Gas-phase chemistry of group 5 elements with bromine

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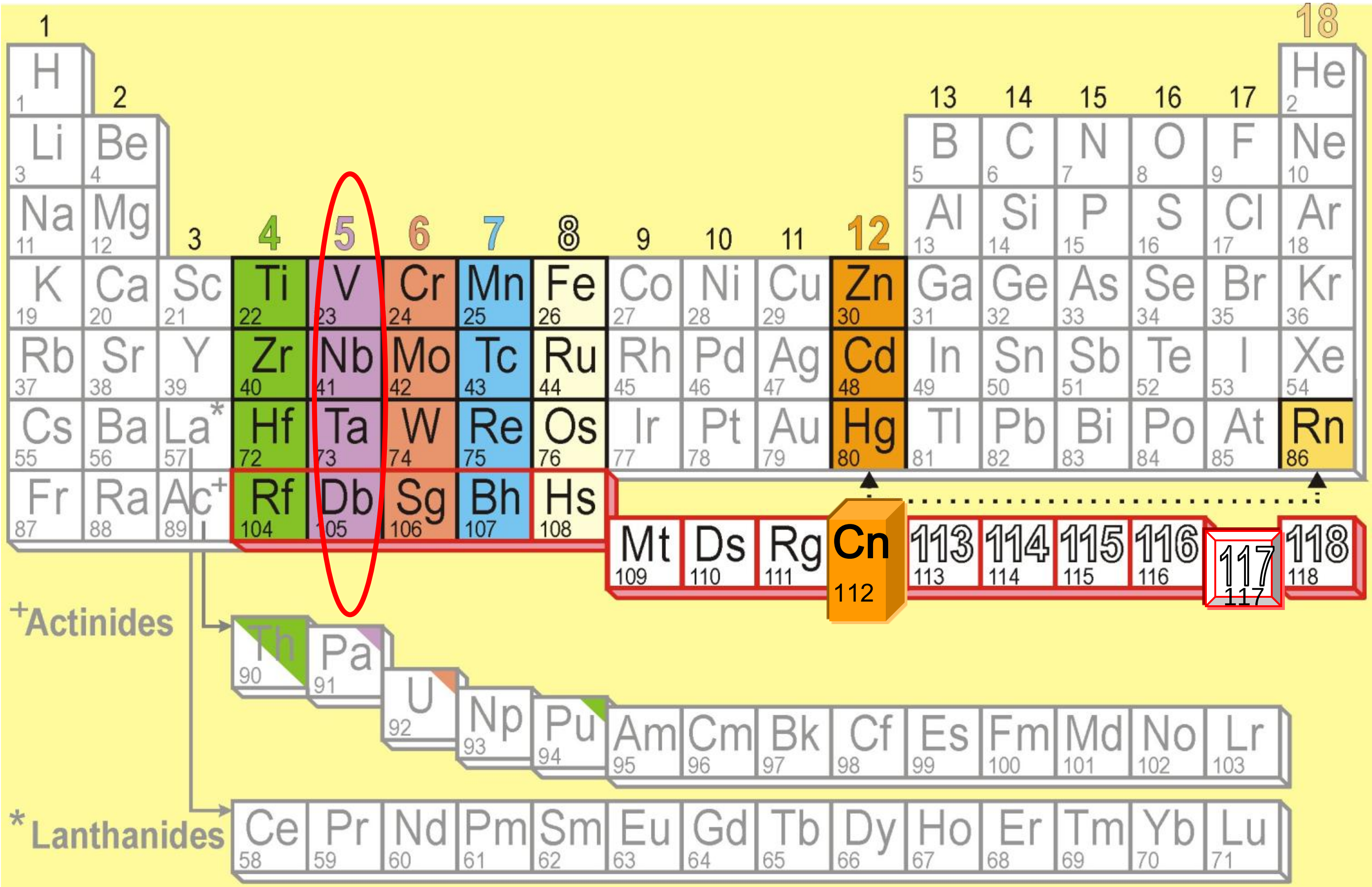
Outline

- Introduction
- Development of the isothermal chromatography at IMP
- Gas-phase chemistry of short-lived isotopes of ^{88}Nb and ^{170}Ta with HBr
- Isothermal chromatographic experiment with ^{258}Db
- Summary

Periodical table of elements



R. Eichler et al, NATURE, Vol.447(2007)72, *Chemical characterization of element 112*

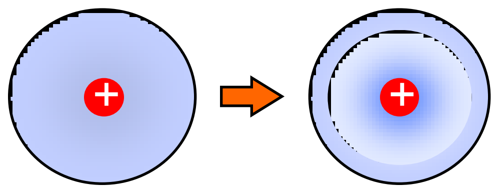
Oganessian et al., Phys. Rev. Lett. 104, 142502 (2010)

Synthesis of a New Element with Atomic Number Z=117

Relativistic effects on SHE

Direct effects

contraction and stabilization of $s_{1/2}$ and $p_{1/2}$ orbitals

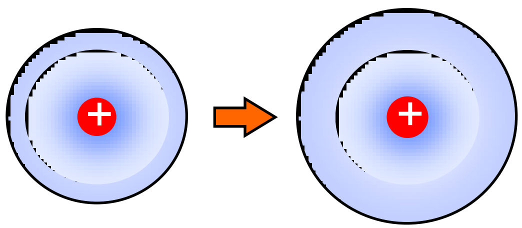


Mass increase
$$m = \frac{m_0}{\sqrt{1-(v/c)^2}}$$

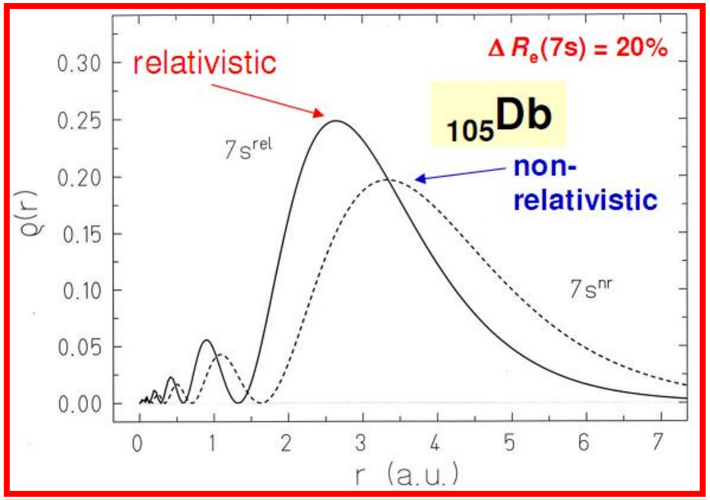
Bohr radii decrease
$$a_B = \frac{\hbar^2}{me^2} = a_B^0\sqrt{1-(v/c)^2}$$

