



105番元素Dbの オンライン等温ガスクロマトグラフ挙動

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Superheavy Elements (SHEs)



- Short half-lives
- Low production rate

$$^{262}\text{Db}: T_{1/2} = 34 \text{ s}, 1 \text{ atom}/10 \text{ min}$$

IUPAC Periodic Table of the Elements

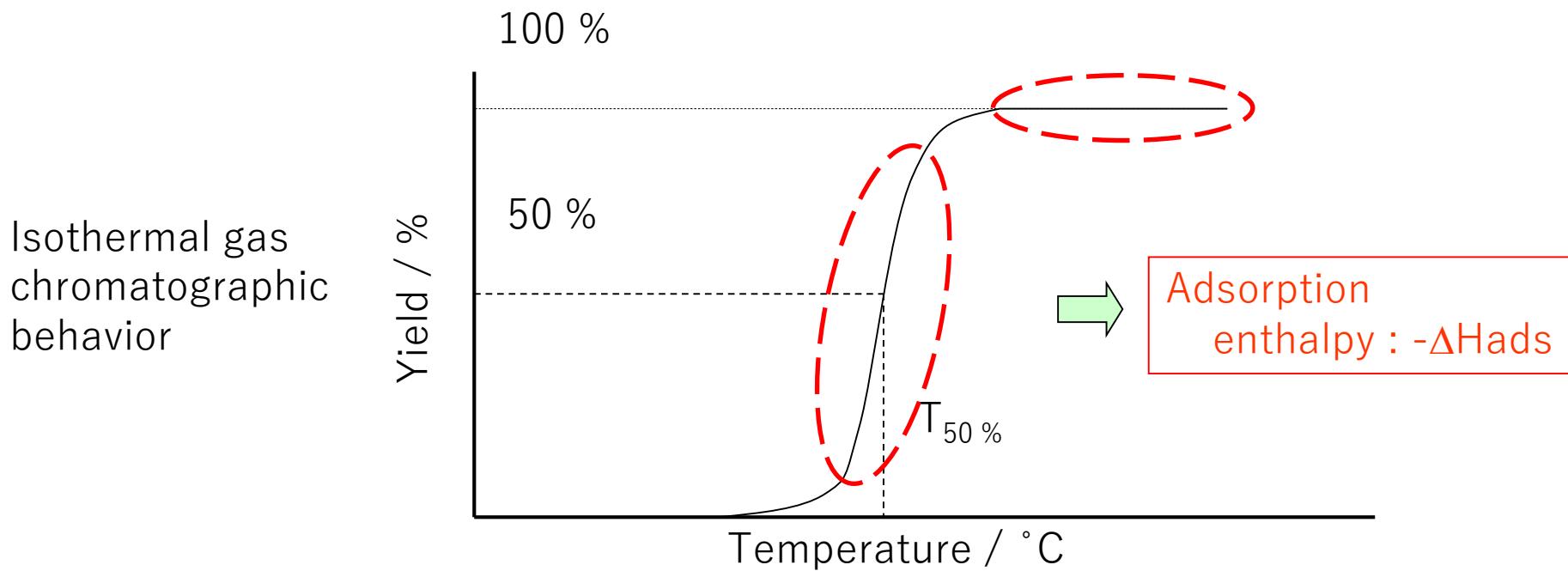
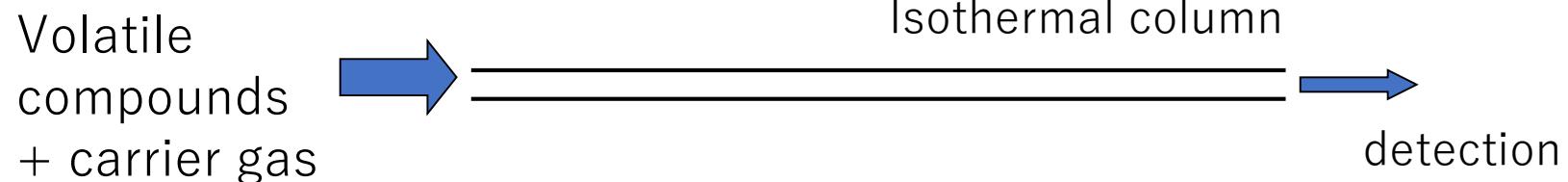
The table includes the following information:

