Investigation of volatile metal complexes @ BGS

Ch.E. Düllmann for the LBNL heavy element group

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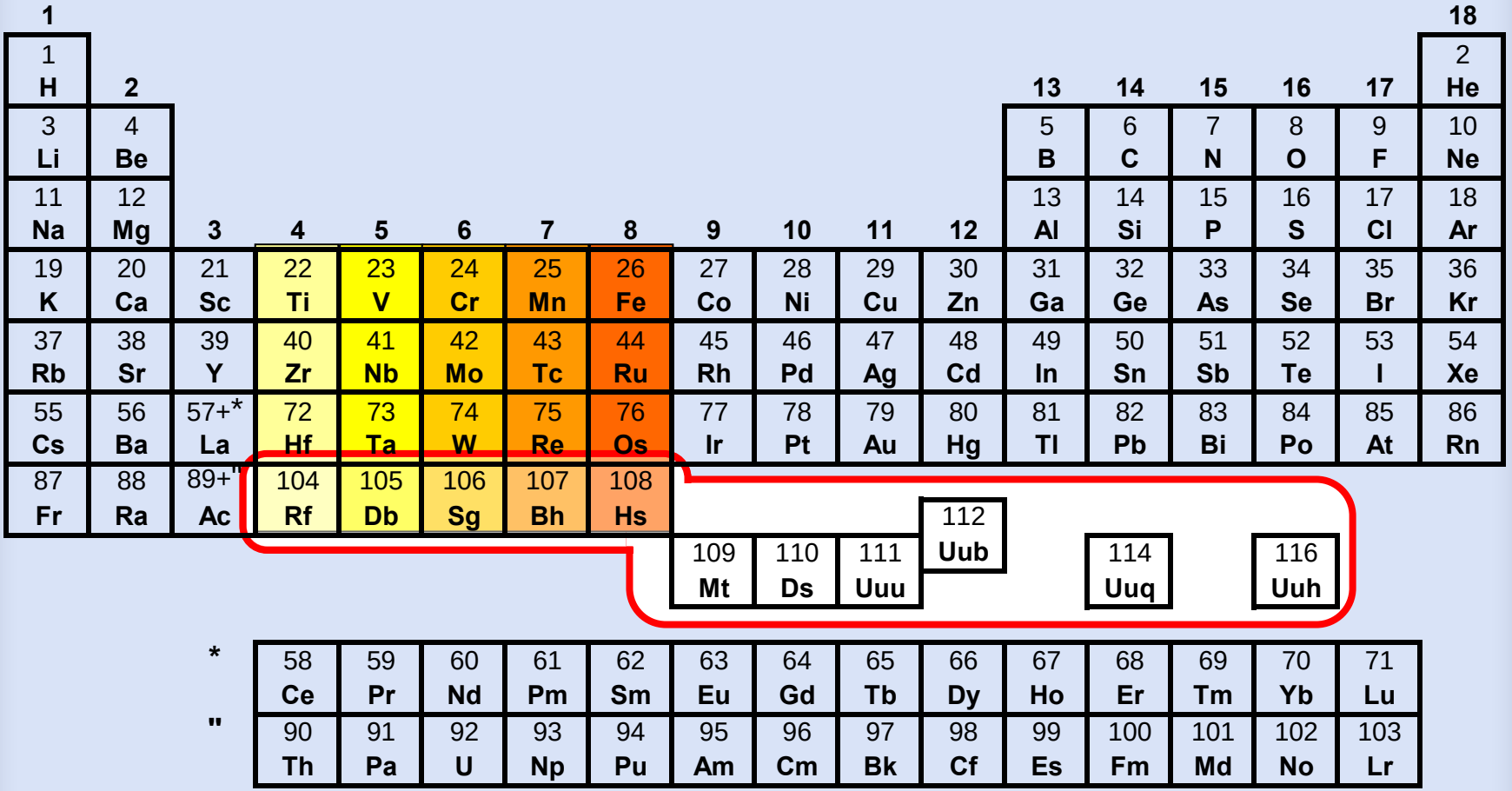
Outline

- Introduction
- Present state of TAN gas-phase chemistry
  - What has been done so far
- Opportunities @ BGS for doing something new
  - Volatile metal complexes, perhaps organometallic TAN compounds
- Experimental
  - The set-up
  - Results
  - Discussion
- Outlook
- Summary