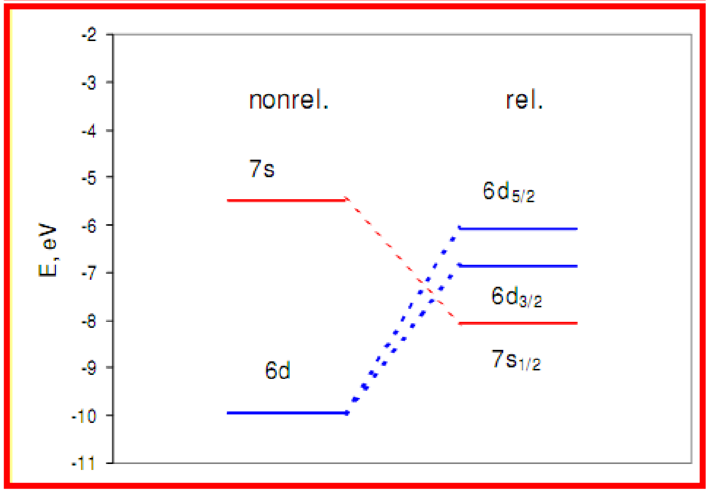
Indirect effects

expansion and destabilization of $p_{3/2}$ and $d_{3/2}$

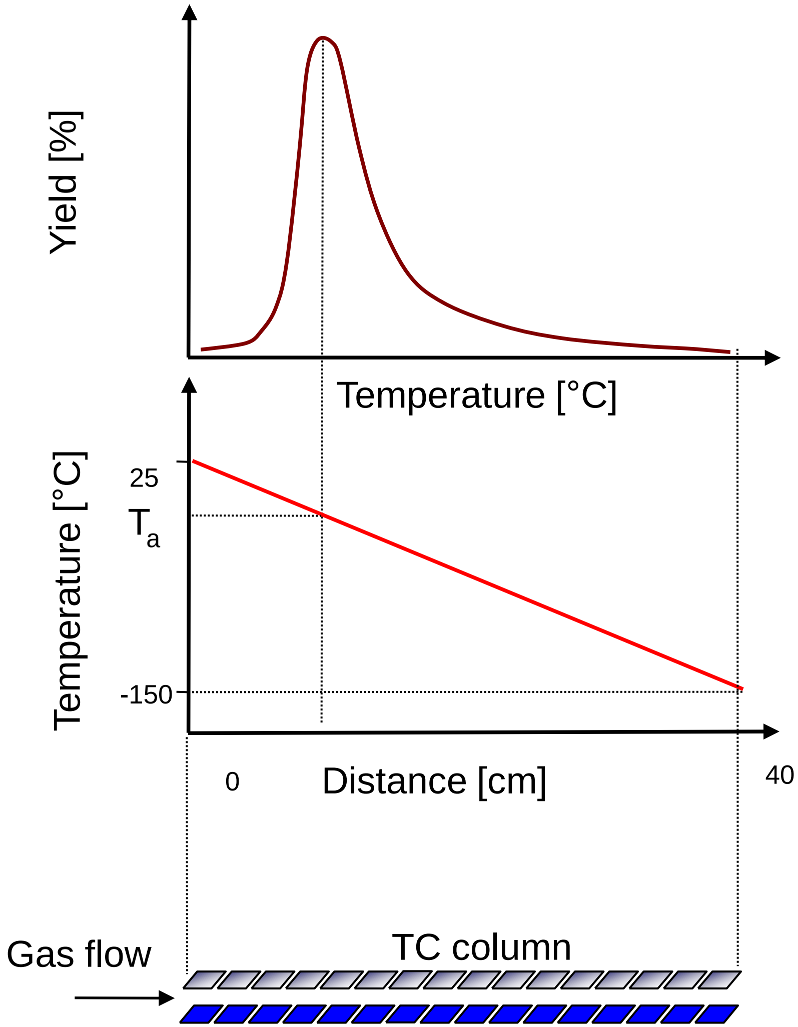


SO splitting of p, d, f orbitals: $j = l \pm s$

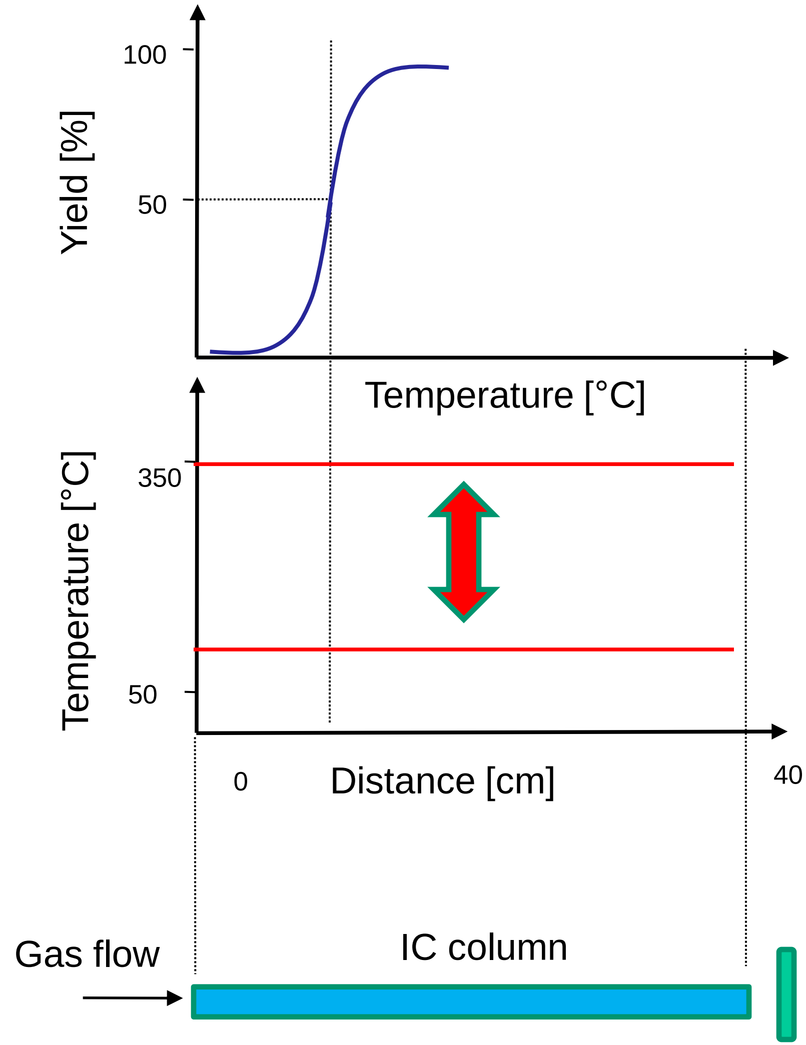




Thermo- chromatography (IC) Isothermalchromatography (IC)



OsO4/ HsO_4 ,Hg/Cn, Pb/114

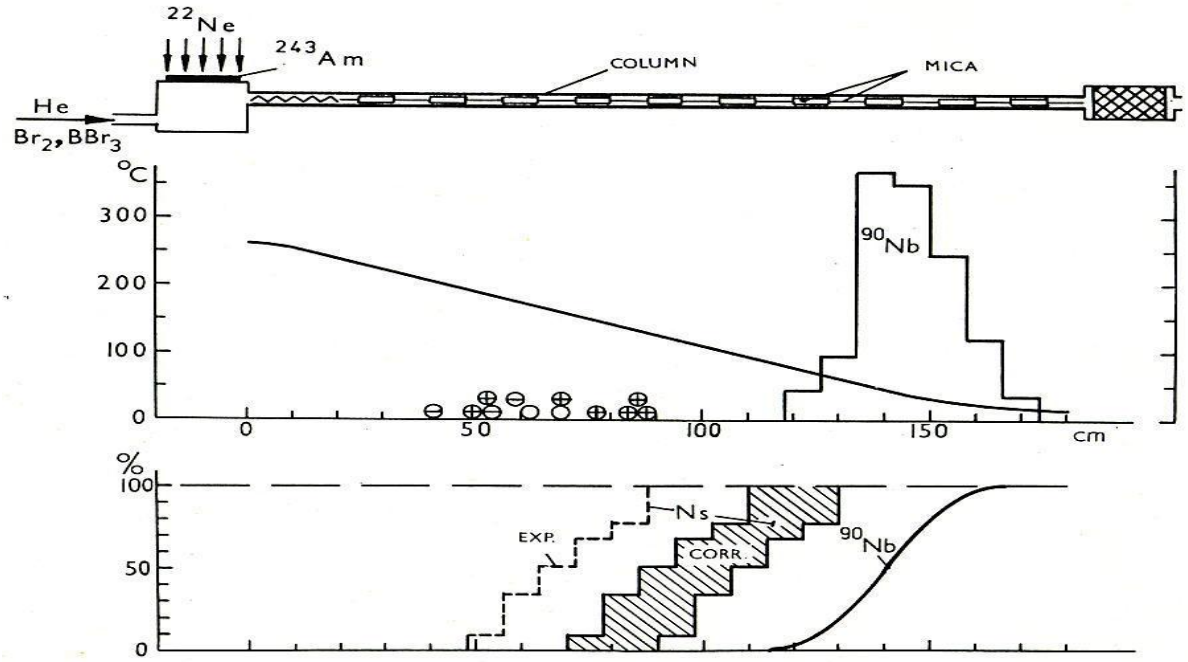


$RfCl_4$, $DbBr_5$, SgO_2Cl_2, BhO_3Cl

Previous gas-phase chemistry (TC) experimental results of Db with bromine

- Dubna(1970)：identification of Db isotopes based on SF track in mica.

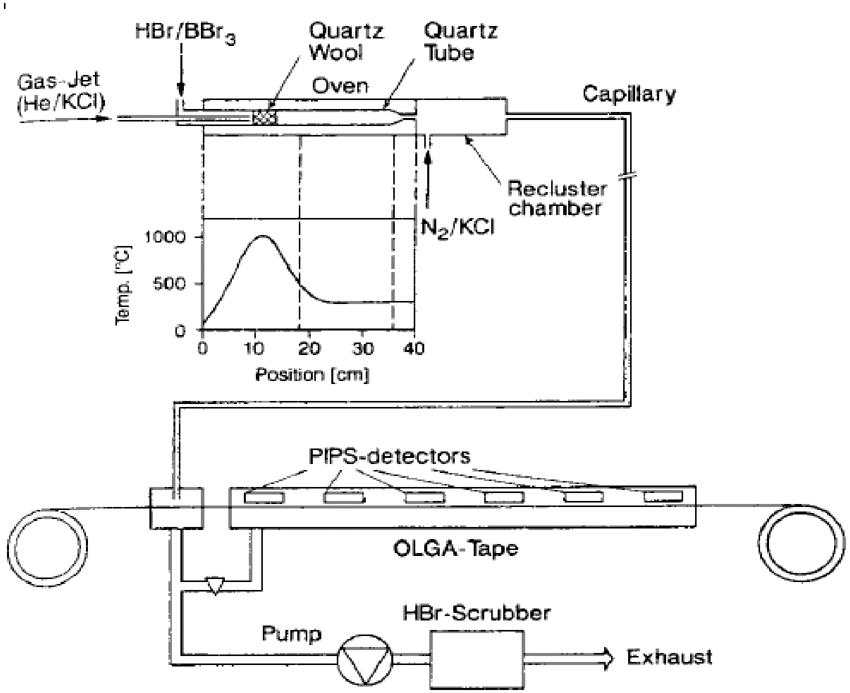
Volatility: $NbBr_5 > DbBr_5 \approx HfBr_4$



Previous gas-phase chemistry (IC) experimental results of Db with bromine

- PSI(1992) : chemical species were probably $DbOBr_3$ rather than pure $DbBr_5$ since trace amount of oxygen exist in carrier gas.

Volatility: $TaBr_5 \approx NbBr_5 \geq DbBr_5$



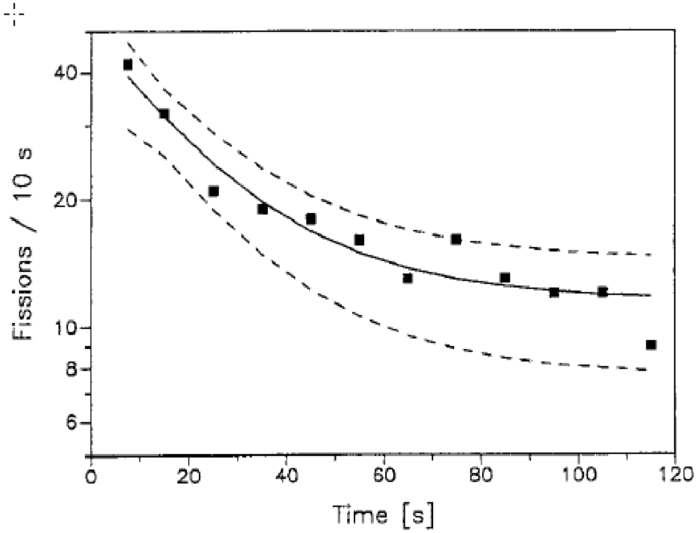
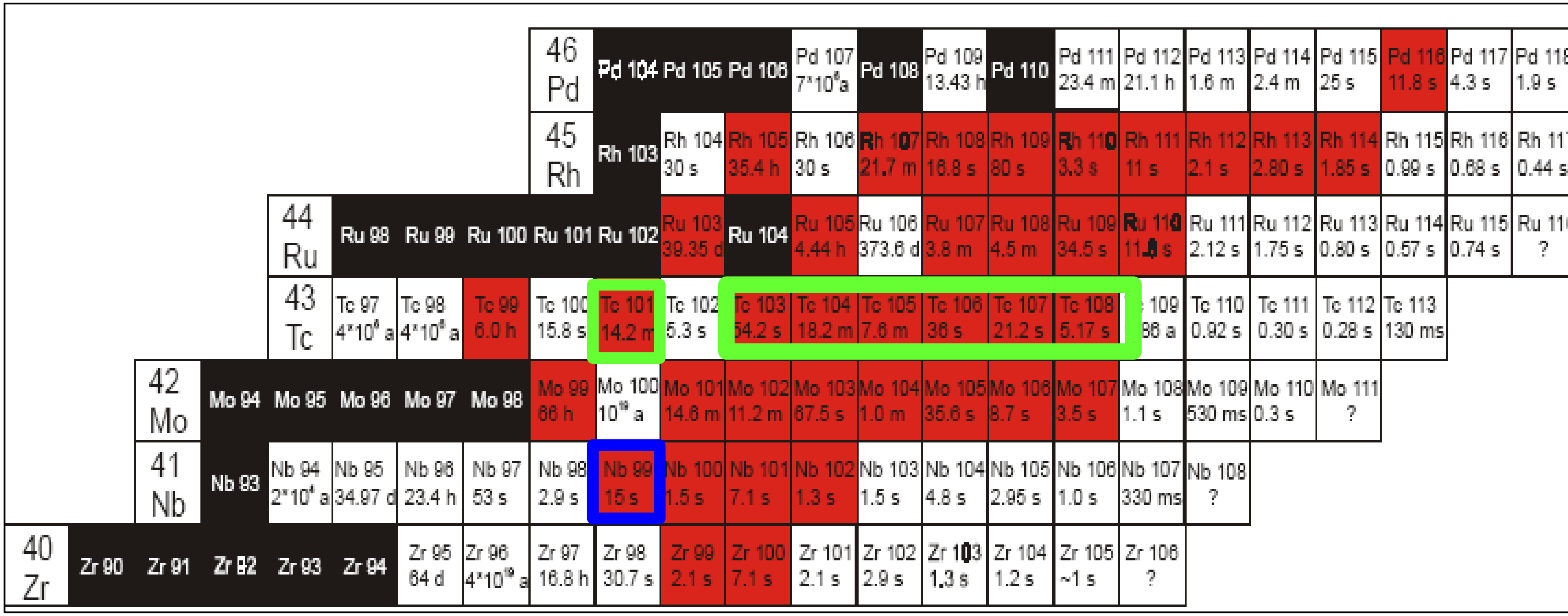


