Chemistry of superheavy elements

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Konferencja Przyszłość fizyki jądrowej niskich energii w Polsce a rozwój krajowej infrastruktury badawczej

Środowiskowe Laboratorium Ciężkich Jonów UW
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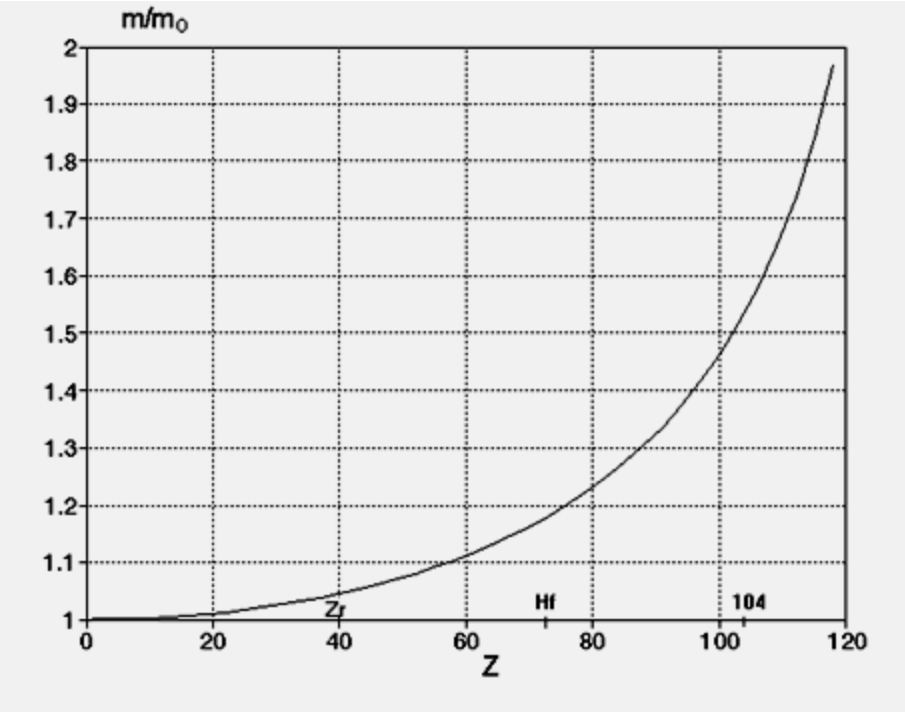
Why we study super-heavy elements?

- How many elements can exist? chemical restrictions
- How relativistic effects can affect the chemical properties of elements
- Construction of the periodic table

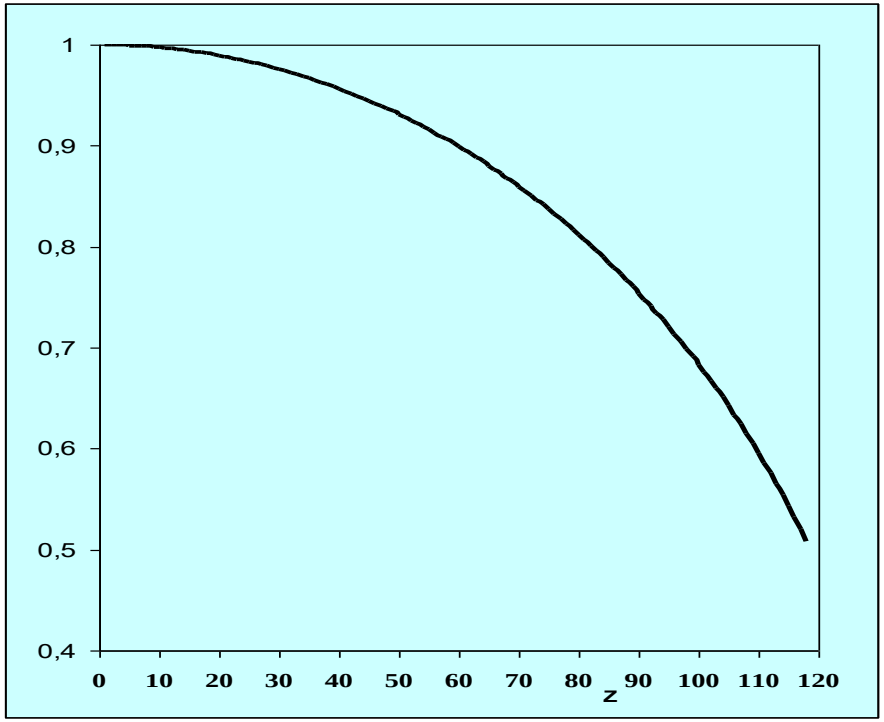
$$\langle V_r \rangle = \frac{Z}{137{,}035}\, c$$ **orbital 1s**

$$m = \frac{m_0}{\sqrt{1-\left(\frac{v}{c}\right)^2}}$$

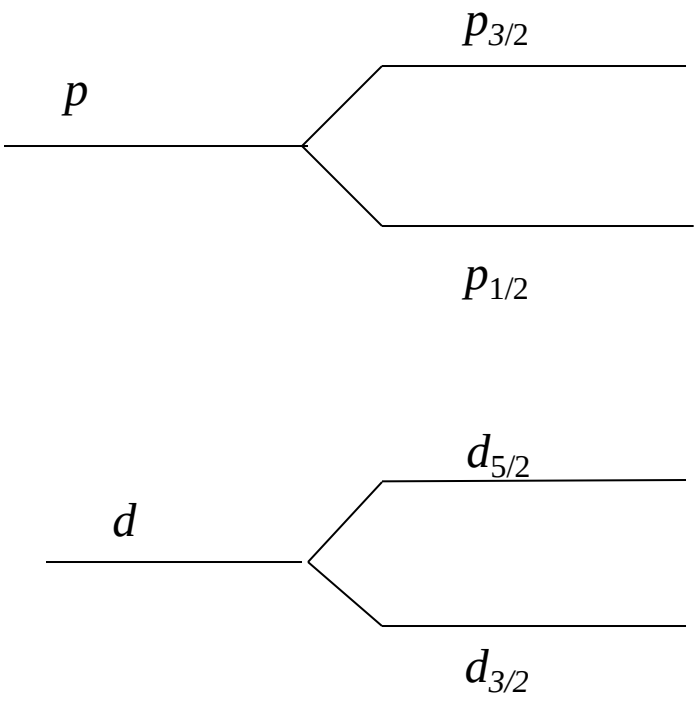
$$r_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$