The Periodic Table of the Elements

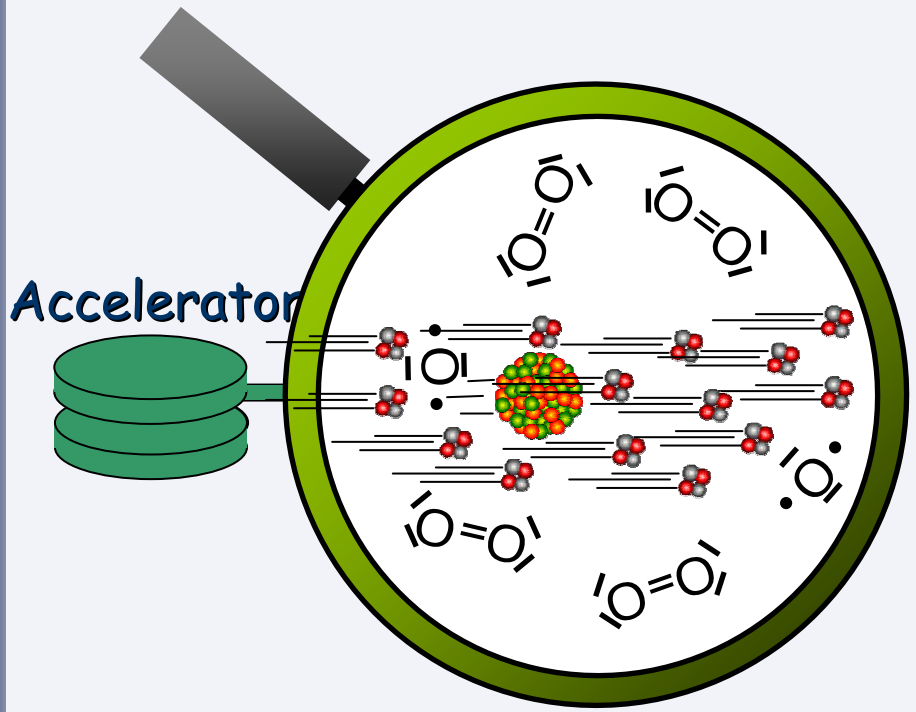


Gas Phase Chemistry of TAN

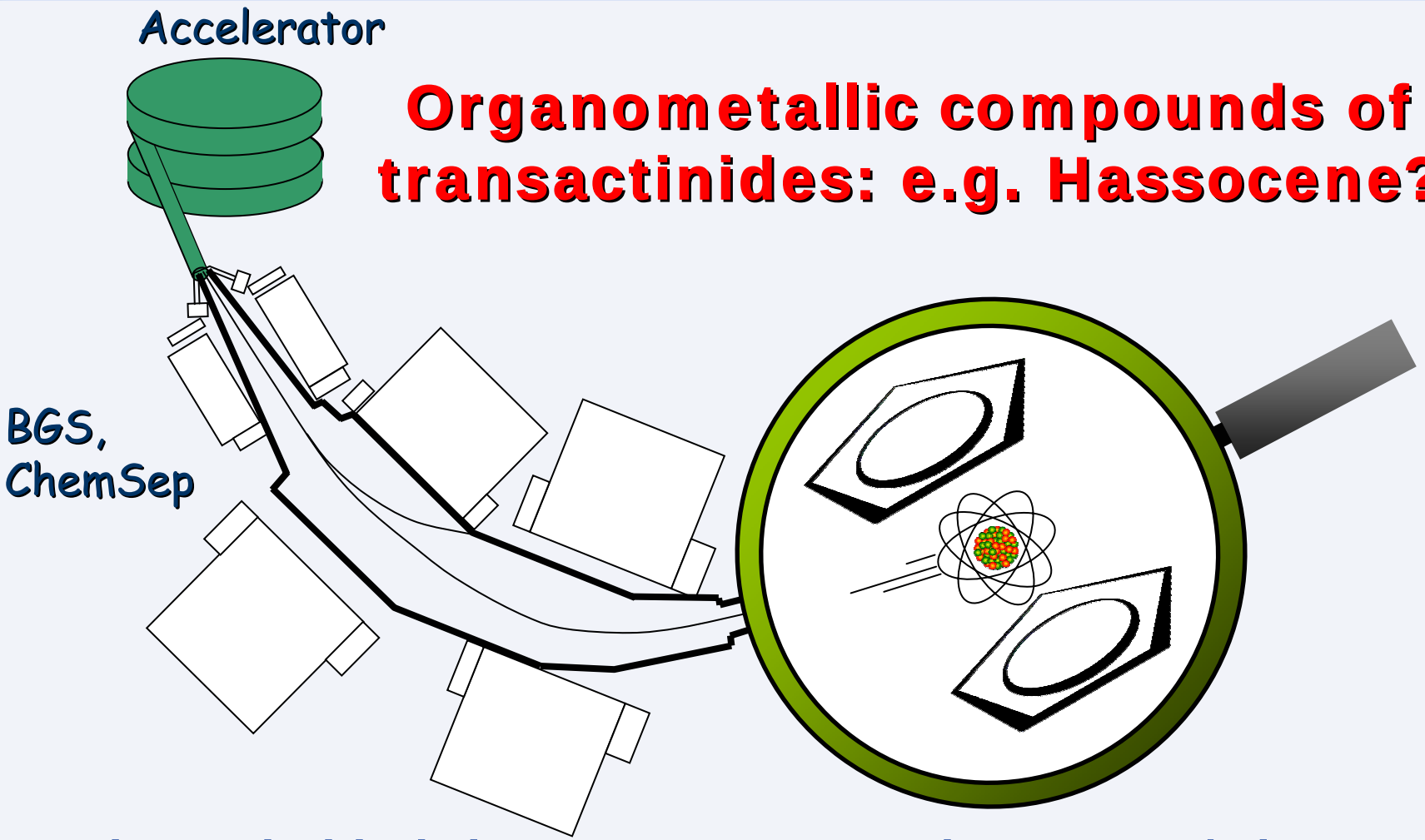
	Rf 104	Db 105	Sg 106	Bh 107	Hs 108		El. 112 112
Elemental state							(112)
Chlorides	$RfCl_4$	$DbCl_5$					
Bromides	$RfBr_4$	$DbBr_5$					
Oxychlorides	$(RfOCl_2)$	$DbOCl_3$	SgO_2Cl_2	BhO_3Cl			
Oxybromids							
Oxides					HsO_4		
Hydroxides			$SgO_2(OH)_2$				

Gas Phase Chemistry: Present

Simple inorganic compounds: e.g. HsO_4



Gas phase chemistry: Future ?



Organometallic compounds of transactinides: e.g. Hassocene?

No beam behind the target!! Separation @ BGS/ChemSep

Presented on the "Workshop on Recoil Separator for Superheavy Element Chemistry". March 20-21, 2002, GSI, Darmstadt, Germany

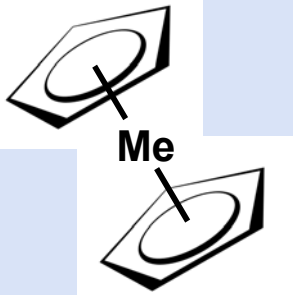
Volatile Compounds of d Elements

Metallocenes $M(cp)_2$

Observed in solid phase:

$Fe(cp)_2 + U(n,f)Ru \rightarrow Ru(cp)_2$

(F. Baumgärtner et al., Z. Naturforsch. 16a (1961) 374)

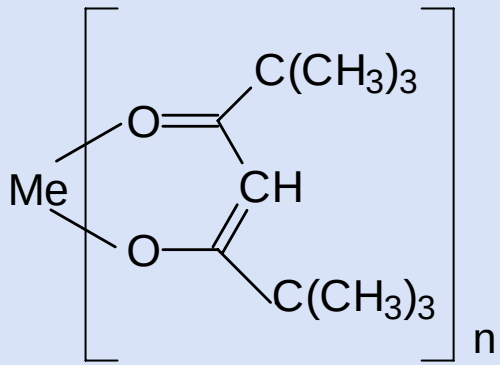


β-diketonates

(e.g. dpm=dipivaloylmethane):

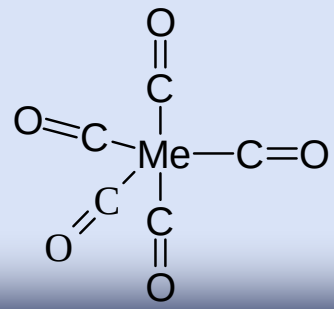
Investigated with IC using carrier-free Ru from ^{252}Cf

(S. Ono et al., J. Radioanal. Nucl. Chem. 255 (2003) 571)



Carbonyles $M(CO)_x$

Well-known, stable (e.g. group 8)



