Boris L. Zhuikov

NEW METHODS OF HIGH TEMPERATURE CHEMICAL SEPARATION IN RADIOCHEMISTRY, ANALYTICAL CHEMISTRY AND NEW ELEMENT RESEARCH

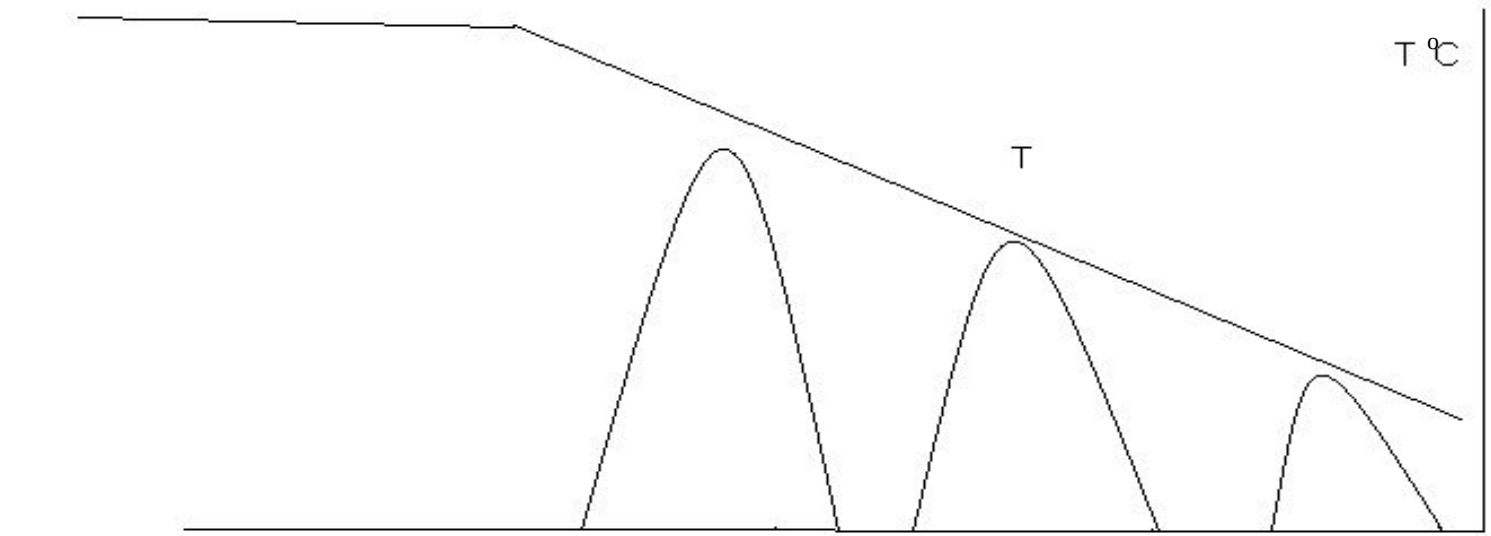
1. **Experimental and theoretical approach.**

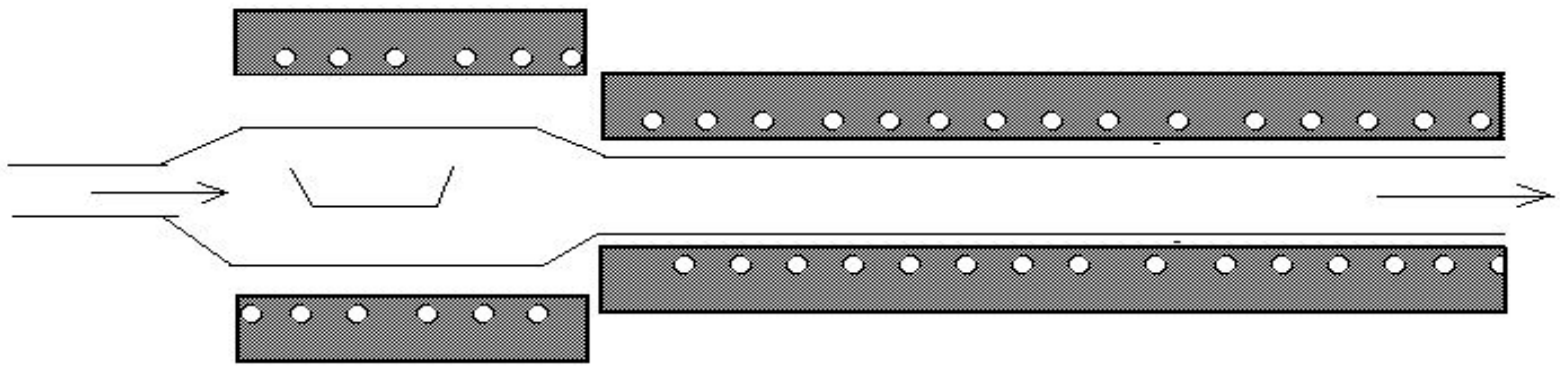
2. **High temperature examples in radioisotope production.**

3. **Analytical system for separation of volatile elements and oxides.**

4. **New element chemistry research.**

THERMOCHROMATOGRAPHY





THEORETICAL APPROACH FOR CARRIER-FREE THERMOCHROMATOGRAPY

Approximate equation:

$$\Delta H_d^0 = T_a \, [\Delta S_d^o + R \ln(0.11 \, t \, Q \, g / s)]$$

$$T_a = \Delta H_d^0 \, [\Delta S_d^o + R \ln(0.11 \, t \, Q \, g / s)]^{-1}$$

ΔH_d^0 - Enthalpy of desorption

ΔS_d^o - Entropy of desorption

T_a - Absolute temperature of peak maximum

Parameters of the experiment:

t – period of separation

Q – gas flow rate

g – temperature gradient

s – support surface per unit of column length

Entropy calculation:

- Theoretical (molecular kinetics) (B.Eichler, 1975 and later) :

$$\Delta S_d^o = R \ln[s \, \nu \, (2\pi M/2RT)^{1/2}]$$

- Semi – theoretical (therodynamics) (B.Zhuikov 1982, 1996):

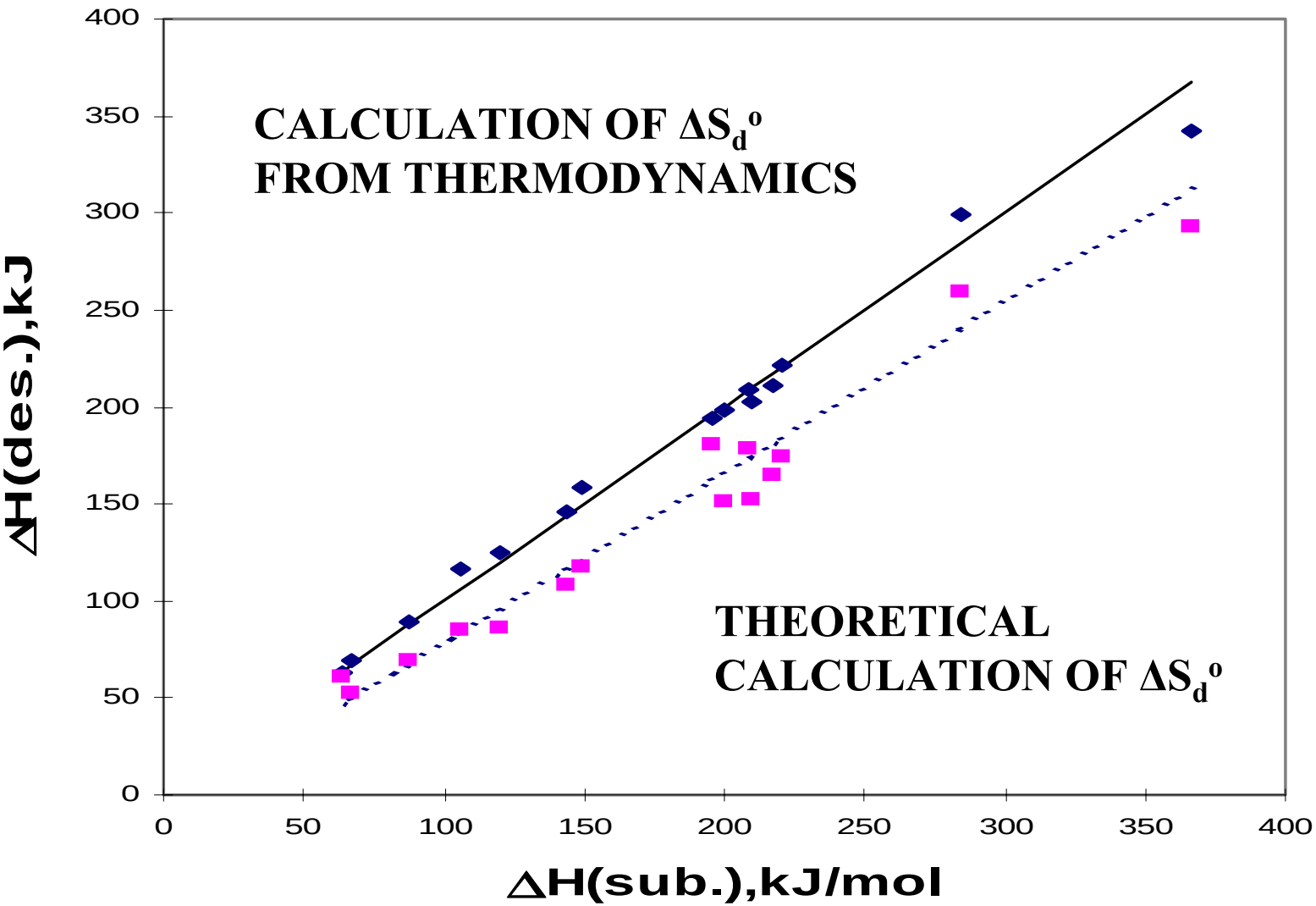
$$\Delta S_d^o = \Delta S_{sub}^o + R \ln[1.02 \cdot 10^6 \, M^{2/3} \, \rho^{-2/3} \, T^{-1})$$

- Experimental: T_a dependence from experimental parameters.

