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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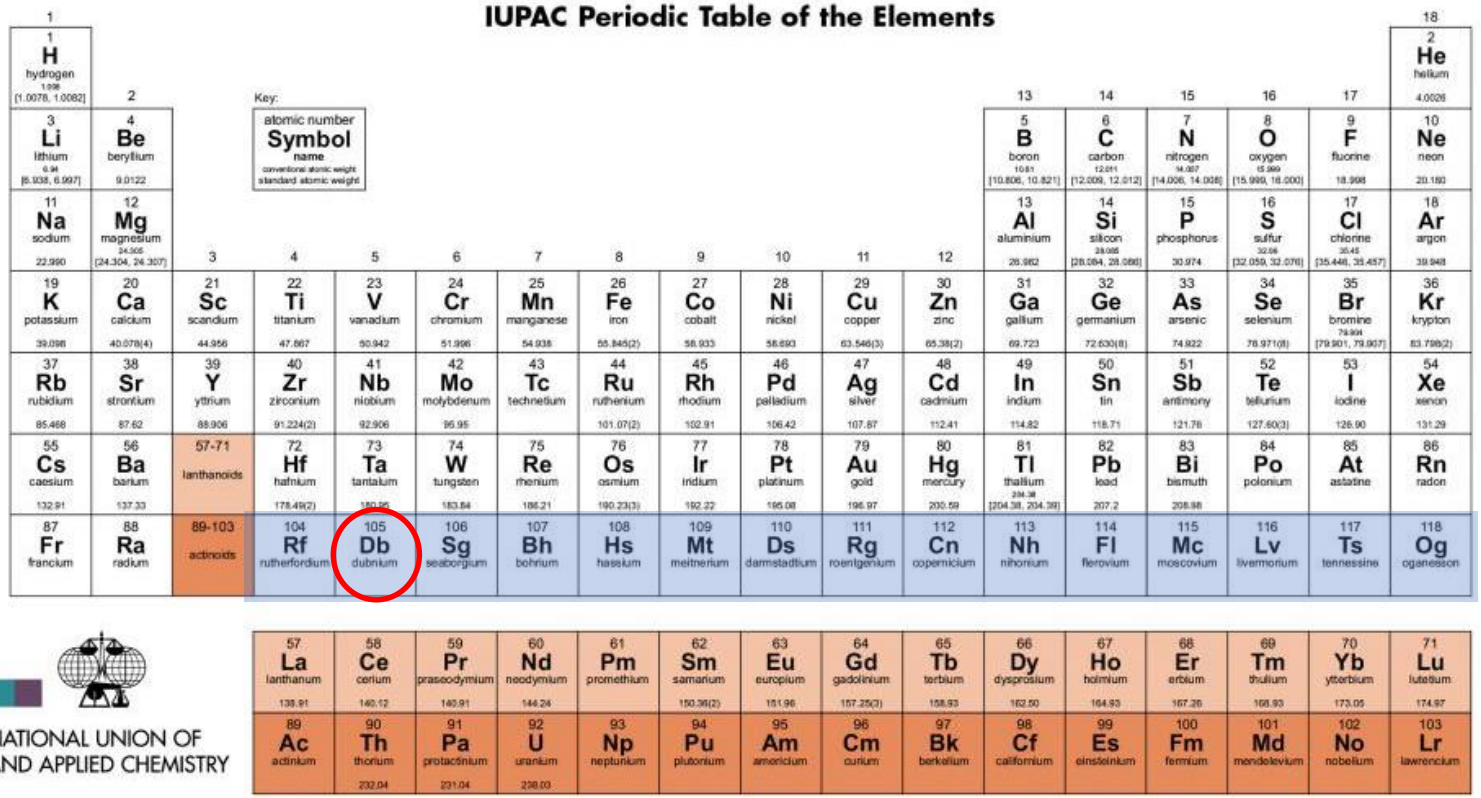
2020 東海・重イオン科学シンポジウム(2020/1/15-16 @ JAEA)

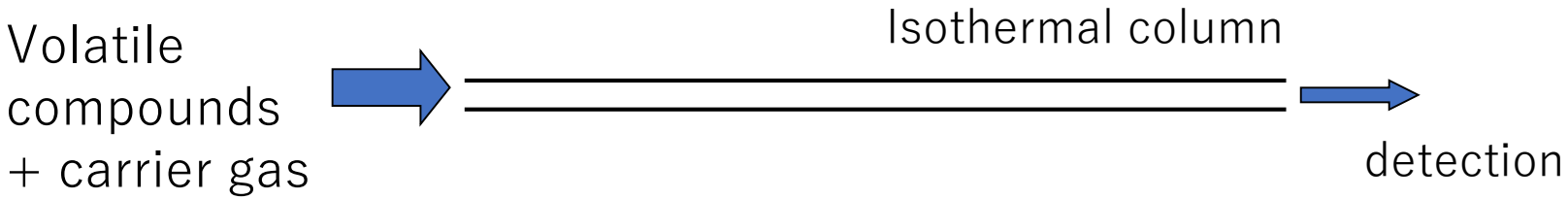
Superheavy Elements (SHEs)