<r1s>rel/<r1s>



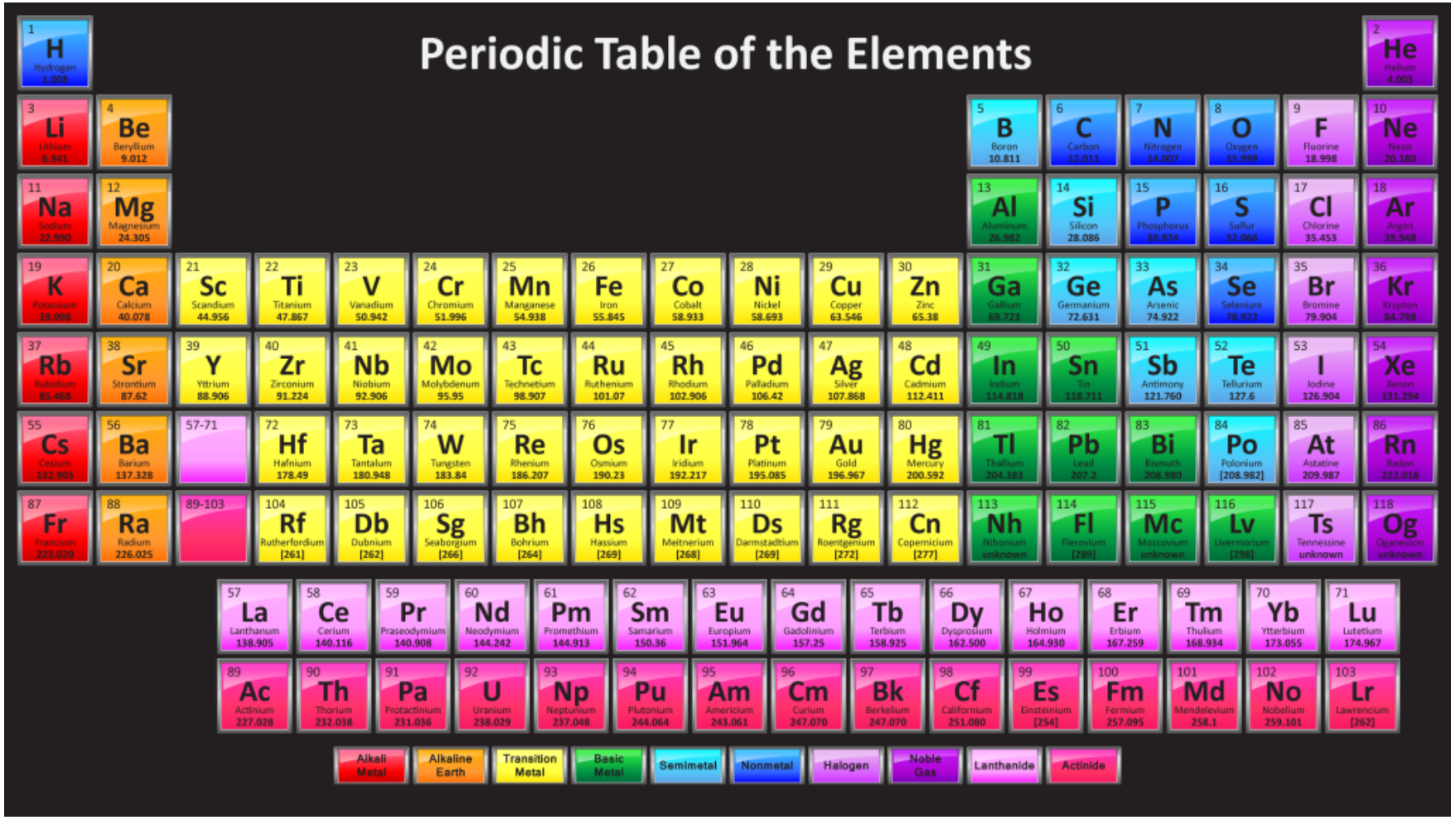
spin-orbital coupling



Relativistic effects in chemistry

- Noble gold $[Xe]5d^{10}6s^{1}$
- Liquid mercury $[Xe]5d^{10}6s^{2}$
- Yellow color of gold and cesium
- Anion Au^{-}
- Low oxidation states
- Tl^{+} , $[Xe]5d^{10}6s^{2}6p_{1/2}$
- Pb^{2+}, $[Xe]5d^{10}6s^{2}6p^{2}_{1/2}$
- Bi^{+}, $[Xe]5d^{10}6s^{2}6p^{2}_{1/2}6p_{3/2}$
- Po^{2+} $[Xe]5d^{10}6s^{2}6p^{2}_{1/2}6p^{2}_{3/2}$