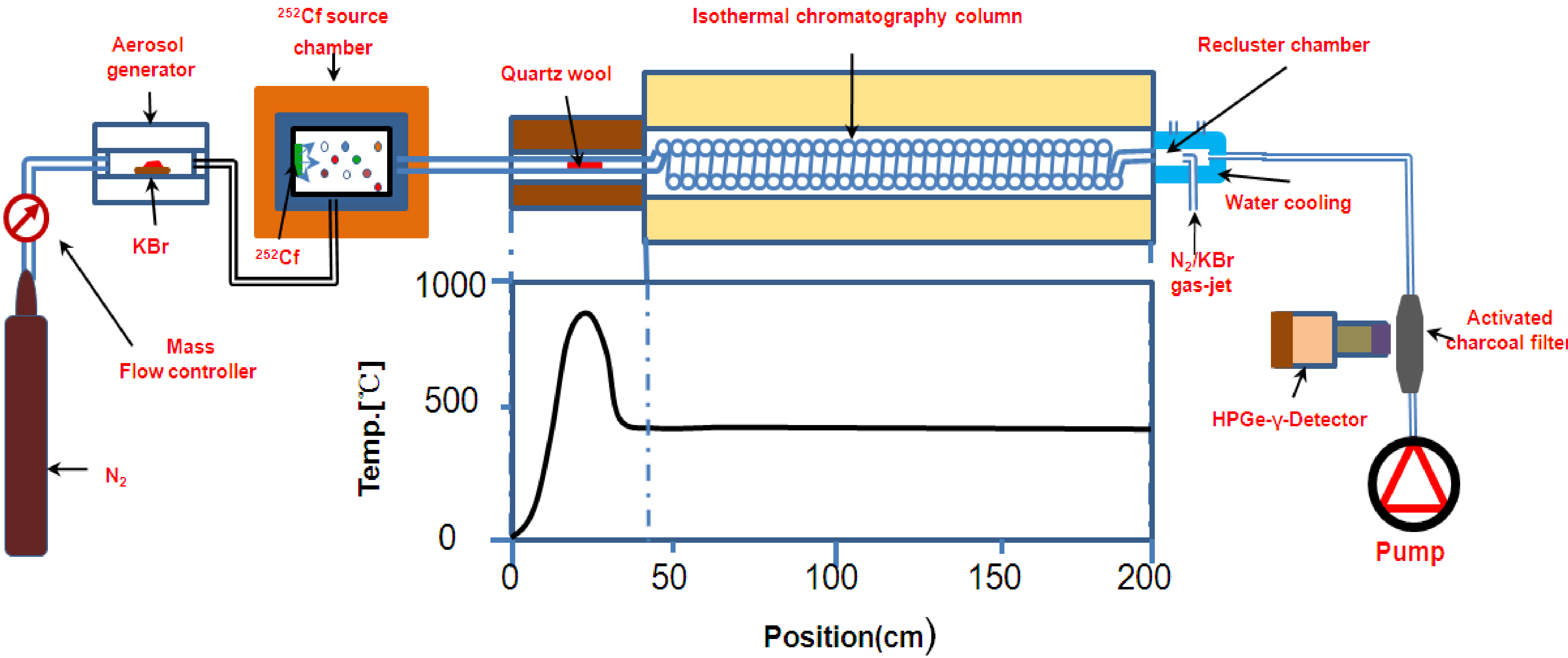
Fig. 2. Spontaneous fission activity measured in the $^{18}O + ^{249}Bk$ reaction during a direct catch experiment with a beam dose of $8.7 \cdot 10^{16}$ particles. The fit to the data results in a short-lived component with $T_{1/2} = 28 \pm 8$ s and a long-lived component from ^{256}Fm, produced in this reaction via ingrowth from ^{256}Md

Light fission products from ^{252}Cf spontaneous fission

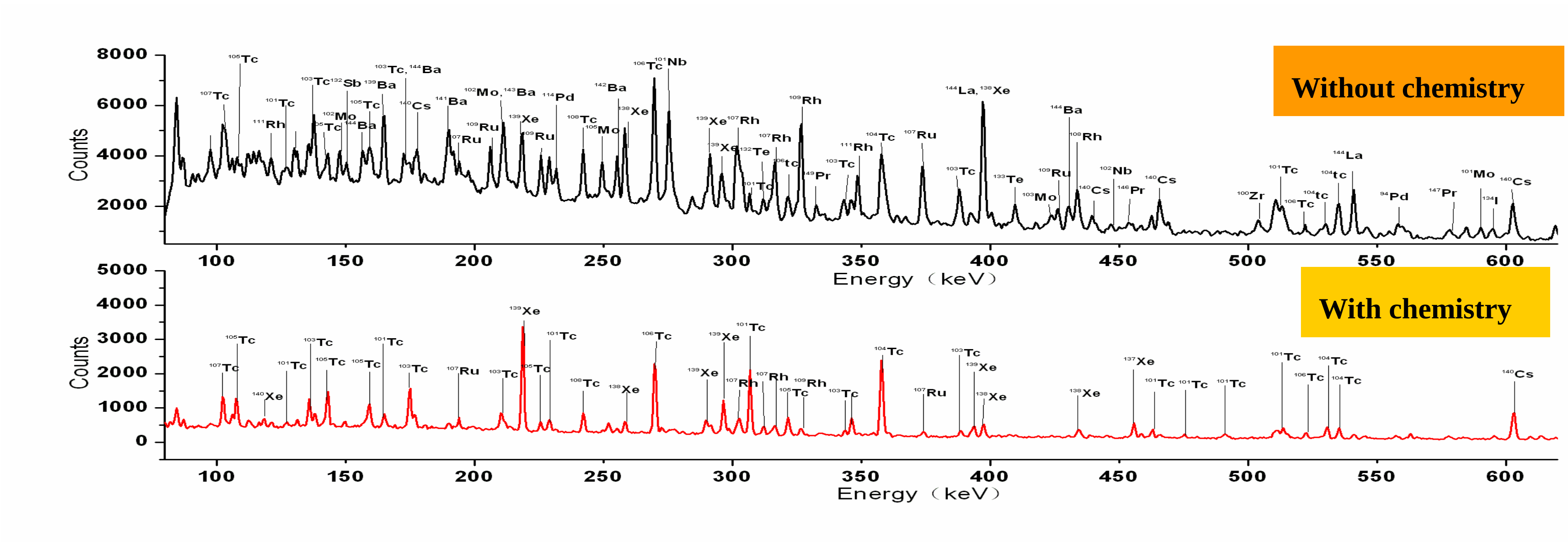


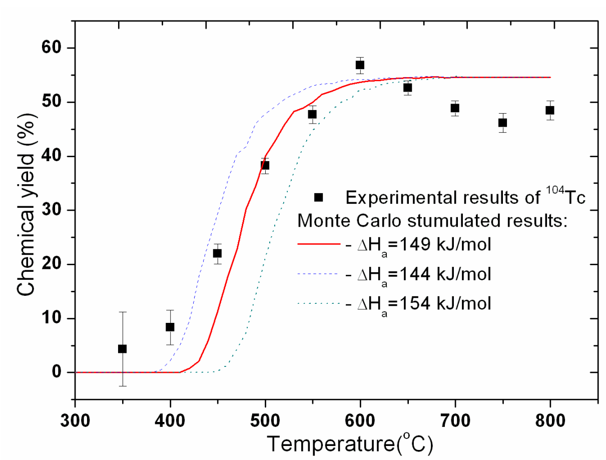
Isotope	^{101}Tc	^{103}Tc	^{104}Tc	^{105}Tc	^{106}Tc	^{107}Tc	^{108}Tc	^{99}Nb
$T_{1/2}$	14.2m	54.2s	18.2m	7.6m	35.6s	21.2s	5.2s	15s
E_γ(keV)	307	346	358	143	270	103	242	138

Isothermal chromatography set-up at IMP



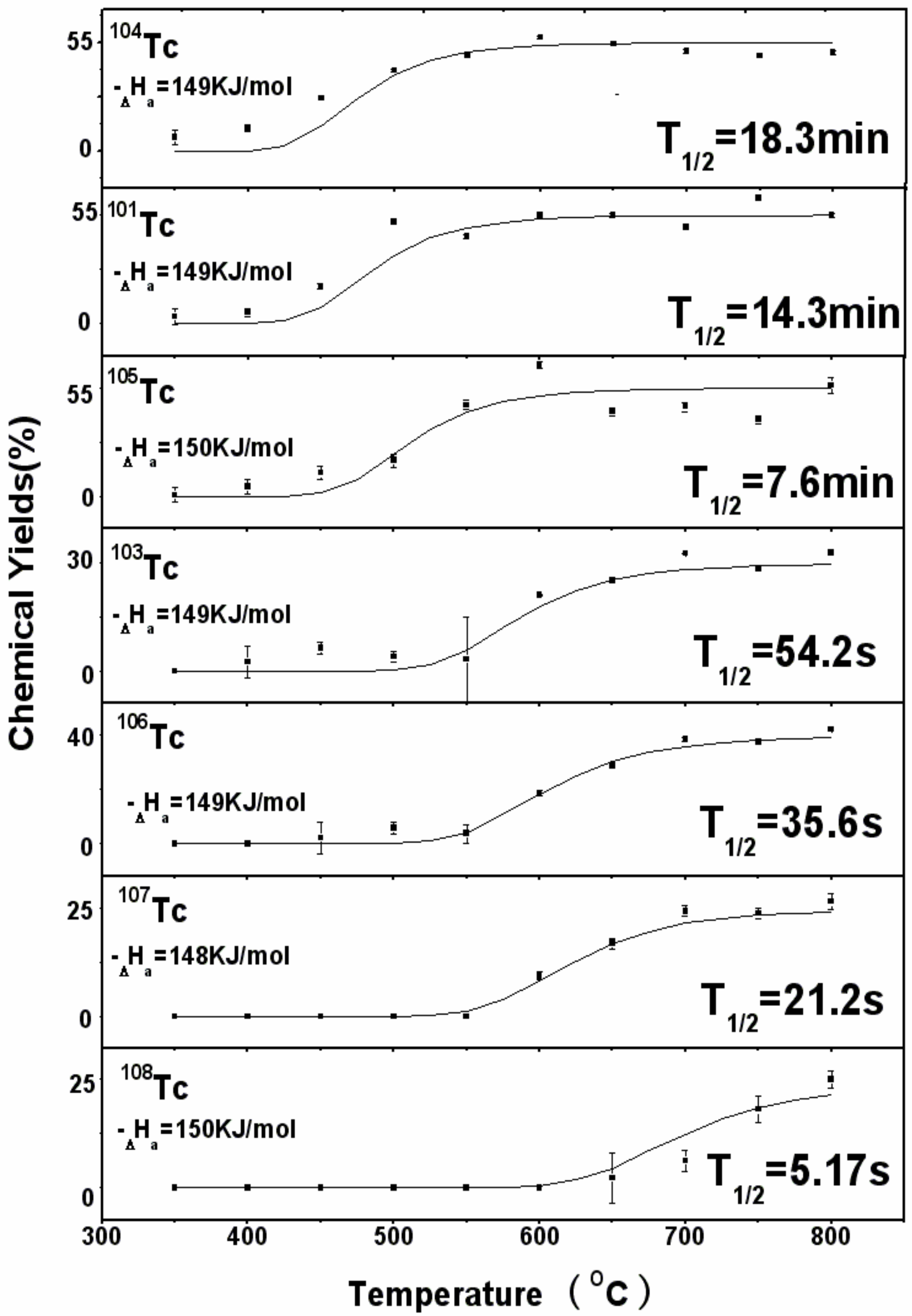
Fast chemical separation of short-lived Tc isotopes in the form of TcO_3