- Key:**
 - atomic number
 - Symbol
 - name
 - conventional atomic weight
 - standard atomic weight
- Elements:**
 - Hydrogen (H)
 - Lithium (Li)
 - Boron (B)
 - Carbon (C)
 - Nitrogen (N)
 - Oxygen (O)
 - Fluorine (F)
 - Neon (Ne)
 - Scandium (Sc)
 - Titanium (Ti)
 - Vanadium (V)
 - Chromium (Cr)
 - Manganese (Mn)
 - Iron (Fe)
 - Cobalt (Co)
 - Nickel (Ni)
 - Copper (Cu)
 - Zinc (Zn)
 - Gallium (Ga)
 - Silicon (Si)
 - Phosphorus (P)
 - Sulfur (S)
 - Chlorine (Cl)
 - Argon (Ar)
 - Calcium (Ca)
 - Scandium (Sc)
 - Titanium (Ti)
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 - Nickel (Ni)
 - Copper (Cu)
 - Zinc (Zn)
 - Gallium (Ga)
 - Silicon (Si)
 - Phosphorus (P)
 - Sulfur (S)
 - Chlorine (Cl)
 - Argon (Ar)
 - Potassium (K)
 - Rubidium (Rb)
 - Sodium (Na)
 - Magnesium (Mg)
 - Calcium (Ca)
 - Scandium (Sc)
 - Titanium (Ti)
 - Vanadium (V)
 - Chromium (Cr)
 - Manganese (Mn)
 - Iron (Fe)
 - Cobalt (Co)
 - Nickel (Ni)
 - Copper (Cu)
 - Zinc (Zn)
 - Gallium (Ga)
 - Silicon (Si)
 - Phosphorus (P)
 - Sulfur (S)
 - Chlorine (Cl)
 - Argon (Ar)
 - Strontium (Sr)
 - Yttrium (Y)
 - Zirconium (Zr)
 - Niobium (Nb)
 - Molybdenum (Mo)
 - Technetium (Tc)
 - Ruthenium (Ru)
 - Rhodium (Rh)
 - Palladium (Pd)
 - Silver (Ag)
 - Cadmium (Cd)
 - Inium (In)
 - Tin (Sn)
 - Antimony (Sb)
 - Te tellurium
 - Iodine (I)
 - Xenon (Xe)
 - Barium (Ba)
 - Lanthanoids
 - Hafnium (Hf)
 - Tantalum (Ta)
 - Tungsten (W)
 - Rhenium (Re)
 - Osmium (Os)
 - Irindium (Ir)
 - Platinum (Pt)
 - Au gold
 - Mercury (Hg)
 - Thallium (Tl)
 - Pb lead
 - Bismuth (Bi)
 - Po polonium
 - At astatine
 - Rn radon
 - Cesium (Cs)
 - Barium (Ba)
 - Lanthanoids
 - Hafnium (Hf)
 - Tantalum (Ta)
 - Tungsten (W)
 - Rhenium (Re)
 - Osmium (Os)
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 - Platinum (Pt)
 - Au gold
 - Mercury (Hg)
 - Thallium (Tl)
 - Pb lead
 - Bismuth (Bi)
 - Po polonium
 - At astatine
 - Rn radon
 - Rutherfordium (Rf)
 - Dubium (Db)
 - Seaborgium (Sg)
 - Bohrium (Bh)
 - Hassium (Hs)
 - Meltinanium (Mt)
 - Darmstadium (Ds)
 - Roerigenium (Rg)
 - Copernicium (Cn)
 - Nihonium (Nh)
 - Rerovium (Fl)
 - Moscovium (Mc)
 - Livermorium (Lv)
 - Tennessine (Ts)
 - Oganesson (Og)



57 La lanthanum	58 Ce cerium	59 Pr praseodymium	60 Nd neodymium	61 Pm promethium	62 Sm samarium	63 Eu europium	64 Gd gadolinium	65 Tb terbium	66 Dy dysprosium	67 Ho holmium	68 Er erbium	69 Tm thulium	70 Yb ytterbium	71 Lu lutetium
138.91	140.12	140.91	144.24	150.36(2)	151.96	157.25(2)	158.93	162.50	164.93	167.26	168.93	173.05	174.97	
Ac actinium	Th thorium	Pa protactinium	U uranium	Np neptunium	Pu plutonium	Am americium	Cm curium	Bk berkelium	Cf californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium
232.04	231.04	238.03												

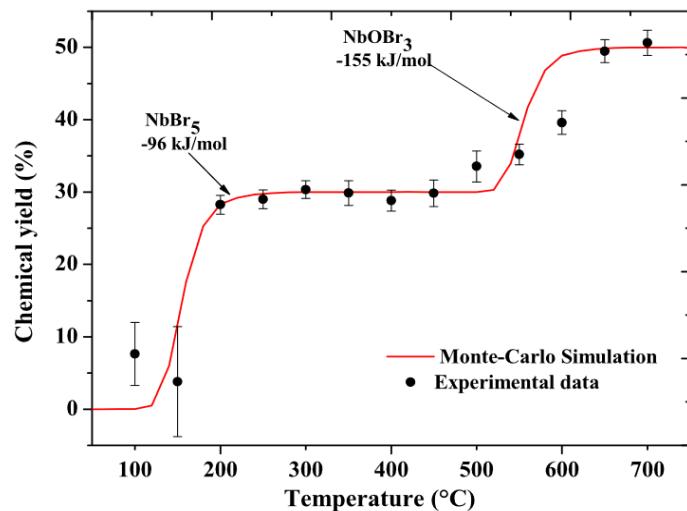
Isothermal gas chromatography



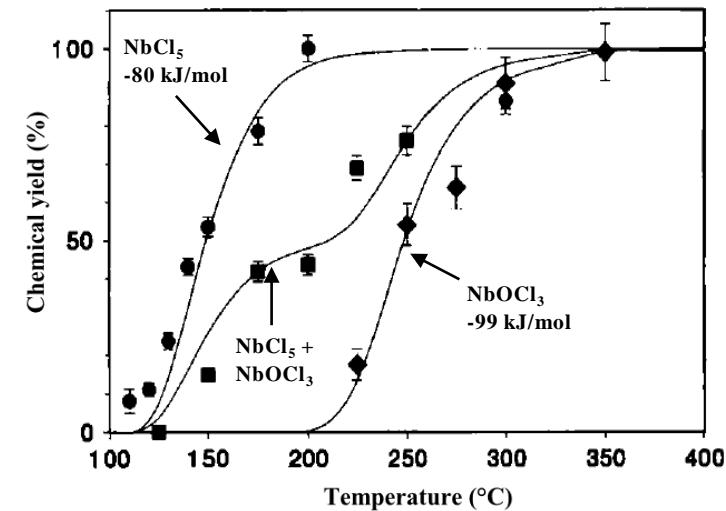
Group-5 halides and oxyhalides

Group-5 elements have a high tendency to react with **halides**, forming **volatile pentahalides** (NbBr_5 , NbCl_5 , TaCl_5 , etc.)

However, even with trace amounts of **oxygen in the gas phase**, the formation of **oxyhalides** (e.g., NbOCl_3 , TaOBr_3 , etc.) is favored.