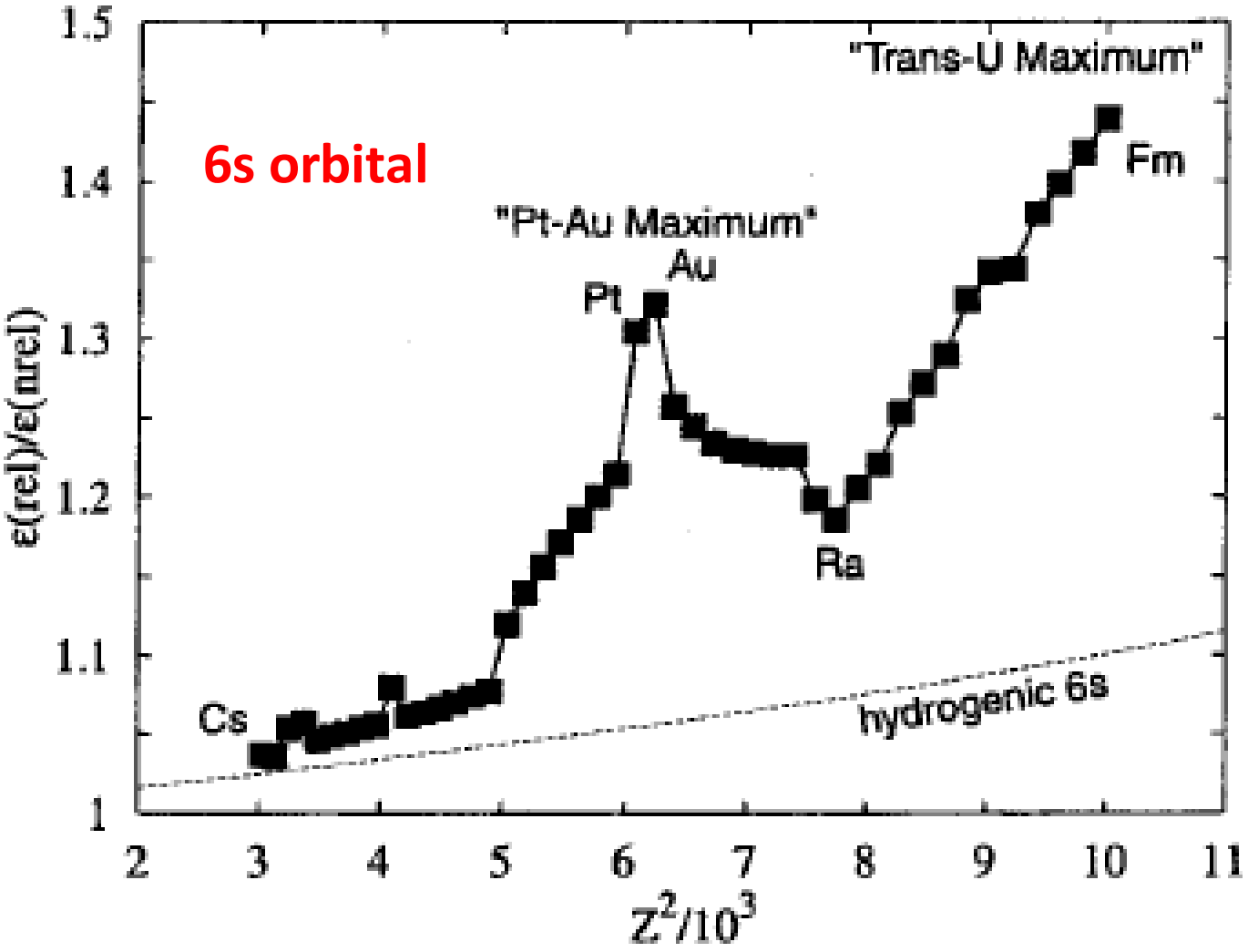
2018



Transaktynowce >103

Transfermowce > 100

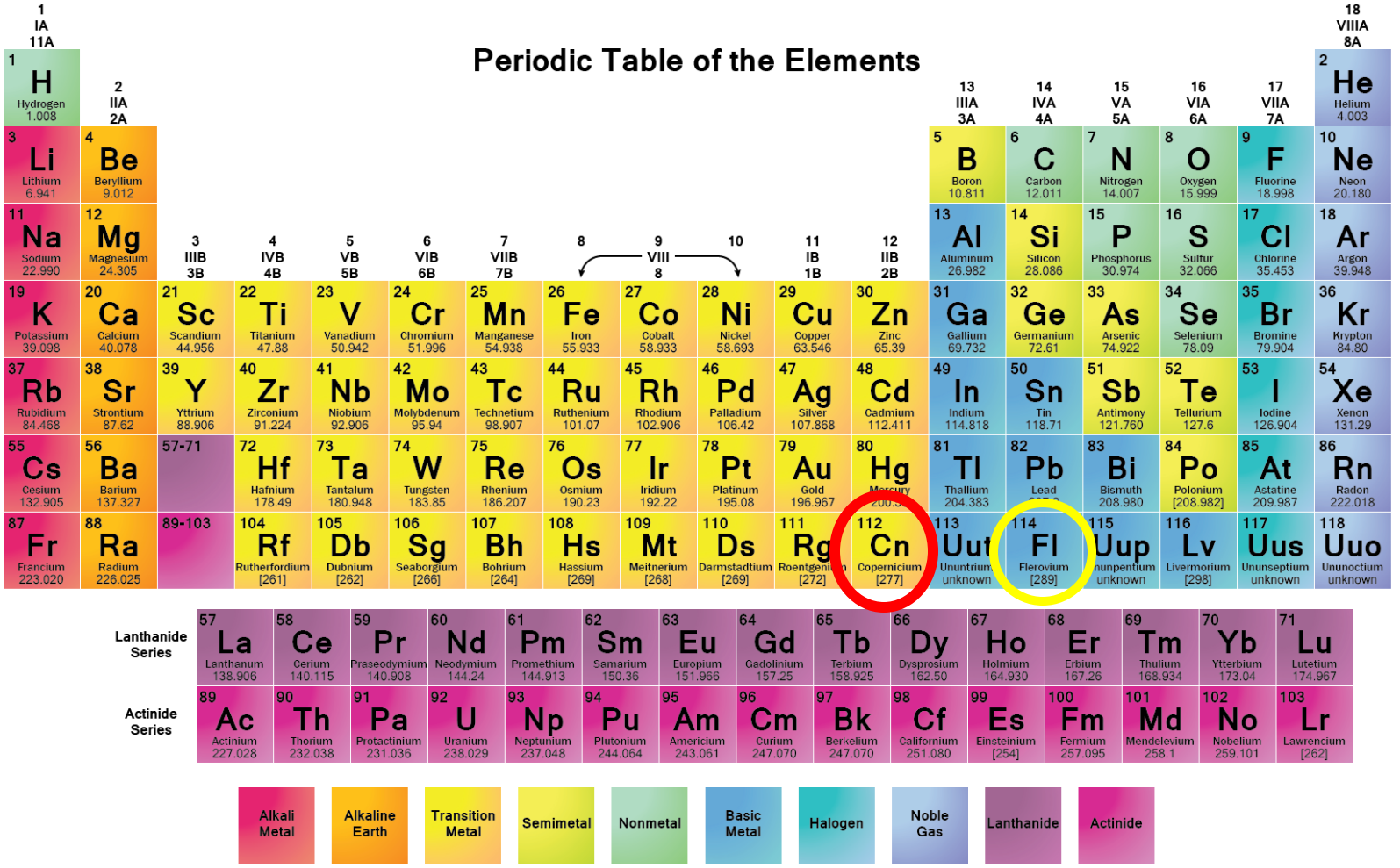
Superciężkie > 103

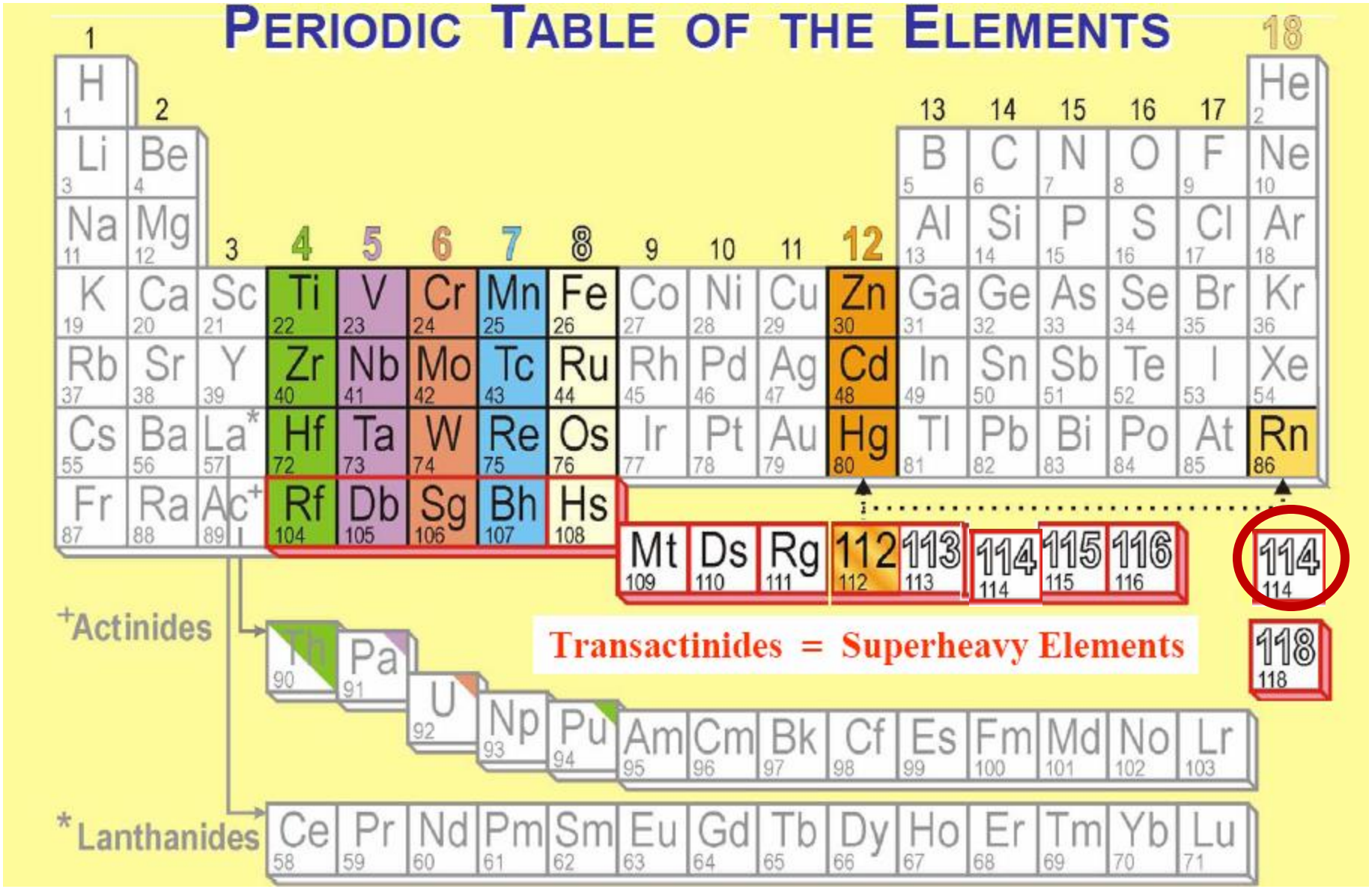


J Autschbach,S Siekierski, J.Coput.Chem. 23 (2002) 808.

Cn - $[Rn]\ 5f^{14}6d^{10}7s^{2}$

Fl - $[Rn]\ 5f^{14}6d^{10}7s^{2}7p_{1/2}{}^{2}$




PERIODIC TABLE OF THE ELEMENTS
1 H 1
2 Li 3 Be 4
Na 11 Mg 12
3 4 5 6 7 8 9 10 11 12
13 14 15 16 17 18
B 5 C 6 N 7 O 8 F 9 He 2 Ne 10
Al 13 Si 14 P 15 S 16 Cl 17 Ar 18
K 19 Ca 20 Sc 21 Ti 22 V 23 Cr 24 Mn 25 Fe 26 Co 27 Ni 28 Cu 29 Zn 30 Ga 31 Ge 32 As 33 Se 34 Br 35 Kr 36
Rb 37 Sr 38 Y 39 Zr 40 Nb 41 Mo 42 Tc 43 Ru 44 Rh 45 Pd 46 Ag 47 Cd 48 In 49 Sn 50 Sb 51 Te 52 I 53 Xe 54
Cs 55 Ba 56 La* 57 Hf 72 Ta 73 W 74 Re 75 Os 76 Ir 77 Pt 78 Au 79 Hg 80 Tl 81 Pb 82 Bi 83 Po 84 At 85 Rn 86
Fr 87 Ra 88 Ac+ 89 Rf 104 Db 105 Sg 106 Bh 107 Hs 108
Mt 109 Ds 110 Rg 111 112 112 113 113 114 114 115 115 116 116
114 114