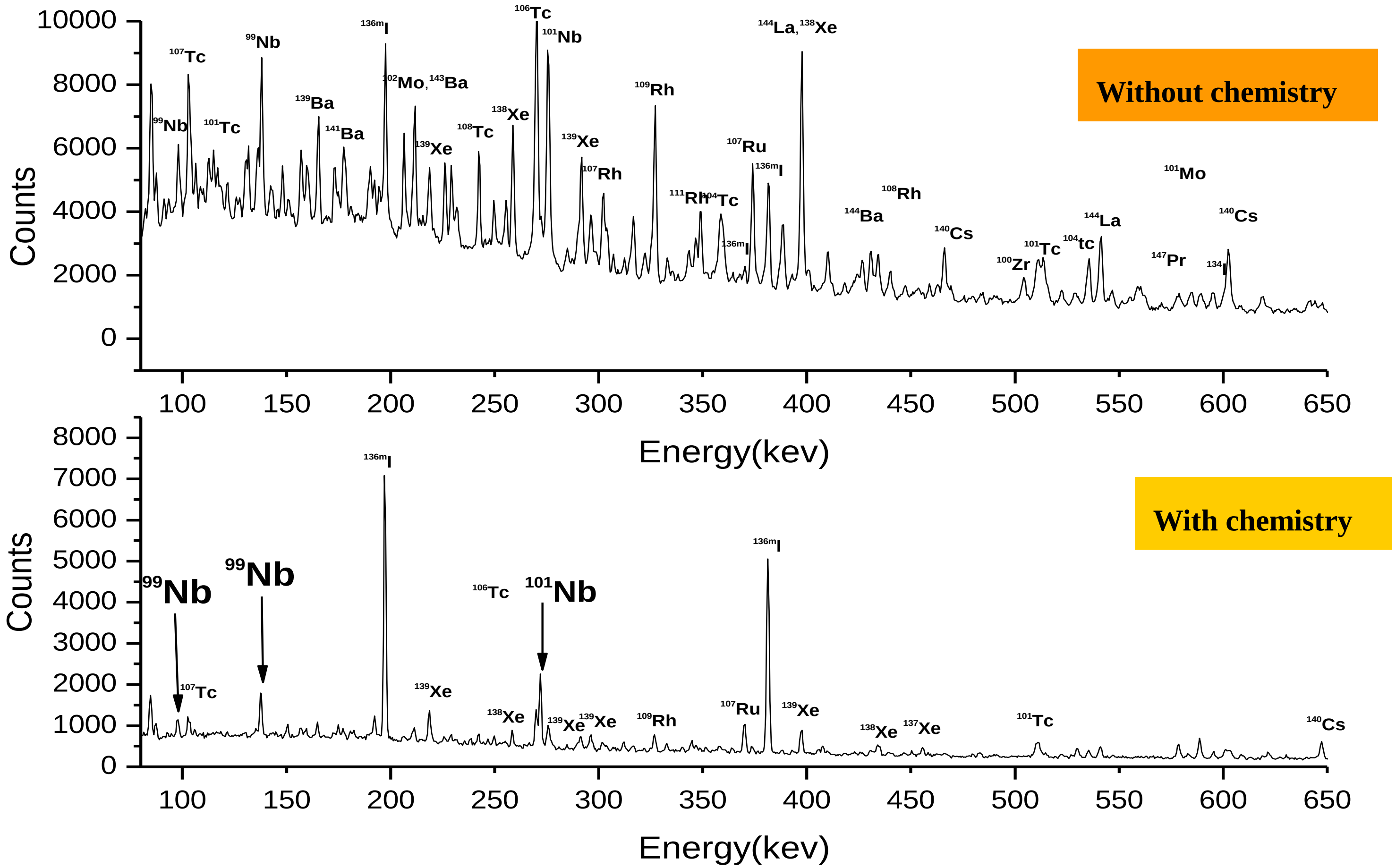
Compounds	$\Delta_f H^0(s)$ [kJ/mol]	$\Delta_f H^0(g)$ [kJ/mol]	ΔH^0_{subl} [kJ/mol]	ΔH^0_{ads} [kJ/mol]
TcO_2	-433	27	460	-319±21
TcO_3	**-540**	**-322**	**218**	**-156±15**
Tc_2O_7	-1115	-982	133	-98±12

M. S. Lin, Z. Qin. *et al.*, ***Radiochimica Acta.*** **2010,98:321-326**



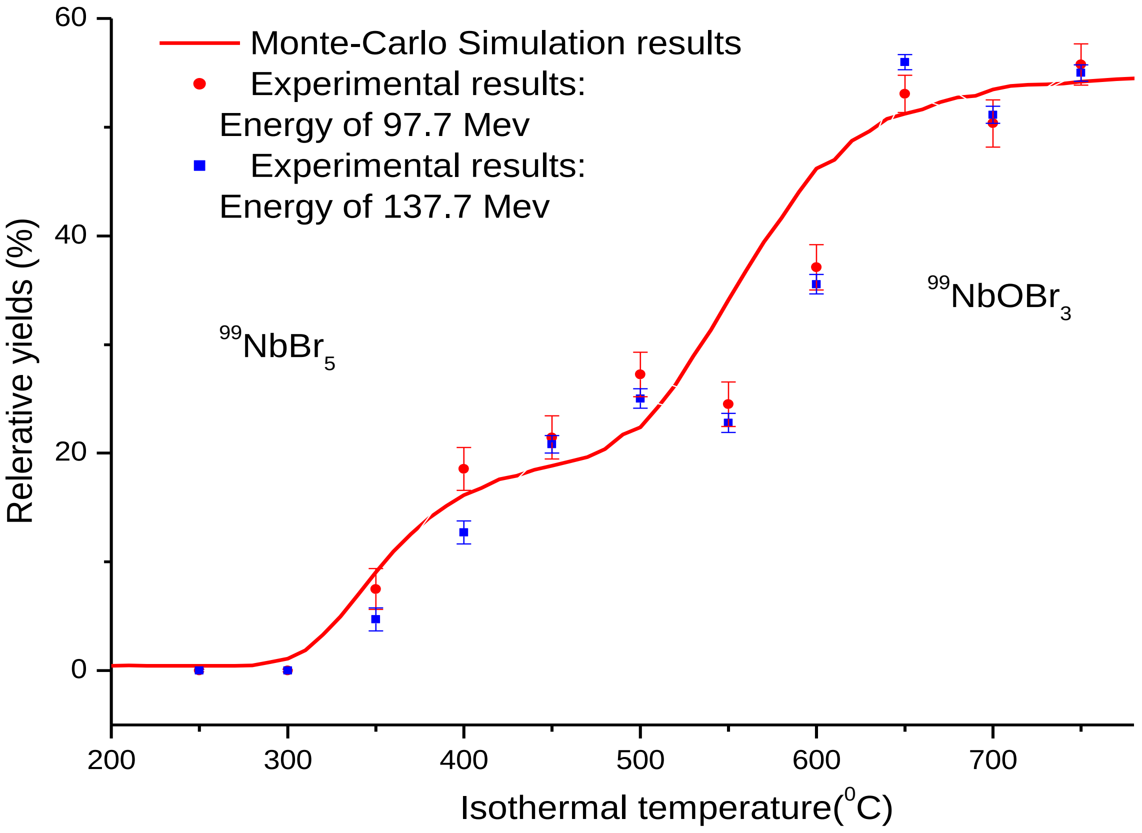
核素	半衰期	γ峰能量 [keV]	分离效率 [%]
^{104}Tc	18.3 min	358; 531; 535	55%
^{101}Tc	14.22 min	307; 545	57%
^{105}Tc	7.6 min	143; 108	56%
^{103}Tc	54.2 s	346; 136	28%
^{106}Tc	35.6 s	270; 2239	34%
^{107}Tc	21.2 s	103; 177	25%
^{108}Tc	5.17 s	242; 466	26%

M. S. Lin, Z. Qin et al., Gas-phase isothermal Chromatography with short-lived technetium isotopes. *Radiochimica Acta.* 2010,98:321-326

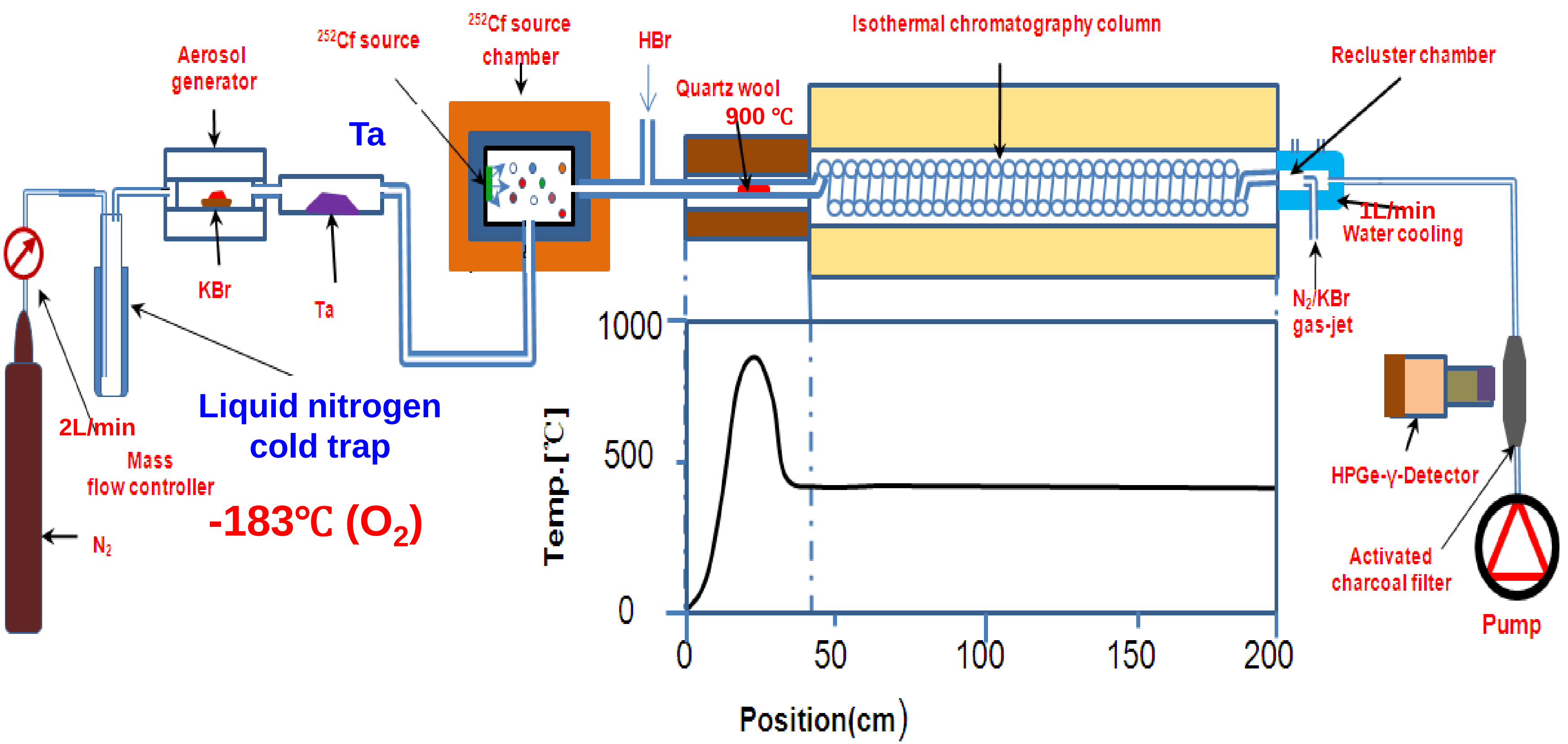


^{99}Nb:$T_{1/2}$= 15 s. E_{γ}=97.7,137.7keV
Aerosol particles: KBr
carrier gas: N_2 (2 l/min)
Reactive gas : HBr (100 ml/min).