Production Rates at 88“ & BGS

Rutherfordium Isotopes

^{257}Rf ($T_{½}$ = 4 s) ; 0.5 Atoms/min behind BGS

Reaction: ^{208}Pb(^{50}Ti, 1n)^{257}Rf, $\sigma \approx$ 10-15 nb

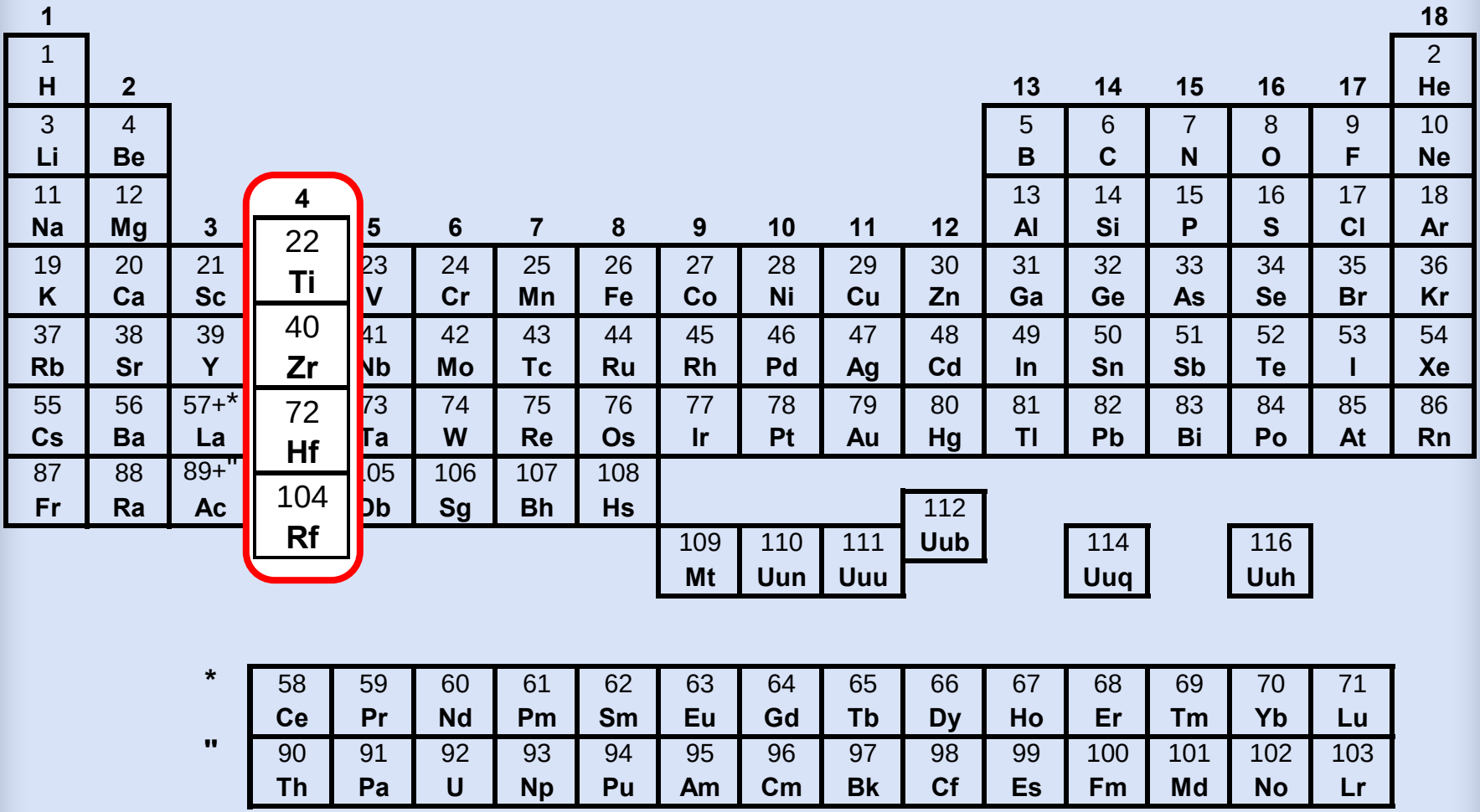
(J.P. Omtvedt et al., J. Nucl. Radiochem. Sci. 3 (2002) 121)

Dubnium isotopes

^{258}Db ($T_{½}$ = 4 s): ^{209}Bi(^{50}Ti,1n)^{258}Db, $\sigma \approx$ 3 nb

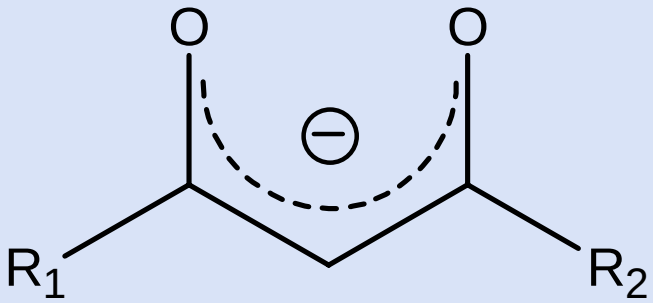
Heavier elements: no isotopes with $T_{½} > 0.5$ s that can be produced and separated with BGS

The Periodic Table of the Elements



Volatile Compounds of Group 4 Elements

β-diketonates:



acac:	$R_1 = R_2 = CH_3$
tfa:	$R_1 = CH_3$, $R_2 = CF_3$
hfa:	$R_1 = R_2 = CF_3$
thd (=dpm):	$R_1 = R_2 = C(CH_3)_3$

hfa compounds:

(hfa=hexafluoroacetylacetonate)

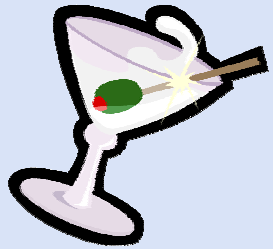
Successful production of carrier-free $Hf(hfa)_4$ is reported. ($T_{½}$ ~ h). However, no separation was achieved! T_{Dep} in TC: 50-100 °C

(E.V. Fedoseev et al., J. Radioanal. Nucl. Chem. Lett. 119 (1987) 347)

Production of Short-Lived Zr and Hf Isotopes

Investigating homologue elements under identical conditions is desirable.

When preseparation is employed, simultaneous production is not possible (differing Bρ).



→ Employ a heavy-ion cocktail!