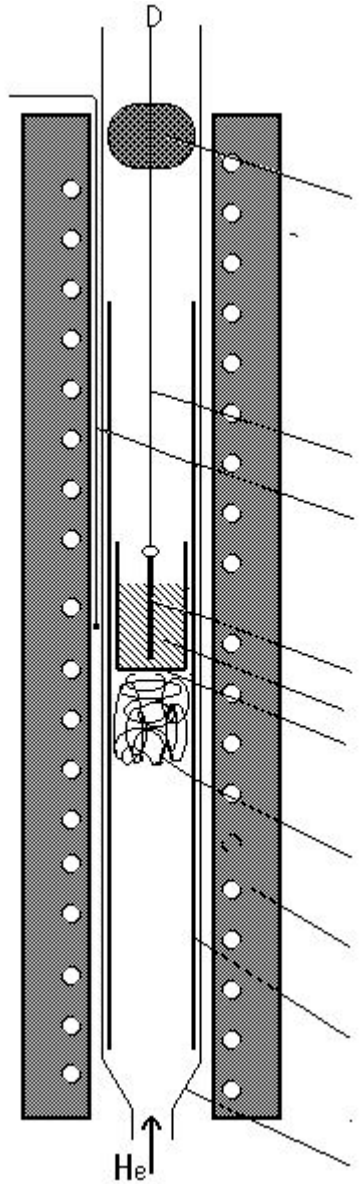
Enthalpy of desorption:

Correlation $\Delta H_d^0 \sim \Delta H_{sub}^0$

CORRELATION BETWEEN HEAT OF SUBLIMATION AND HEAT OF DESORPTION IN THERMOCHROMATOGRAPHY



A Simple Experiment on Direct Adsorption from Liquid Metal



Quartz or metallic wool

Steel wire

Thermocouple

Catcher foil

Molten metal

Quartz or metallic vial

Quartz or metallic wool

Electrical furnace

Niobium foil

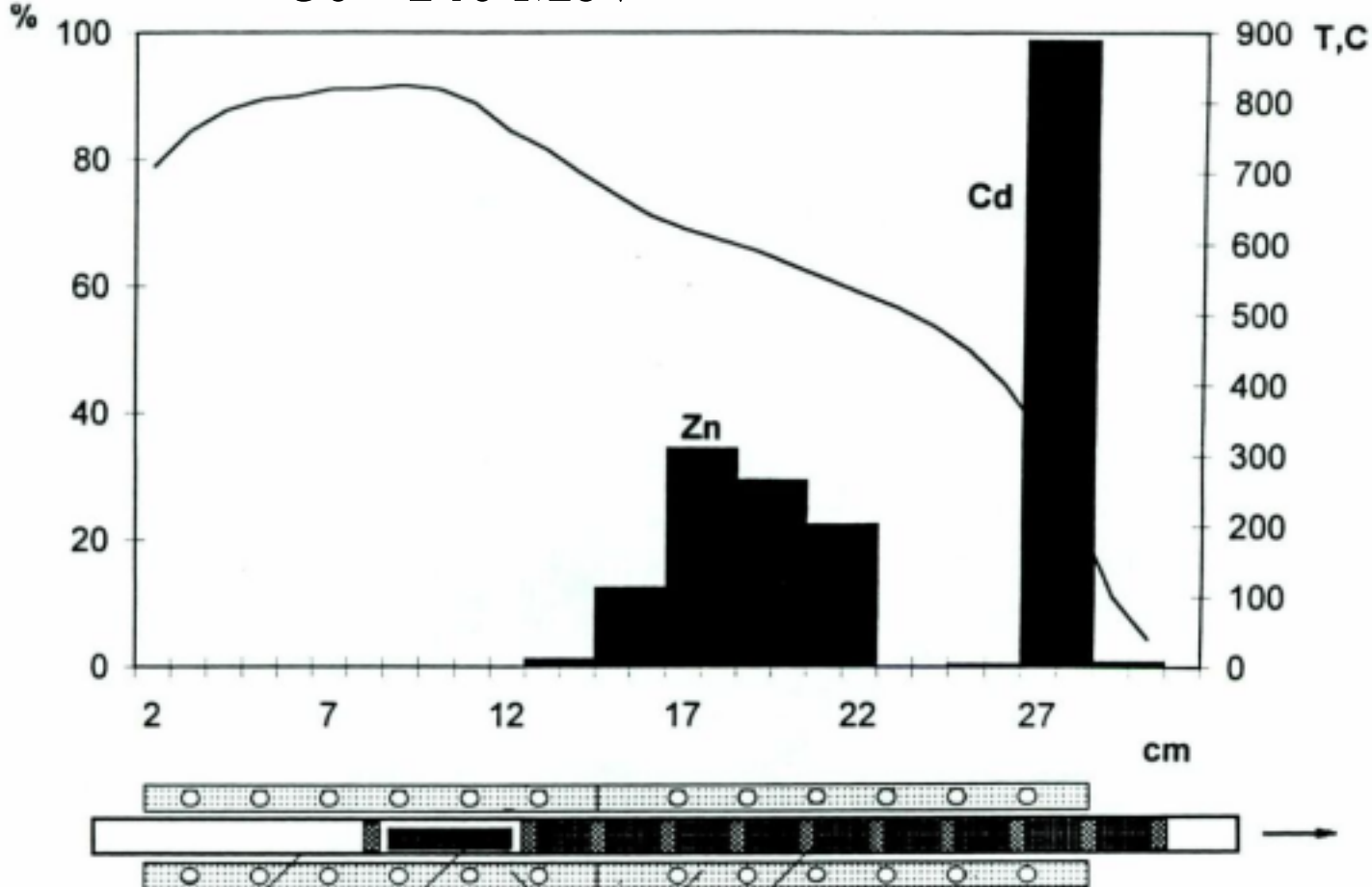
Quartz or metallic tube

He-gas flow

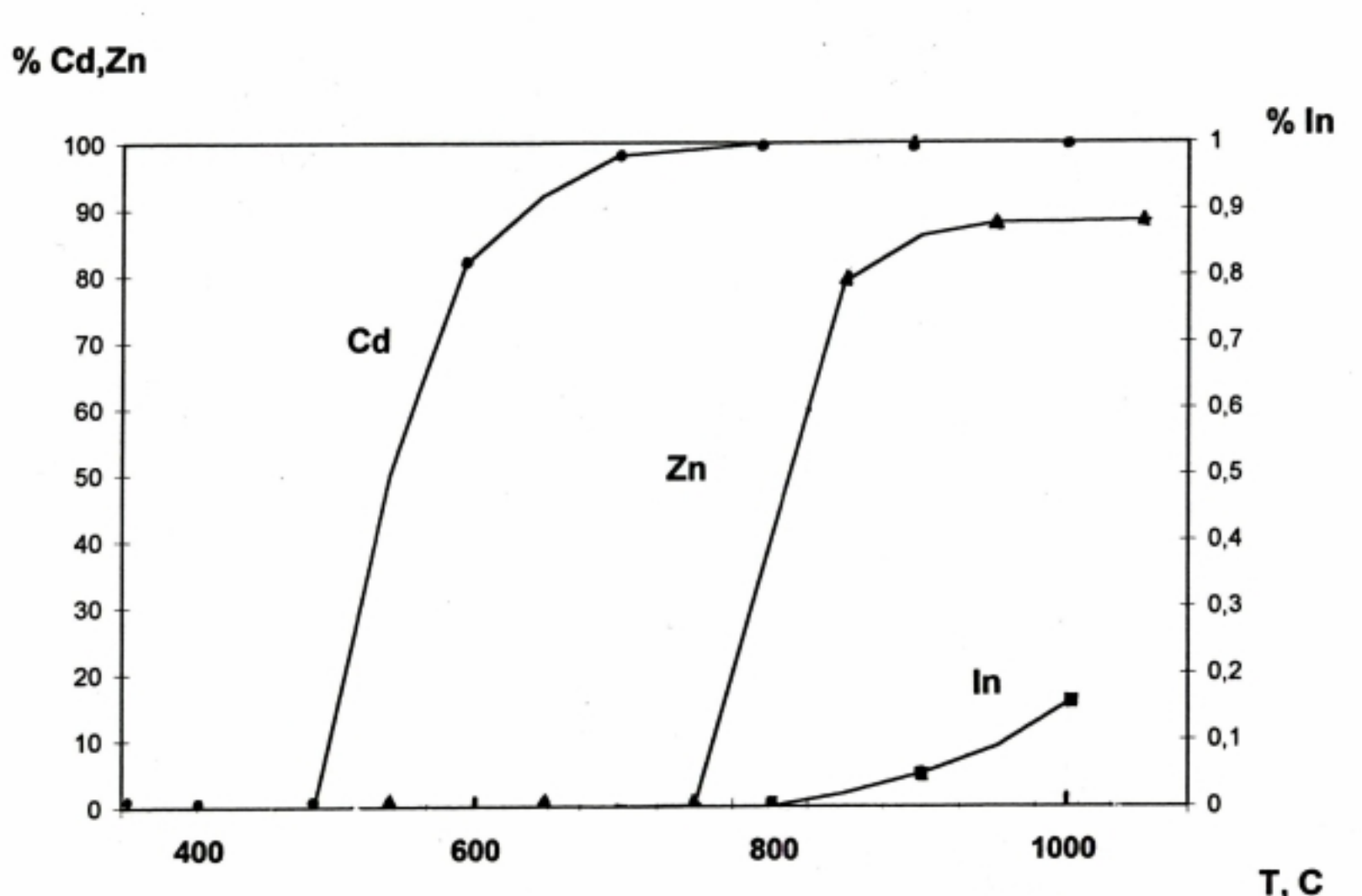
Thermochromatographic Separation of Cd and Zn from Indium Metal

