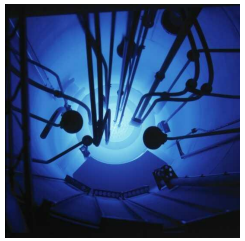

Undepotential deposition - a new method to study the chemistry of hassium!?

J. Even, J.V. Kratz, J. Ballof, W. Brüchle, R.A. Buda, Ch.E. Düllmann, K. Eberhardt, E. Gromm, D. Hild, E. Jäger, J.Krier, J. Khuyagbaatar, T. Lauer, D. Liebe, M. Mendel, D. Nayak, P. Reichert, M. Schädel, B. Schausten, E. Schimpf, A. Semchenkov, P. Thörle-Pospiech, A.Toyoshima, A. Türler, V. Vicente Vilas, N. Wiehl, T. Wunderlich, A. Yakushev

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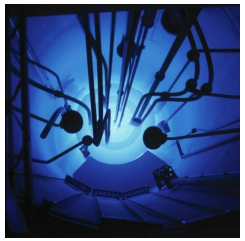
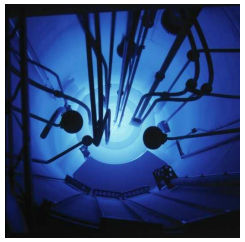


Electrodeposition of TANs?

- Theoretical predictions: the elements 108 - 116[1)] are suitable for electrodeposition experiments
- Hummrich et al.[2)] studied the influence of various parameters on deposition kinetics.

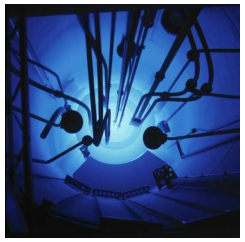
  Result: minimum electrolysis time is 10 s
- Choose long-lived ^{270}Hs ($t_{1/2}$~23 s)[3)] for electrochemistry

1) B. Eichler, J. V. Kratz, Radiochim. Acta **88**, 475 (2000). 2) H. Hummrich et al., Radiochim. Acta **96**, 73 (2008). 3) J. Dvorak et al., Phys. Rev. Lett. **100**, 132503 (2008).

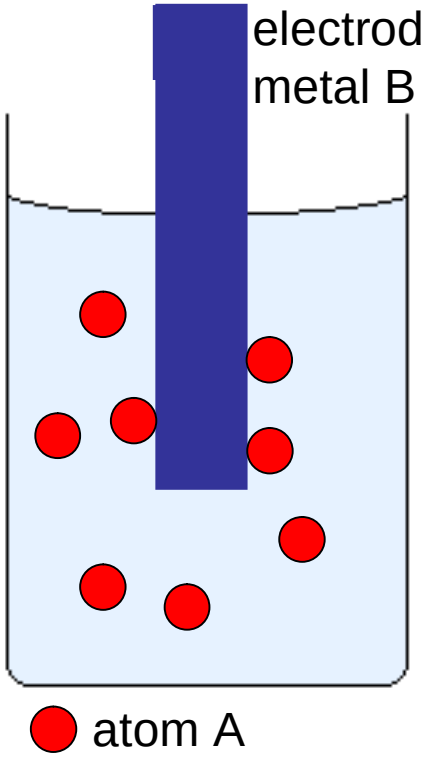


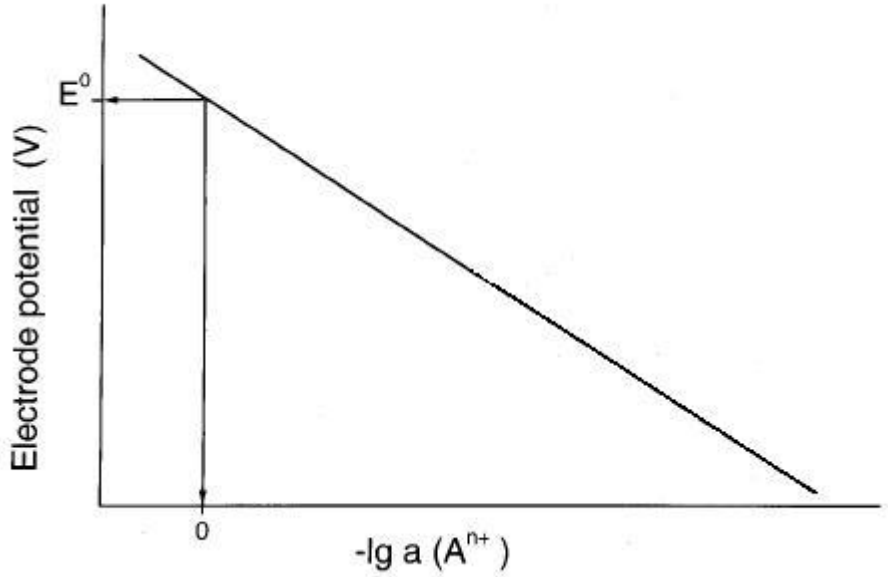
Steps to a hassium electrodeposition experiment

- Underpotential deposition - theory
- Test experiments with Os and Ru - the lighter homologues
- Proof that a transactinide chemistry experiment is feasible at the physical preseparator TASCA
- Construction of an automated setup



Beyond the limits of the Nernst equation

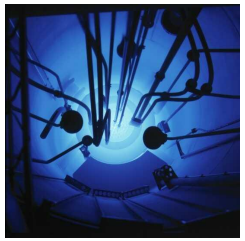




$$E = E^\circ + \frac{RT}{nF} \ln a_{ox}$$

U

E: electrode potential E°: standard potential
R: ideal gas constant T: temperature
n: transfered charges F: Faraday constant
a_{ox}: chemical activity oxidized spezies