- **Short half-lives**
- **Low production rate**

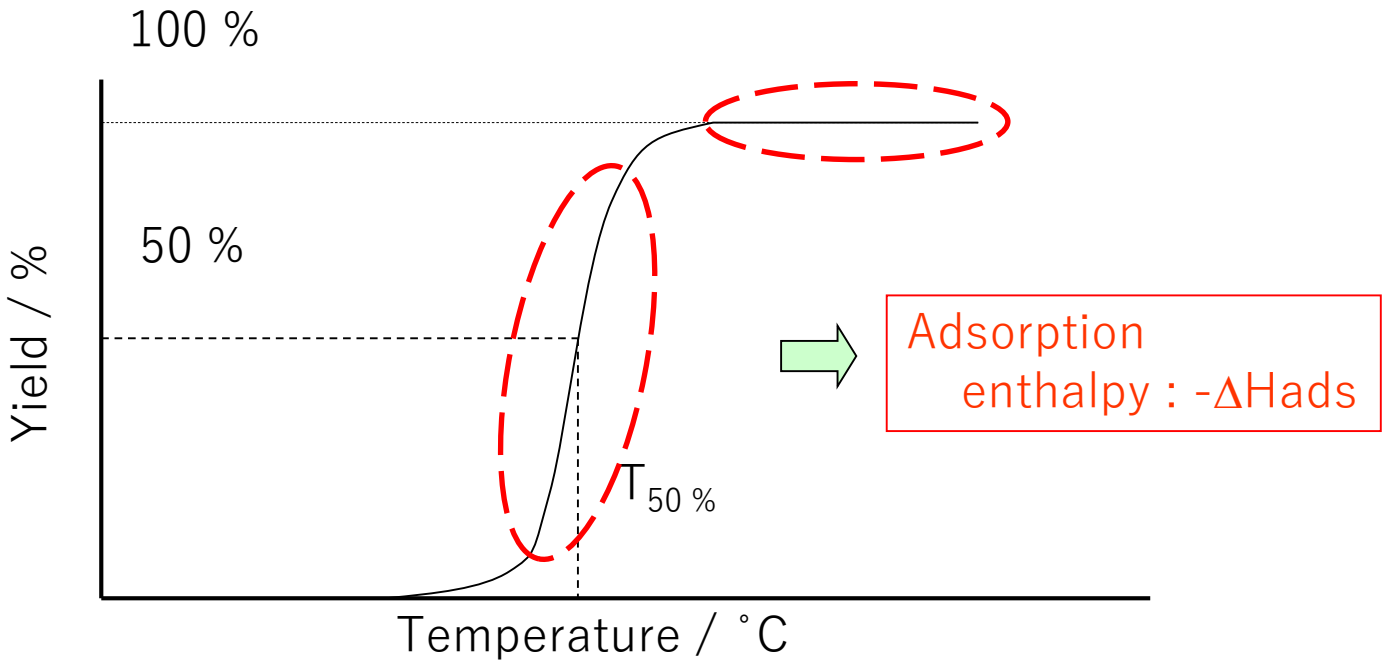
^{262}Db: $T_{1/2}$ = 34 s, 1 atom/10 min



Isothermal gas chromatography

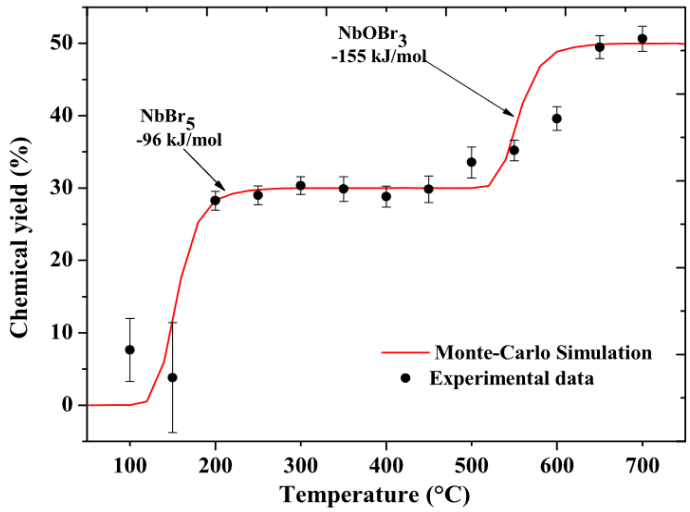


Isothermal gas chromatographic behavior

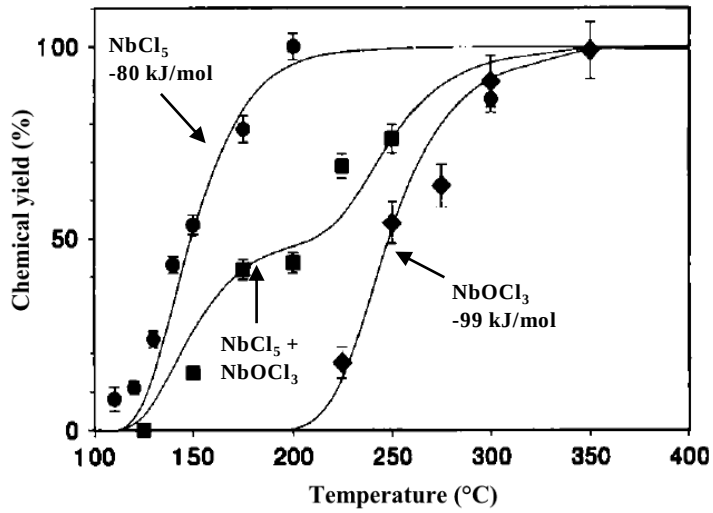


Group-5 halides and oxyhalides

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.