^{nat}In (p,xn)$\rightarrow$^{109}In$\rightarrow$ ^{109}Cd

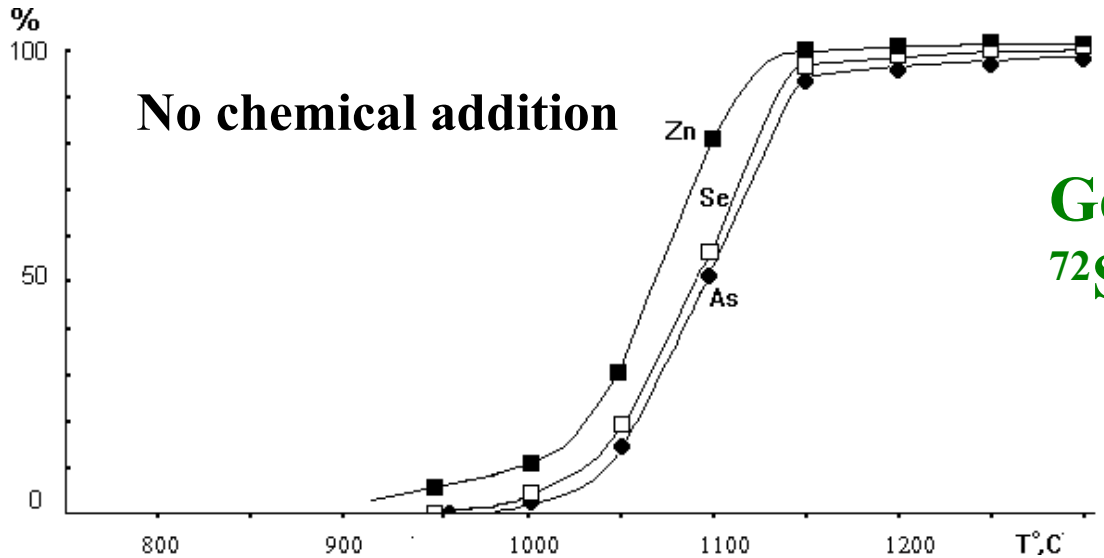
50 - 140 MeV



Temperature Dependence of Cd-109 and Zn-65 Evaporation from Indium and Gallium

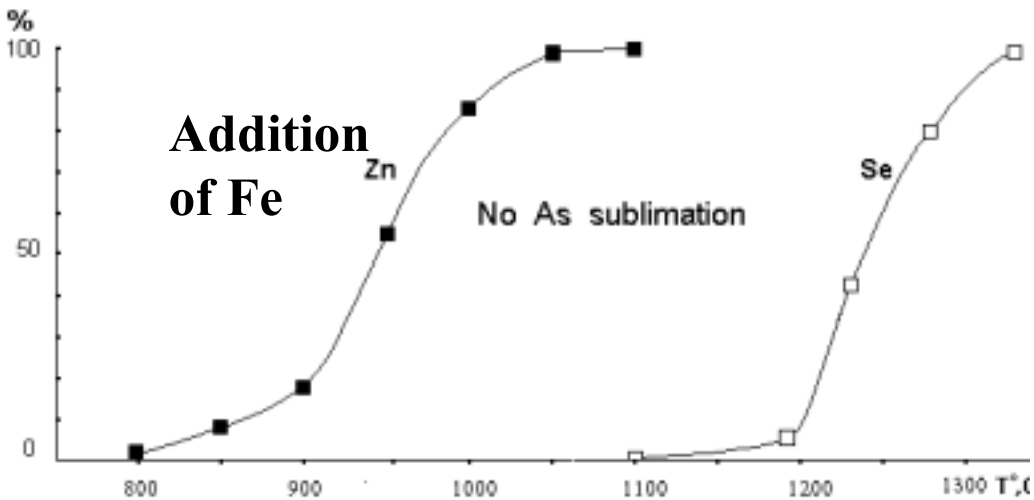


Se-72, Zn-65 and As Sublimation from Gallium Arsenide Target vs. Temperature in Helium Stream



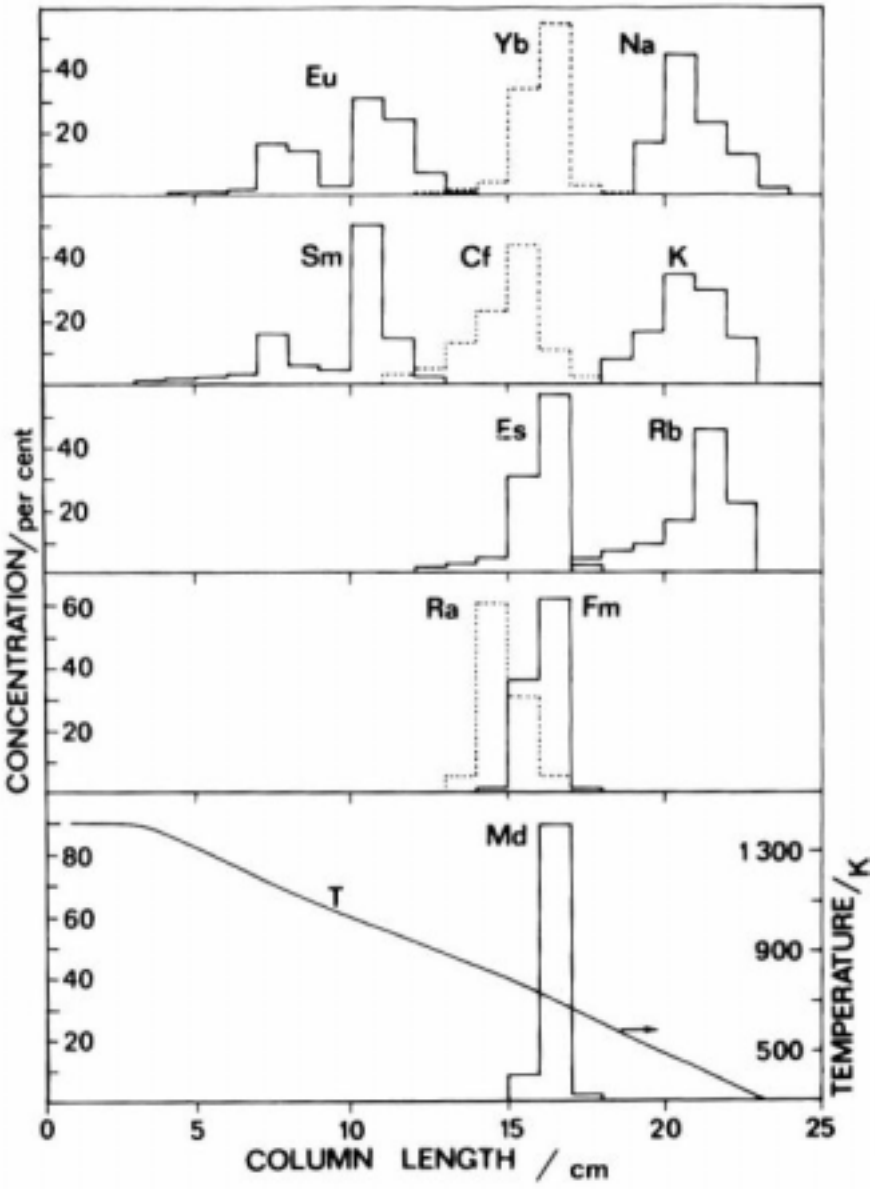
^{nat}As (p, 4n) ^{72}Se

Generator for PET imaging:
^{72}Se (8.5 days) → ^{72}As(26 hr)