118 118
+Actinides
Th 90 Pa 91 U 92 Np 93 Pu 94 Am 95 Cm 96 Bk 97 Cf 98 Es 99 Fm 100 Md 101 No 102 Lr 103
*Lanthanides
Ce 58 Pr 59 Nd 60 Pm 61 Sm 62 Eu 63 Gd 64 Tb 65 Dy 66 Ho 67 Er 68 Tm 69 Yb 70 Lu 71
Transactinides = Superheavy Elements

Rutherfordium	^{267}Rf	2.5 hours
Dubnium	^{268}Db	29 hours
Seaborgium	^{269}Sg	14 minutes
Bohrium	^{270}Bh	1 minute
Hassium	^{270}Hs	10 seconds
Meitnerium	^{278}Mt	7.6 seconds
Darmstadtium	^{281}Ds	9.6 seconds
Roentgenium	^{282}Rg	1.6 minutes
Copernicium	^{285}Cn	29 seconds
Nihonium	^{286}Nh	9.5 seconds
Flerovium	^{289}Fl	1.9 seconds
Moscovium	^{290}Mc	650 milliseconds
Livermorium	^{293}Lv	57 milliseconds
Tennessine	^{294}Ts	51 milliseconds
Oganesson	^{294}Og	0.69 milliseconds[1]

Criteria for chemical studies to be carried out on a transactinide,

- at least four atoms must be produced,
- the half-life of the isotope must be at least 1 second,
- rate of production must be at least one atom per week.