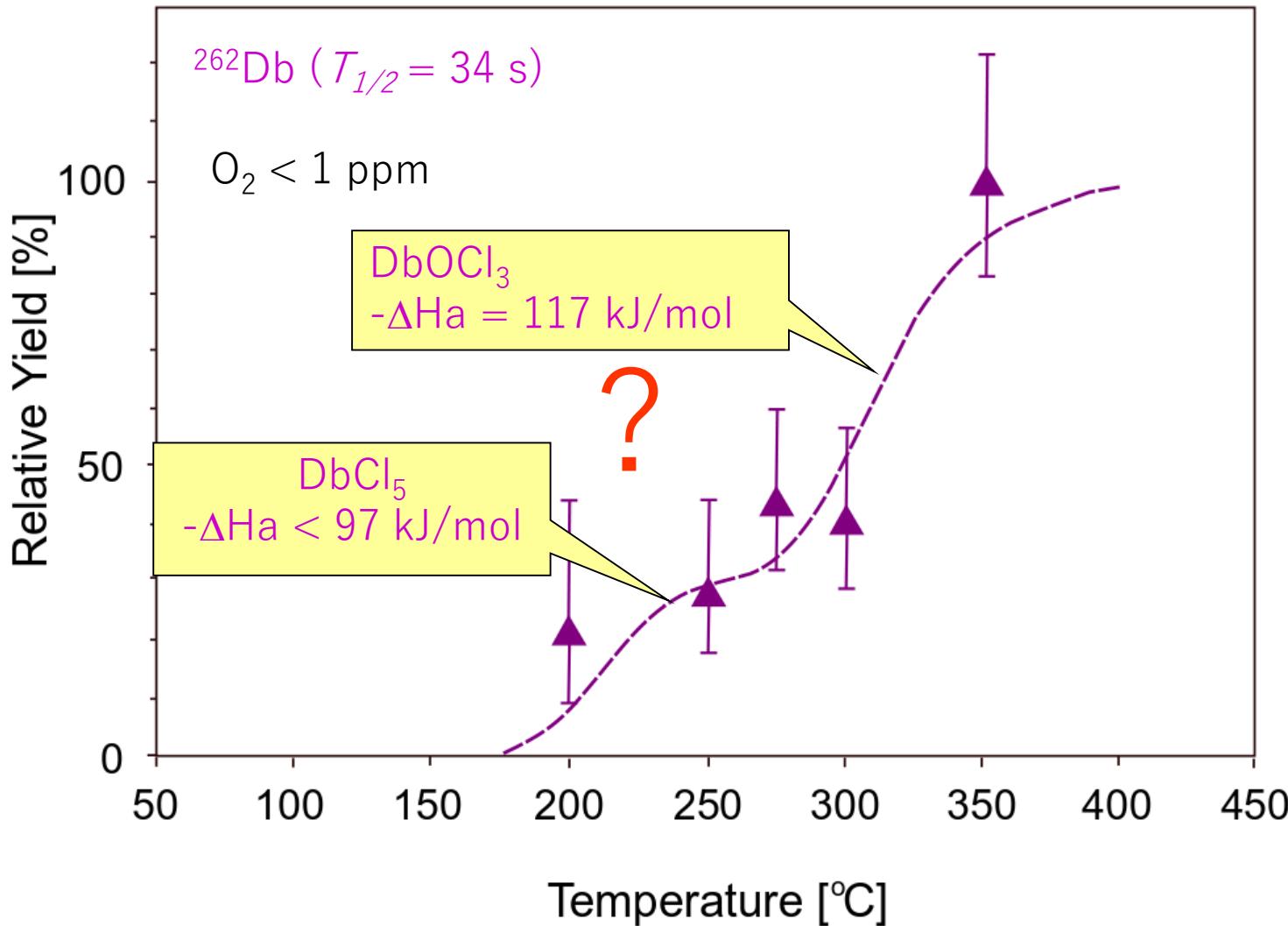
Qin et al., 2012



Türler et al., 1996

Group-5 halides and oxyhalides

A. Türler et al. Radiochim. Acta 73, 55 (1996)



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Results up-to-now (relative volatility):

$\text{NbCl}_5 \approx \text{DbCl}_5$	$\text{NbBr}_5 \approx \text{DbBr}_5$	Zvara et al., 1973
$\text{NbCl}_5 > \text{DbCl}_5$	$\text{NbBr}_5 > \text{DbBr}_5$	Zvara et al., 1991
$\text{NbBr}_5 > \text{TaOBr}_3 > \text{DbOBr}_3$		Gäggeler et al., 1992
$\text{NbCl}_5 \approx \text{DbCl}_5 > \text{TaOCl}_3$		Kadkhodayan et al., 1993
$\text{NbCl}_5 \geq \text{DbCl}_5 > \text{NbOCl}_3 > \text{DbOCl}_3$		Türler et al., 1996
$\text{DbBr}_5 > \text{NbBr}_5 > \text{TaBr}_5 > \text{NbOBr}_3$		Lin et al., 2012