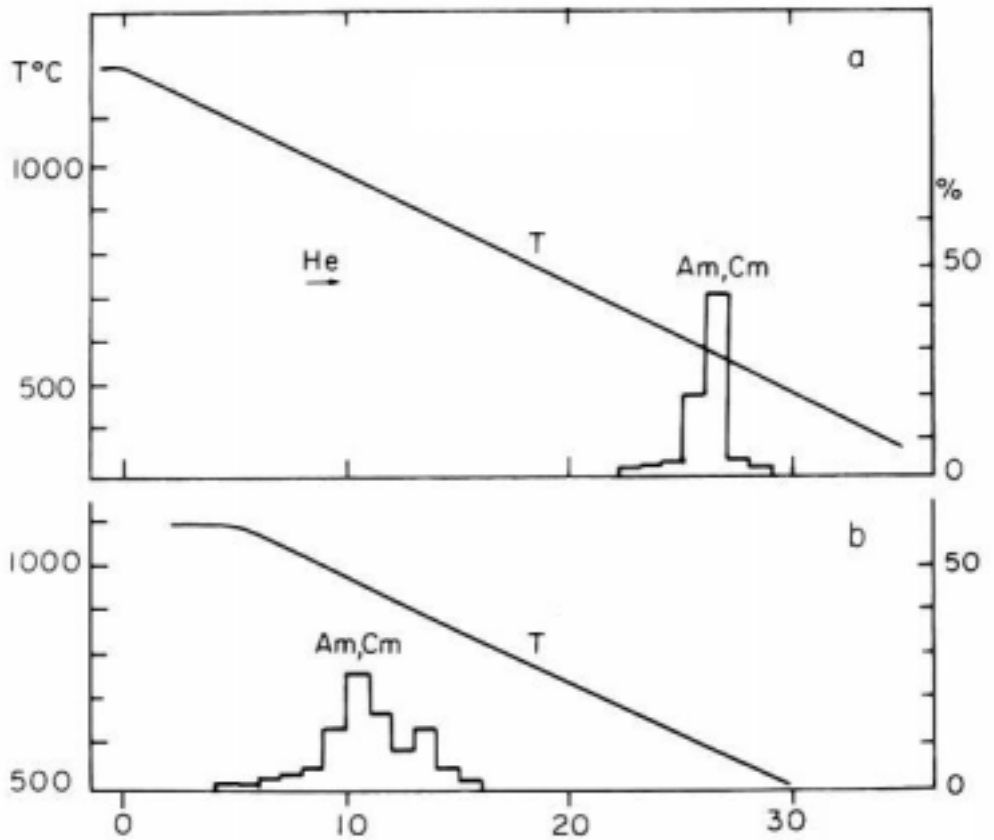


Thermochromatography of Lanthanides and Actinides on Ti - Column

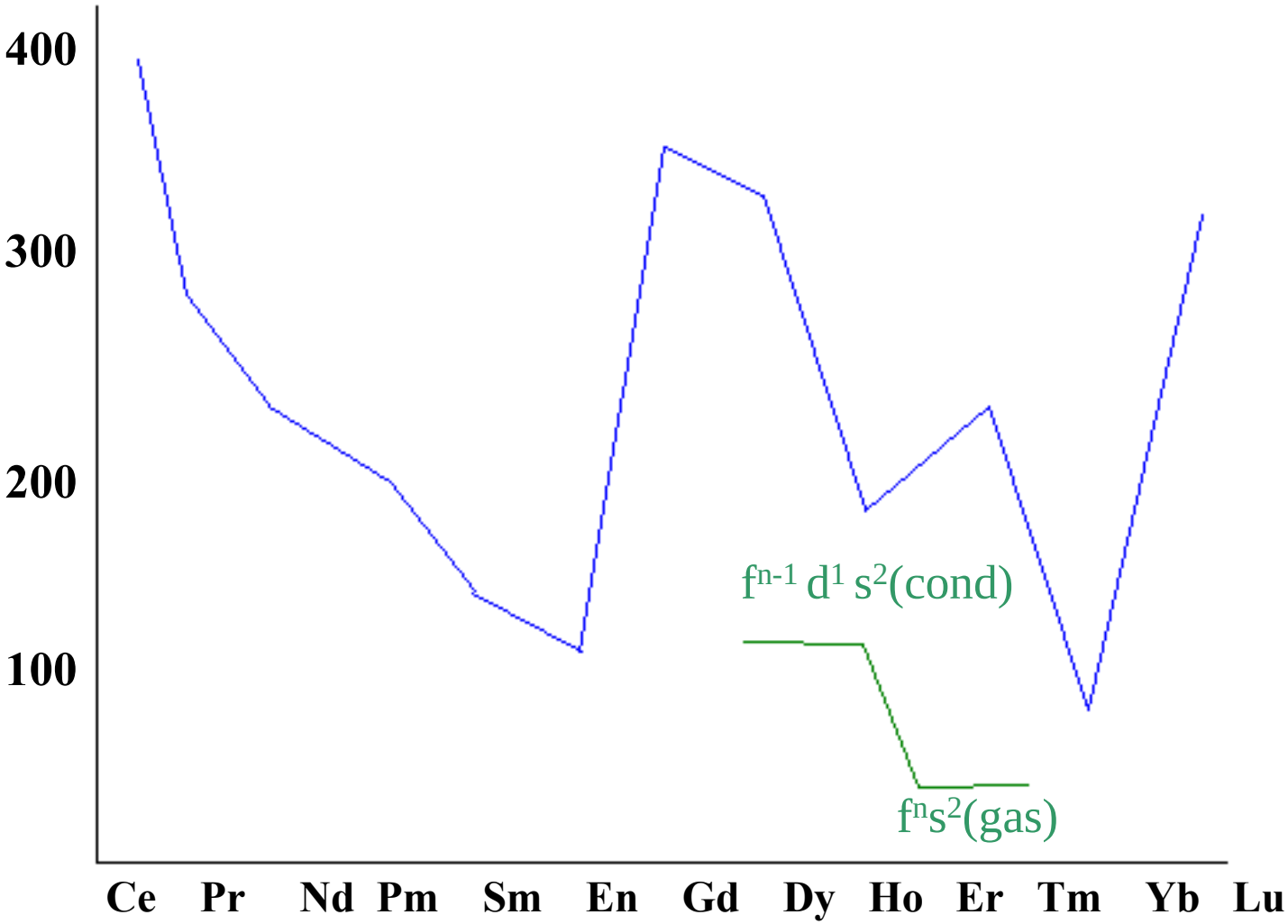
Elements (He-gas with Ca-vapor) *(S. Hubener et al.)*



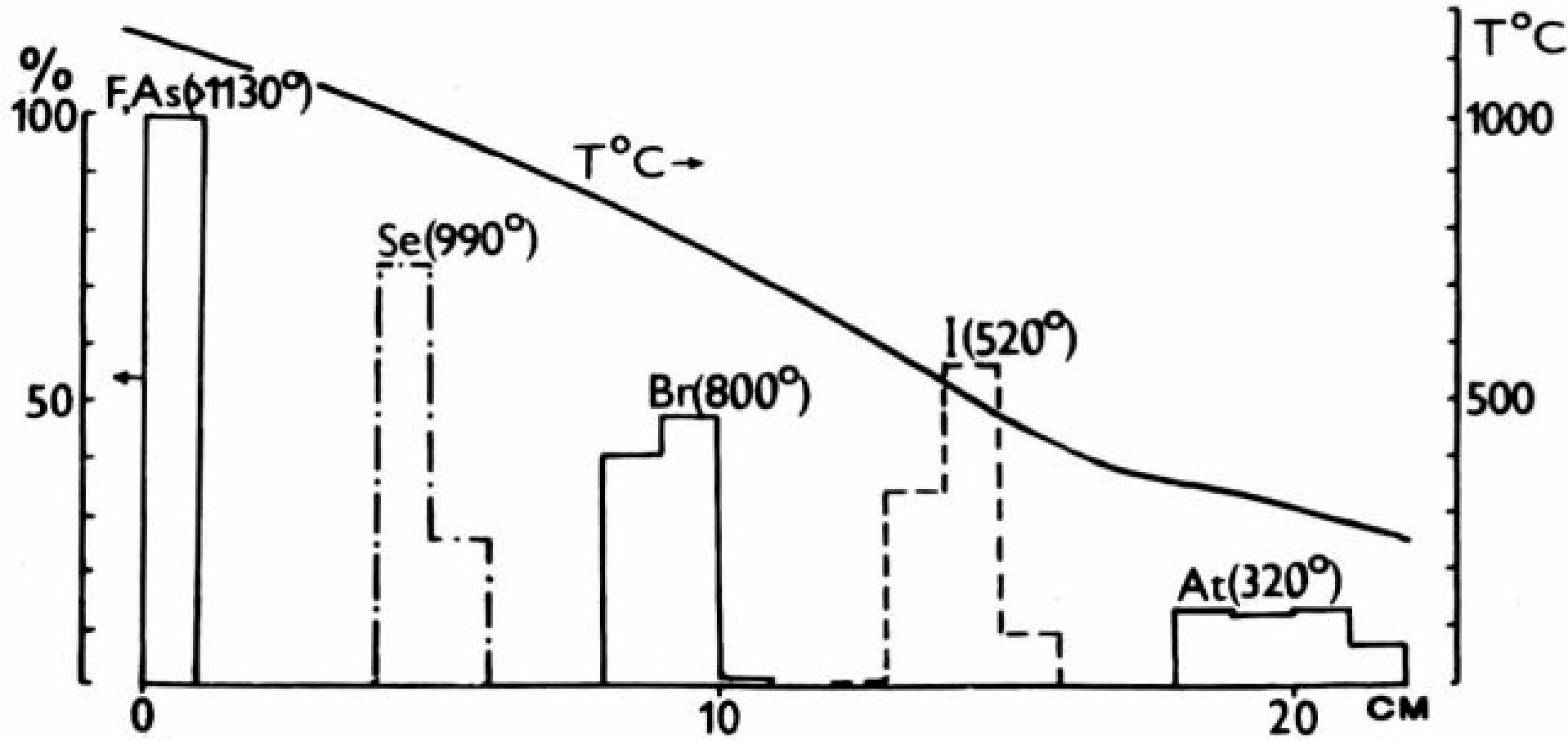
Lower oxides (He-gas) *(B.Zhuikov et al.)*