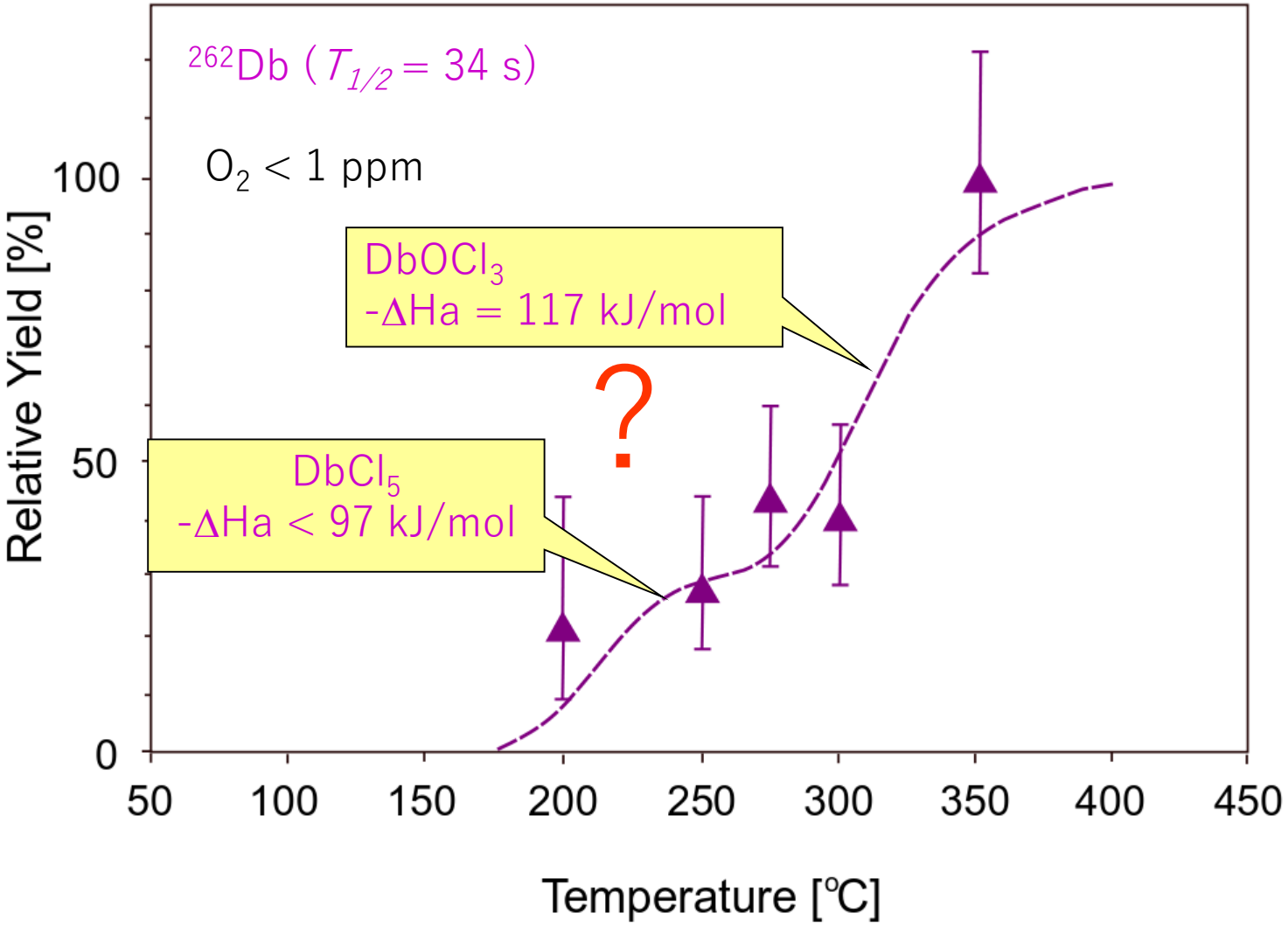
Qin et al., 2012



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):