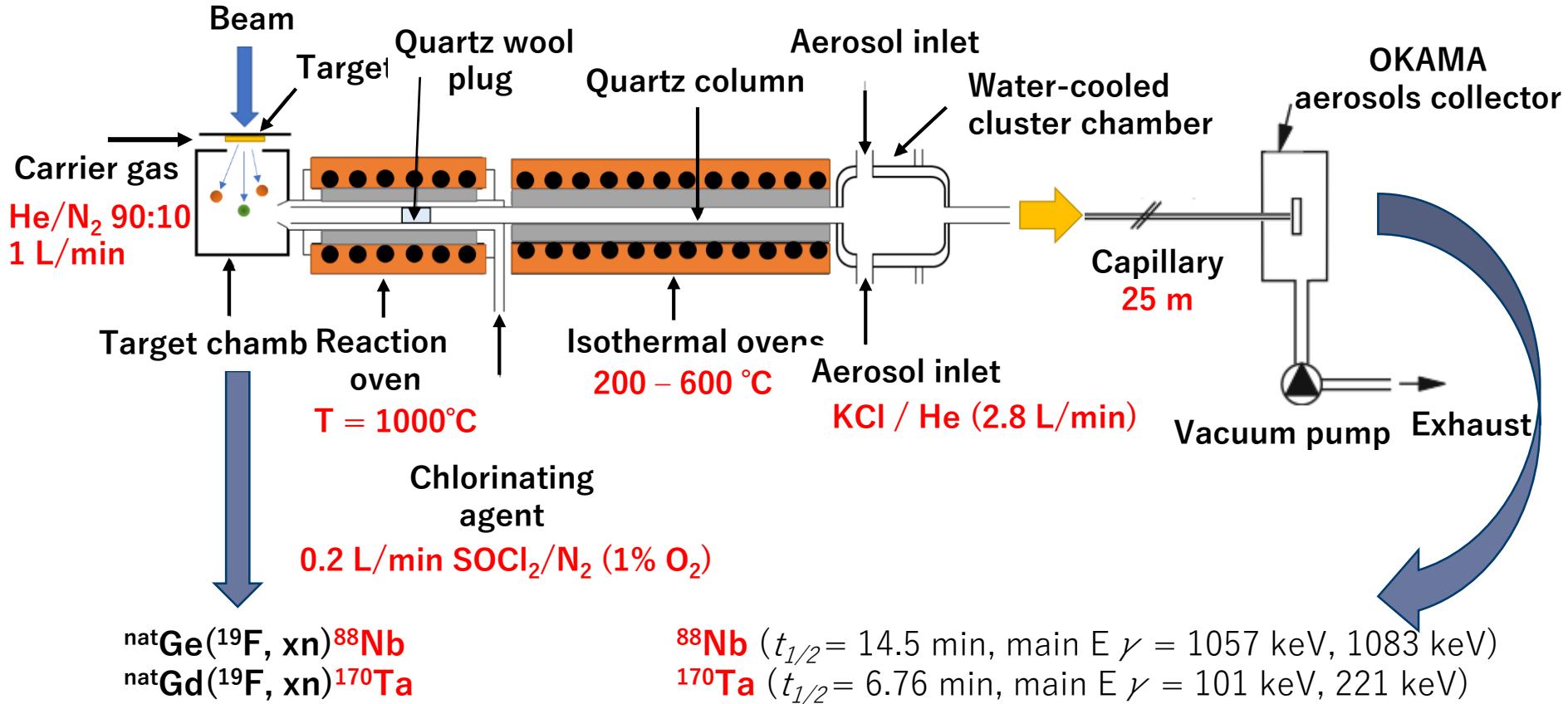
Objectives of this study

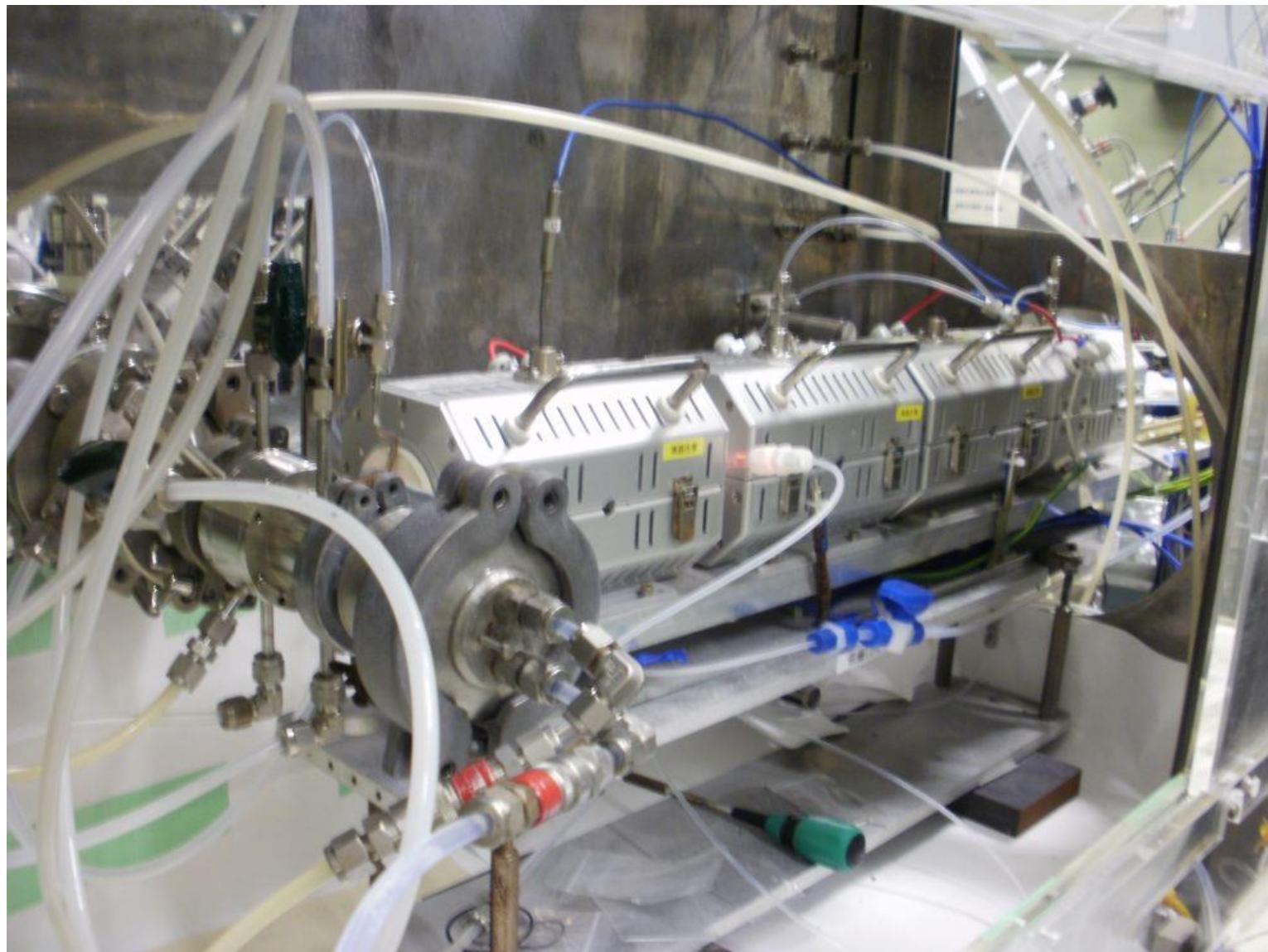


- Systematic gas-phase chemical exploration of Ta-, Nb-, and Db- oxychlorides (i.e., TaOCl_3 , NbOCl_3 , DbOCl_3) in the temperature range 200-600°C