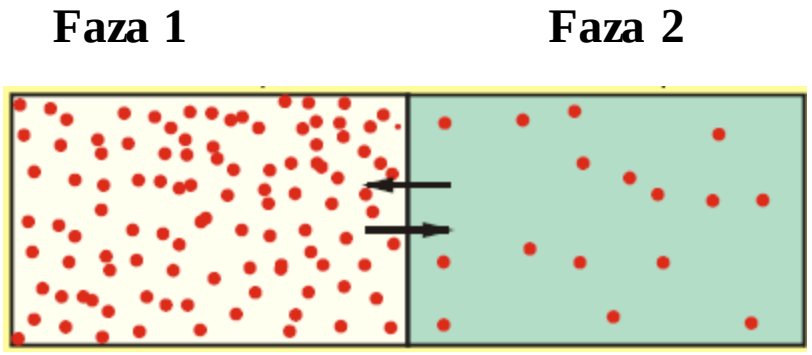
Partition

technique

Solid state– gas

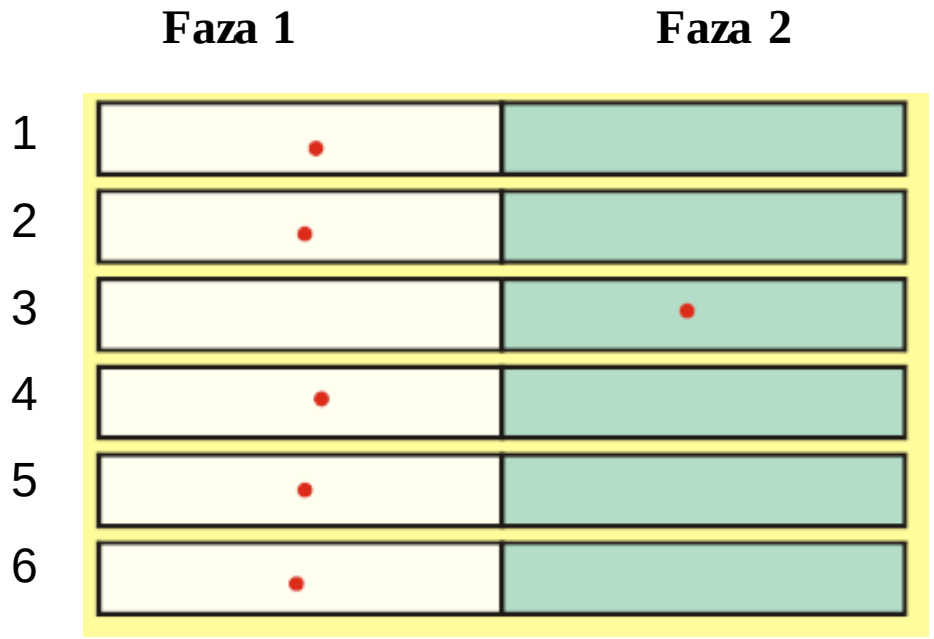
liquid – liquid

liquid – solid state



Classical system

$$K_d = \frac{C_{F1}}{C_{F2}} = \mathbf{5}$$



$K_d = \infty$

$K_d = \infty$

$K_d = 0$

$K_d = \infty$

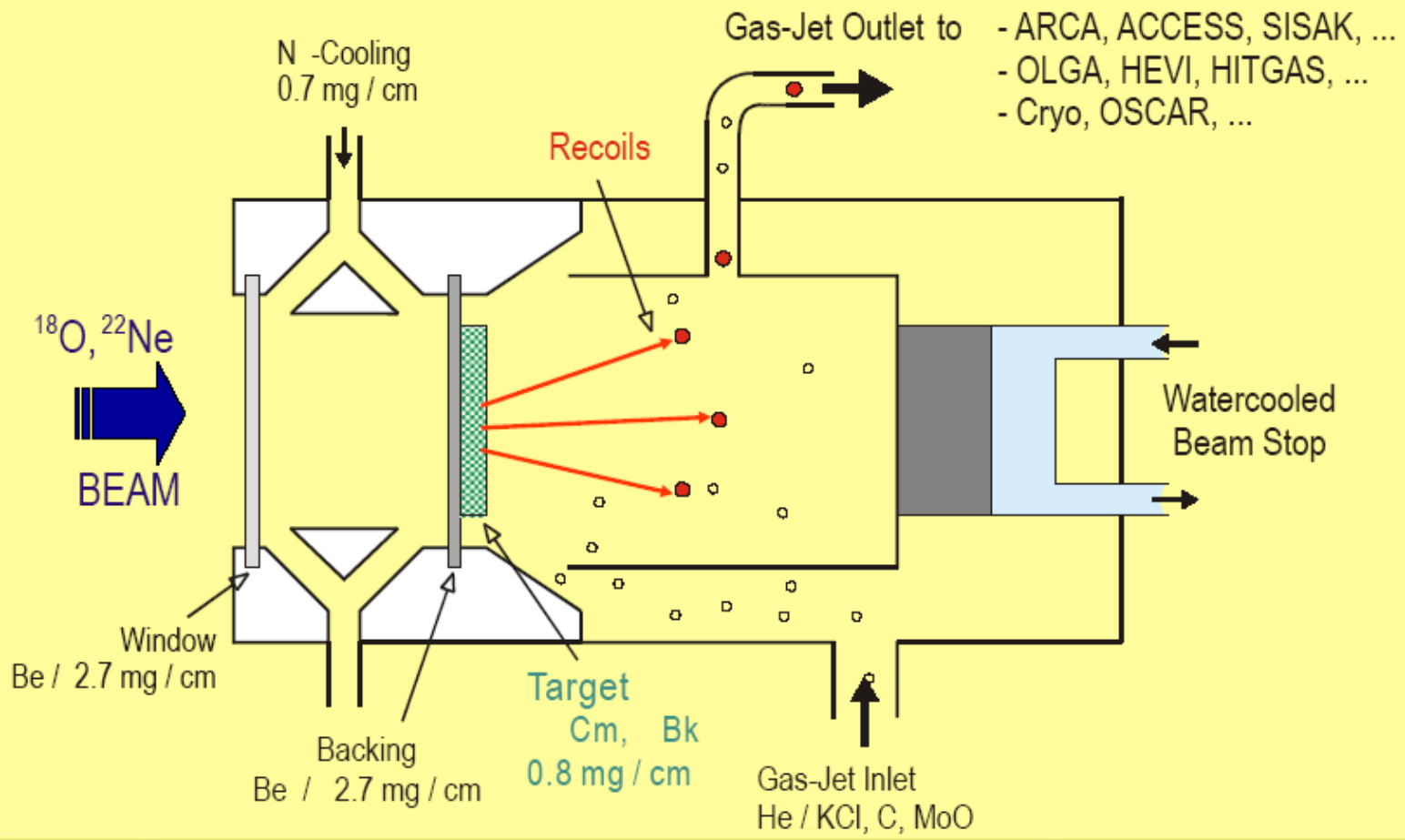
$K_d = \infty$

$K_d = \infty$

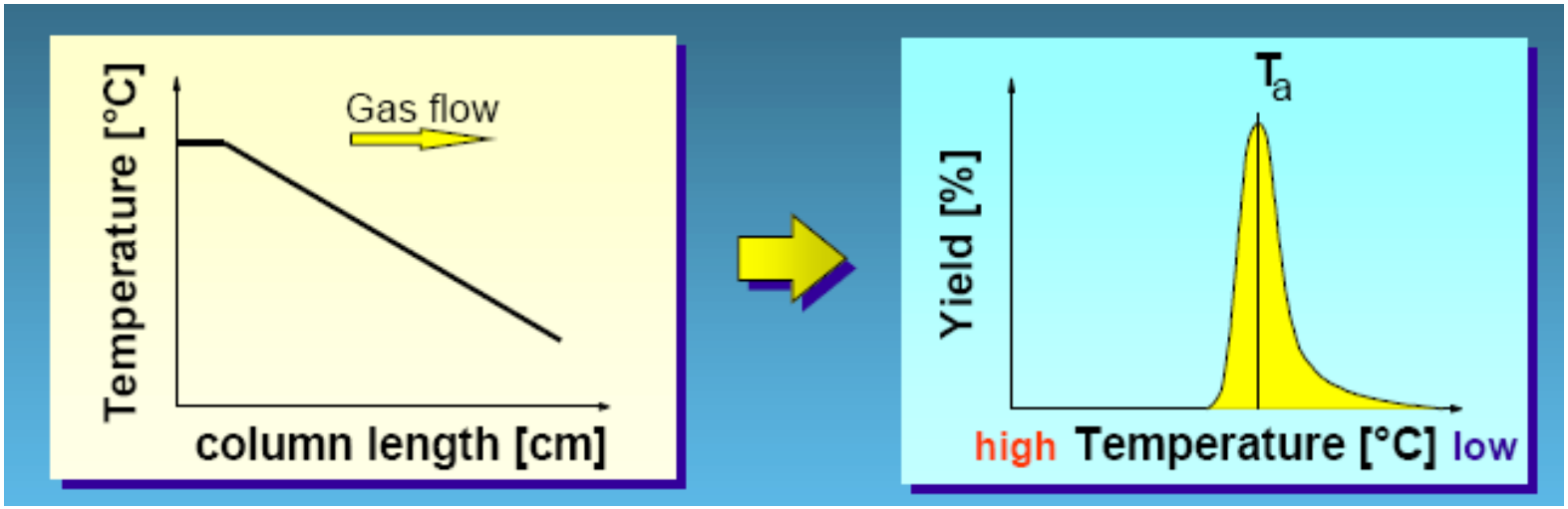
