Calcium Isotope Separation with Crown Ether via LLE and SLE method: Cool Plasma ICP-MS Analysis

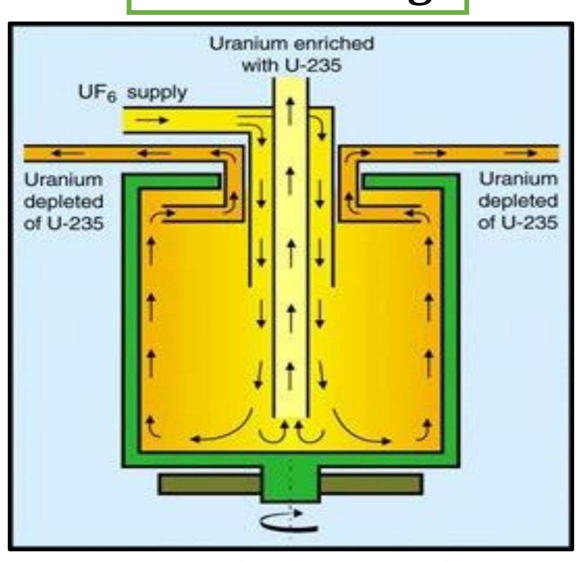
○ Pantiwa Kumsut[1], Ryuta Hazama[1], Takaaki Yoshimoto [1], Kanyanan Kosinarkaranun[1], Chonlada Pitakchaianan[1], Anawat Rittirong[2], Tadafumi Kishimoto[2], Toshiyuki Fujii[2], Yoichi Sakuma[3], Satoshi Fukutani[4], Yuji Shibahara[4]

大阪産業大学 OSAKA SANGYO UNIVERSITY　大阪大学 OSAKA UNIVERSITY　京都大学複合原子力科学研究所 Kyoto University Research Reactor Institute　東京工業大学 Tokyo Institute of Technology

Calcium isotope enrichment via chemical exchange

❖ Applicable ways to isotope enrichment

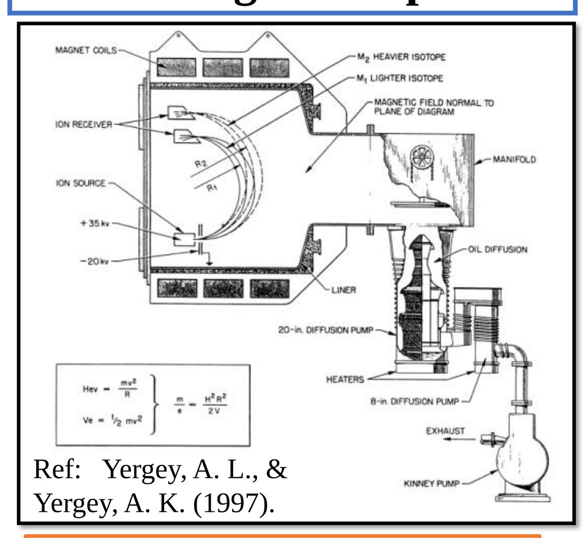
Gas centrifuge



Ref: European Nuclear Society Newsletter

- Required a gaseous compound
- × Calcium no gas compound

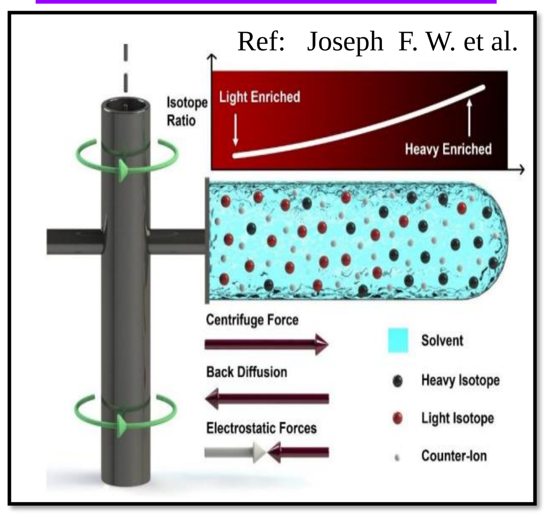
Electromagnetic separator



Ref: Yergey, A. L., & Yergey, A. K. (1997).