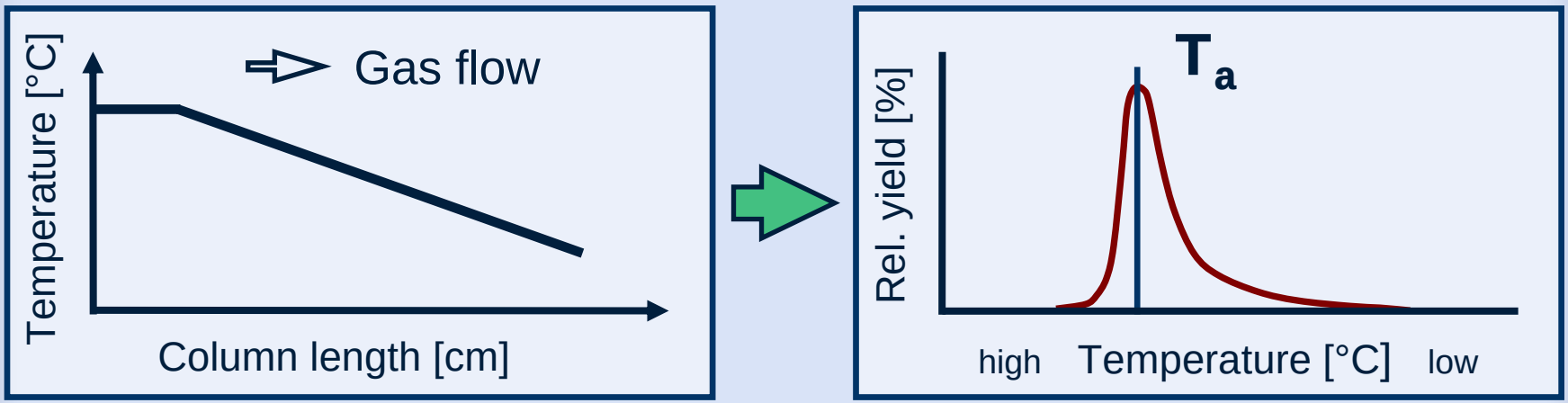
^{nat}Ge(^{18}O,xn)$^{85;85m;87m}$Zr

$^{112;116;120;124}$Sn(^{50}Ti, 4-5n)$^{158;162;165;169}$Hf

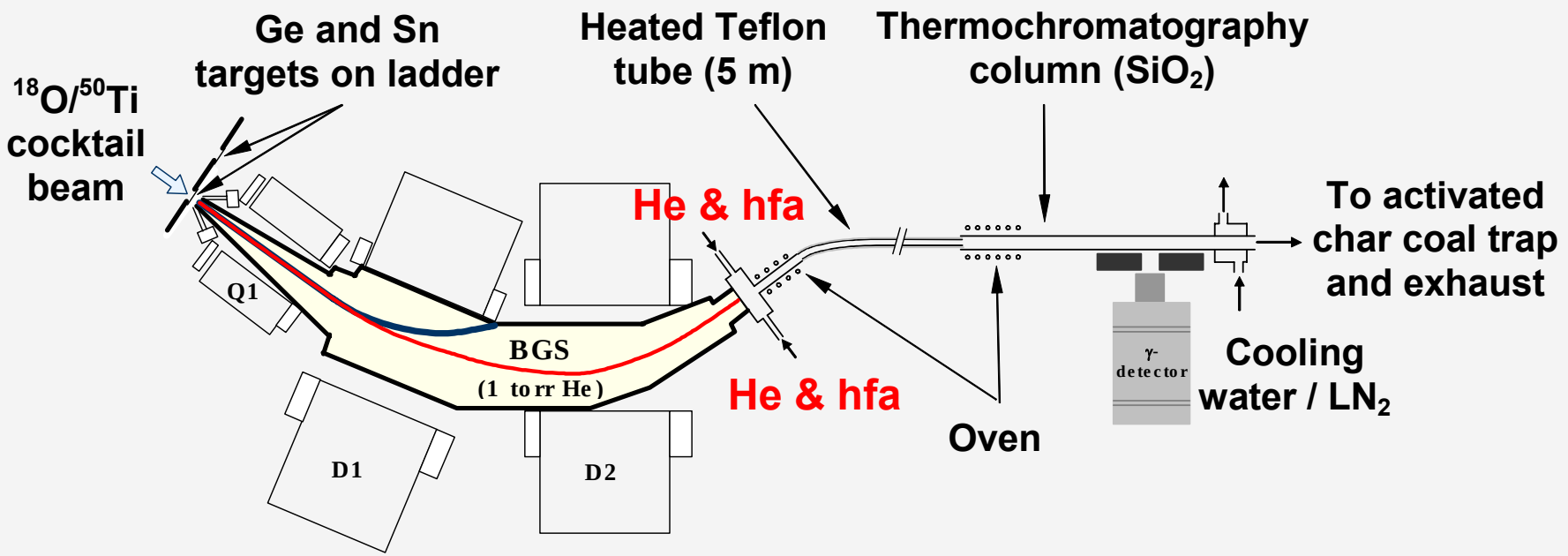
Ion	Q	M/Q	nat. Abund. %	Energy (MeV)	MeV/n	Frequency (MHz)
^{18}O	4+	4.50	0.2	83.6	4.64	14.3875
^{50}Ti	11+	4.55	5.4	228.0	4.56	14.5162

Using the target ladder (max. 5 different targets), switching between Zr and Hf takes a few min.