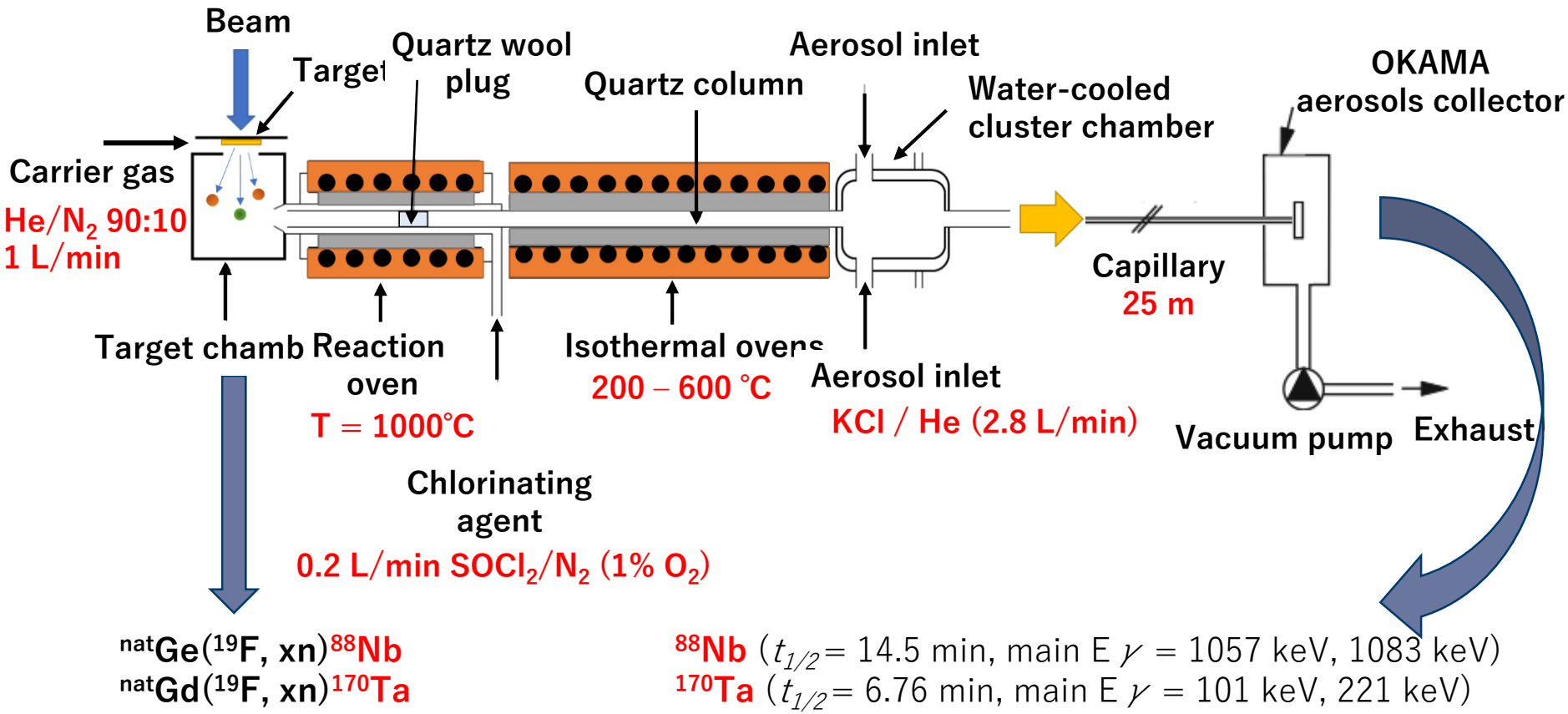
$NbCl_5 \approx DbCl_5$	$NbBr_5 \approx DbBr_5$	Zvara et al., 1973
$NbCl_5 > DbCl_5$	$NbBr_5 > DbBr_5$	Zvara et al., 1991
$NbBr_5 > TaOBr_3 > DbOBr_3$		Gäggeler et al., 1992
$NbCl_5 \approx DbCl_5 > TaOCl_3$		Kadkhodayan et al., 1993
$NbCl_5 \geq DbCl_5 > NbOCl_3 > DbOCl_3$		Türler et al., 1996
$DbBr_5 > NbBr_5 > TaBr_5 > NbOBr_3$		Lin et al., 2012