Tracer amount of O_2 exist in N_2 gas



Purify the N_2 carrier gas with liquid nitrogen trap and high temperature Ta-getter



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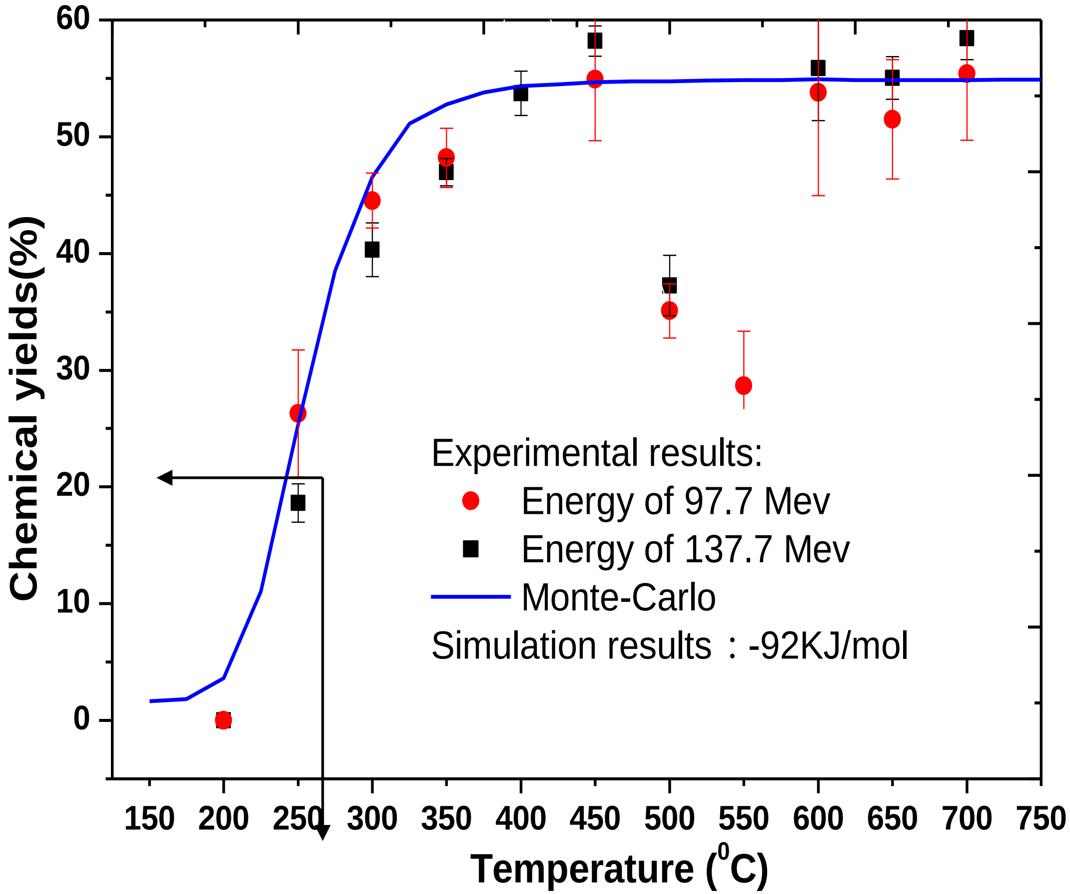
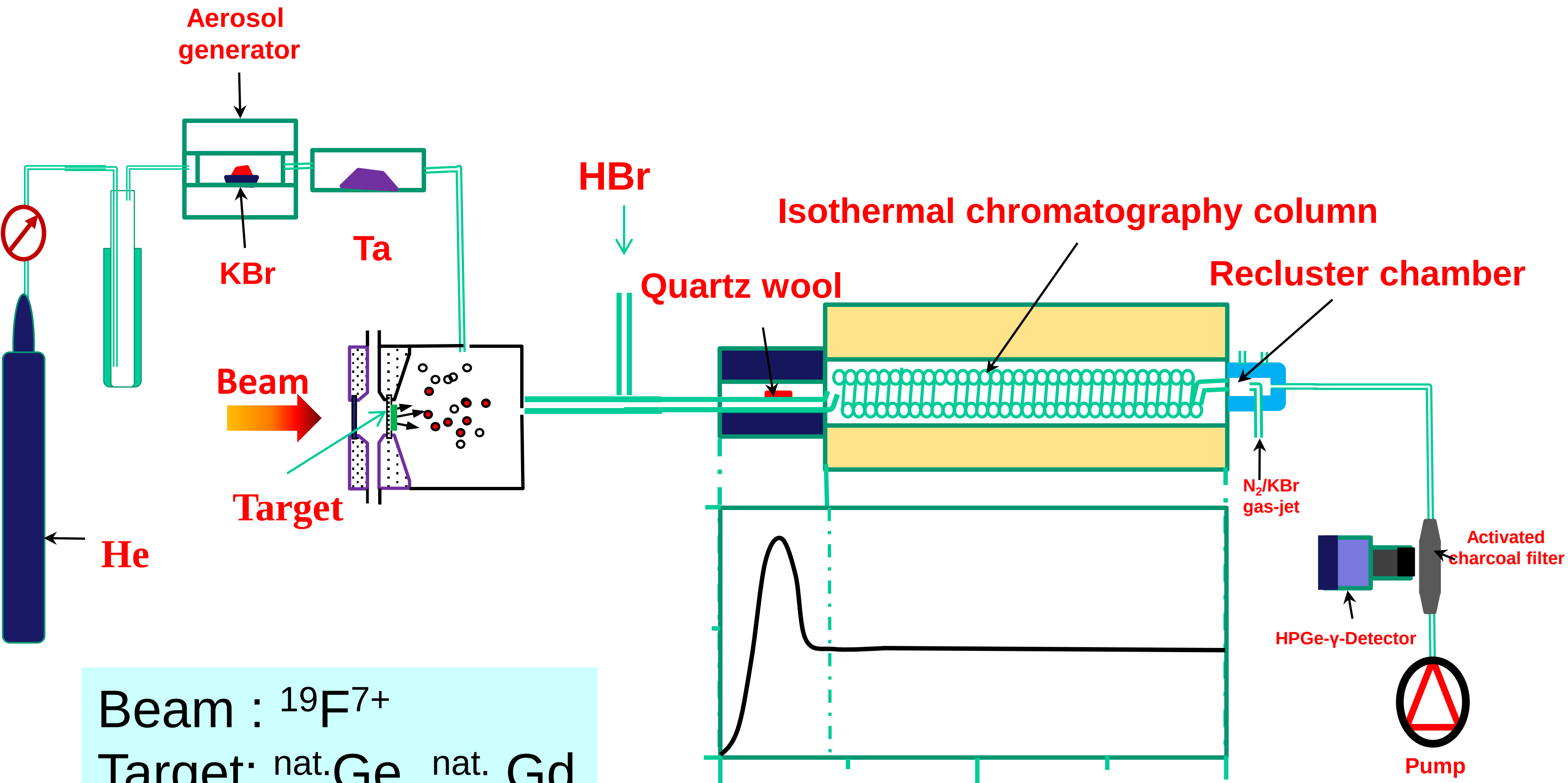
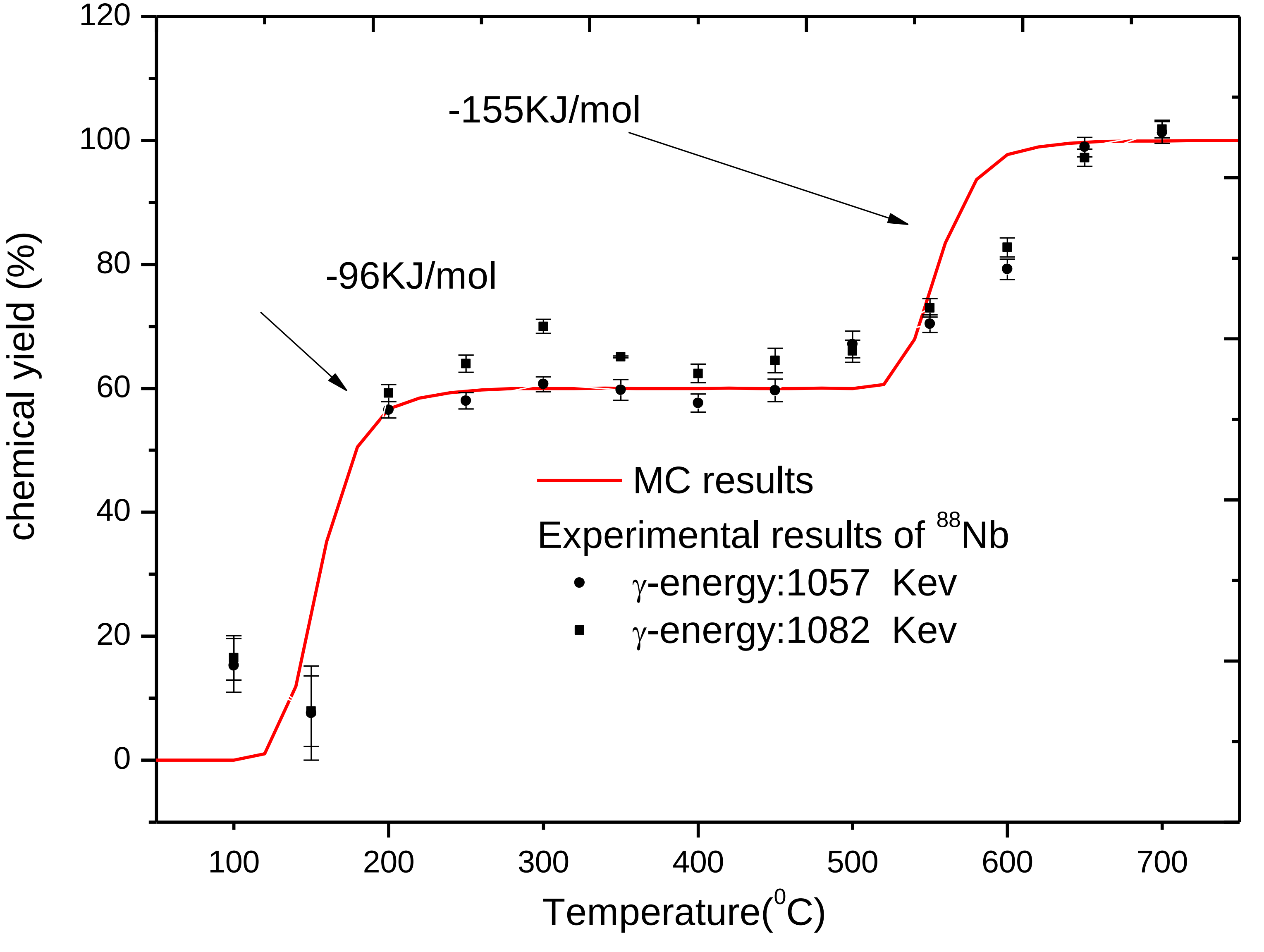