Underpotential deposition – kinetics and thermodynamics

- Thermodynamical aspects: Shift of the potential compared to the prediction of the Nernst equation:

$$\Delta E = \frac{-\Delta\bar{H}(A-B) + T\Delta\bar{S}_{vib}}{nF}$$

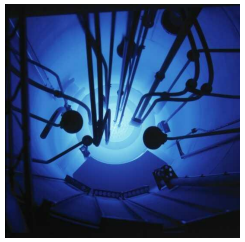
- Kinetic aspects:

$$t_{50\%} = \frac{6 \cdot \pi \cdot V \cdot a \cdot \delta \cdot \eta \cdot \ln 2}{F_E \cdot k_B \cdot T}$$

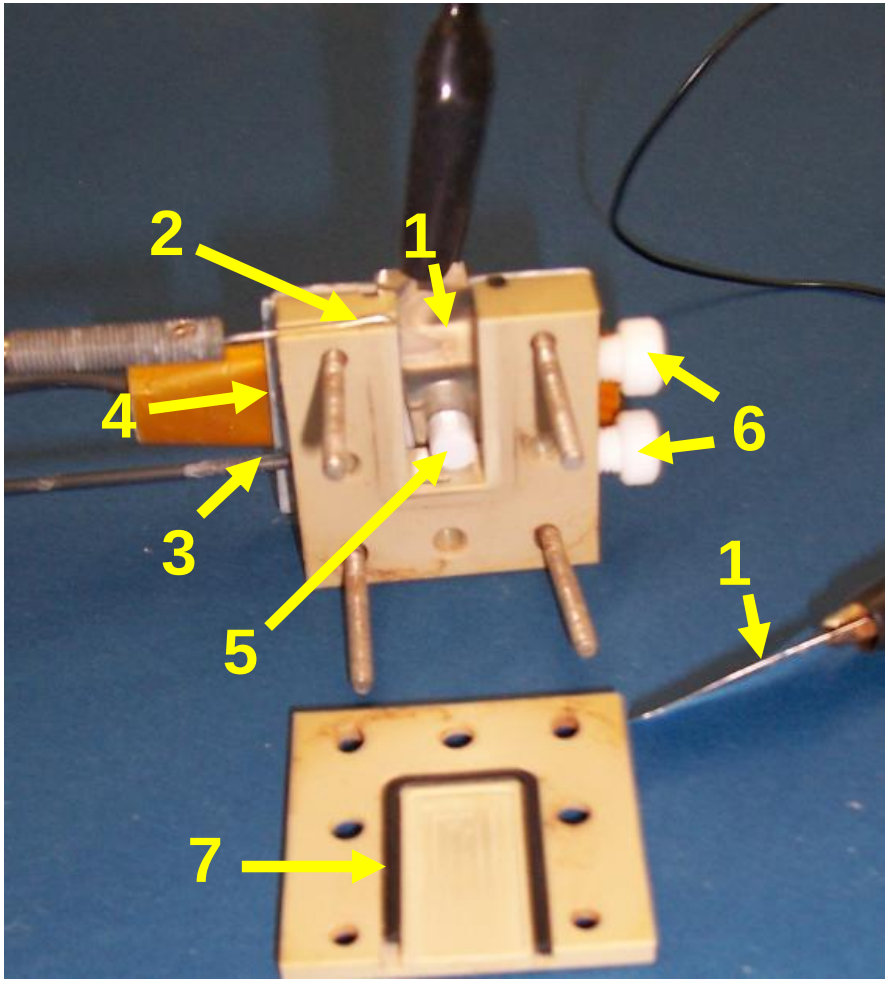
ΔE:	Shift of critical potential
$\Delta\bar{H}(A\text{-}B)$:	partial molar net adsorption enthalpy
$\Delta\bar{S}_{vib}$:	difference in vibrational entropies
n:	number of transfered charges
F:	Faraday constant

F_E:	electrode area	V:	electrolyte volume
δ:	Nernst diffusion layer	k_B:	Boltzmann constant
T:	absolute temperature	a:	hydrodynamic radius
η:	dynamic viscosity	$t_{50\%}$:	time at which 50% are deposited

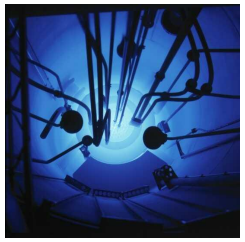
Goal: construct an optimized electrolytical cell!!!