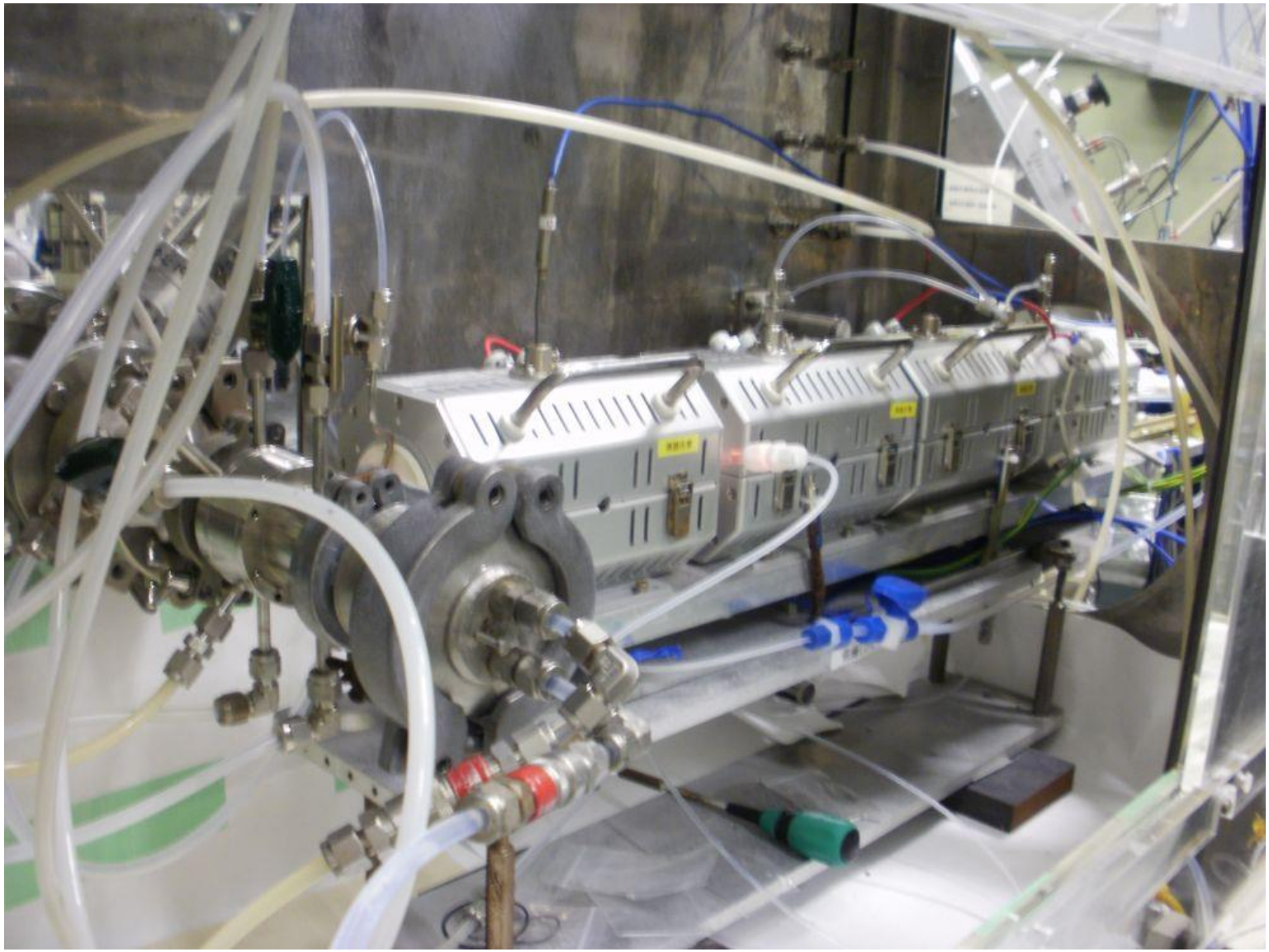
Objectives of this study

- 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

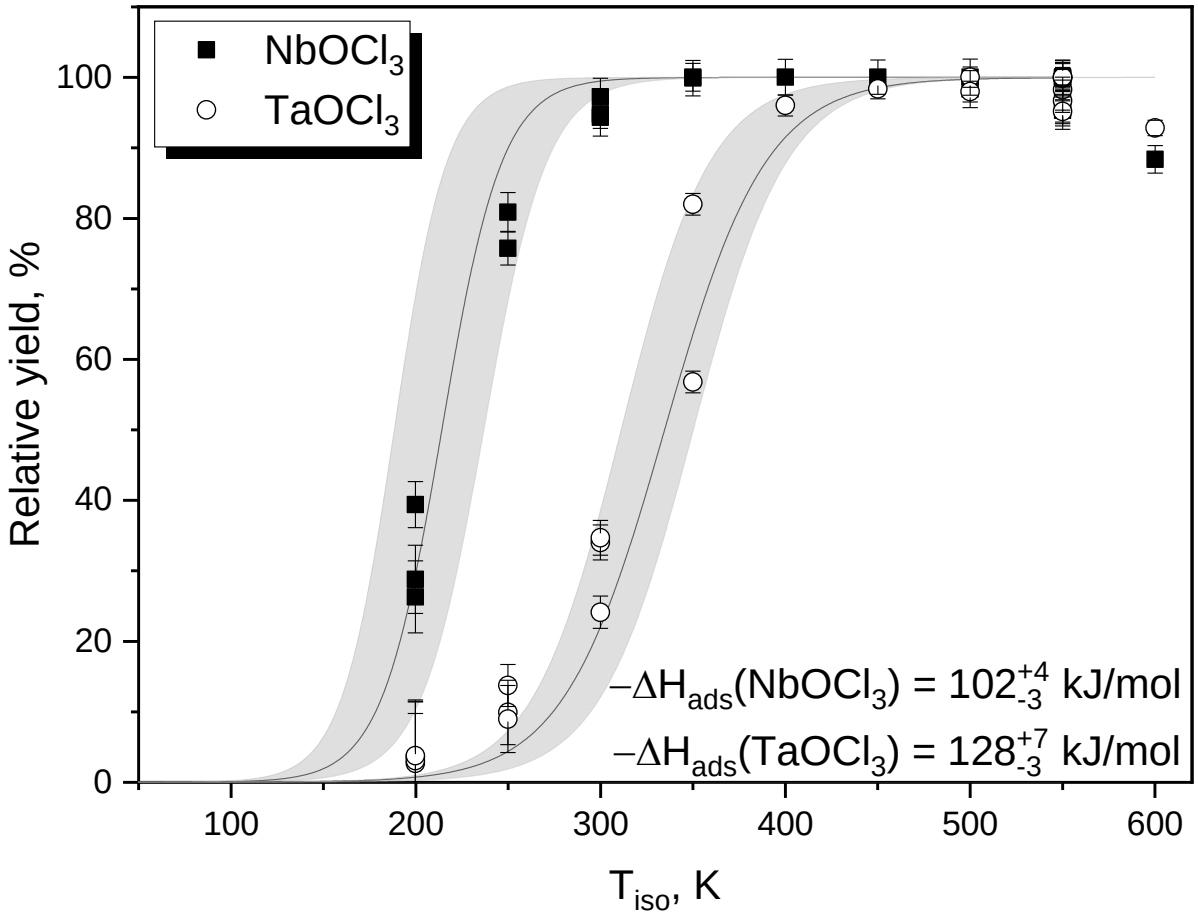
- Obtainment of **thermochemical information (adsorption and sublimation enthalpies)**
- Unambiguous establishment of the **volatility trend in Group-5 elements**