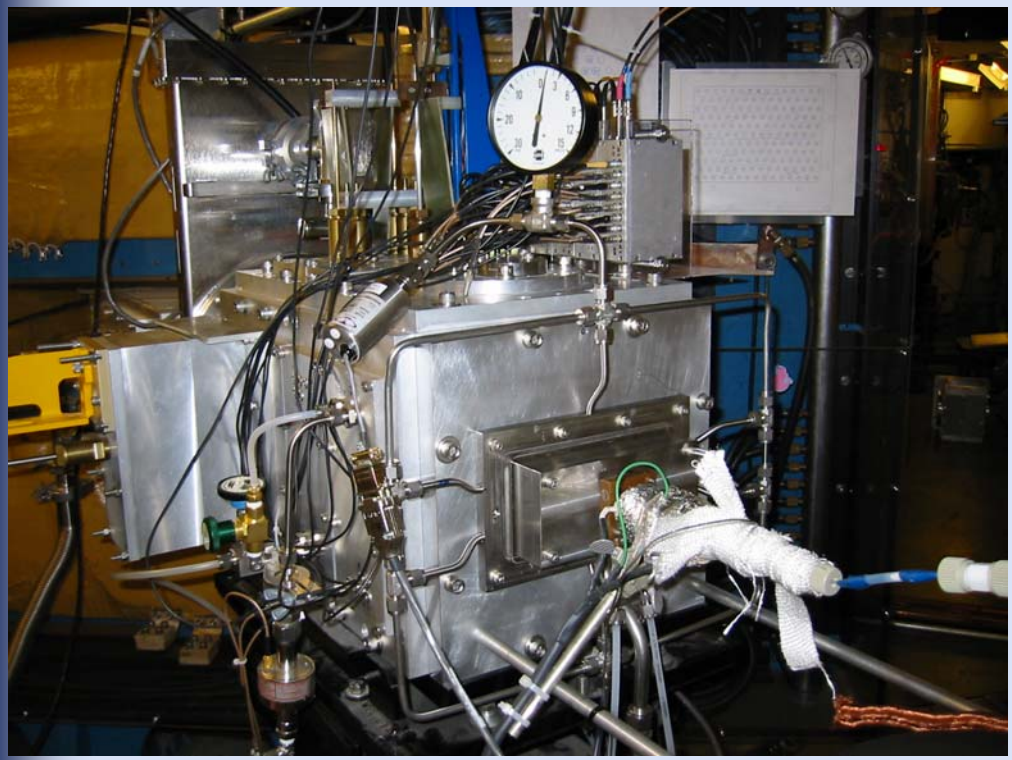
Thermochromatography



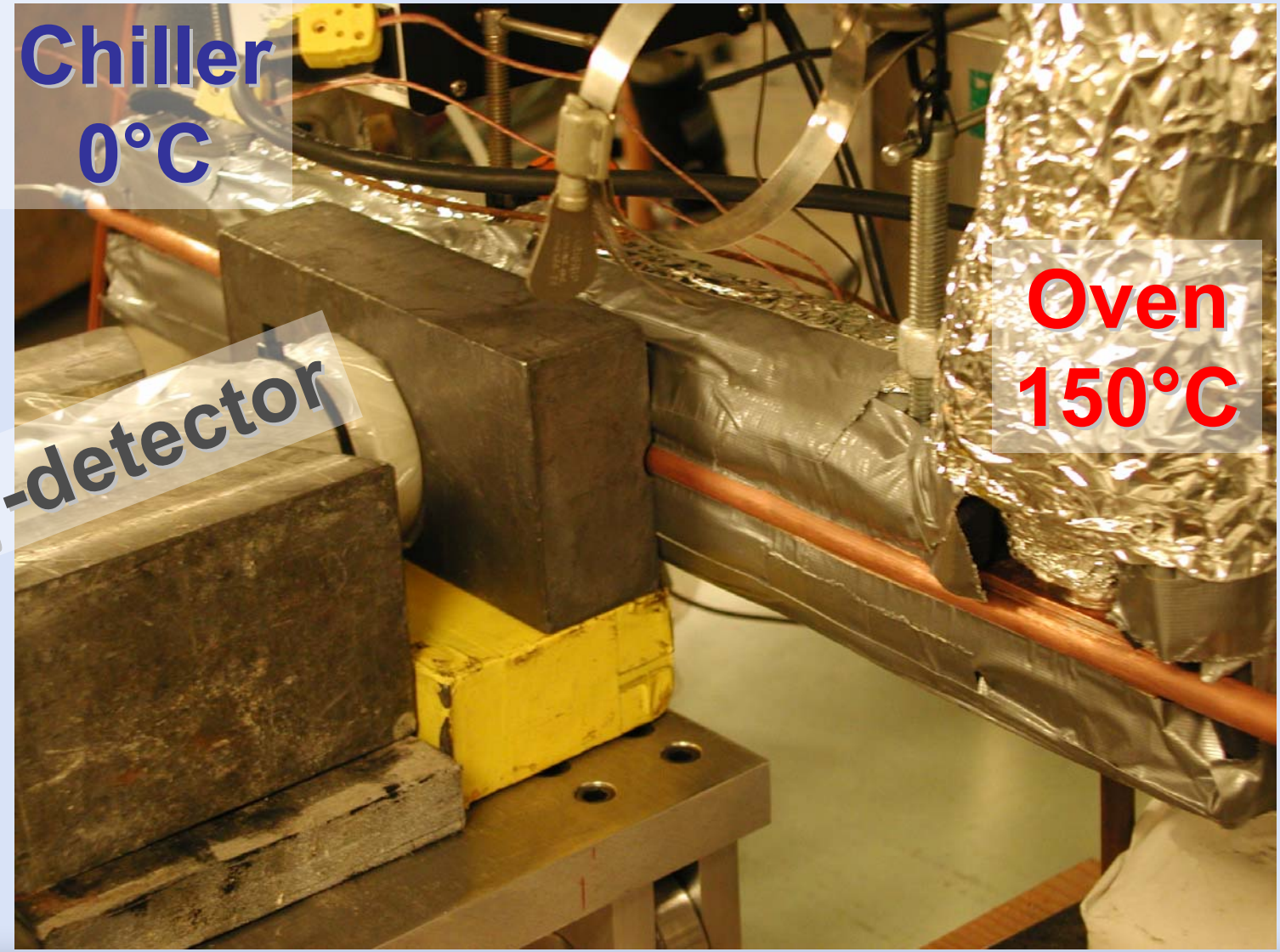
Experimental Set-Up



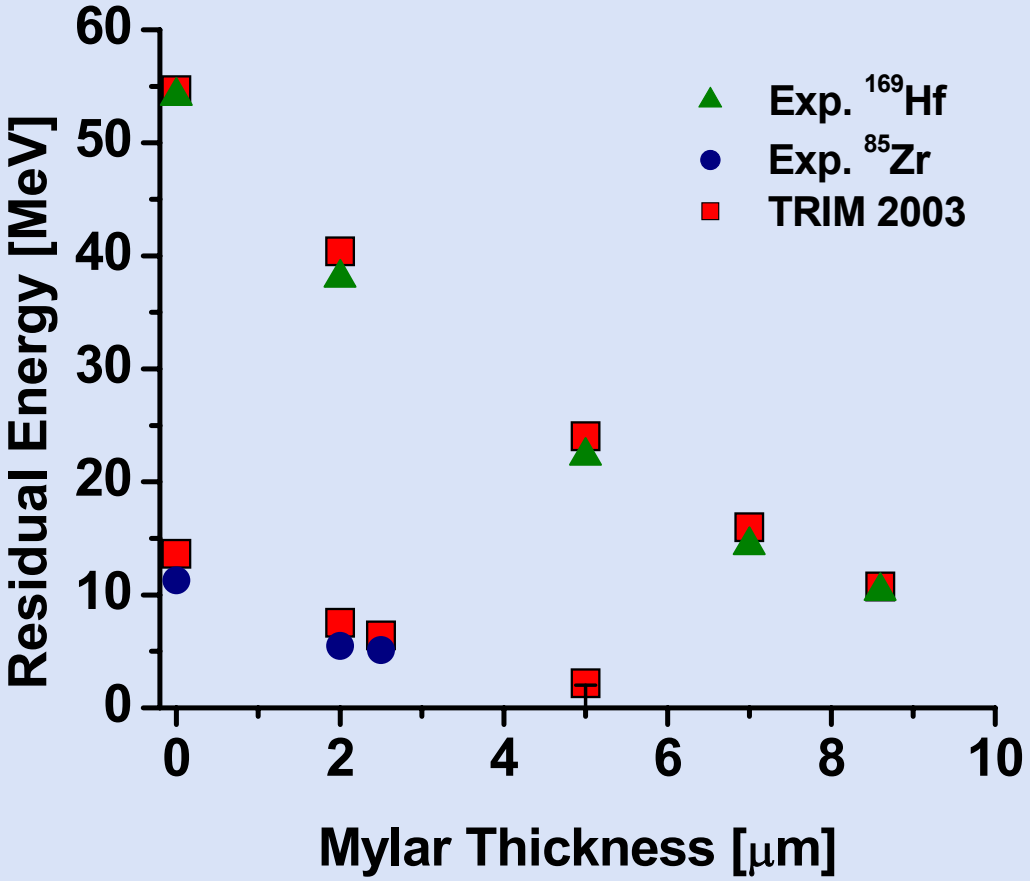
Modified Recoil Transfer Chamber RTC



On-Line TC Apparatus (γ-detection)