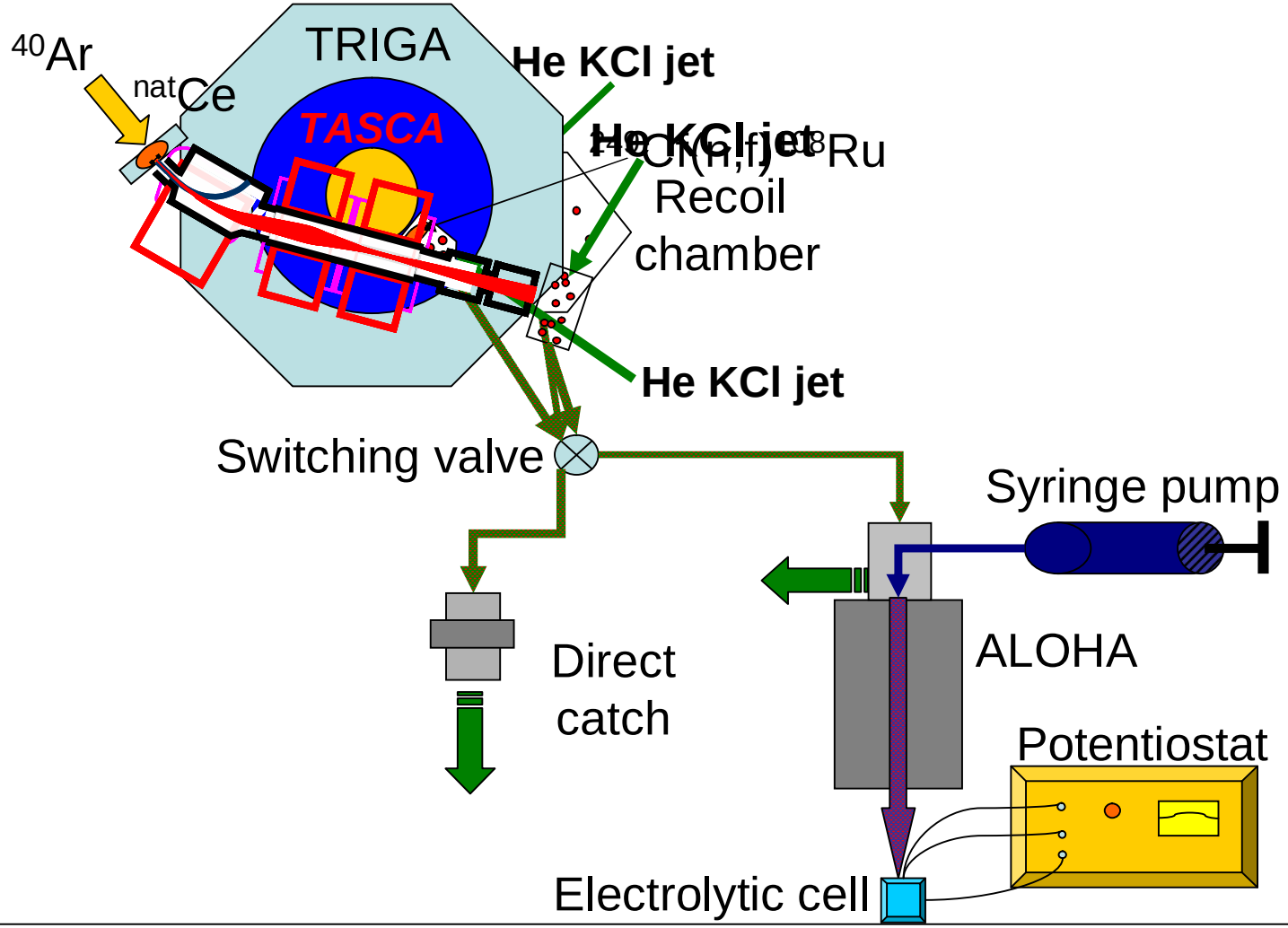
The electrolysis cell

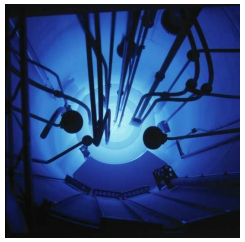


1) working electrodes;
2) counter electrode;
3) reference electrode;
4) heating;
5) stir bar;
6) electrolyte in- and outlet;
7) viton sealing