Short-lived isotopes of ^{88}Nb and ^{170}Ta produced at SFC of HIRFL



Beam : $^{19}F^{7+}$

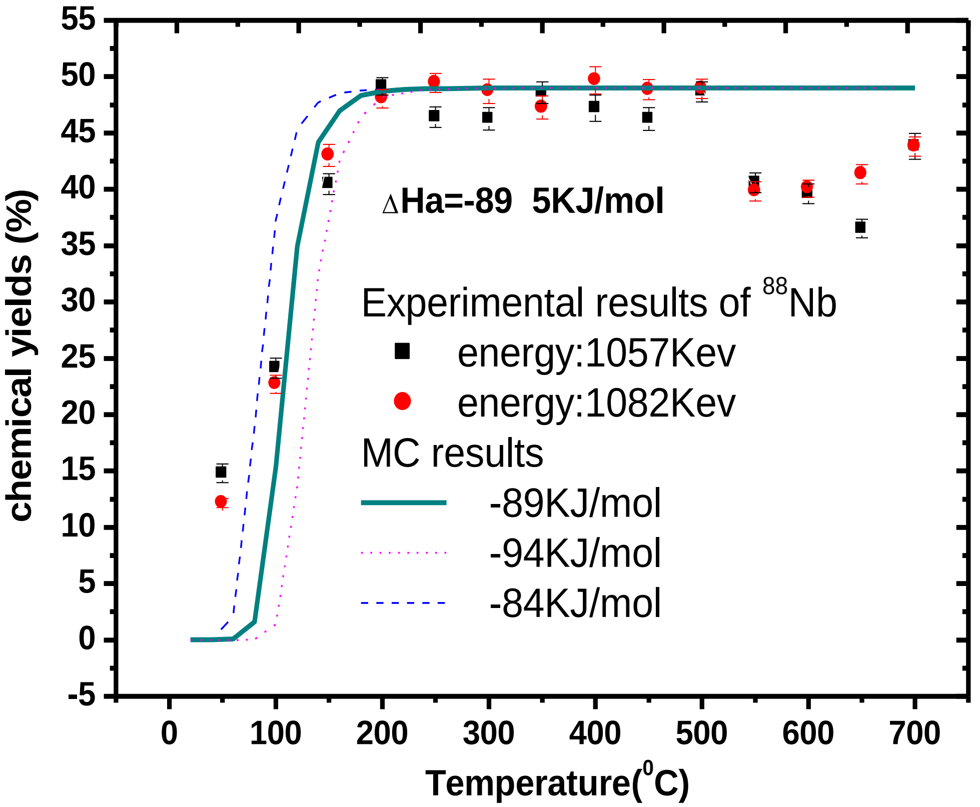
Target: $^{nat.}Ge$, $^{nat.}$ Gd



-155KJ/mol
-96KJ/mol
MC results
Experimental results of 88Nb
γ-energy:1057 Kev
γ-energy:1082 Kev
chemical yield (%)
Temperature(0C)
0
20
40
60
80
100
120
100
200
300
400
500
600
700

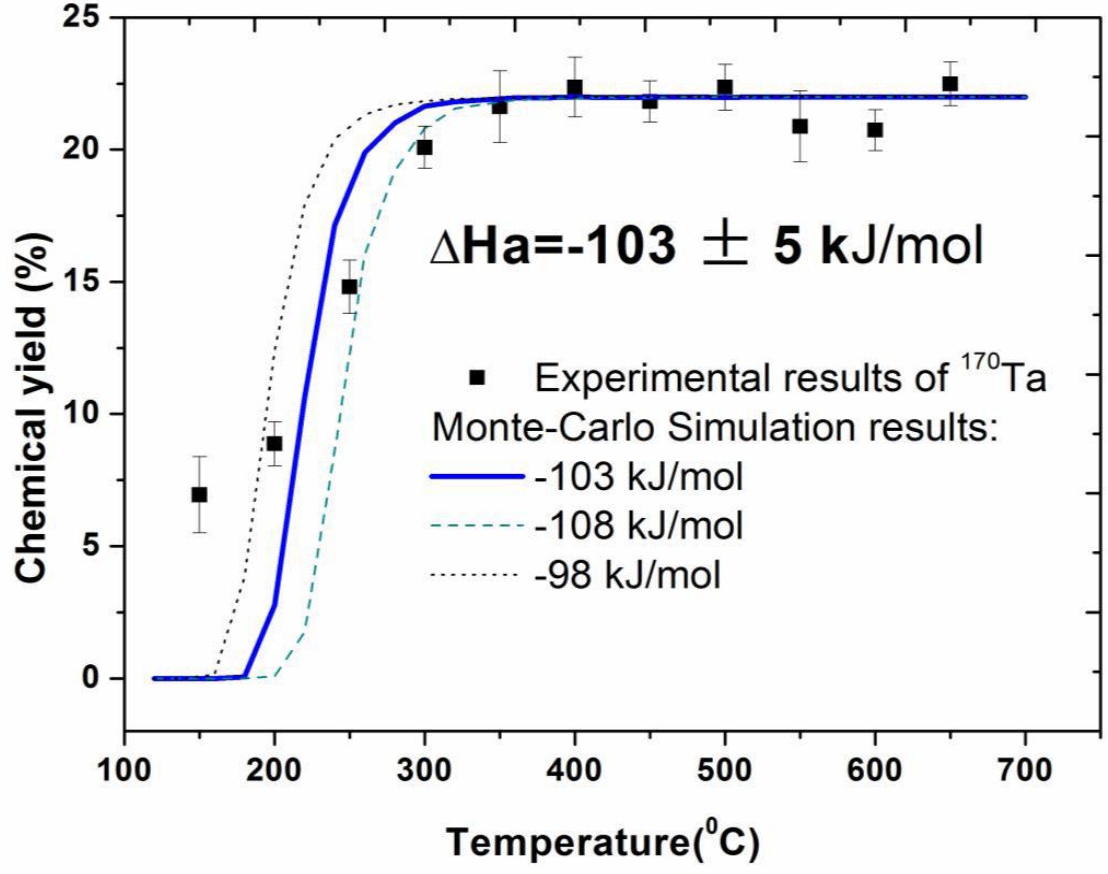
$^{nat}Ge(^{19}F,xn)\ ^{88}Nb$: $T_{1/2}$=14.5 m, E_γ=1082,1057 keV

Aerosol particles: KBr
carrier gas: He =2 L/min
Reactive gas :
HBr =100 mL/min
Measure time :15 min



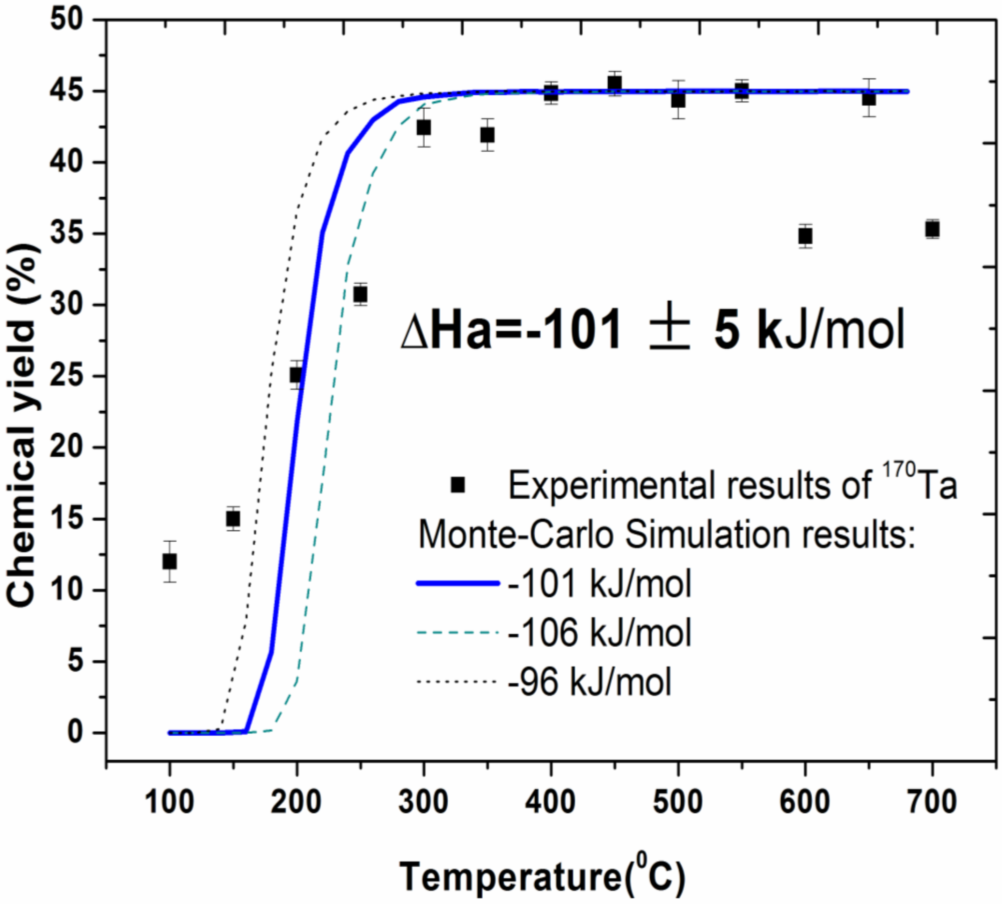
$^{nat}Gd(^{19}F,xn)\ ^{170}Ta$: $T_{1/2}$=6.76 m, Eγ=100.8,221 keV

Aerosol particles: KBr
carrier gas: He = 2 L/min
Reactive gas :
HBr = 100 mL/min
Measure time :15 min