Hf EVR residual energy after passing through MYLAR



SRIM2003 range predictions:

^{169}Hf: 12.40 μm

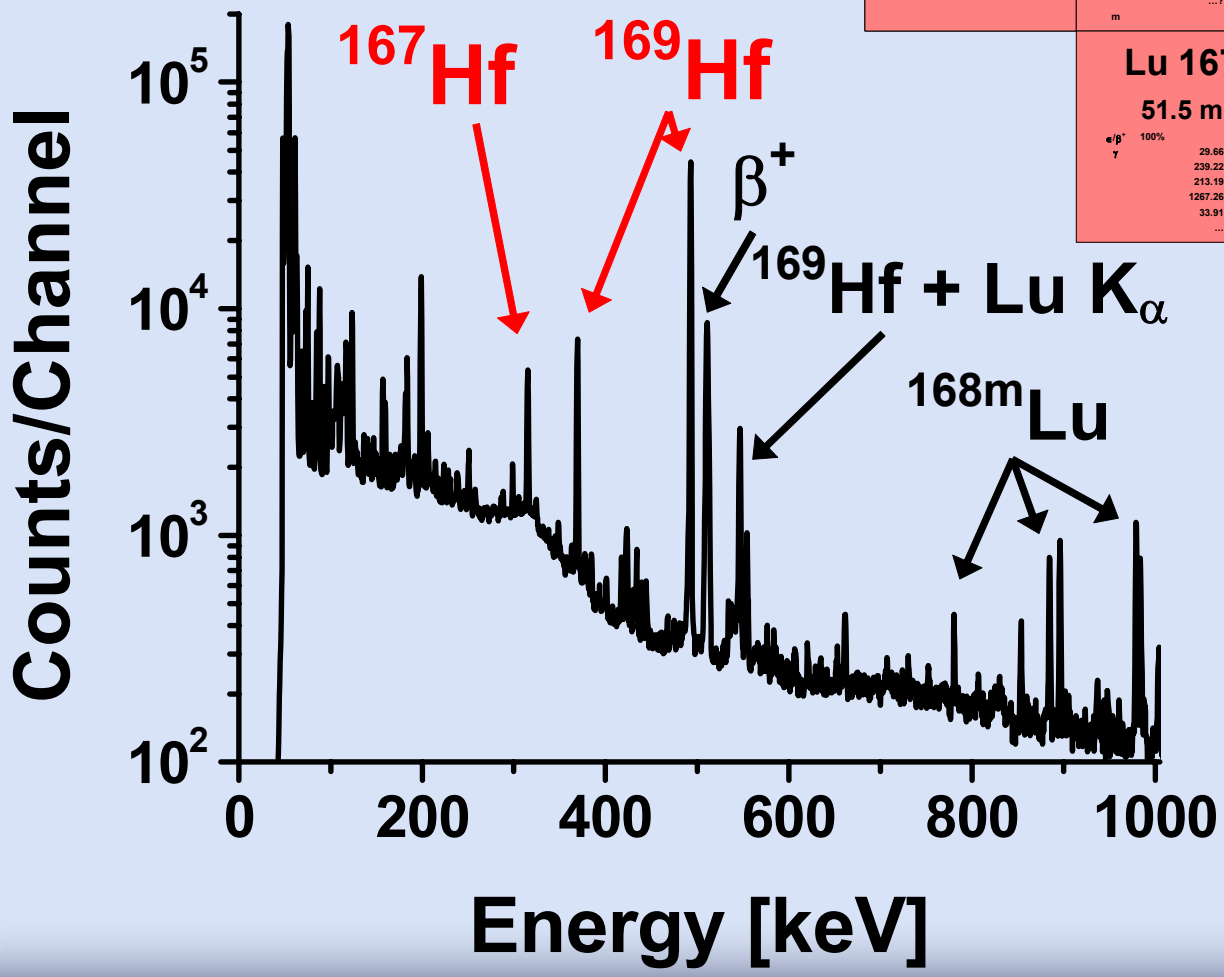
^{85}Zr: 6.64 μm

However, using a 6 μm window didn‘t allow for the observation of Zr.