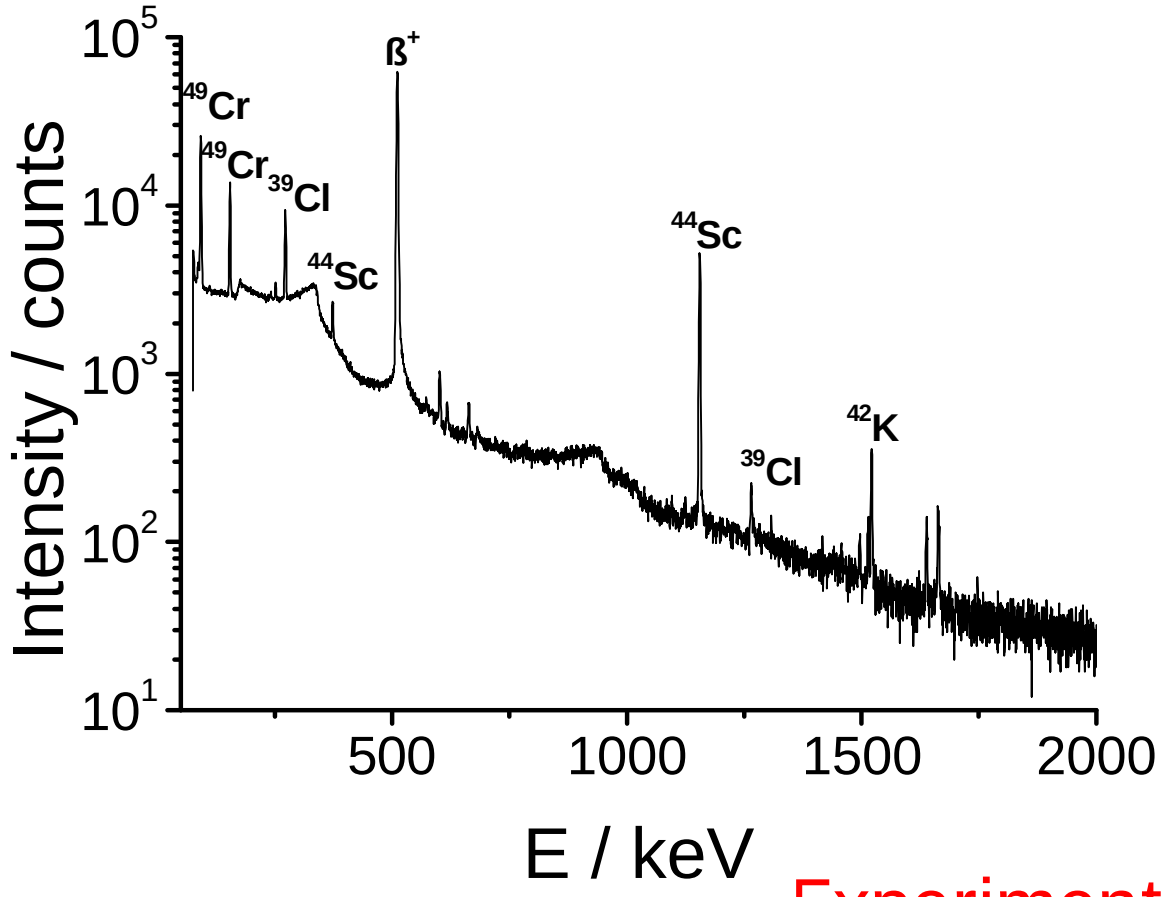


Experimental setup

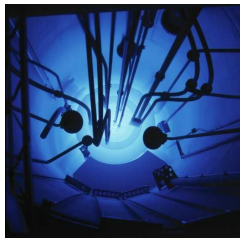




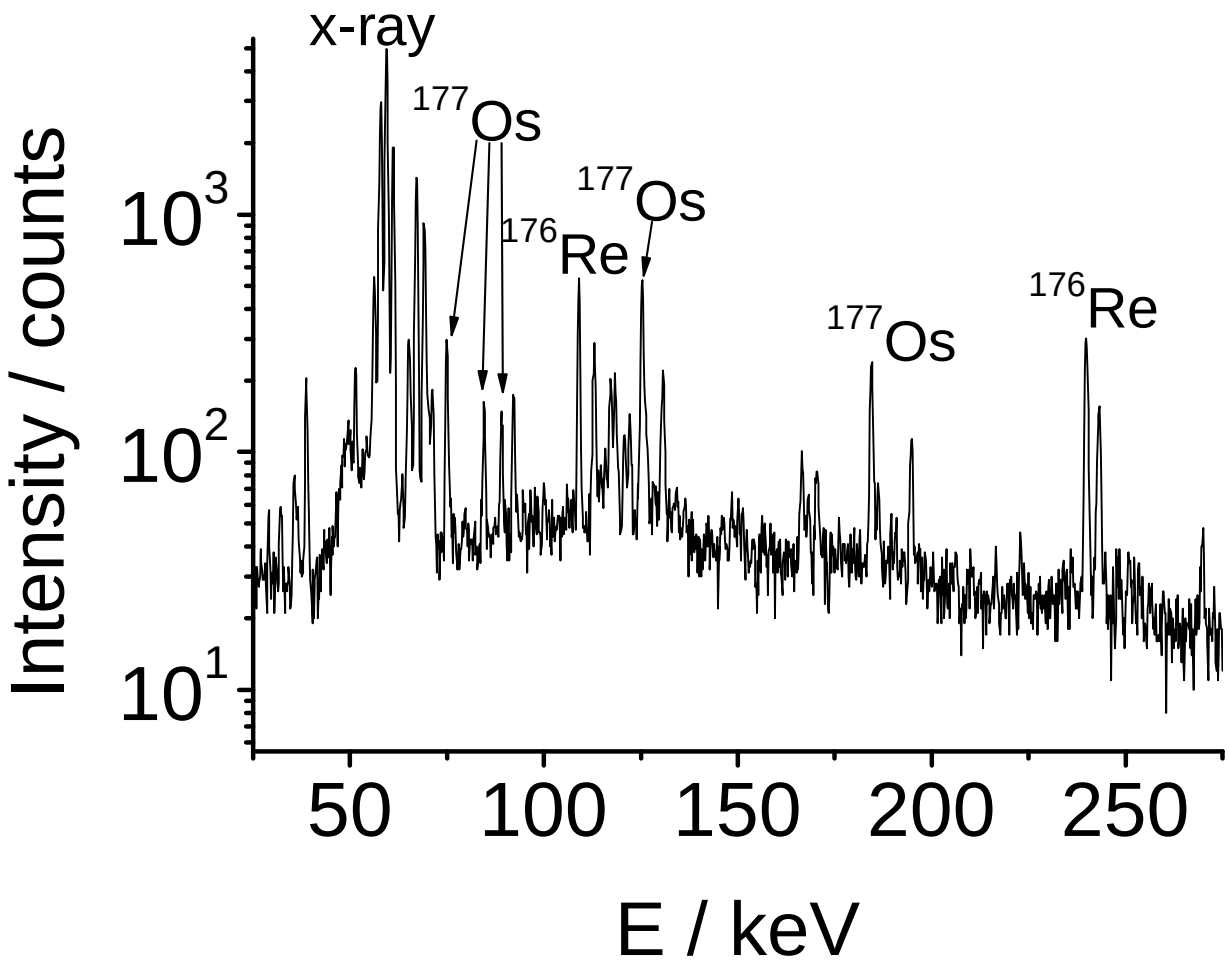
$^{nat}Ce(^{40}Ar,xn)^{\sim 176}Os$ without preseparation

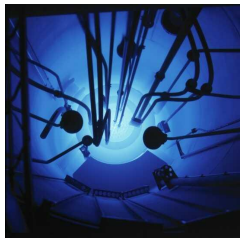


Experiment @ TASCA!!!!!

