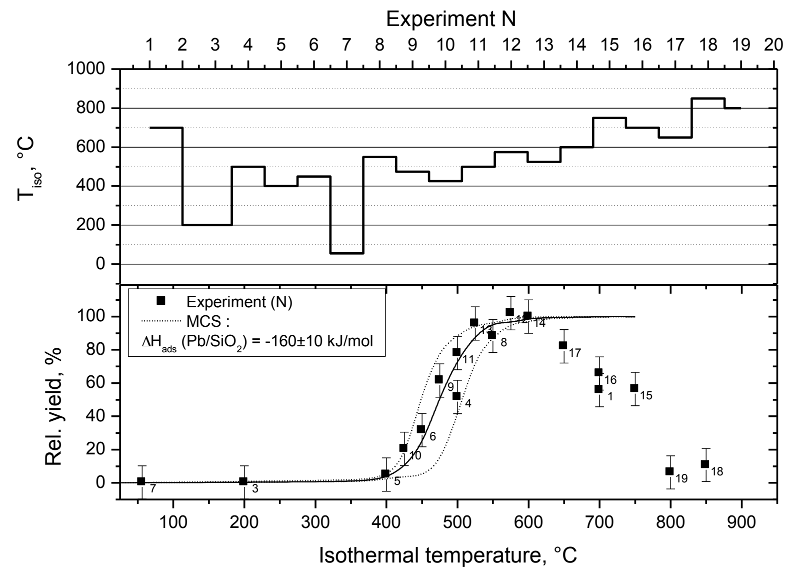



$^{227}Ac/Ta$ →→ $^{211}Pb$

Quartz column

CVD Diamond Detector



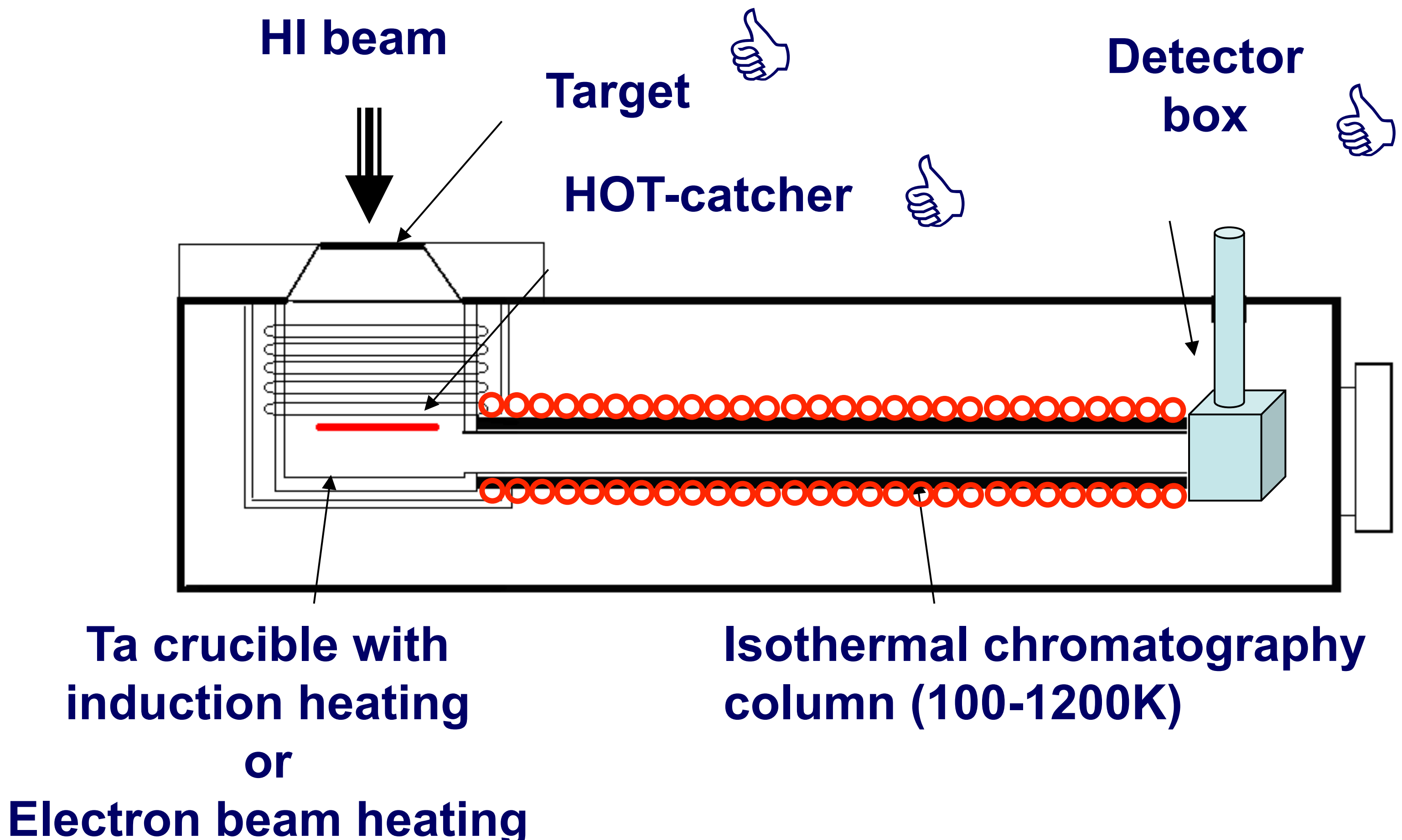

Adsorption of Pb on quartz &
@ T>600°C reaction of Pb with Quartz

Operation of the detector in the vicinity of a hot oven (IR-vis light) possible.

*P. Steinegger 2011*

# Vision:

## Isothermal On-line Vacuum Chromatography




R&D of a first setup coming soon!