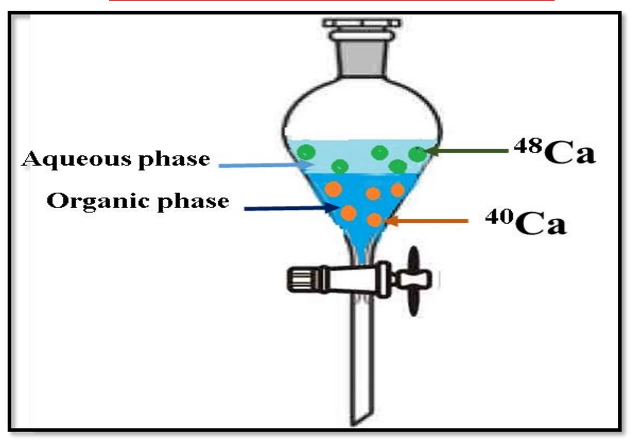
- ❑Small production yield
- ❑Costly material
- (200,000 $/g (~2千万円/g)

Liquid centrifugation



- Spend a long time for centrifugation (72 hours)
- Low Ca concentration

Chemical exchange



Liquid-liquid extraction (LLE) using crown-ether

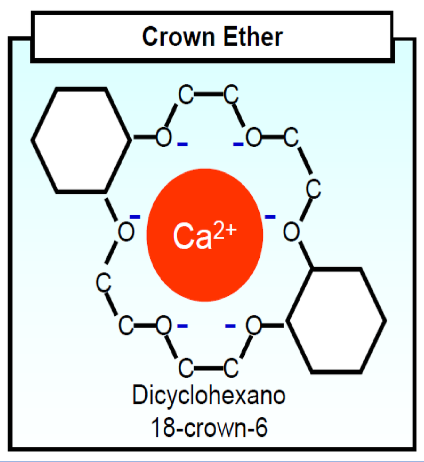
- ✓Inexpensive (low-cost)
- ✓Easy to handle
- ✓Fast and high productivity

❑ Calcium Isotope Enrichment

Separation techniques	Filed of use	Production efficiency (y^{-1})	Cost	Separation coefficient (ε)
Electromagnetic by mass spectroscopy	Universal	ten of grams	High	Large
Chemical processes	Light elements	tons	Low	Small
Laser separation	Elements having isotope shift from spectrum lines	kilograms	middle	Large

- The most advantage of LLE using an organic solvent containing crown-ether is that it can be applied to microchip separation
- The microchip provides fast and high conversion of the extraction process, resulting in mass production feasibility

Crown-Ether



Dicyclohexano-18-crown-6: DC18C6

Total atoms in the ring　Oxygen atoms in the ring

Hold by electrostatic attraction between Oxygen atoms (negative charge) and cation (Ca^{2+})