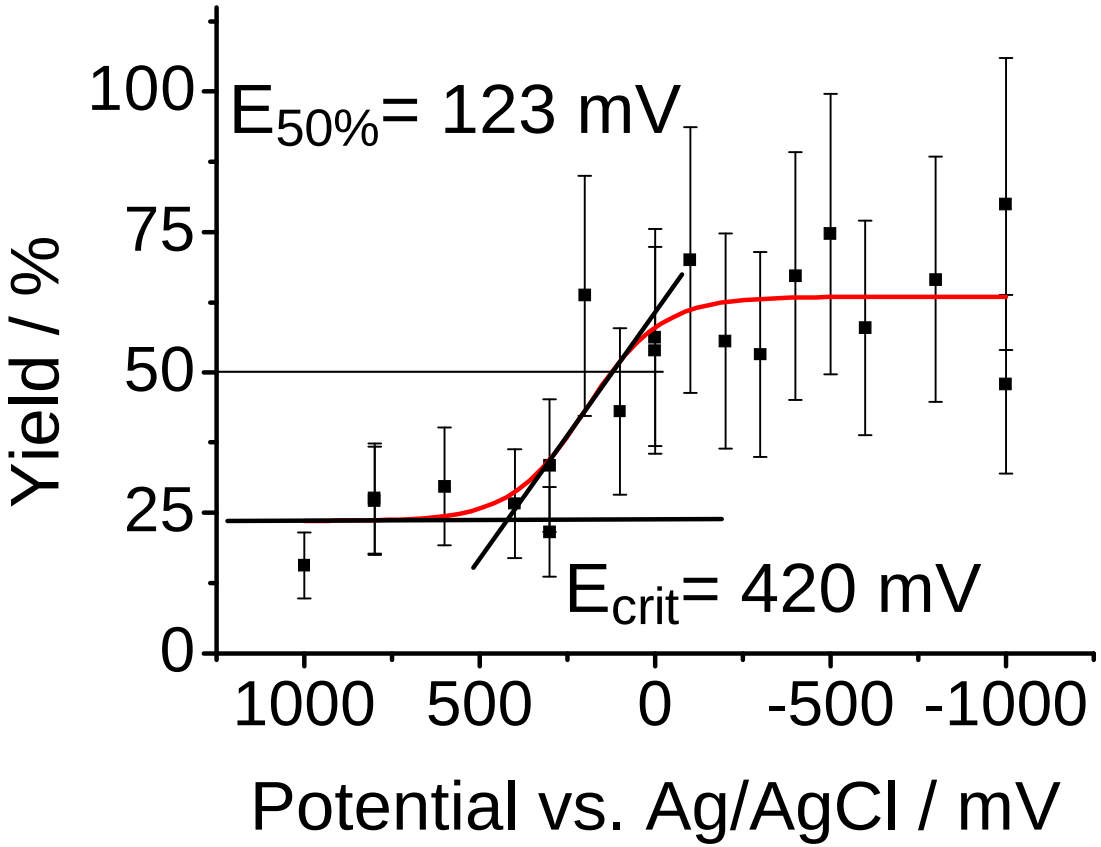


$^{nat}Ce(^{40}Ar,xn)^{\sim 176}Os$ behind TASCA



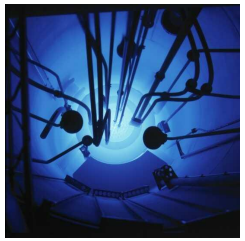


Deposition of Os on Pd

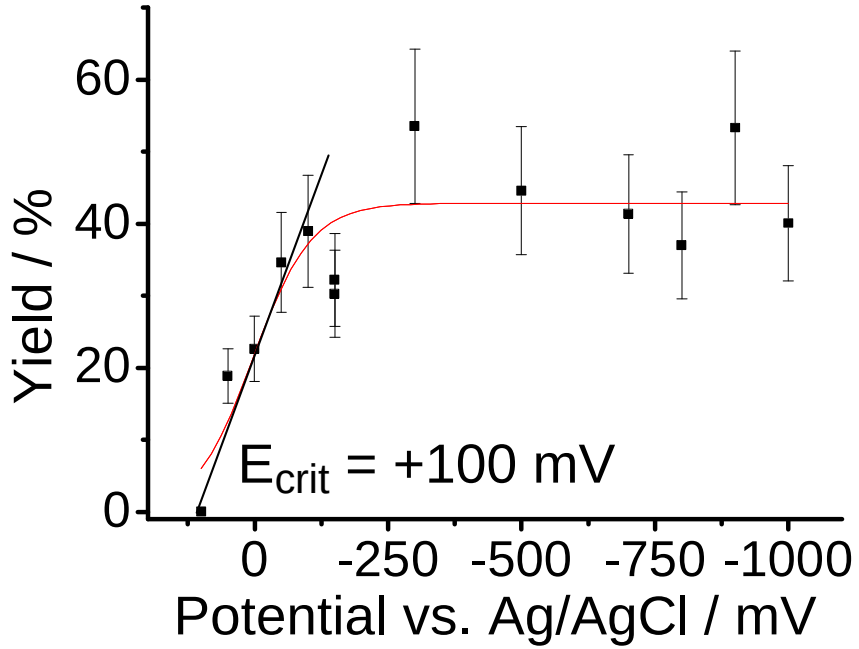


Conditions:

Pd electrodes
0.1 M HCl
71 °C
2 min

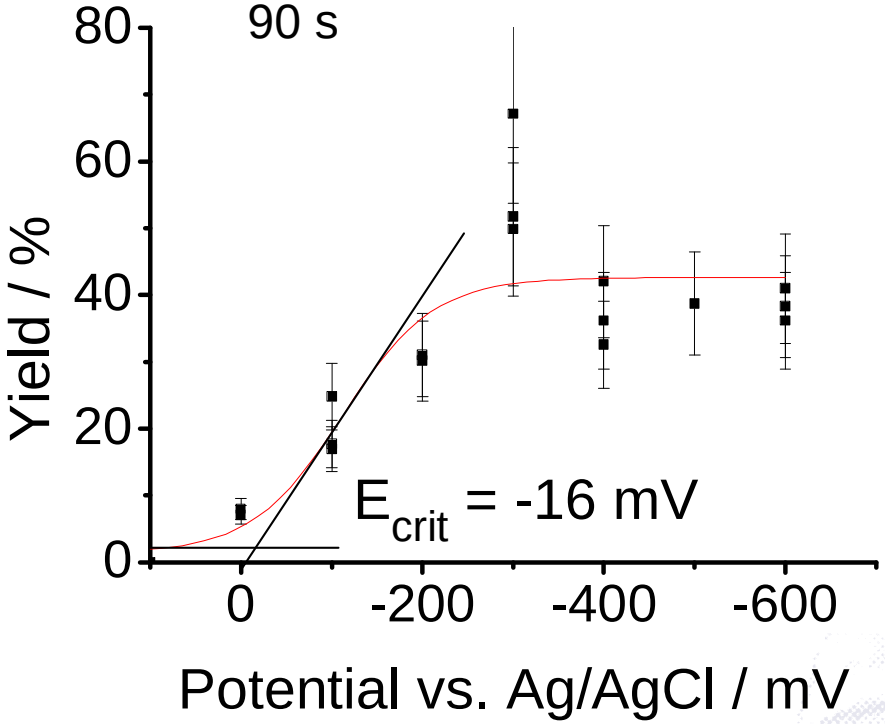


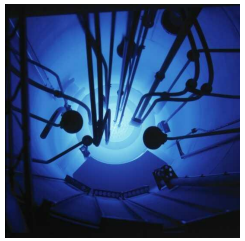
Deposition of Ru on Pd and Au



Pd-electrodes
0.1 M HCl
54 °C
90 s electrolysis time

Au-electrodes
0.1 M HCl
54 °C
90 s



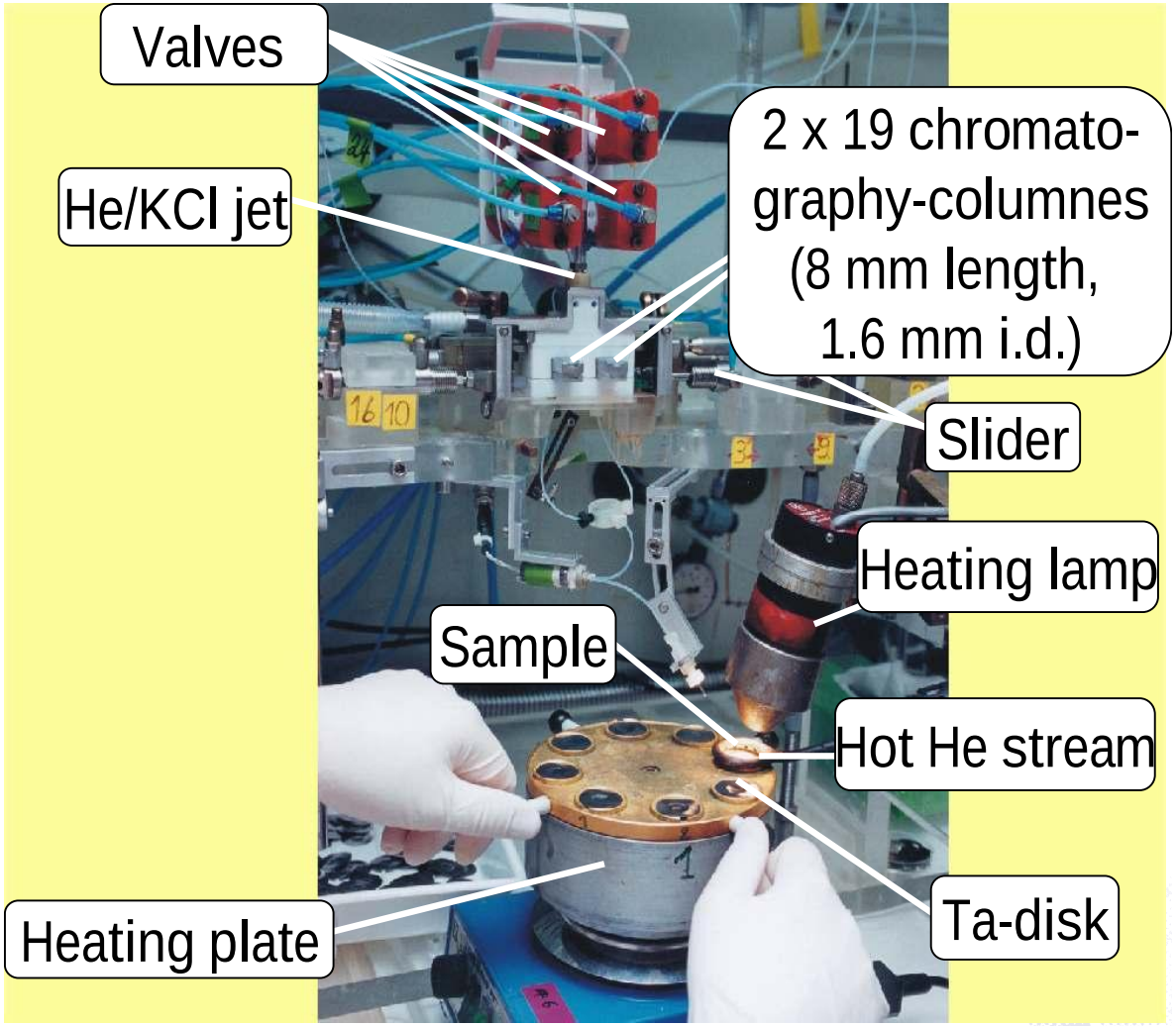


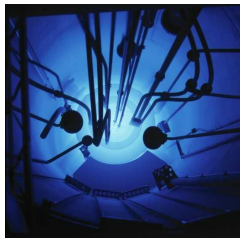
First TAN chemistry @ TASCA

Fluoride complexation of Rf

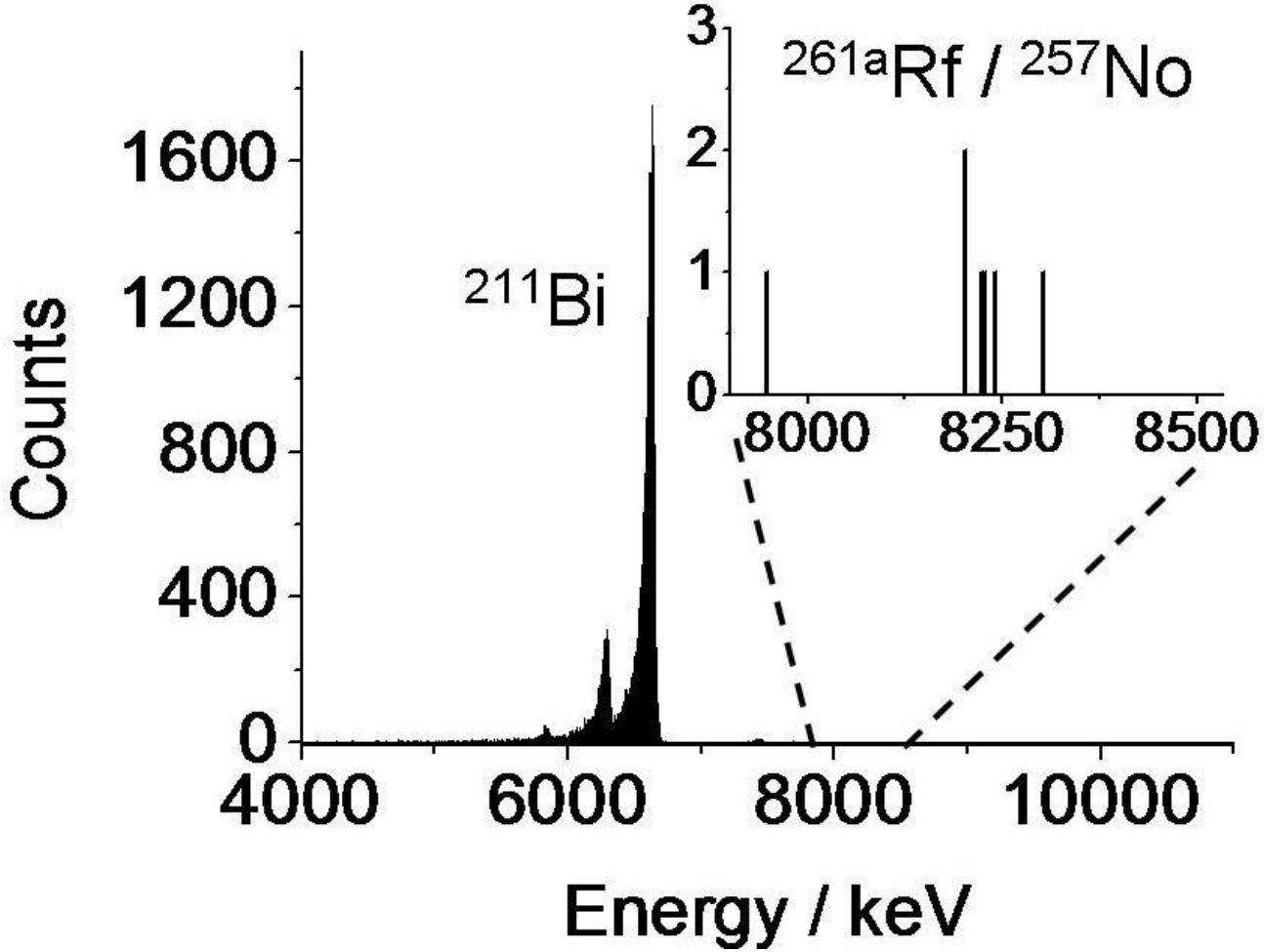
$^{244}Pu(^{22}Ne,5n)^{261a}Rf$