Heat of Evaporation of Lanthanides (kJ/mol)



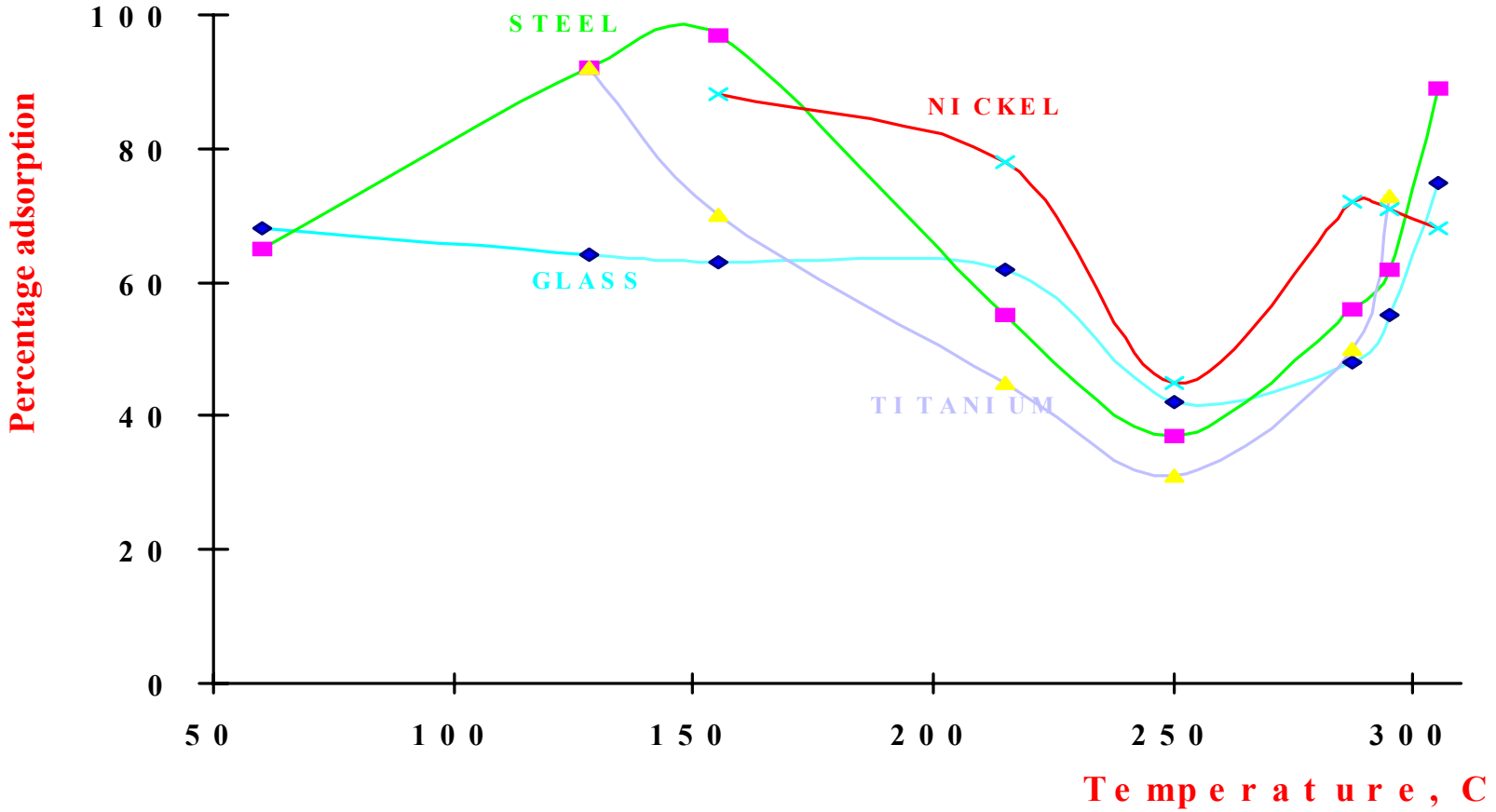
Thermochromatography of Non-Metals on CaO - Column in Oxygen Stream



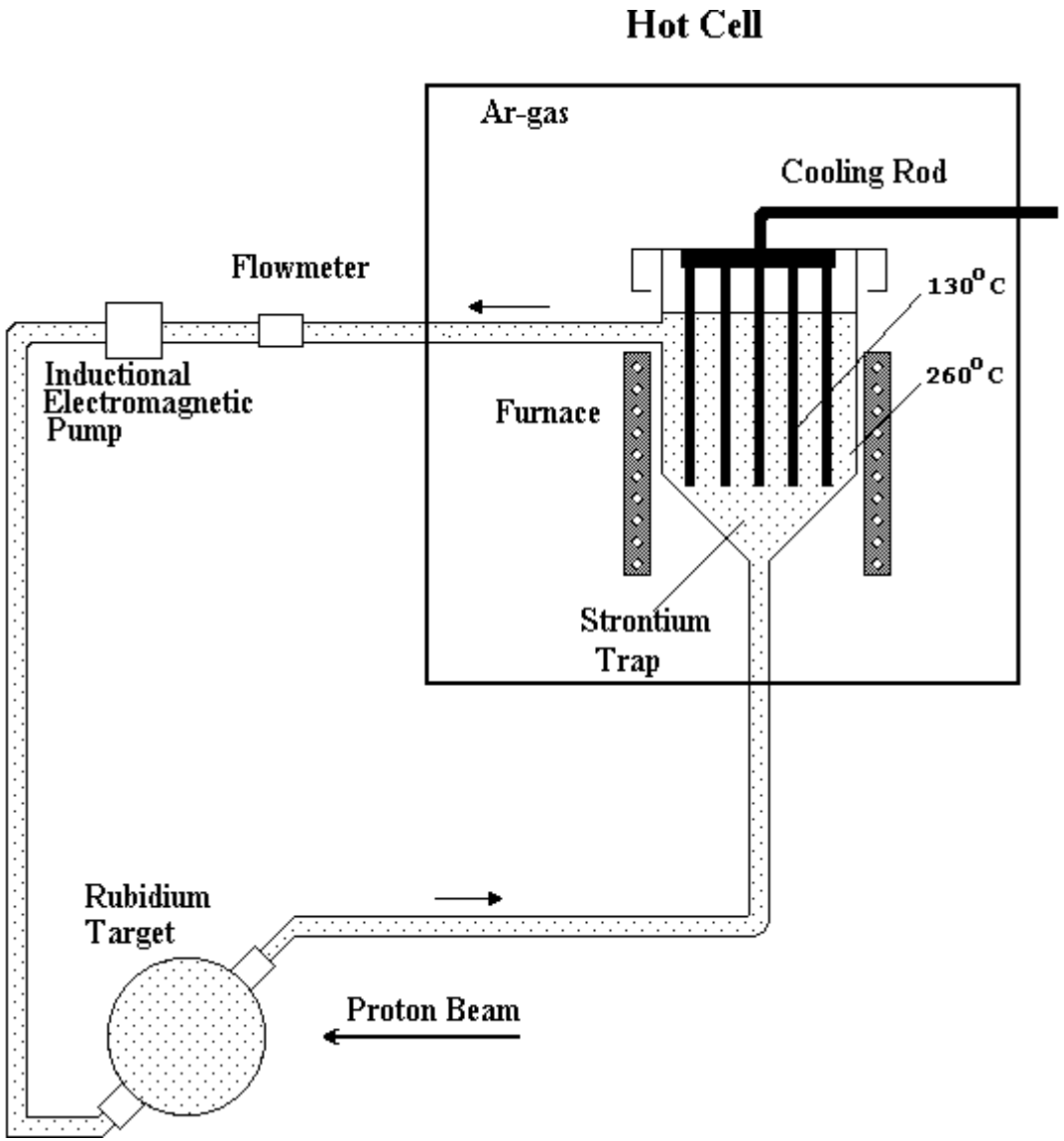
Temperature Dependence of Radio-Strontium Adsorption from Metallic Rubidium onto Several Different Surfaces