 - Deliberate **addition of O_2** in the system

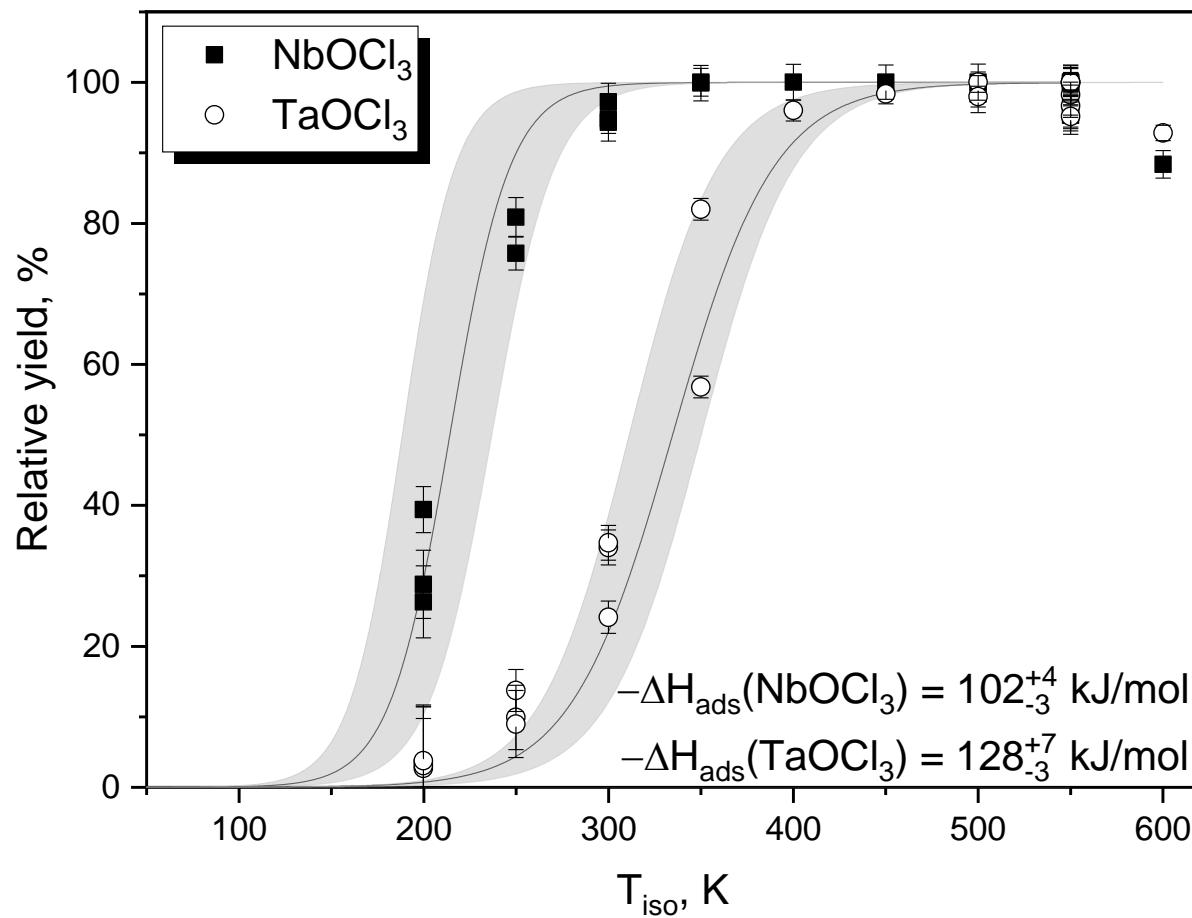


- Obtainment of **thermochemical information (adsorption and sublimation enthalpies)**
- Unambiguous establishment of the **volatility trend in Group-5 elements**