Anion exchanger (MCI GEL CA08Y - OH^- form)

1) Extraction with $7x10^{-4}$ M HF, stripping solution 5 M HNO_3
2) Extraction with $1x10^{-3}$ M HF, stripping solution 5 M HNO_3





Results of the ARCA experiment



- %ads ≥ 62.5 % in 7×10^{-4} M HF
- %ads ≥ 72.5 % in 1×10^{-3} M HF.

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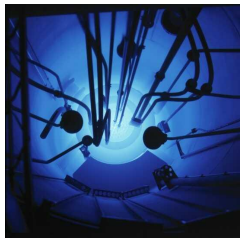
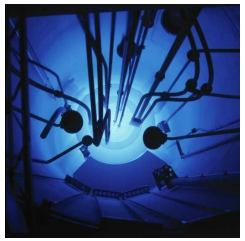
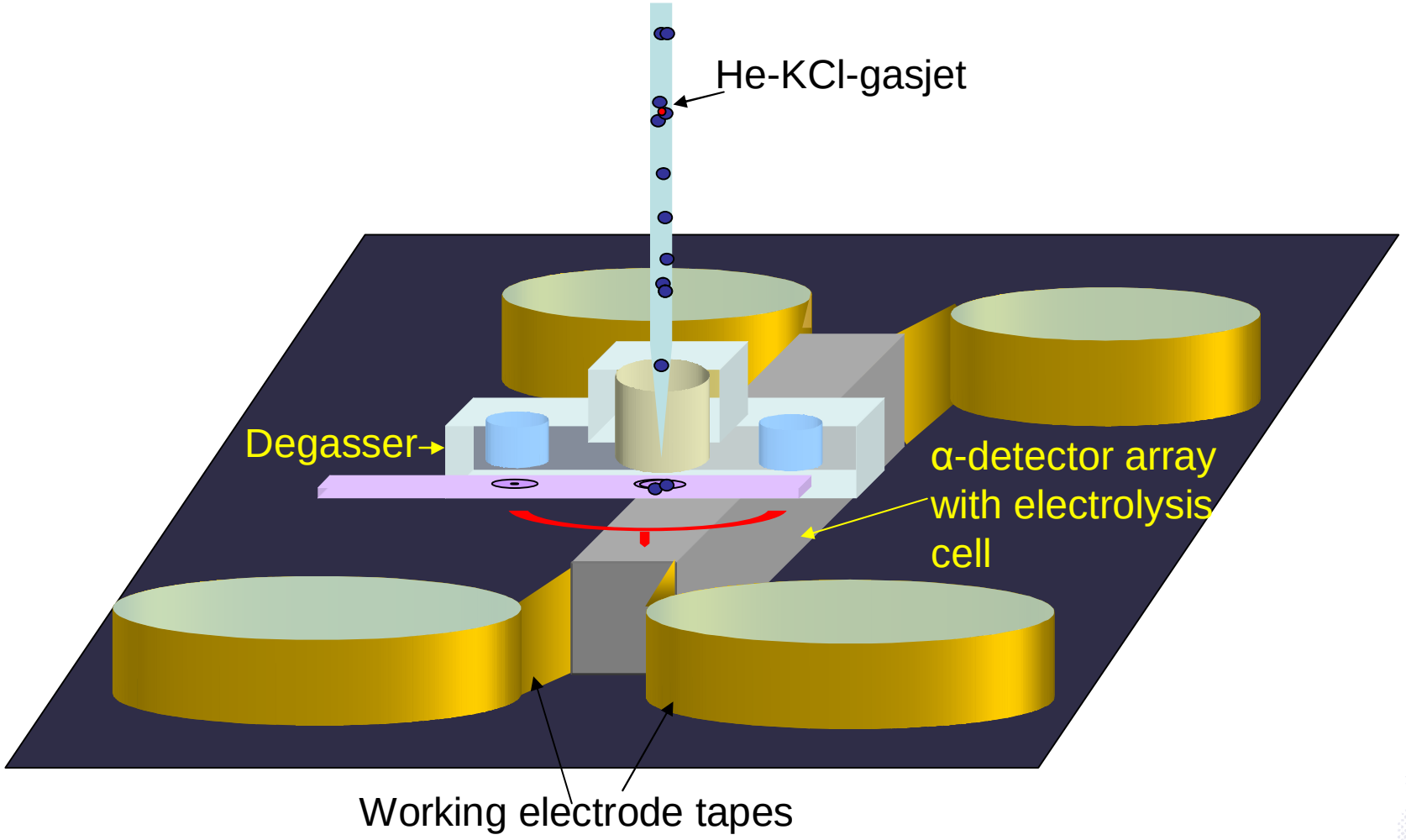