^{nat}Rb (p, 4-6n) $\rightarrow$ ^{82}Sr

PET generator for cardio diagnostics ^{82}Sr(25days) $\rightarrow$ ^{82}Rb (1.3 min)

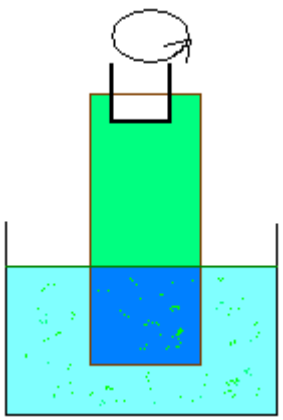


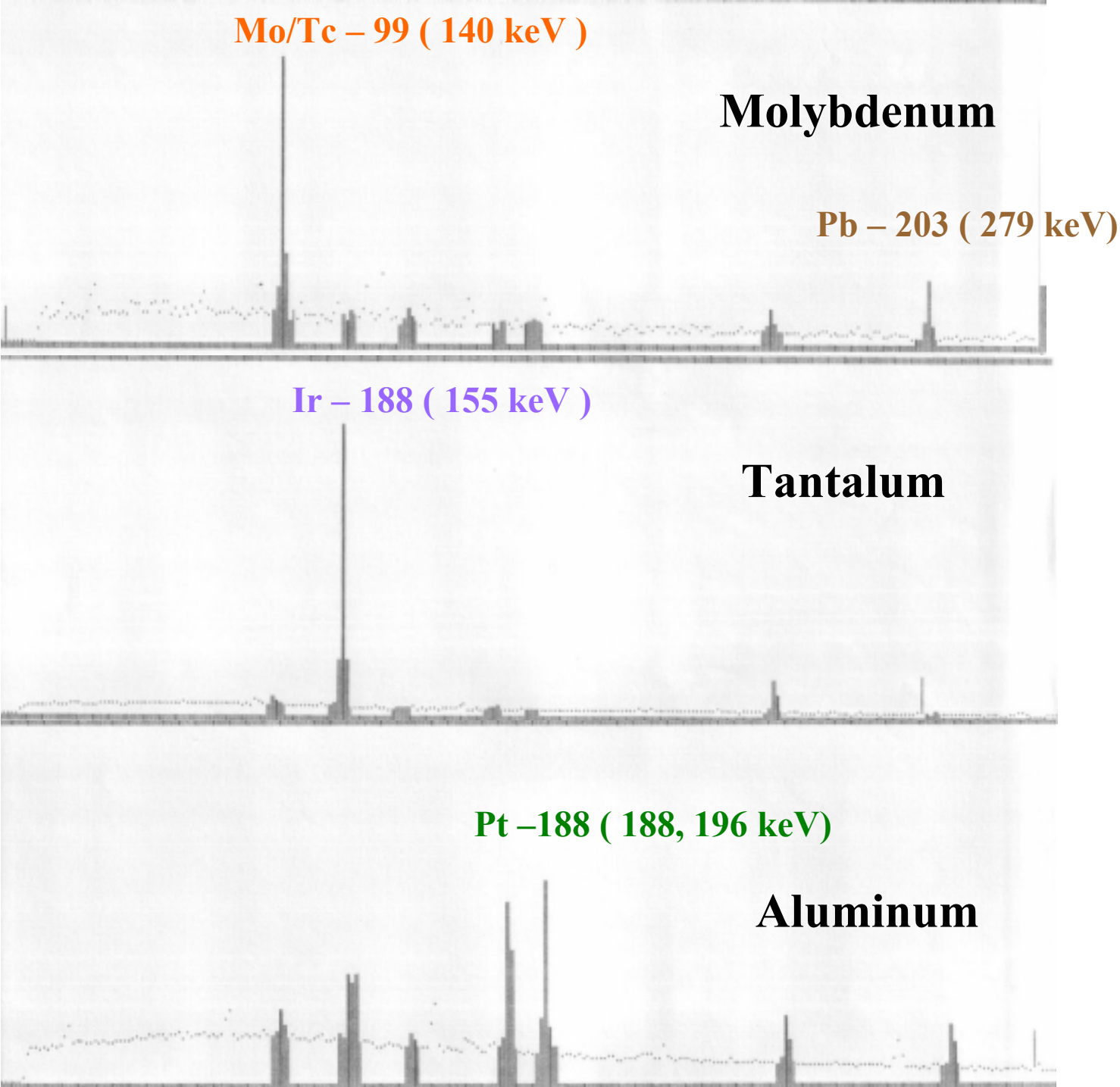
Proposed Scheme for On-Line Isotope Extraction from Liquid Metal Irradiated by Protons



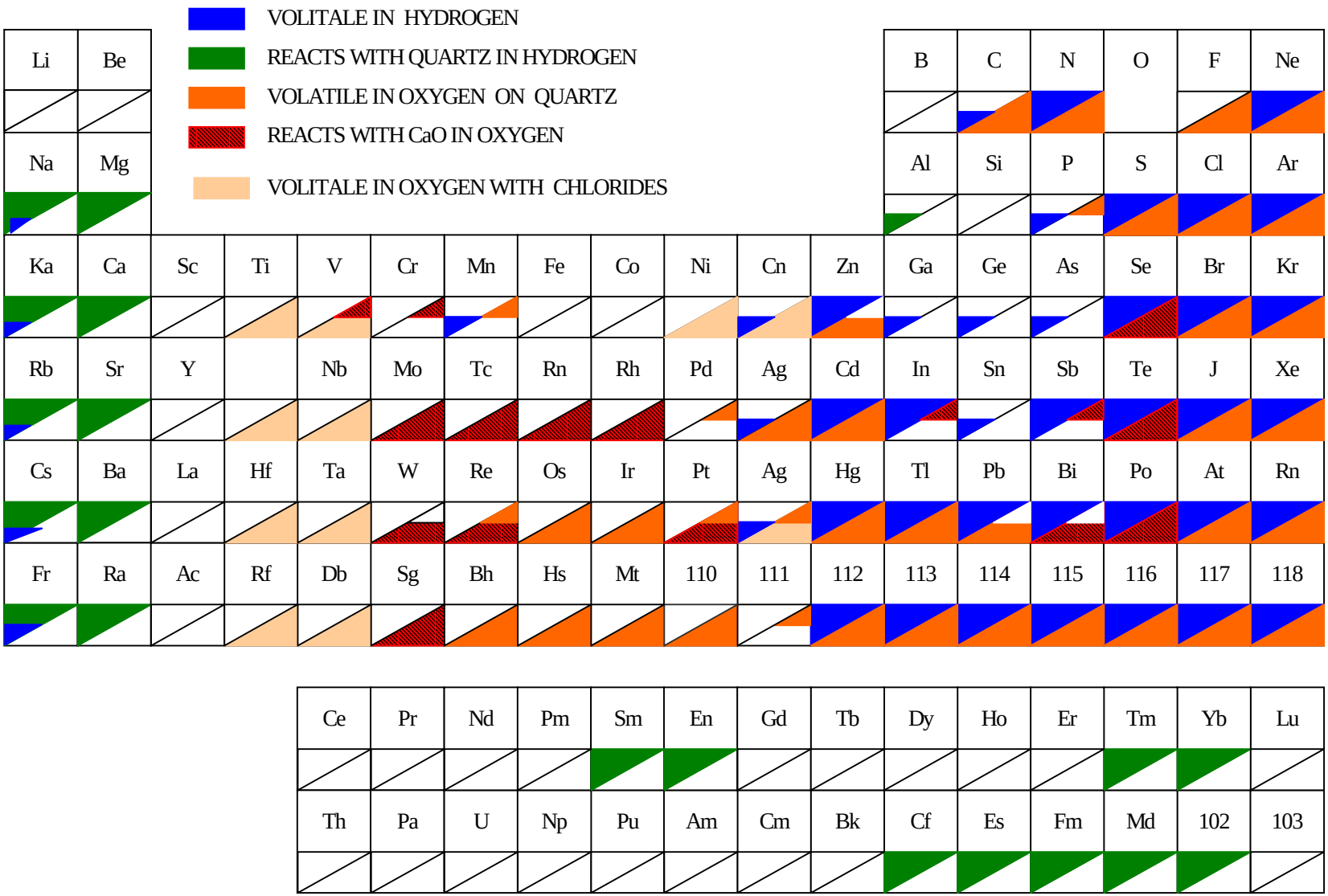
Adsorption of Various Isotopes from Liquid Metallic Lead at 500^0C

Surface inside liquid phase	Isotopes extracted
Ta	Ir-188, 189
Quartz	Mo/Tc –99
Mo	Mo/Tc –99
Ti	Hf – 173
Al	Pt-188, 189
	Os - 185, Ru – 97
Surface in Gas Phase	
Ti	Tl- 201, 200, 202
Au	Hg- 203