Macrocyclic polyether for Calcium extraction

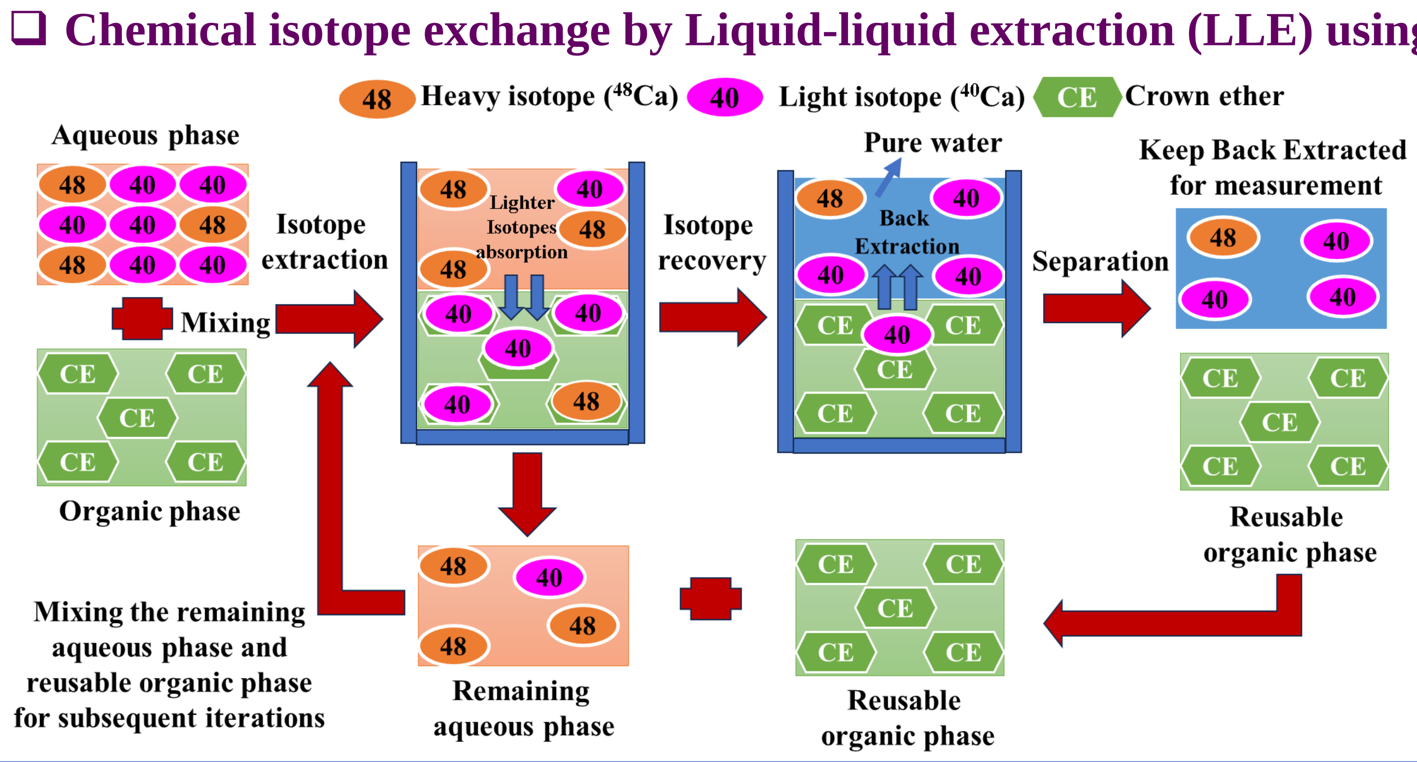
- Appropriate cavity size to calcium ion
- High selective extraction to the Ca-ion

The cavity size of crown-ether in Angstrom unit [94]

Crown-ether molecule	Cavity size (Å)
12-crown-4	1.2 – 1.5
15-crown-5	1.7 – 2.2
18-crown-6	2.6 – 3.2
21-crown-7	3.4 – 4.3

Calcium isotope enrichment

❑ Chemical isotope exchange by Liquid-liquid extraction (LLE) using crown-ether



❖ Chemical exchange reaction

$$^{40}Ca^{2+}_{(aq)} + {}^{48}CaL^{2+}_{(org)} \rightarrow {}^{48}Ca^{2+}_{(aq)} + {}^{40}CaL^{2+}_{(org)}$$

Where; L is macrocyclic crown-ether

❖ In solid-liquid extraction (SLE) using calcium in solid form instead of aqueous phase

Measurement

- ❑ Ion concentration measurement by AAS
- ❑ Isotopic analysis by cool-plasma ICP-MS (Agilent 7900)

Current measurement technique

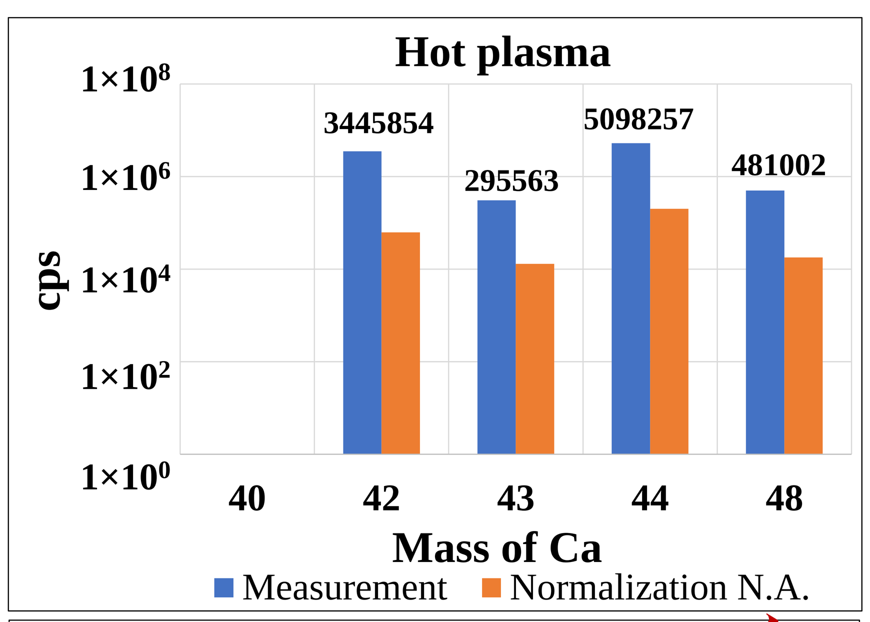
- Apply the "cool plasma" technique
- Reduce the RF from 1500 W to 600 W
- To suppress and free from isobaric interference such as which the problematic in ICP-MS measurement for calcium measurement