$NbOCl_3$ and $TaOCl_3$ simultaneous chemical exploration with the IGC setup



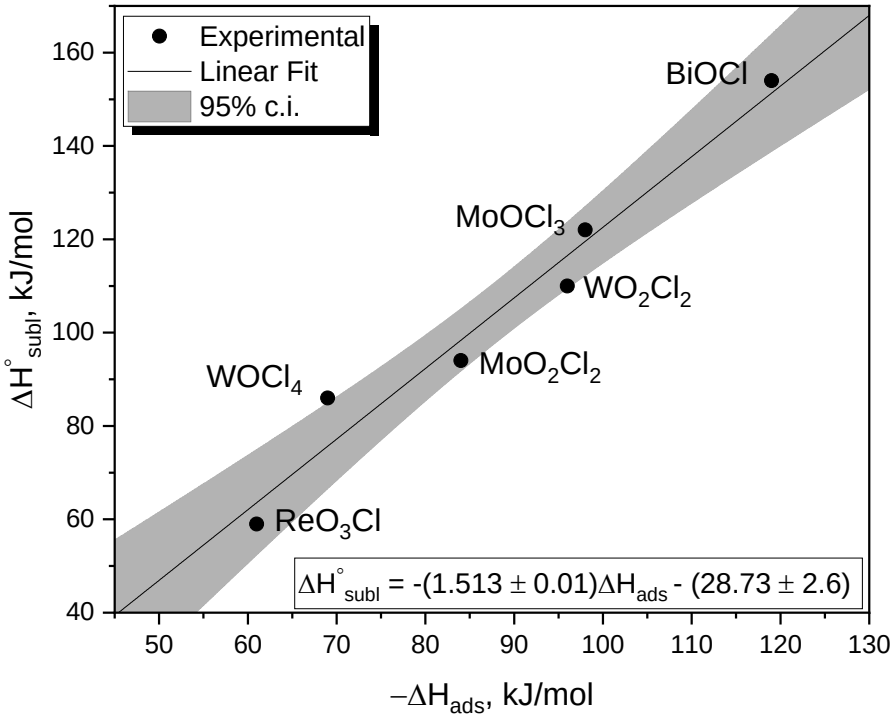


Adsorption enthalpies (ΔH_{ads}) of $NbOCl_3$ and $TaOCl_3$ on quartz

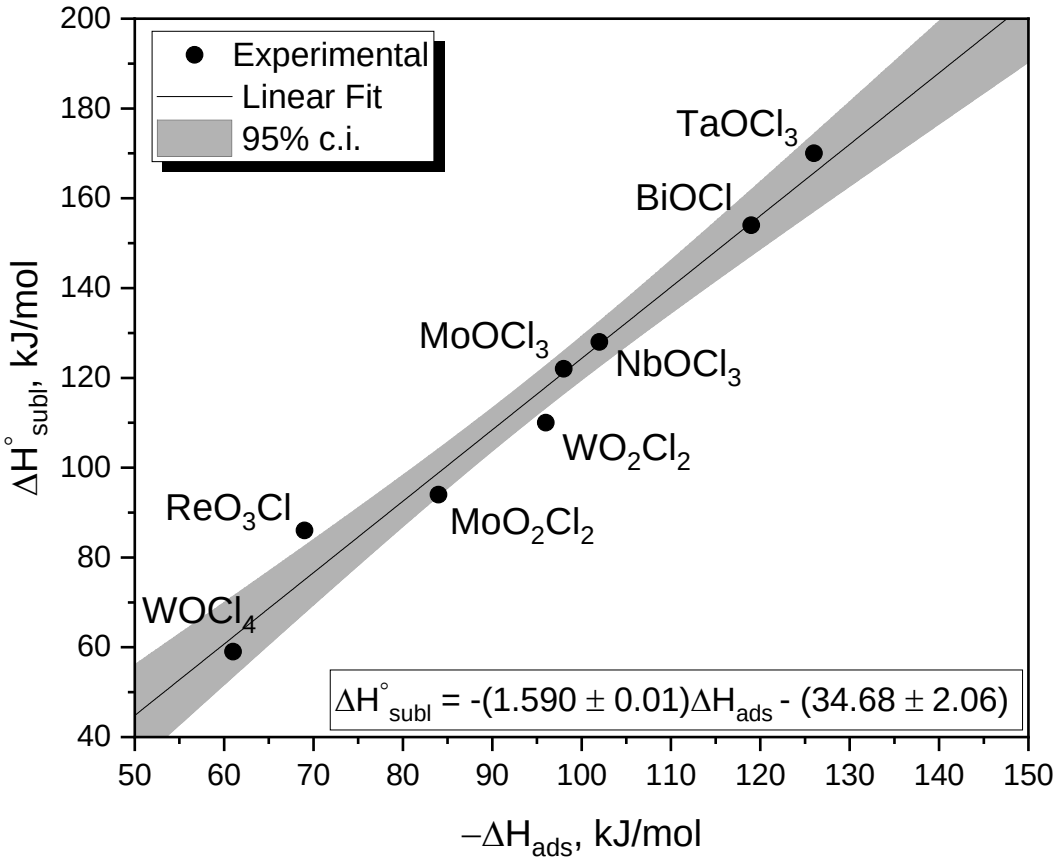


Sublimation enthalpies (ΔH_{subl}) of $NbOCl_3$ and $TaOCl_3$

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



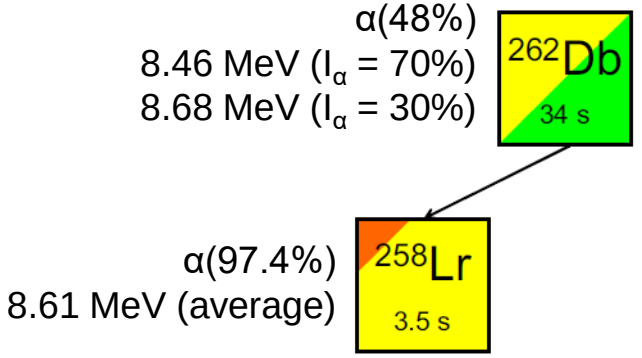
Updated empirical - ΔH_{ads} vs. ΔH_{subl} correlation for oxychlorides