Now in use: 3.6 μm window

Pulse height defect corrected according to Moulton et al. NIM 157 (1978) 325

Hf Catcher-Foil: $^{124}Sn(^{50}Ti;\sim 5n)^{\sim 169}Hf$

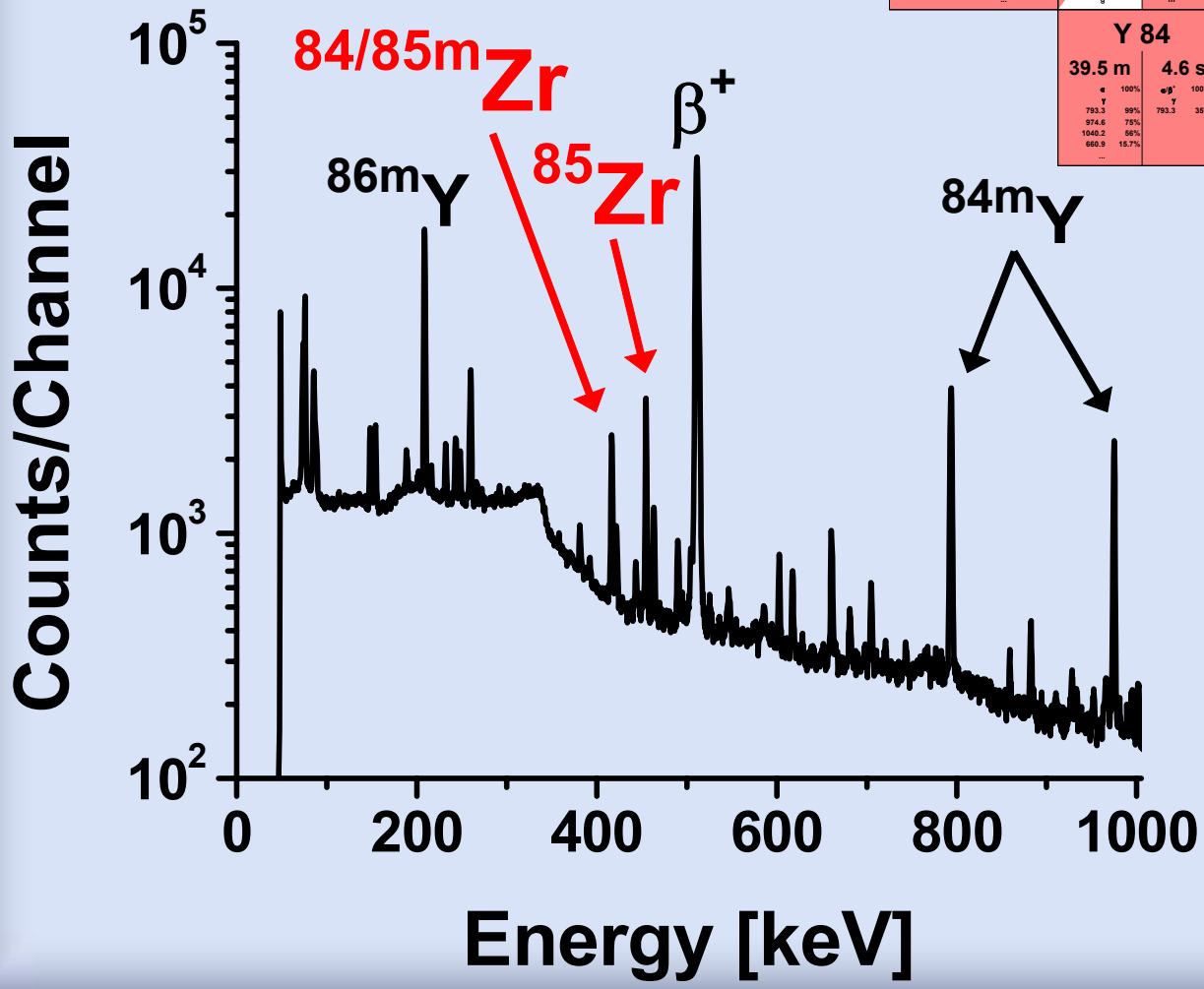


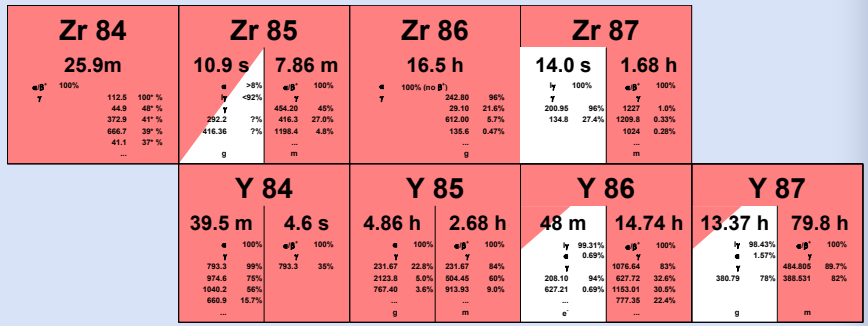
Hf 167	Hf 168	Hf 169
2.05 m	25.95 m	3.24 m
ε/β+ 100% 3.685…	ε/β+? 100%	ε/β+ 100% 2.777…
γ 315.24 100%	γ 183.8 147* %	γ 492.86 84%
175.4 6%	157.2 100* %	369.5 9.7%
139.9 3.8%	57 ?%	123.5 3.9%
	117 ?%	68.4 1.6%
	…?	72.9 0.6%
	m	g …

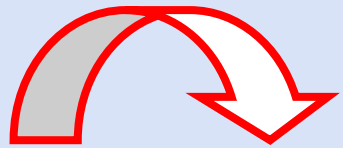
Lu 167	Lu 168		Lu 169	
51.5 m	6.7 m	5.5 m	2.7 m	1.44 d
ε/β+ 100%	ε >95%	ε/β+ 100%	Iγ 100%	ε/β+ 100%
γ 29.66 14.4%	Iγ <5%	γ	γ	γ
239.22 8.6%	γ	1483.65 72* %	29.0 0.0010%	960.62 23.4%
213.19 3.6%	198.82 28%	228.58 70* %		191.21 20.6%
1267.26 3.25%	979.22 20%	111.79 49* %		1449.74 9.92%
33.91 3.2%	896.12 15%	539.87 47* %		889.75 5.36%
…	…	…	e-	g; m

Works well, also for wet chemistry

Zr Catcher-Foil: $^{nat}Ge(^{18}O,xn)^{85/85m/87m}Zr$

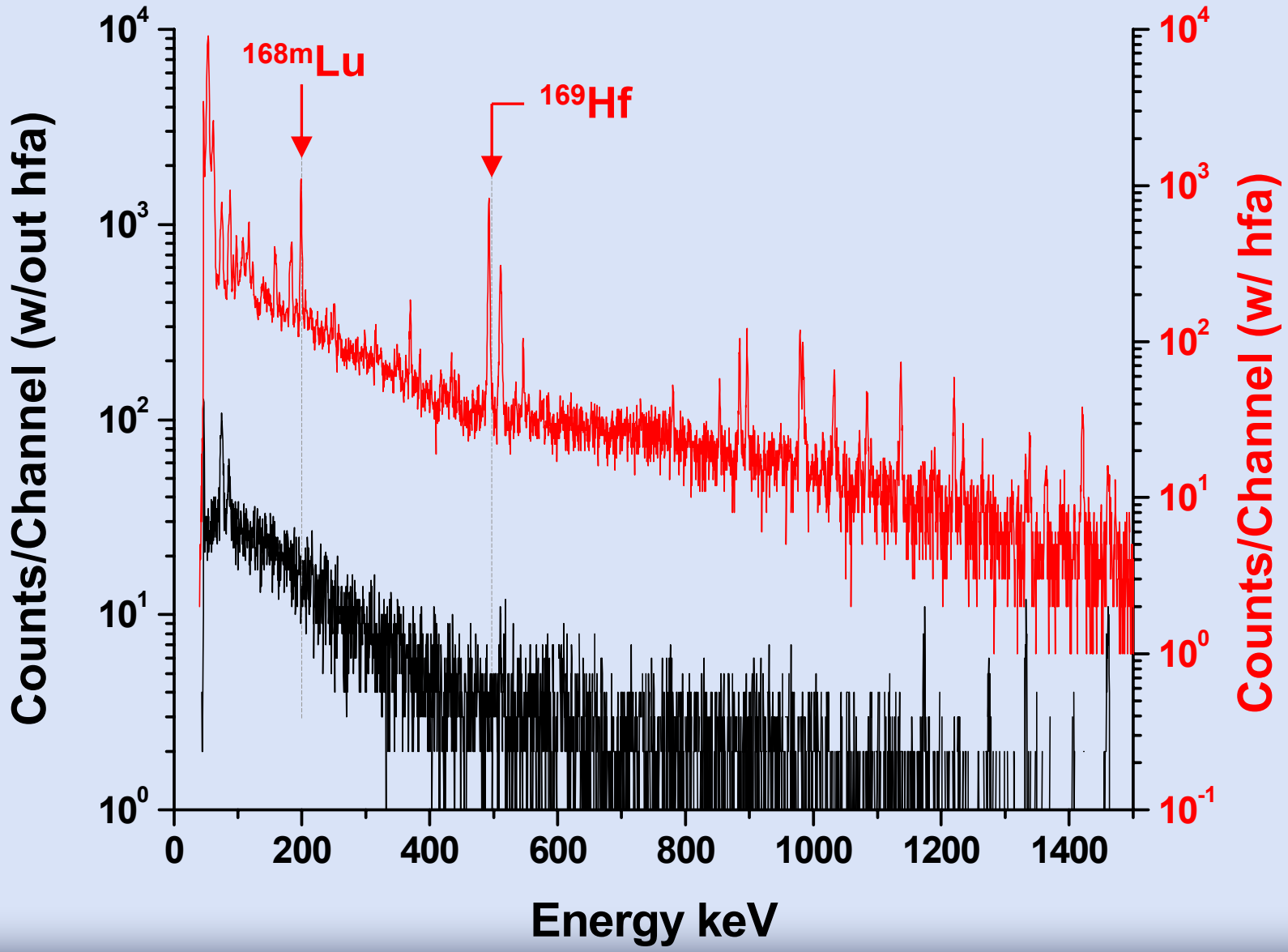






Using enriched Ge target is favorable.