One atom chemistry

$K_d = 5$

Techniki badań



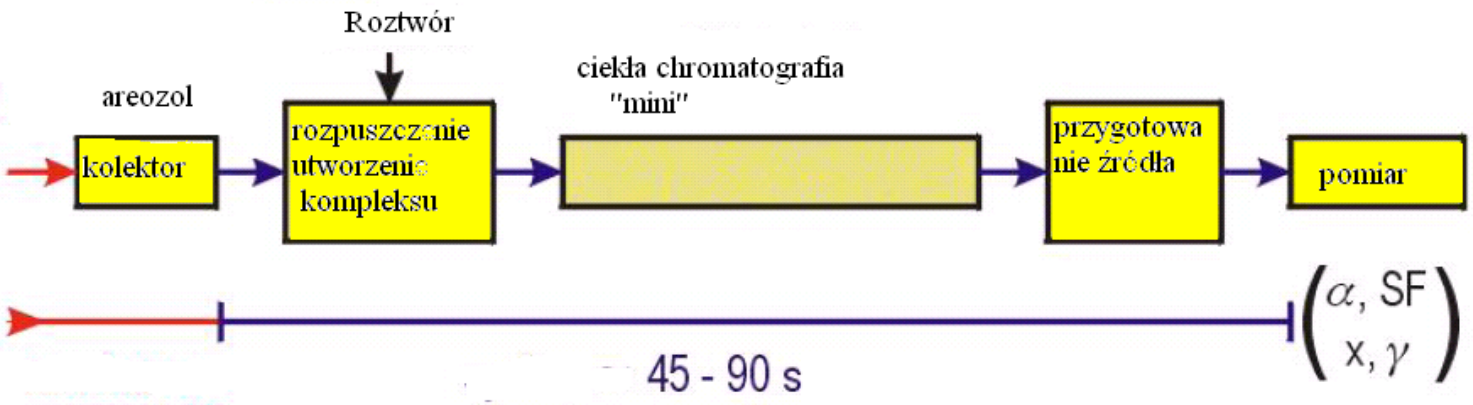
Termochromatography



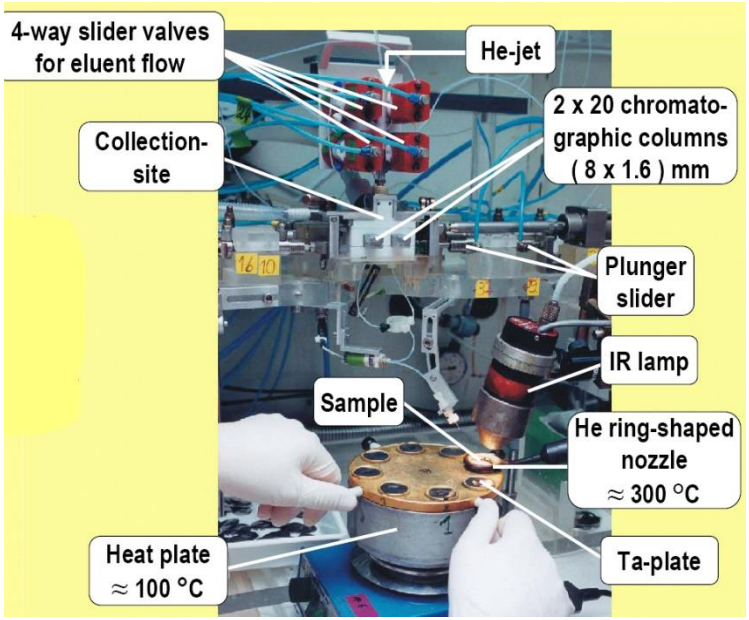
Liquid chromatography

ARCA Rf - Sg

AIDA Rf

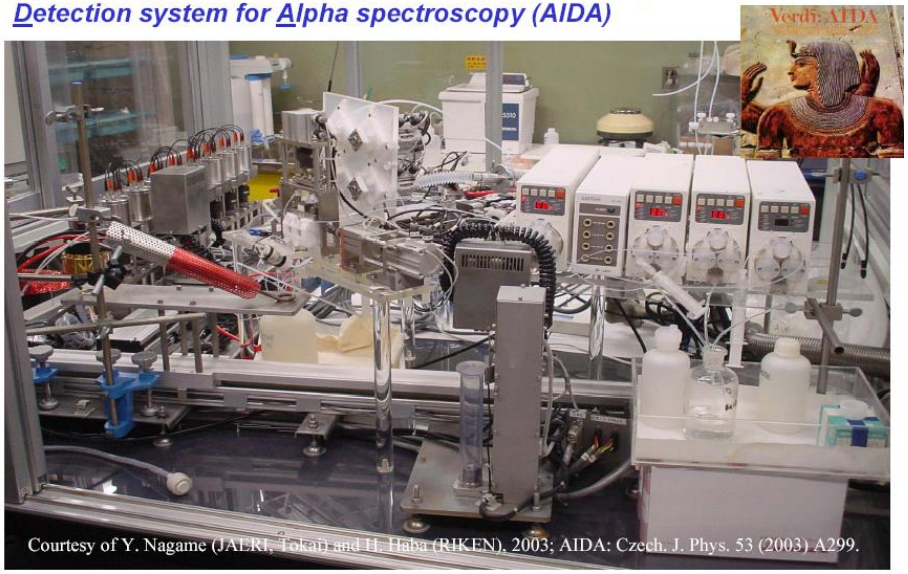


A R C A



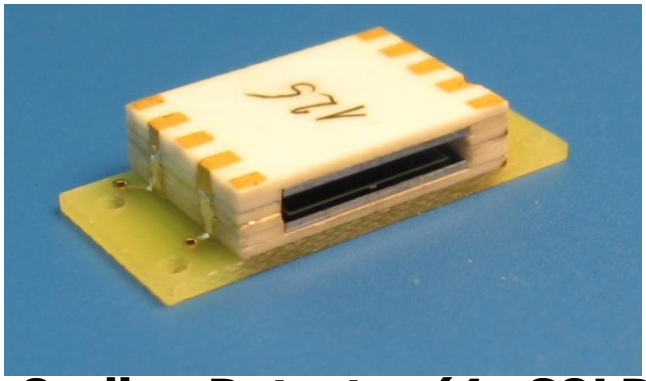
A I D A

Automated Ion exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA)