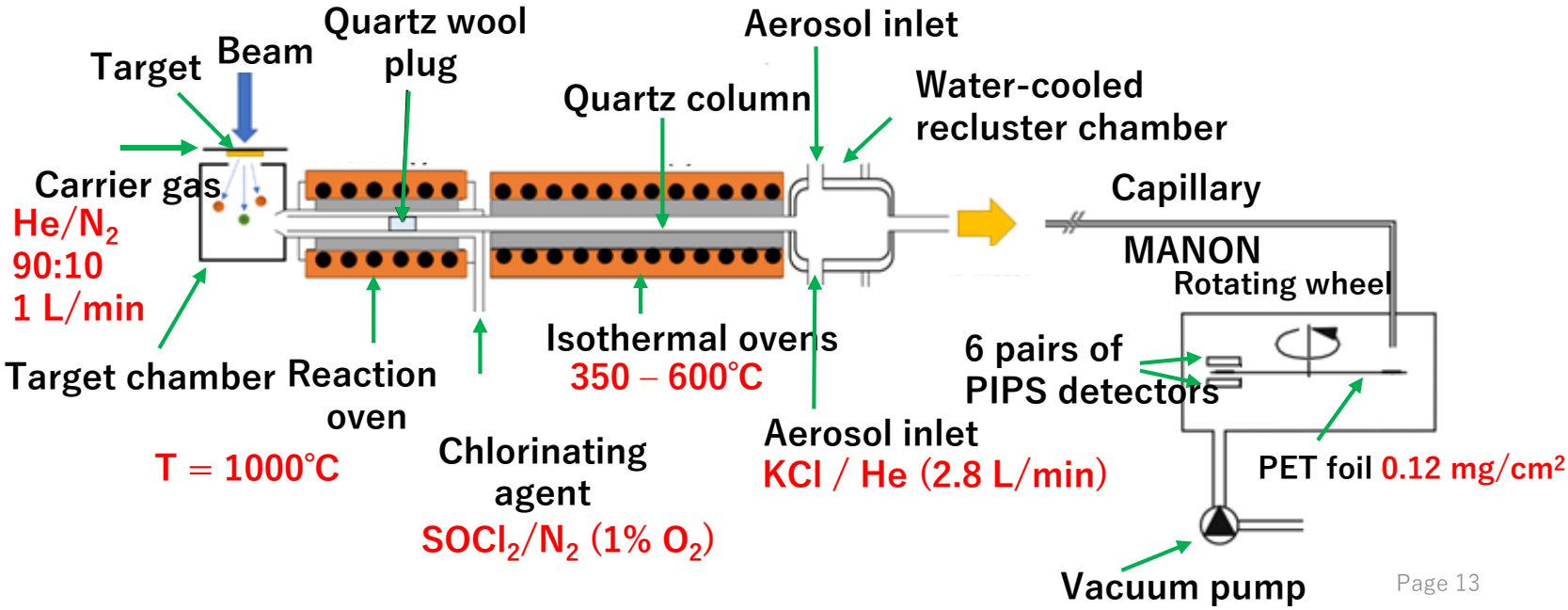
Relative volatility:
$NbOCl_3 > TaOCl_3$
? $DbOCl_3$

Experiments with $DbOCl_3$ with the IGC setup @Tandem, JAEA

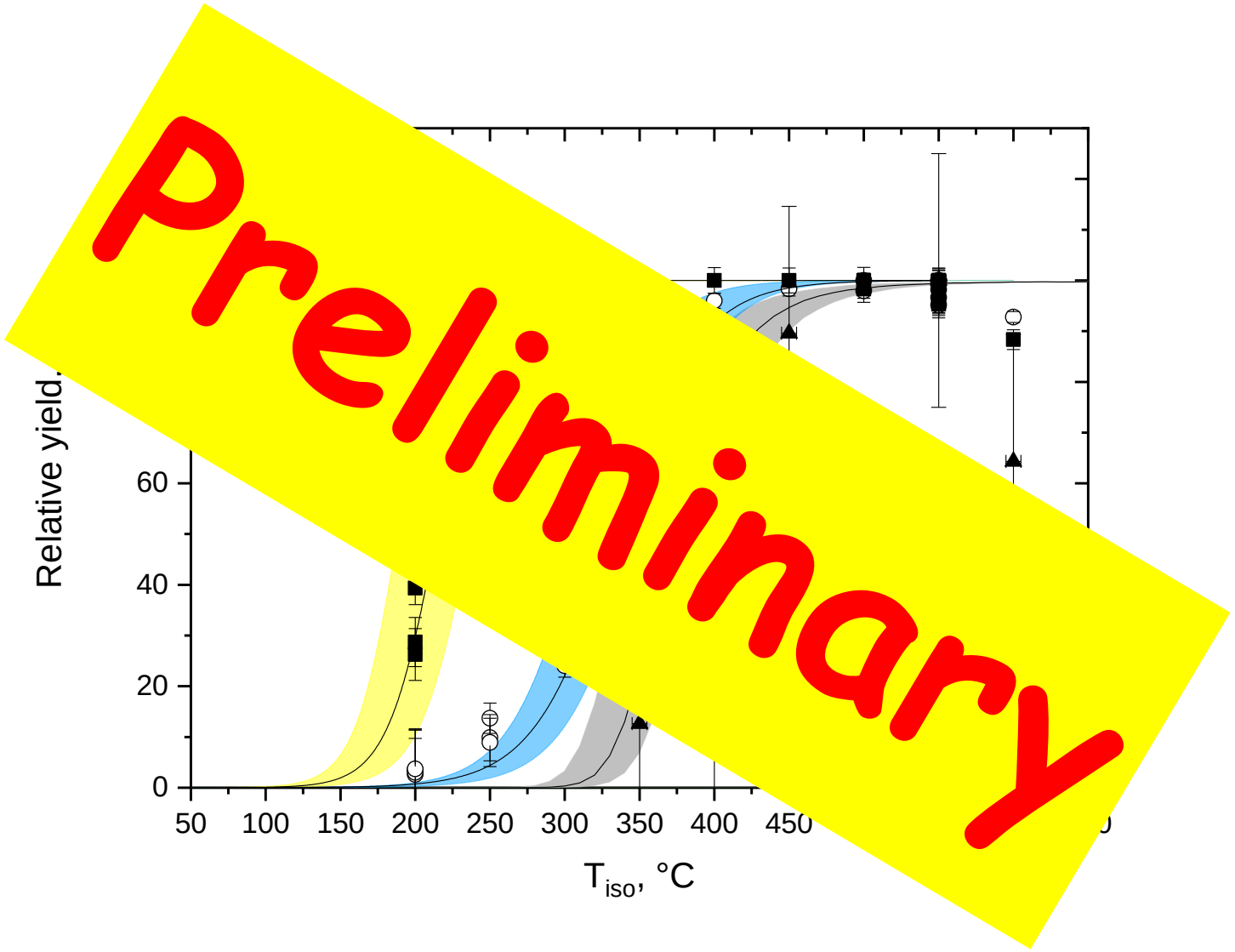
$^{248}Cm(^{19}F, 5n)^{262}Db$
$^{19}F^{7+}$ @103 MeV, 350 pnA
σ = 210 pb @103 MeV
Target thickness: 550 μg/cm²
Chemical efficiency with MANON: 4%