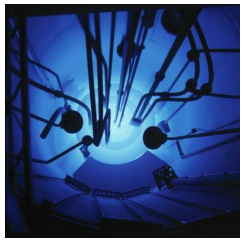
Requirement for an electrodeposition experiment with TANs

- Physical preseparation
- Fully automated setup
- Reproducible electrode surface
- Small dead volume between degasser and electrolysis cell
- Small electrolyte volume
- Constant, elevated temperature
- Constant stirring
- Fast transport of the samples in front of the Si detectors
- High detection efficiency

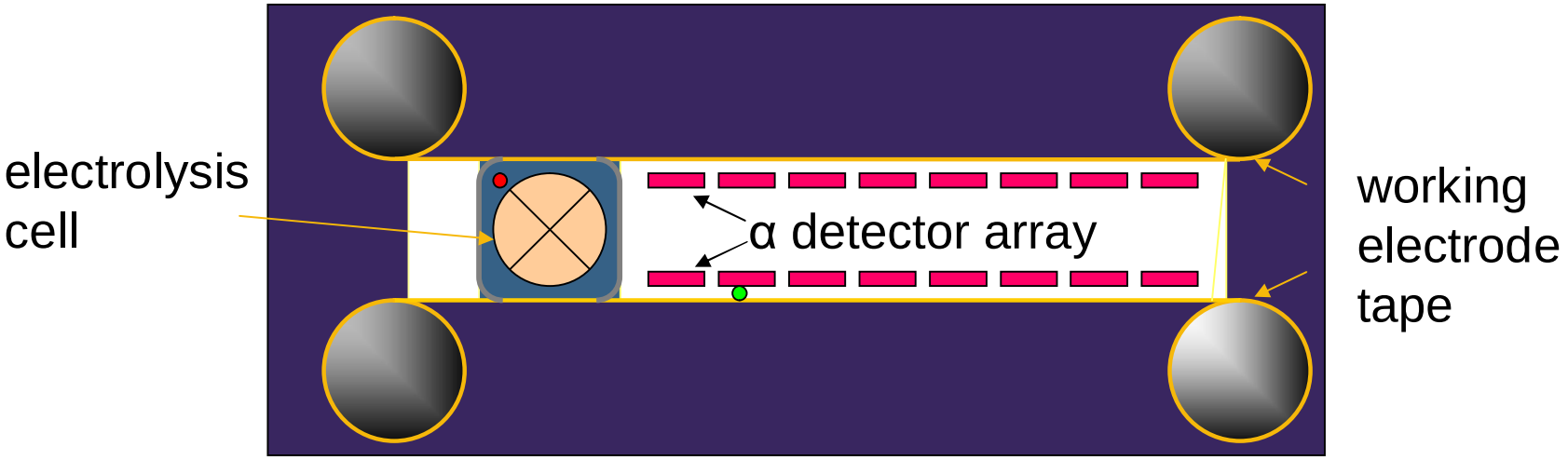


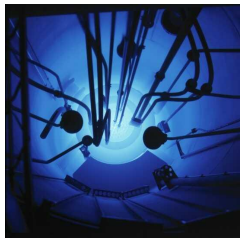
ELCH - ELectroCHemistry apparatus





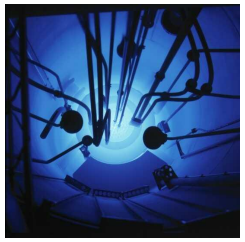
ELCH - ELectroCHemistry apparatus





Summary and outlook

- The advantage of physical preseparation has been demonstrated
- TASCA is ready for TAN chemistry
- Pd and Au seem to be the best electrode materials for underpotential deposition of group 8 elements
- A new apparatus for automated electrolysis experiment - ELCH - is developed and will be tested @ TASCA in the next year



Thanks to...

- The mechanical and electronical workshops at the institute of nuclear chemistry at the University Mainz
- The operators of the TRIGA reactor in Mainz and the operators of the UNILAC at GSI
- The whole TASCA community
- The BMBF for the financial support

Thank you for your attention!