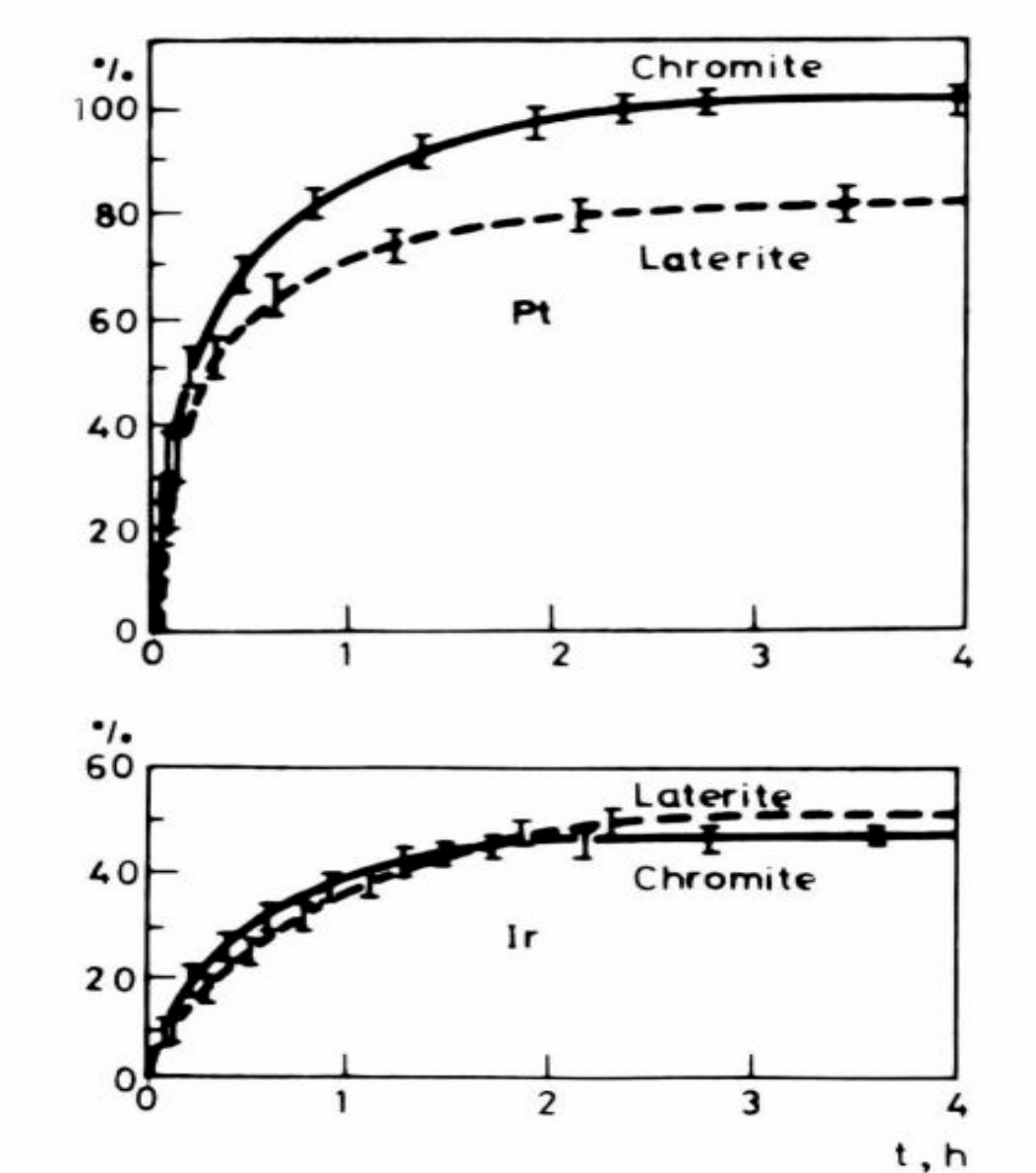



Mo/Tc – 99 (140 keV)
Molybdenum
Pb – 203 (279 keV)
Ir – 188 (155 keV)
Tantalum
Pt –188 (188, 196 keV)
Aluminum

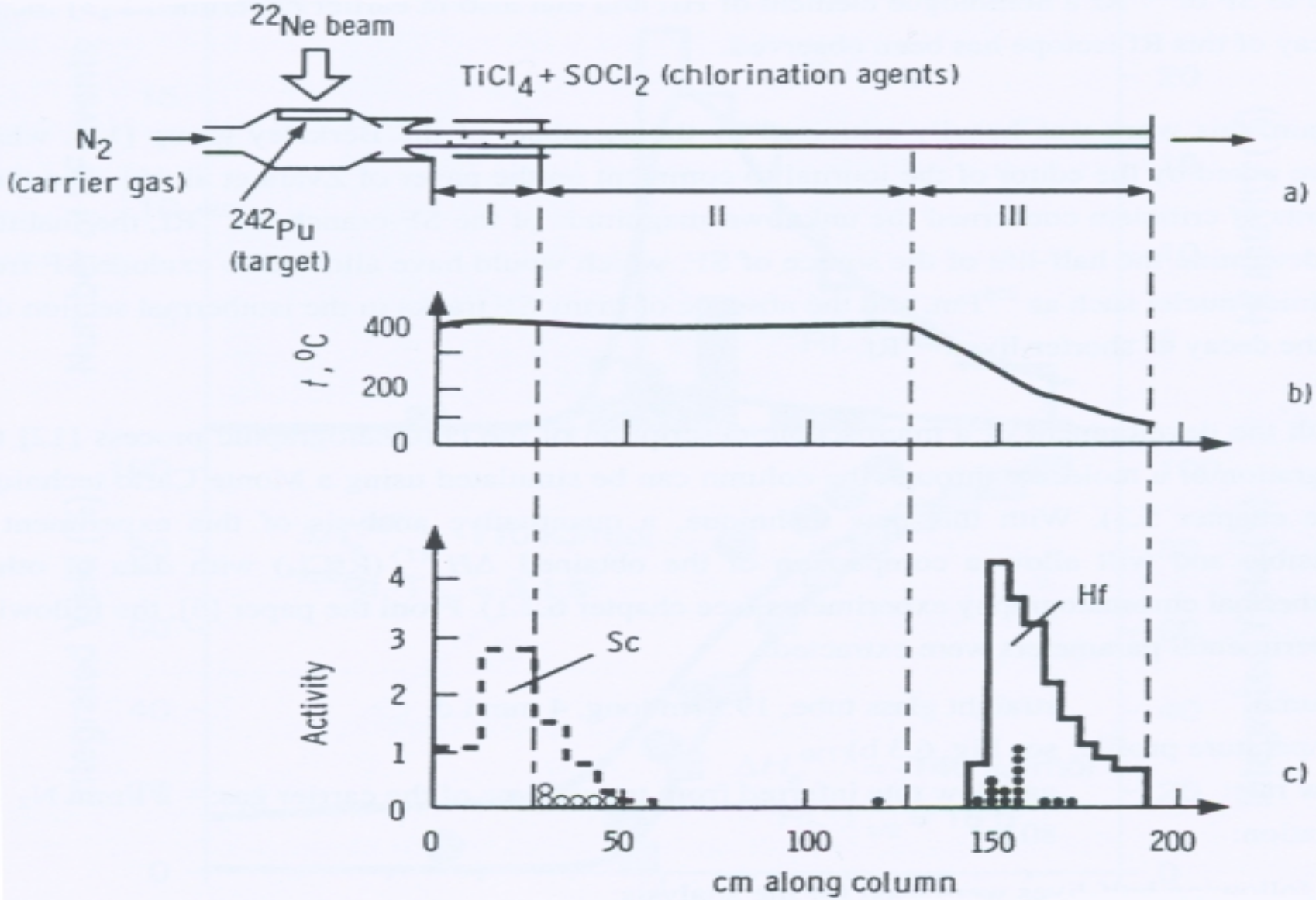
VOLATILITY OF ELEMENTS IN HYDROGEN AND OXYGEN STREAM AT 1100 ^{O}C