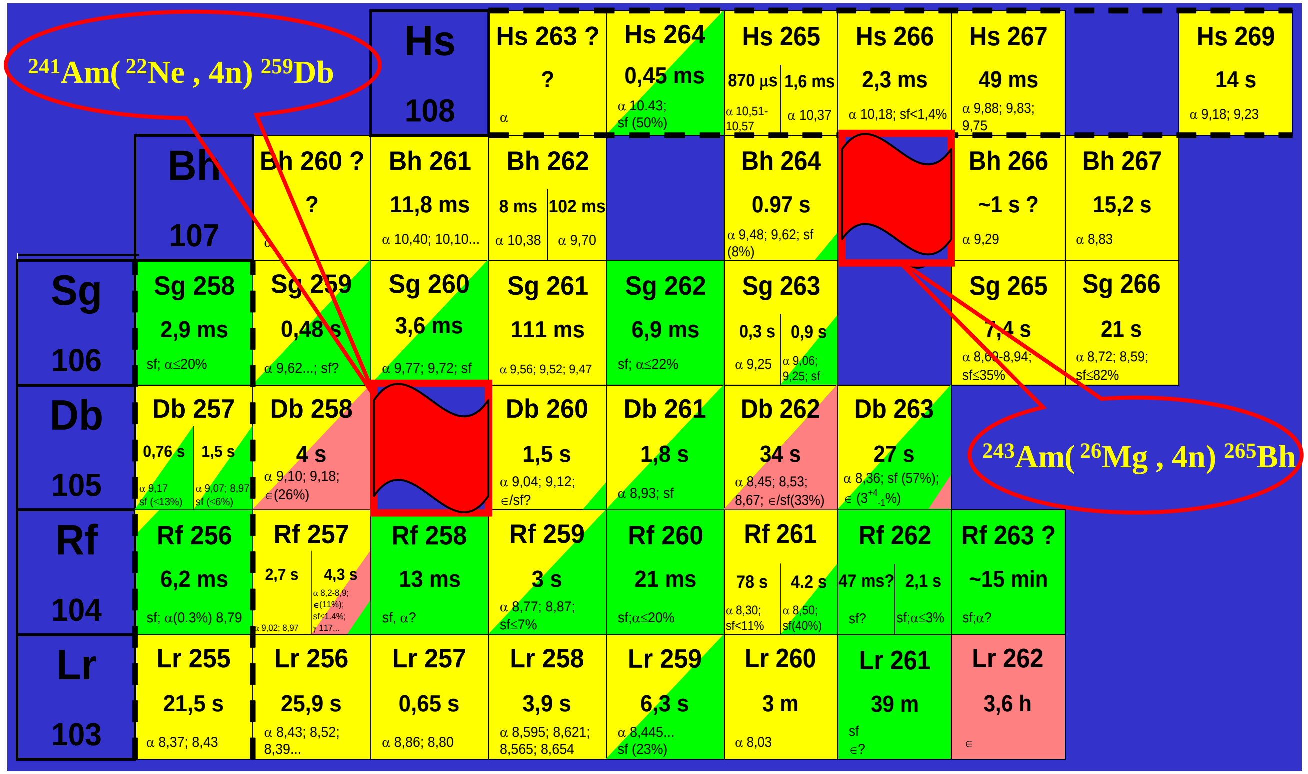


$^{nat}Gd(^{19}F,xn)\ ^{170}Ta$: $T_{1/2}$=6.76 m, Eγ=100.8,221 keV

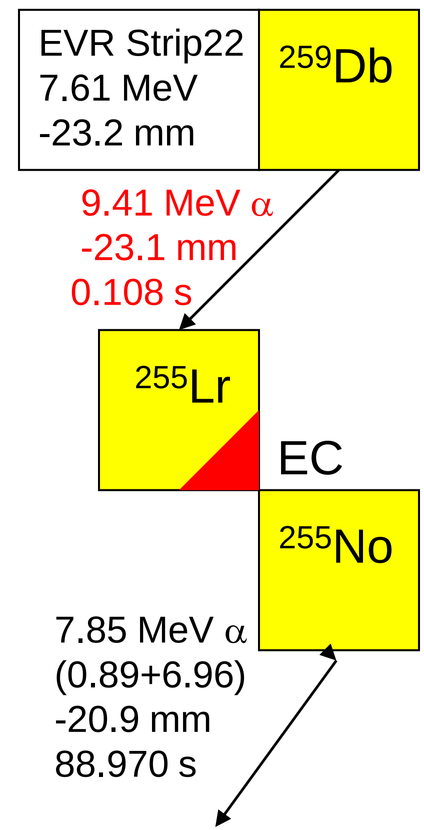
Aerosol particles: KBr
carrier gas: He =2 L/min
Reactive gas :
HBr/BBr_3 =100 mL/min)
Measure time :15 min



^{258,259}Db were produced via reaction of ^{241}Am(^{22}Ne, 4,5n) at SFC of HIRFL



151 MeV ^{27}Al + ^{238}U,
E_{lab}(cot) = 145.2 MeV

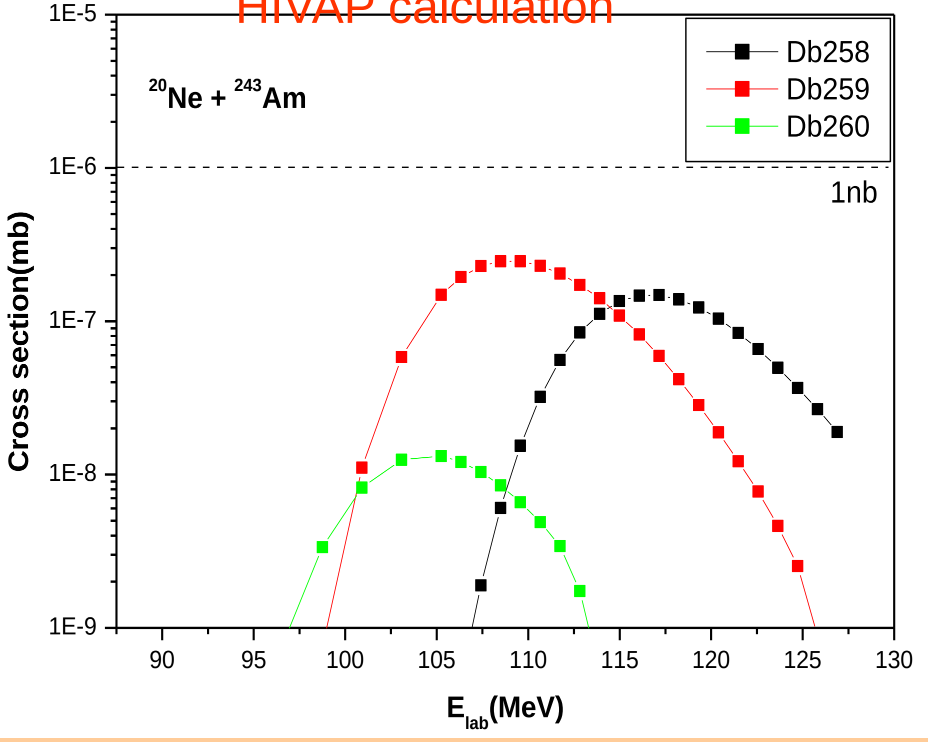


^{259}Db: $T_{1/2}$=0.5s,
E_{α}=9.47MeV
EPJA10，（2001）21

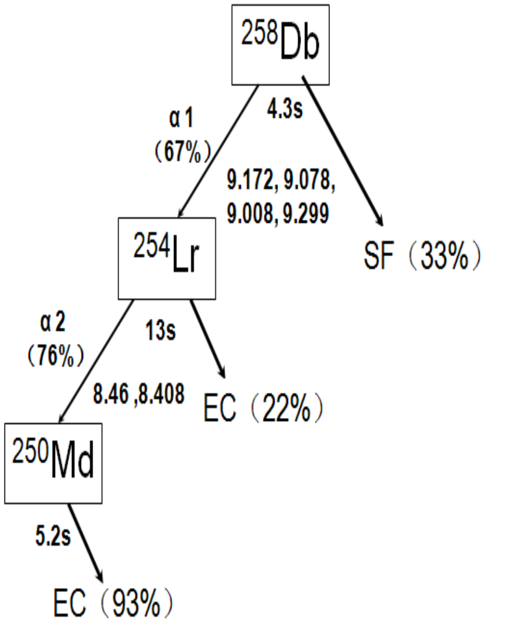
^{265}Bh: $T_{1/2}$=0.9s,
E_{α}=9.24MeV
EPJA20，（2004） 385

Short-lived ^{258}Db produced via ^{243}Am(^{20}Ne, 5n) reaction

HIVAP calculation



Decay properties of ^{258}Db



Beam: **148 MeV $^{20}Ne^{7+}$ from the SFC, intensity: 0.5 puA**

Beam time: **200 hours**

Beam dose: **1.05×10^{18}**

Target: **1mg/cm^2 ^{243}Am on 19μm Be foil prepared by means of electrodeposition method**

Energy loss: 2.3mg/cm^2 Havar windows + cooling gas (He) + 19μm Be

Energy in the center of target: 120 MeV

Rotating wheel detector system: 3 pairs of PIPS detector,

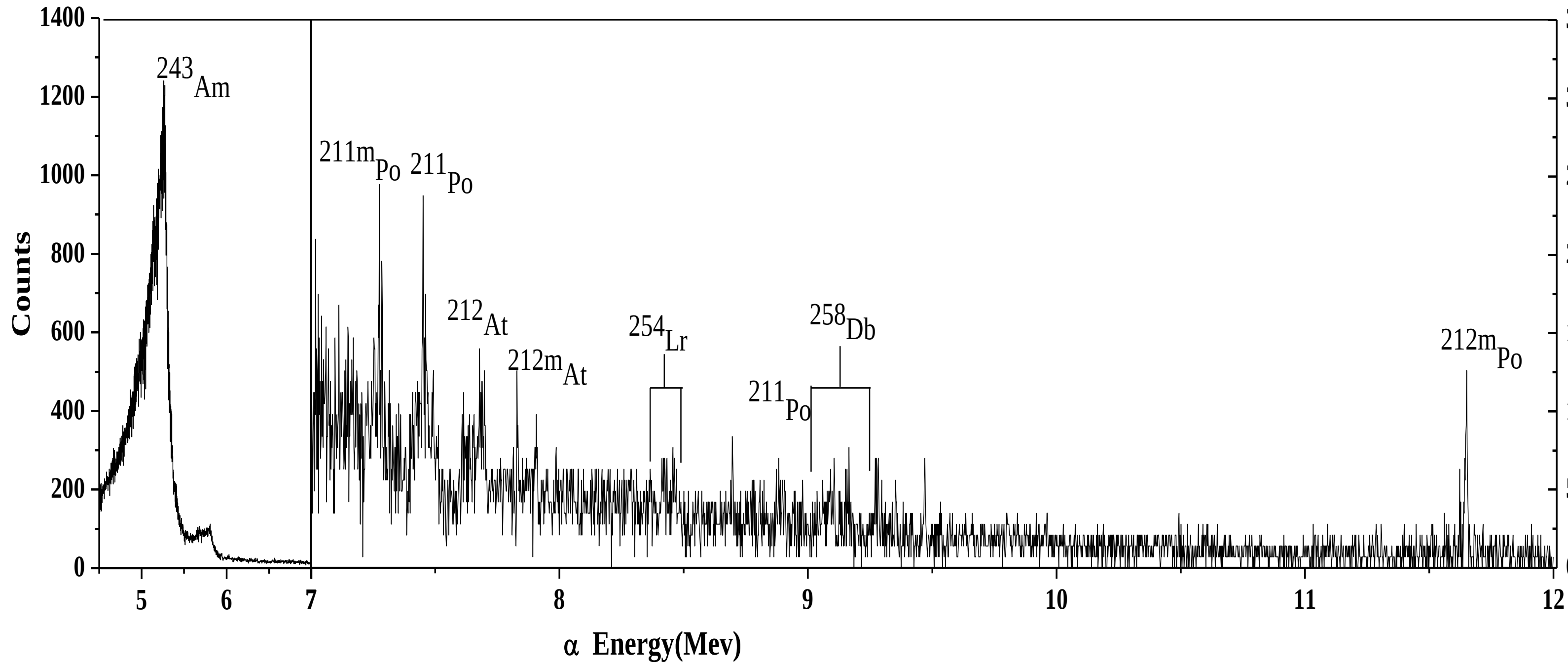
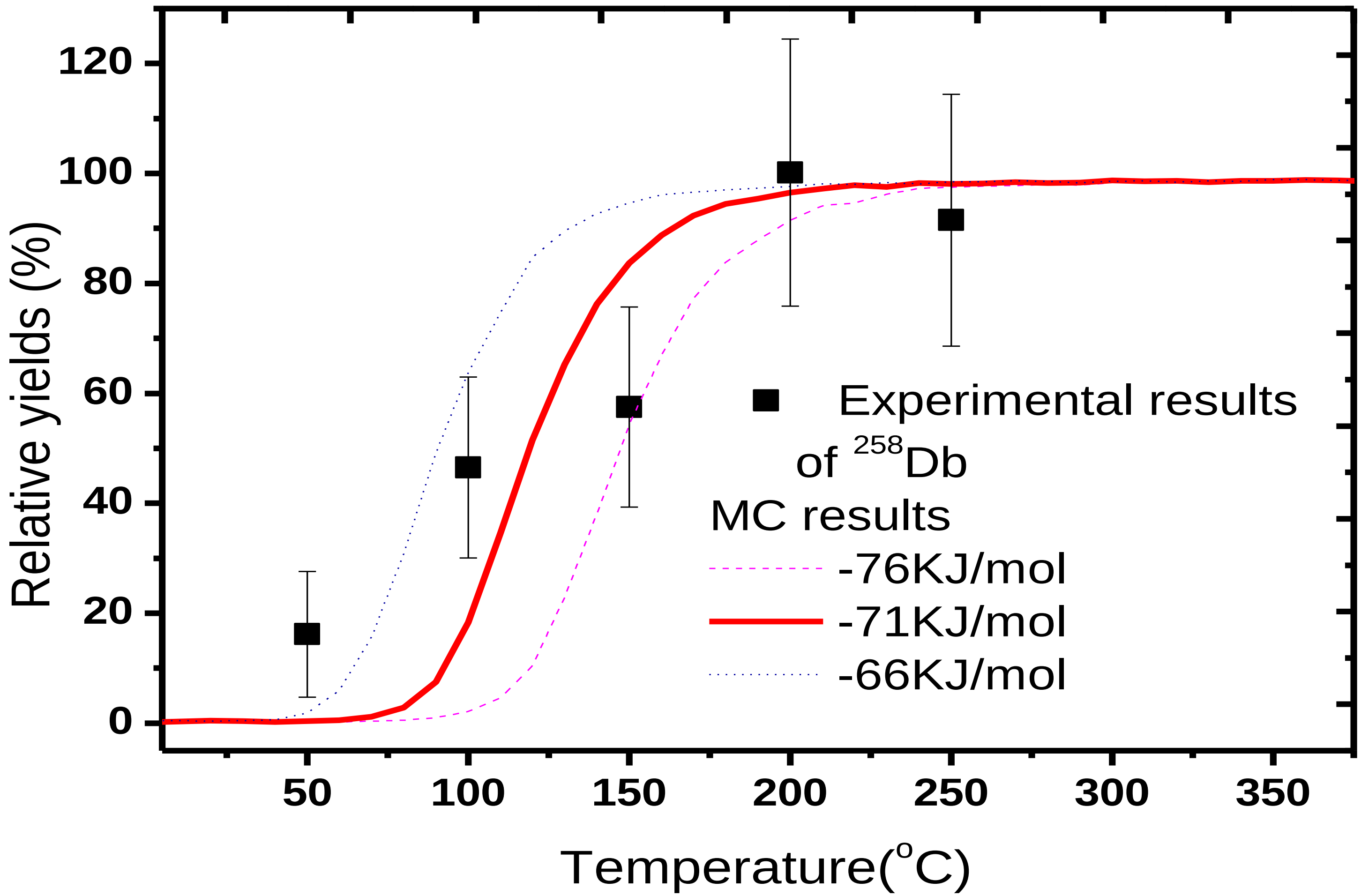