H. Haba et al., 2014



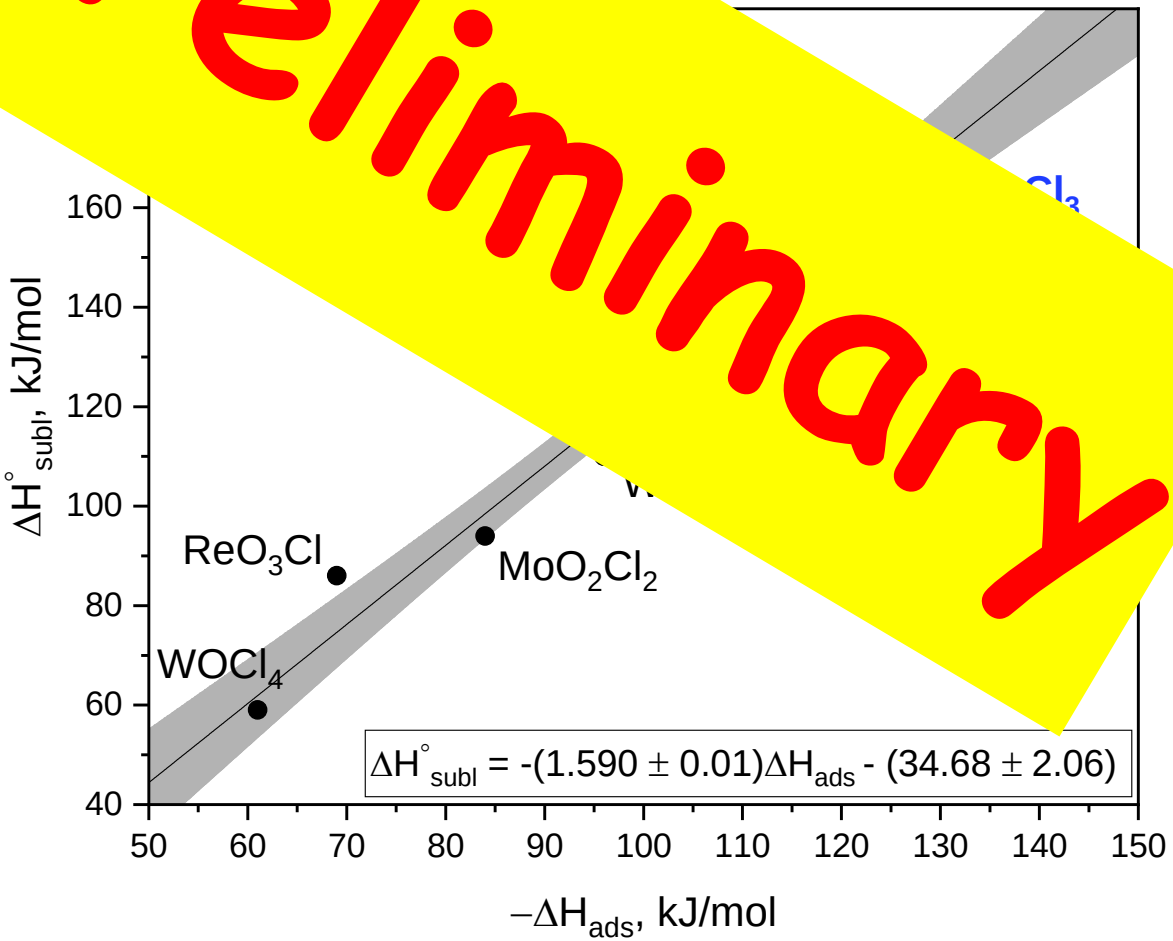
$NbOCl_3$, $TaOCl_3$, $DbOCl_3$ isothermal chromatograms



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

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

Preliminary



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 **$NbOCl_3 > TaOCl_3 \approx DbOCl_3$ adsorption interaction strength** was observed;

•The estimated volatility sequence in Group-5 is **Nb > Ta ≥ Db.**