Volatilization of Pt and Ir in Oxygen Stream at 1200°C from Natural Rock Samples



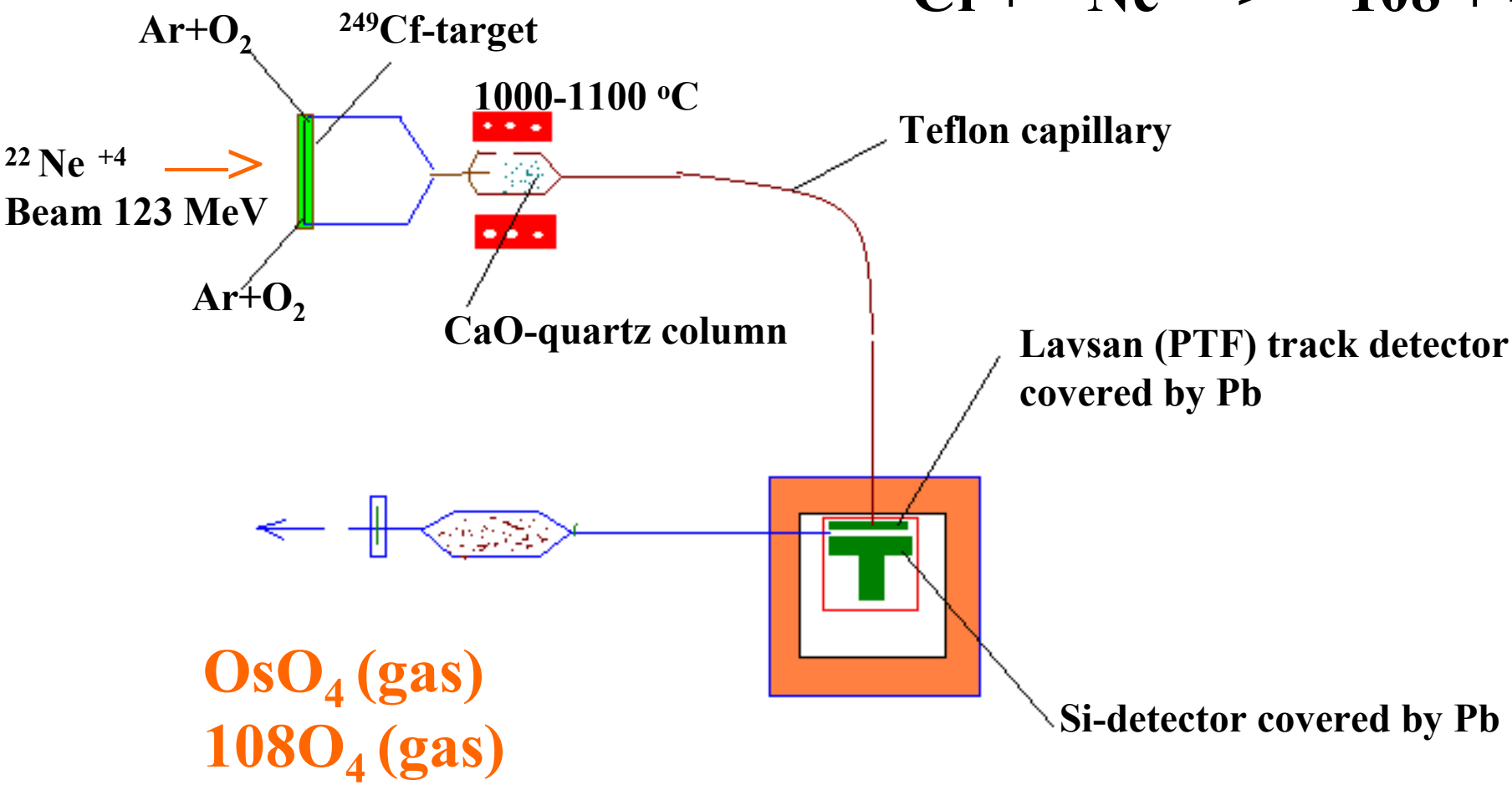
Experiment for Element -104 (Rf) Chemical Identification via Volatile Chlorides *(I.Zvara et al., 1970)*



No.	Element name (Chemical analog)		Other names suggested or previously used	Gas chemistry performed
102	**Nobelium** (Ytterbium)	**No** (Yb)	Joliotium Flerovium	**Chloride (1968)** **Elemental form (1992)**
103	**Lawrencium** (Lutetium)	**Lr** (Lu)		**Chloride (1968)**
104	**Rutherfordium** (Hafnium)	**Rf** (Hf)	Kurchatovium, Ku Dubnium, Db	**Chloride-oxychloride (1969)** **Bromide (1976)** **Element (1987)**
105	**Dubnium** (Tantalum)	**Db** (Ta)	Hahnium, Ha Nielsbohrium, Ns Joliotium, Jl	**Oxychloride (1970)** **Bromide (1976)**
106	**Seaborgium** (Tungsten)	**Sg** (W)	Rutherfordium, Rf	**Oxychloride (1993)** **Hydroxide**
107	**Bohrium** (Rhenium)	**Bh** (Re)	Nielsbohrium, Ns	**Oxychloride (1999)** **Hydroxides**
108	**Hassium** (Osmium)	**Hs** (Os)	Hahnium, Ha	**Oxide (2001)**
109	**Meitnerium** (Iridium)	**Mt** (Ir)		

AN ATTEMPT TO ISOLATE CHEMICALLY AND DETECT SF- AND α-ACTIVE ISOTOPES OF ELEMENT-108 *(B.Zhuikov et al., 1985)*

$^{249}Cf + {}^{22}Ne \longrightarrow {}^{267}108 + 4n$

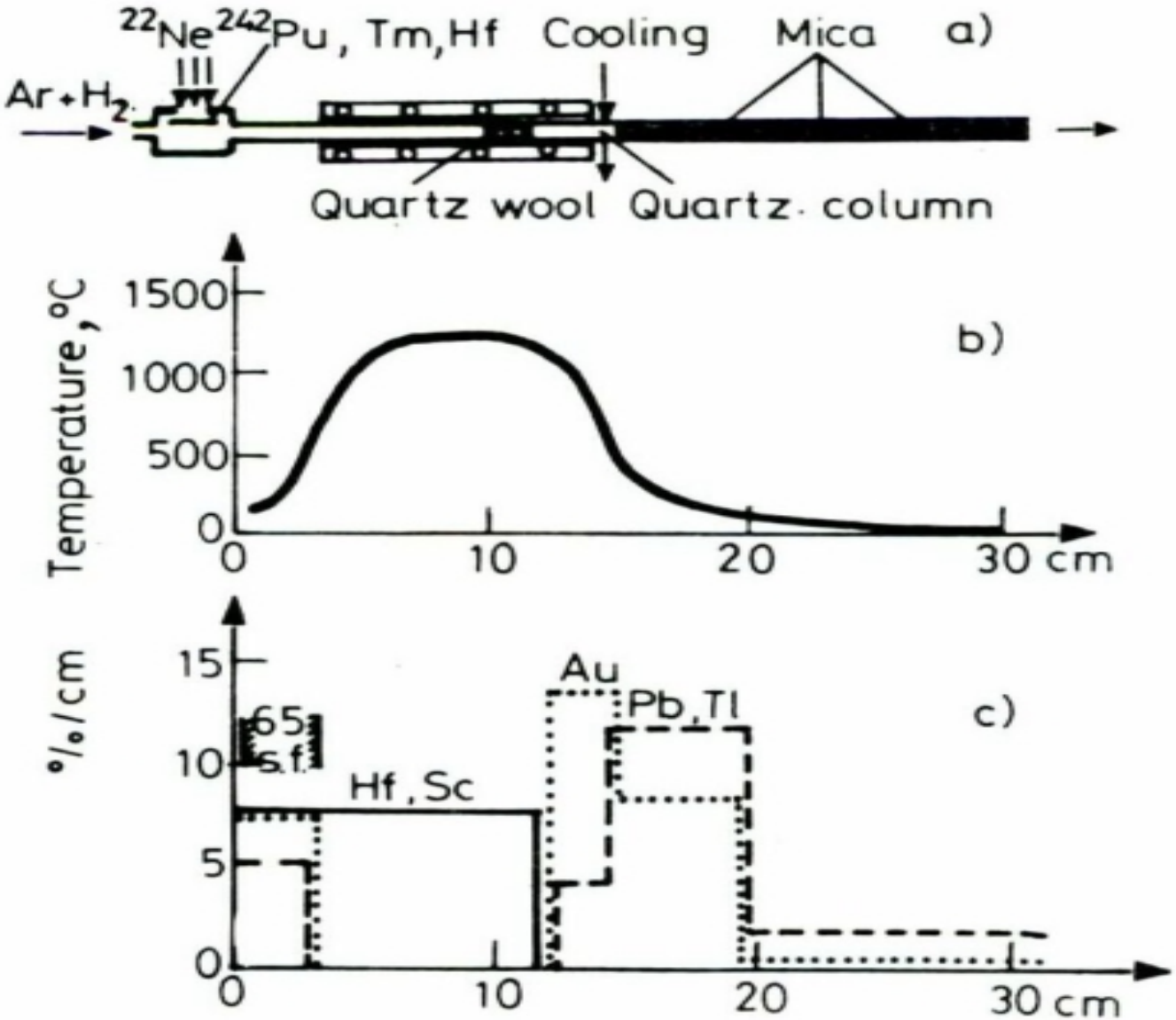


RELATIVISTIC DIRAC-FOCK ATOMIC CALCULATIONS

d-elements	p-elements
Lu	Lr
ds^2	s^2p (Desclaux calc.)
Ti	Sn
Zr	Ge
Hf	Pb
d^2s^2	s^2p^2

Rf (104) ?

Study of Volatility of Element-104 (Rf) in Elemental Form *(B.Zhuikov et al., 1989)*



Multi-Configuration Dirac-Fock Computations *(V.Glebov, B.Zhuikov et al.)*

Ground State: ds^2p

Atomic radius: 1.79A

Ionic radius: 0.89A

Sublimation heat: >370 kJ/mol (experimental)
610±21 kJ/mol (predicted)

Structure of electron levels:

CONCLUSION: Rf IS A TYPICAL d-ELEMENT

Structure of Energy Levels of Excited Configuration for Elements of IV Group