The Cn and Fl experiments

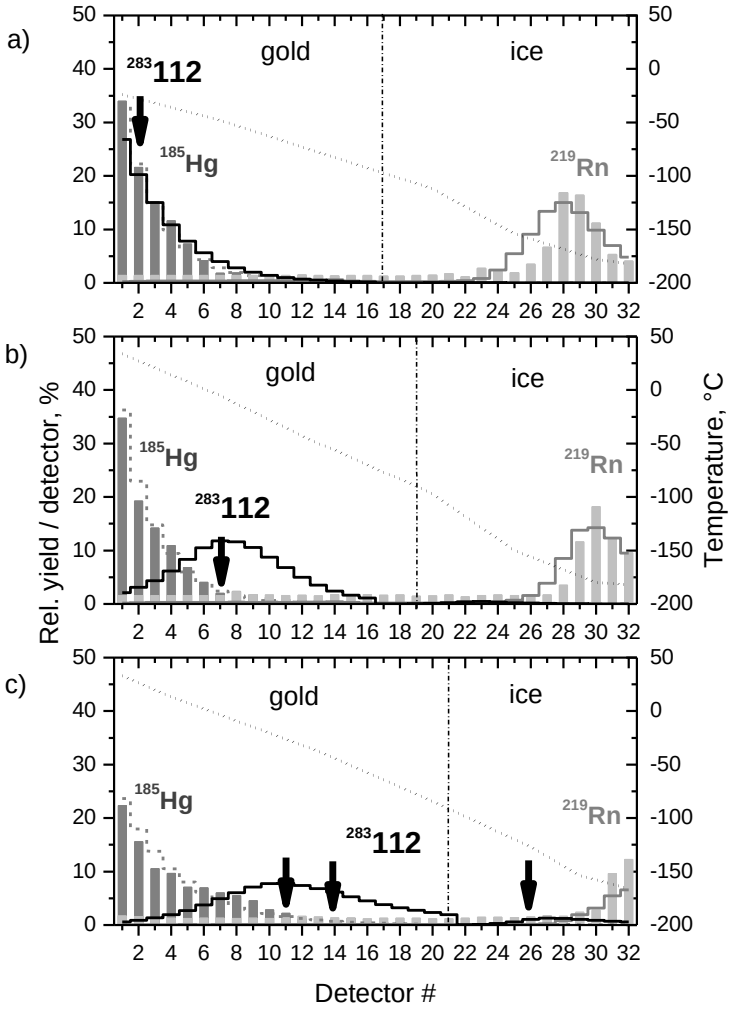
^{242}Pu (^{48}Ca,3n)^{287}Fl - 3.5 pb



Cryo On-line Detector (4π COLD)

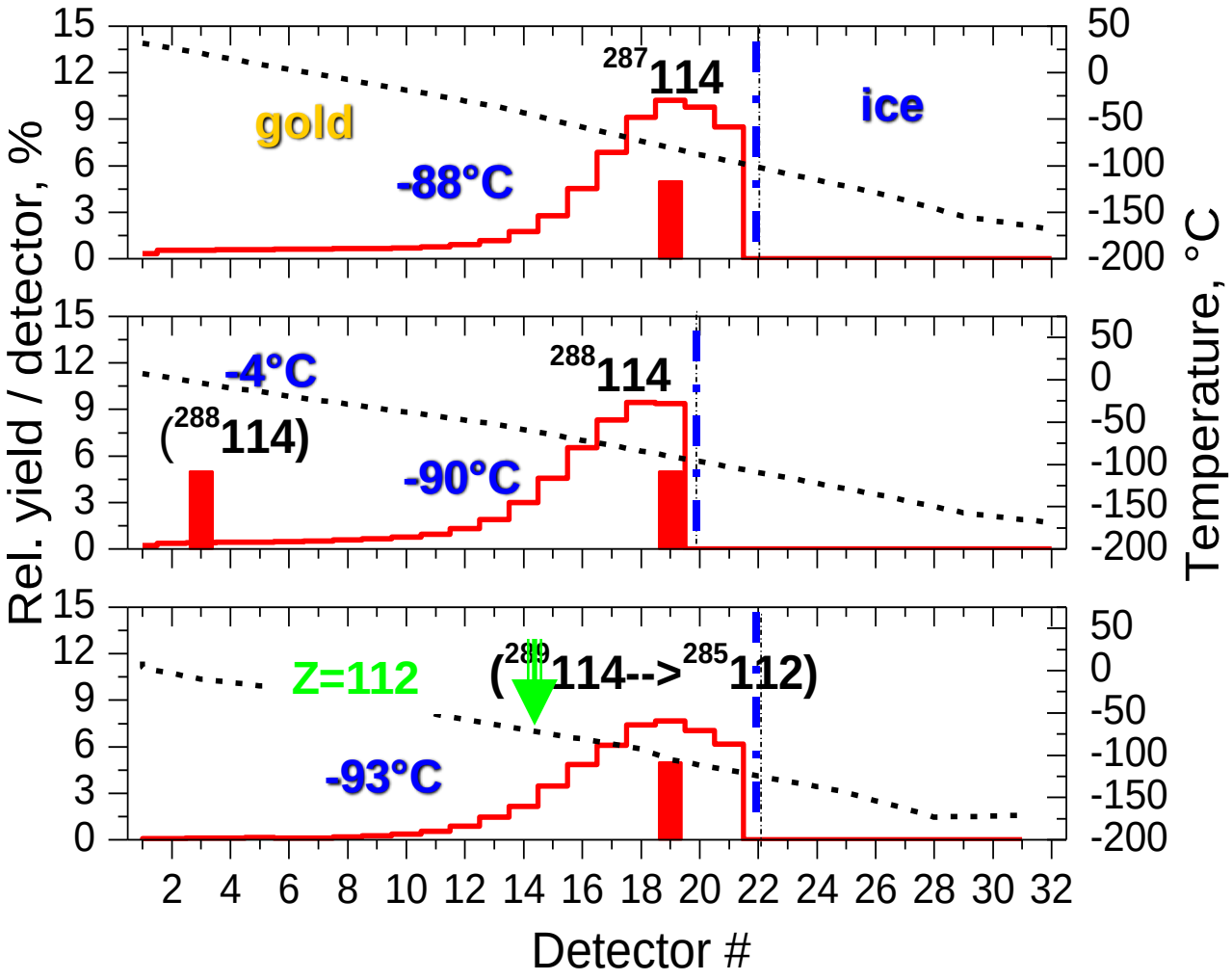
(32 pairs PIN diodes, one side gold covered)