Chemistry Results I – Influence of hfa



Chem. Results II – Yield *vs.* ...

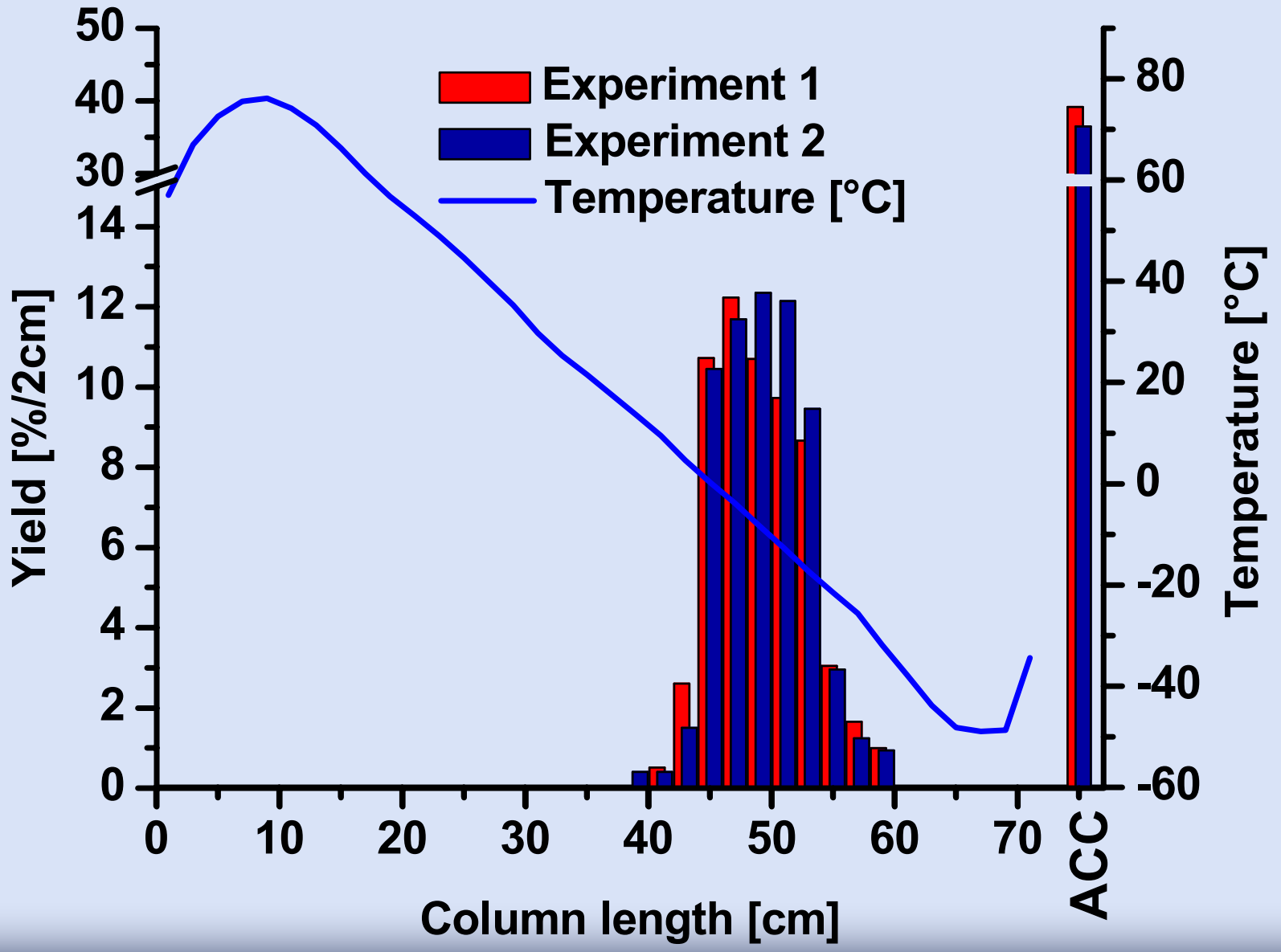
Maximum yield is achieved at the following experimental parameters:

- **T_{RTC}-Oven: 240 °C**
- **T_{hfa}: 30 °C (yield high, consumption rate ok)**
- **"Age" of hfa: new!**

Maximum yields for ^{169}Hf ($T_{½}$ = 3.24 min):

Sample Position	Yield
Catcher Foil at BGS Exit	(100 %)
Formation of $Hf(hfa)_4$	>95 %
Transport to Chemistry Setup	>95 %
Overall Yield	>90 %

Thermochromatography



Thermochromatography

- No adsorption of Hf/Zr complexes at 50-100°C, but deposition between 0 °C and -20°C was observed.
- Due to traces of water in the carrier gas, deposition of ice was observed below -10°C.
- hfa and presumably hfa-complexes react strongly with water → Did we observe chemisorption?
- A substantial amount of Hf was found in the ACC after the TC. → Is there more than one chemical species present?
- Macroamounts of hfa deposit at -65°C, preventing TC to lower temperatures.
- In experiments with Zr, a ACC trap was attached to the TC column which covered a temperature down to -5°C. Zr was observed in the trap, but no Y. → Good separation Y/Zr
- $-\Delta H_{ads}$ of (60±3) kJ/mol was deduced using the model of mobile adsorption.

What have we learnt? / Our problems...

It is indeed possible to form volatile metal complexes of reaction products of HI induced reactions!

- **hfa complexes are very volatile.**
- **Question 1: What is the chemical state of our observed Hf?**
- **Question 2: Does the system look promising for a Rf experiment?**
- **Question 3: Should we rather investigate less volatile compounds (e.g. tfa complexes?)**
- **Main problem: macroamounts of hfa deposit at higher temperature than microamounts of $M(hfa)_4$.**

Summary

The BGS should allow the production of "fragile" compounds of TAN

First experiments aimed at the investigation of hfa-compounds of the Rf homologs Zr and Hf

Short-lived isotopes of these elements are produced with a $^{18}O/^{50}Ti$ cocktail beam

hfa compounds are formed in-situ in the RTC with high yield. They are very volatile and can be transported to a chemistry setup at room temperature.

First TC experiments indicate the formation of two different chemical species, both volatile.