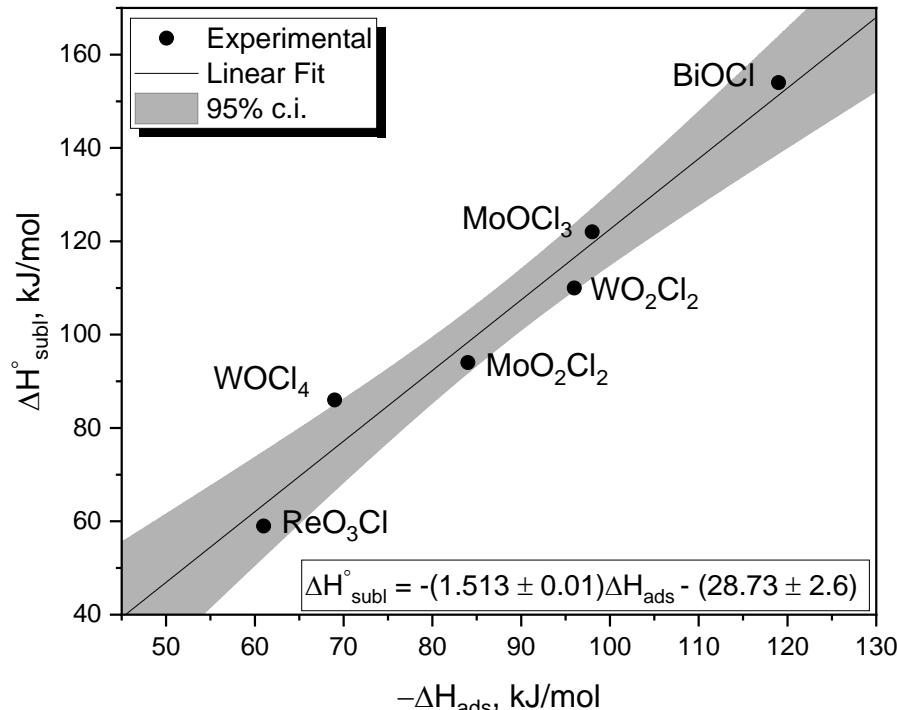


Adsorption enthalpies (ΔH_{ads}) of NbOCl_3 and TaOCl_3 on quartz

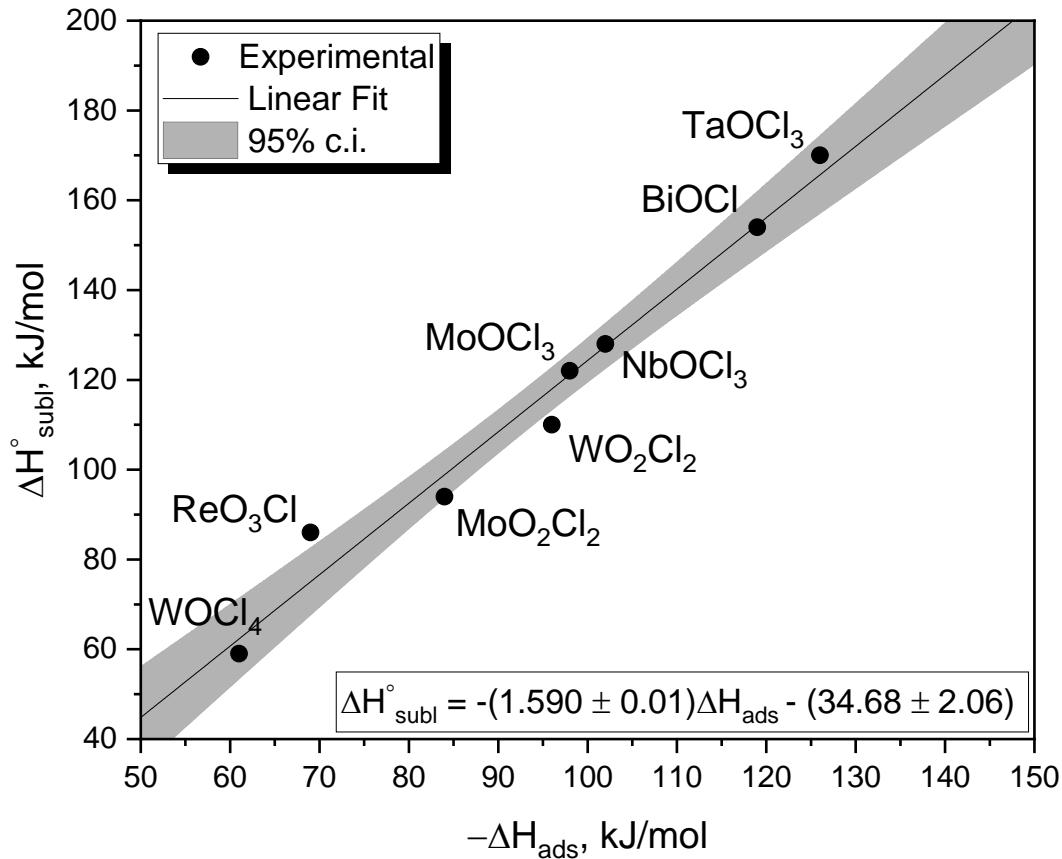


Sublimation enthalpies (ΔH_{subl}) of NbOCl_3 and TaOCl_3

Chemical species	$-\Delta H_{ads}$ [this work]	ΔH_{subl} [this work]
NbOCl_3	102^{+4}_{-3} kJ/mol	126^{+7}_{-5} kJ/mol
TaOCl_3	128^{+7}_{-3} kJ/mol	165^{+11}_{-6} kJ/mol