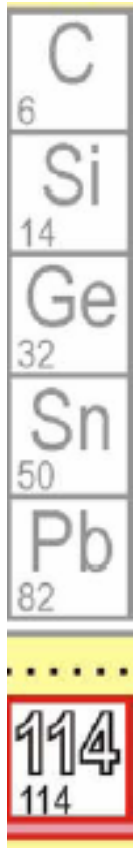
Adsorption of Cn on gold surface



Cn is similar to Hg but more volatile

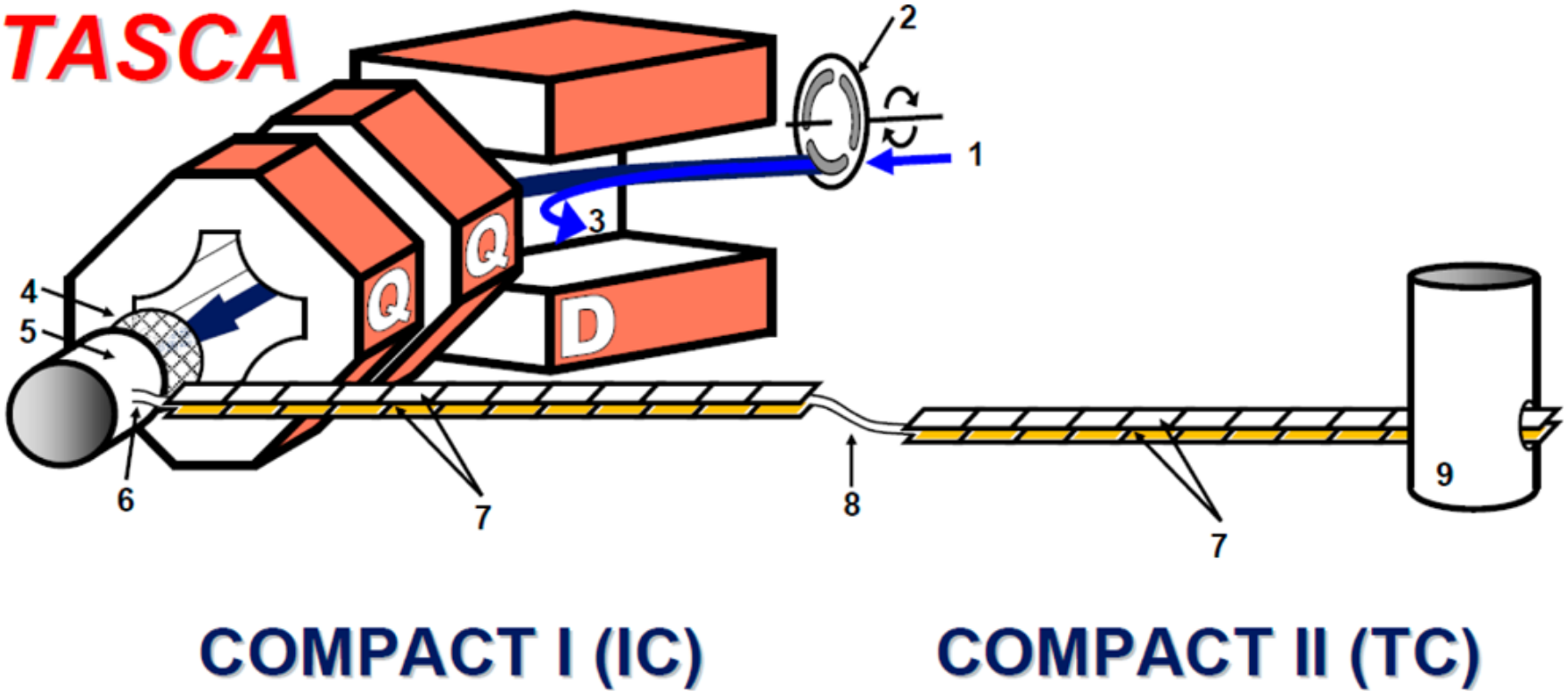
R.Eichler et al. Nature 447 (2007) 72–75





A. Yakushev et al. Inorg. Chem. 2014, 53, 1624−1629

Fl gas chemistry



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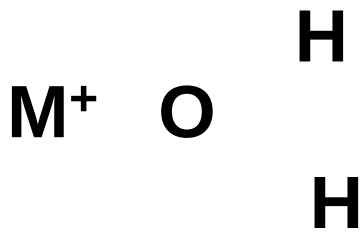
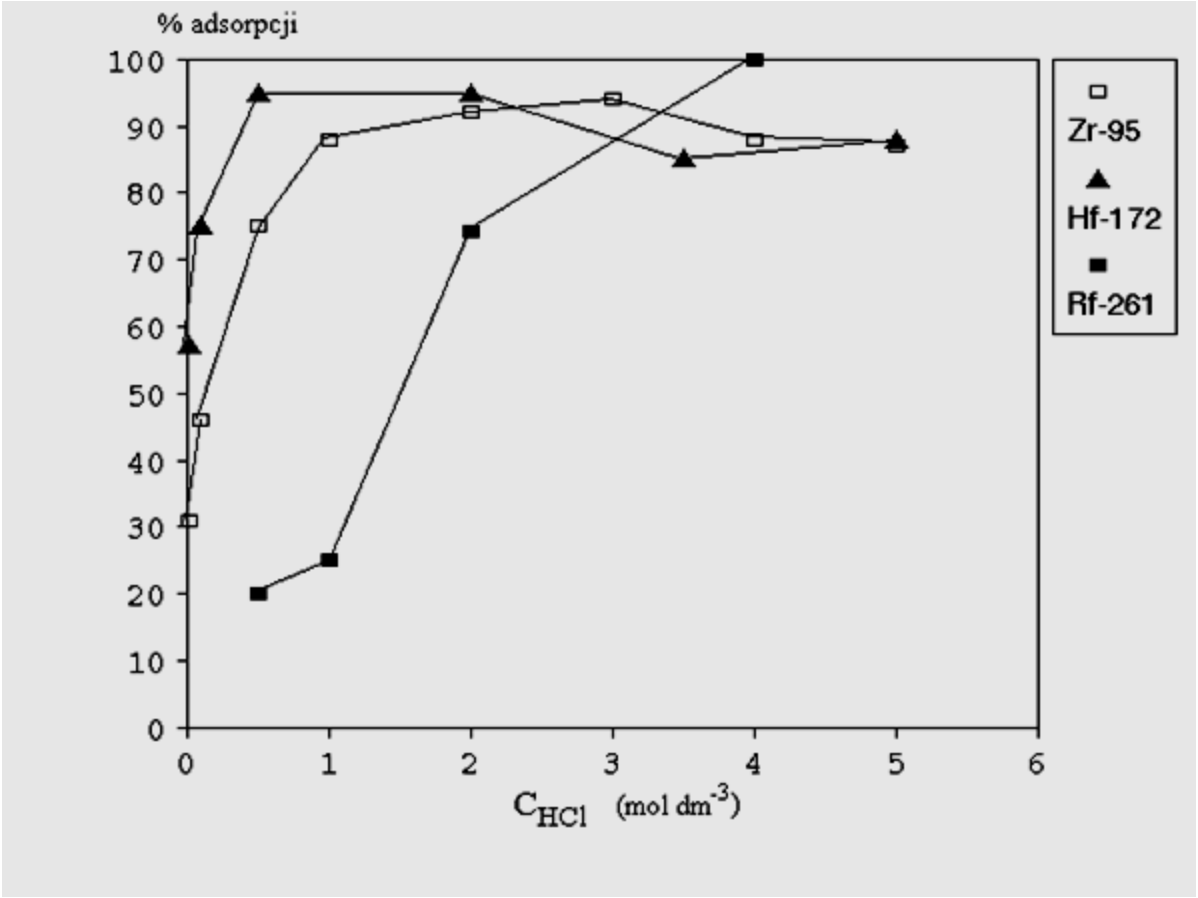


Ionic radius - r_j

$Rf^{4+} > Hf^{4+} > Zr^{4+} > Ti^{4+}$



Hydrolysis in Group 4 Ti>Rf>Zr>Hf

Stałe hydrolizy

Grupa 11

kation	r_i, pm	pK_{1h}
Cu^{+}	77	-
Ag^{+}	115	12
Au^{+}	137	3.8

Grupa 12

kation	r_i, pm	pK_{1h}
Zn^{2+}	74	8.96
Cd^{2+}	95	10.08
Hg^{2+}	102	3.40

Grupa 13

kation	r_i, pm	pK_{1h}
Ga^{3+}	62.0	3.6
In^{3+}	80.0	4.0
Tl^{3+}	88.5	0.6

Grupa 2

kation	**r_i (pm) (CN=8)**	**pK_{1h}**
Ca^{2+}	**112**	**13,22**
Sr^{2+}	**126**	**13,83**
Ba^{2+}	**142**	**14,07**
Ra^{2+}	**148**	**14,07**

Perspectives of SHE research in Poland

1. Studies on Cn^{2+} hydrolysis
2. Termochromatography studies of chelates Rf, Db, Fl
3. Electrochemical studies of Cn and Fl