Figure. The sum α -spectrum of detector 1 at isothermal temperature of 200 °Cand 150 °Cfor 63 hours

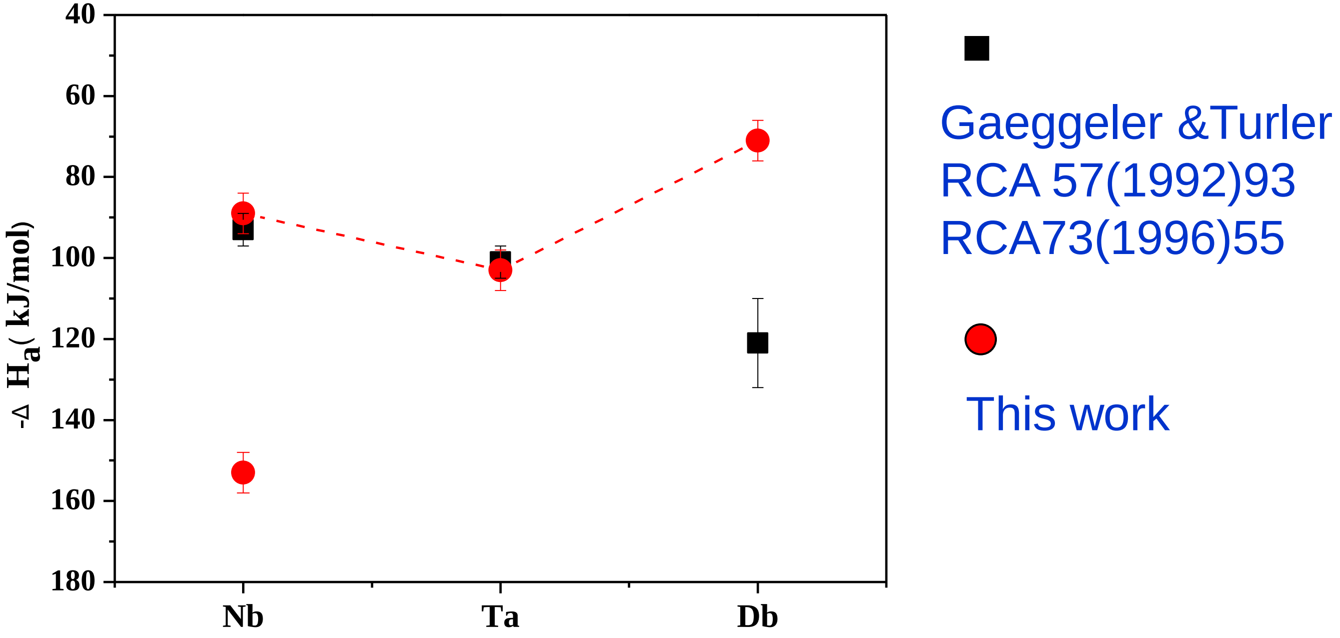
Temperature / ℃	Dose $\times 10^{17}$	α- αcorrelation events
250	2.1759	16
200	2.1416	17
150	2.1688	10
100	2.1569	8
50	1.8392	2

Energy windows: Mother 8.9-9.3MeV， Daughter 8.3-8.5MeV
Correlation time windows: Mother 0-10s， Daughter 0-30s



Volatility :	**$DbBr_5$ 》**	**$NbBr_5$ >**	**$TaBr_5$**
$-\Delta H_{ads}$(kJ/mol)	**71**	**89**	**101**

Adsorption enthalpy of the group V bromides on quartz surface



Summary

1. Pure bromide of group V elements were formed after purifying Carrier gas.
2. Volatility： $DbBr_5$ > $NbBr_5$ >$TaBr_5$, just as theoretical calculation predicted that $DbBr_5$ is more volatile than its light homologous.


兰州重离子加速器国家实验室
HIRFL
江泽民
2009/02/26


Thank you for attention

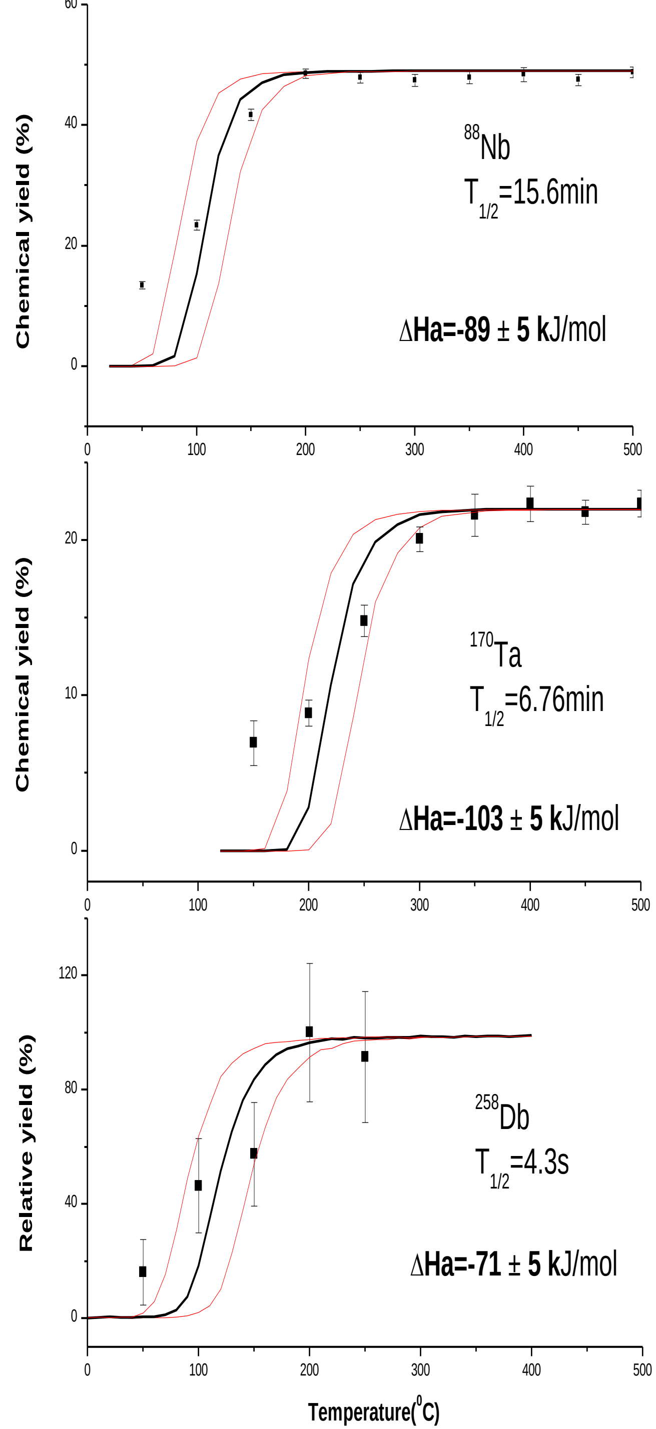
Adsorption of Bromides on Quartz Surface

$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon-1}{\varepsilon+2}\right)\frac{\alpha_{mol}}{\left(\frac{1}{IP_{slab}}+\frac{1}{IP_{mol}}\right)x^3}$$

Property	$NbBr_5$	$TaBr_5$	$DbBr_5$	Ref.
IP, eV	9.35	9.33	9.37	calc.
α_x, a.u.	162.257	155.563	156.828	calc.
α_y, a.u.	163.124	156.477	157.736	calc.
α_z, a.u.	195.885	187.265	188.117	calc.
$\langle\alpha\rangle$, a.u.	173.755	166.435	167.650	calc.
R_e(ax/eq), Å	2.500/2.448	2.495/2.442	2.550/2.496	calc.
R_e(ax/eq), Å	-	2.473/2.412	-	exp.
x, Å	2.783	2.769	2.788	calc.
$-\Delta H_{ads}(SiO_2)$, kJ/mol	66	64	63.2	calc.
$-\Delta H_{ads}(SiO_2\text{-}KBr)$, kJ/mol	77	74.7	74	calc.
$-\Delta H_{ads}$, kJ/mol	**89.2 ± 8**	**101 ± 8**	**71 ±8**	**exp.**

Volatily as adsorption (predictions): $NbBr_5 \le TaBr_5 \le DbBr_5$
Macrochemistry: $NbBr_5 \le TaBr_5 \le DbBr_5$

V. Pershina, privite comunication



Chemical yield (%)
^{88}Nb
$T_{1/2}$=15.6min
ΔHa=-89 ± 5 kJ/mol
Chemical yield (%)
^{170}Ta
$T_{1/2}$=6.76min
ΔHa=-103 ± 5 kJ/mol
Relative yield (%)
^{258}Db
$T_{1/2}$=4.3s
ΔHa=-71 ± 5 kJ/mol
Temperature(^{0}C)

Volatility of group 5 element with bromide