Updated empirical - ΔH_{ads} vs. ΔH_{subl} correlation for oxychlorides



Relative volatility:
NbOCl₃ > TaOCl₃
? DbOCl₃

Experiments with DbOCl_3 with the IGC setup @Tandem, JAEA

$^{248}\text{Cm}(^{19}\text{F}, 5\text{n})^{262}\text{Db}$

$^{19}\text{F}^{7+}$ @103 MeV, 350 pnA

$\sigma = 210 \text{ pb}$ @103 MeV

Target thickness: 550 $\mu\text{g}/\text{cm}^2$

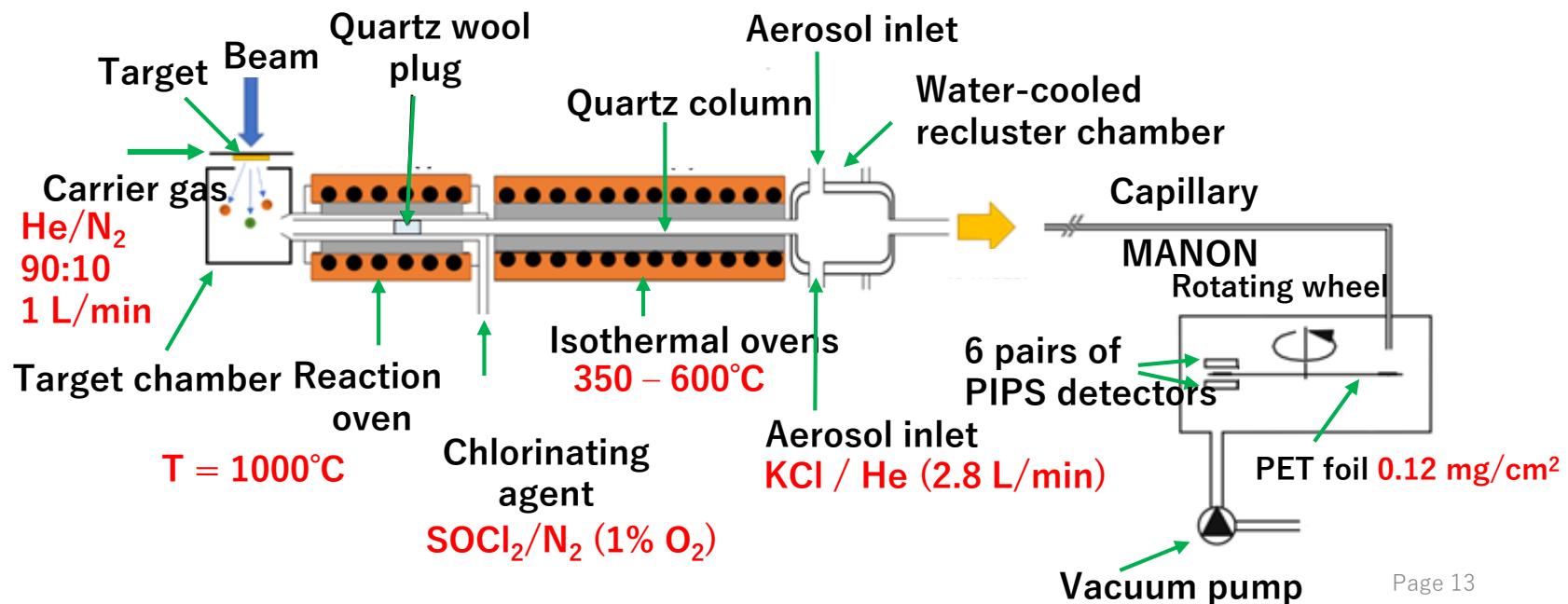
Chemical efficiency with MANON: 4%

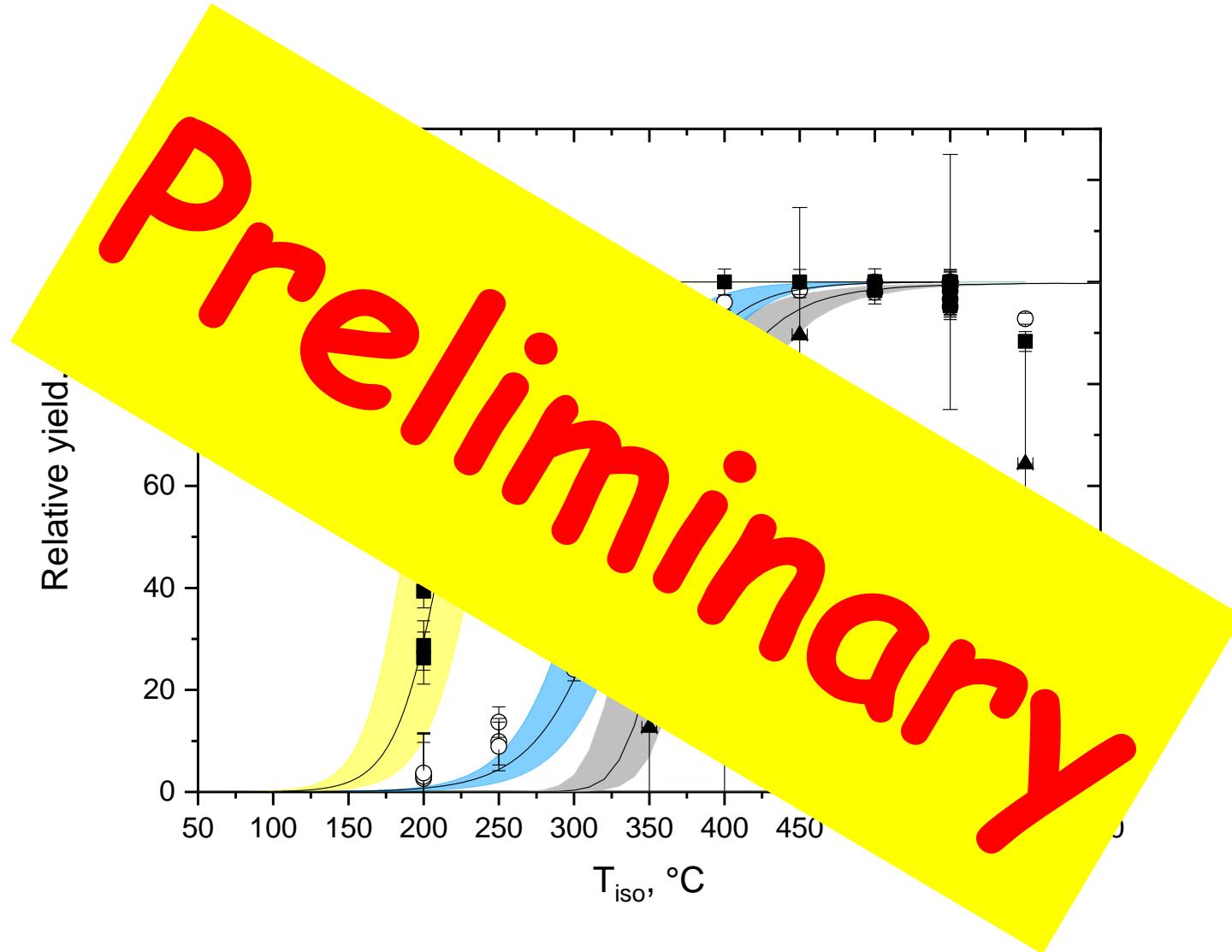
$\alpha(48\%)$
8.46 MeV ($I_\alpha = 70\%$)
8.68 MeV ($I_\alpha = 30\%$)

^{262}Db
34 s

$\alpha(97.4\%)$
8.61 MeV (average)

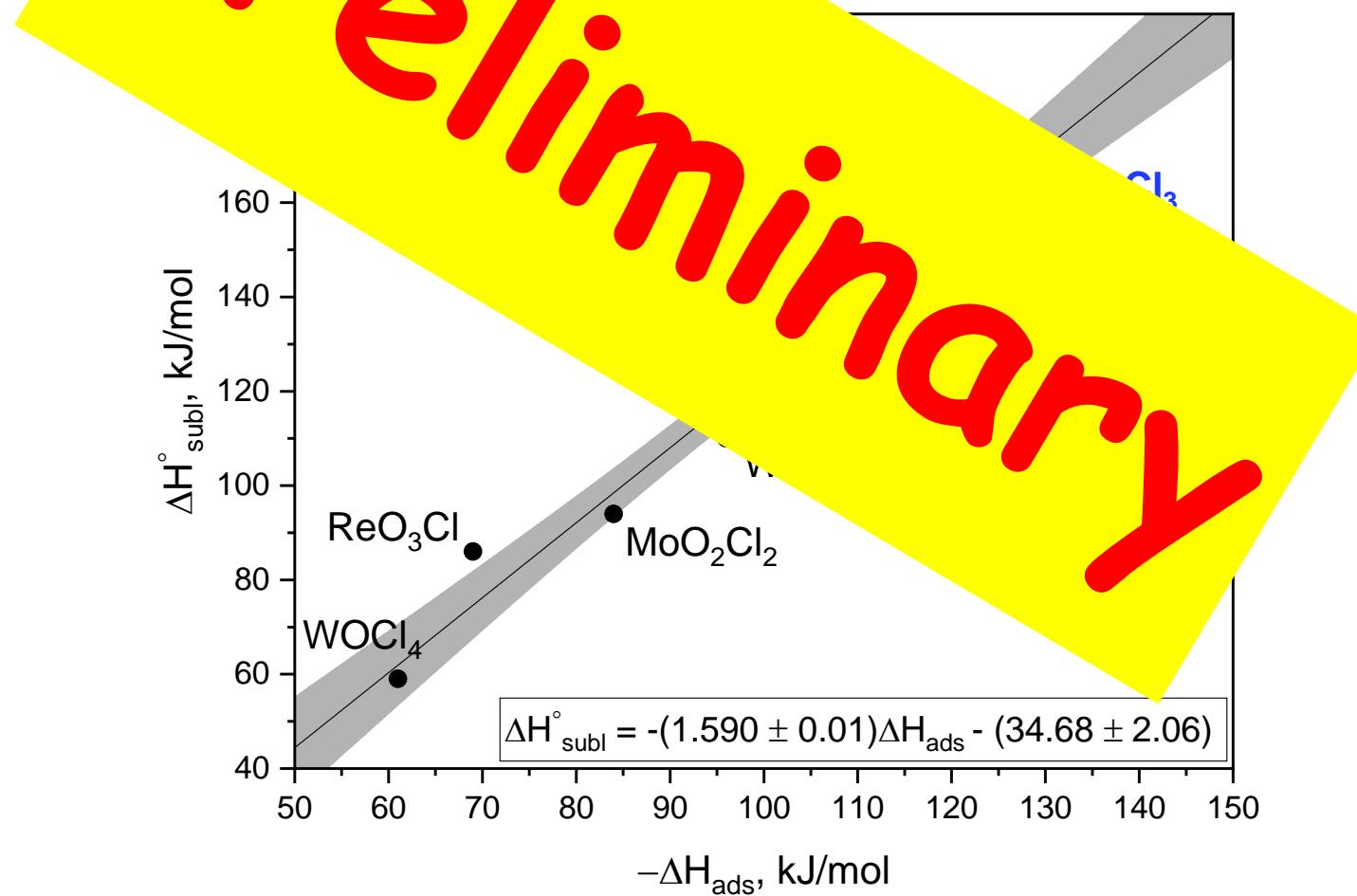
H. Haba et al., 2014





- ΔH_{ads} vs. ΔH_{subl} correlation for oxychlorides

	$-\Delta H_{ads}$ on quartz [kJ/mol]	Reference
DbOCl		Eichler B., 1995
		This work



Summary and conclusions



- Isothermal gas-chromatographic studies on the volatility of NbOCl_3 , TaOCl_3 were performed → **reproducible results**;
- Thermodynamic information for NbOCl_3 and TaOCl_3 was deduced in **agreement with literature** data;
- Experimentally, a **$\text{NbOCl}_3 > \text{TaOCl}_3 \approx \text{DbOCl}_3$ adsorption interaction strength** was observed;
- The estimated volatility sequence in Group-5 is **$\text{Nb} > \text{Ta} \geq \text{Db}$** .