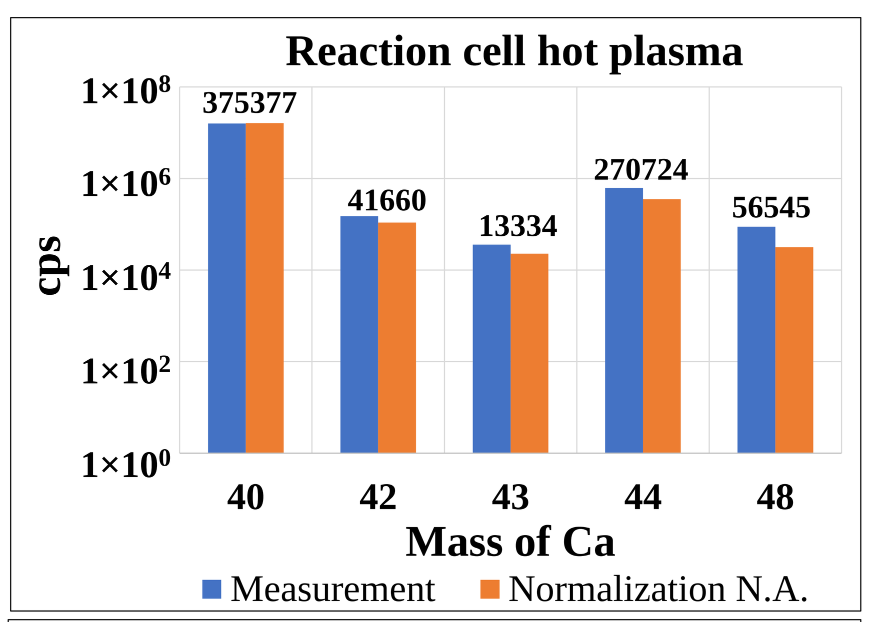
$$\alpha_{aq} = \frac{IR(^{48}Ca/^{40}Ca)_{aq}}{IR(^{48}Ca/^{40}Ca)_{feed}}$$

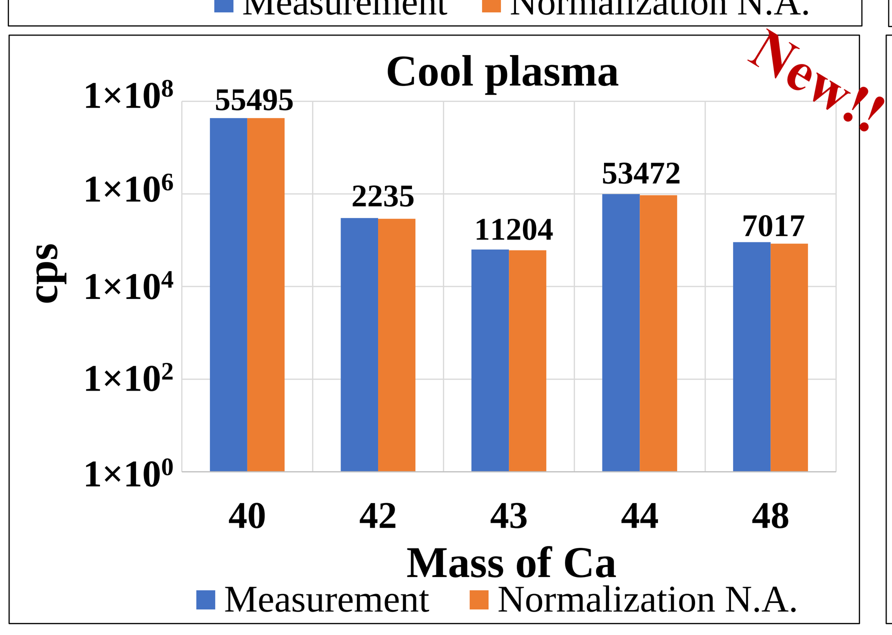
Heavier enriched: $\alpha_{aq} > 1$
Final GOAL!!

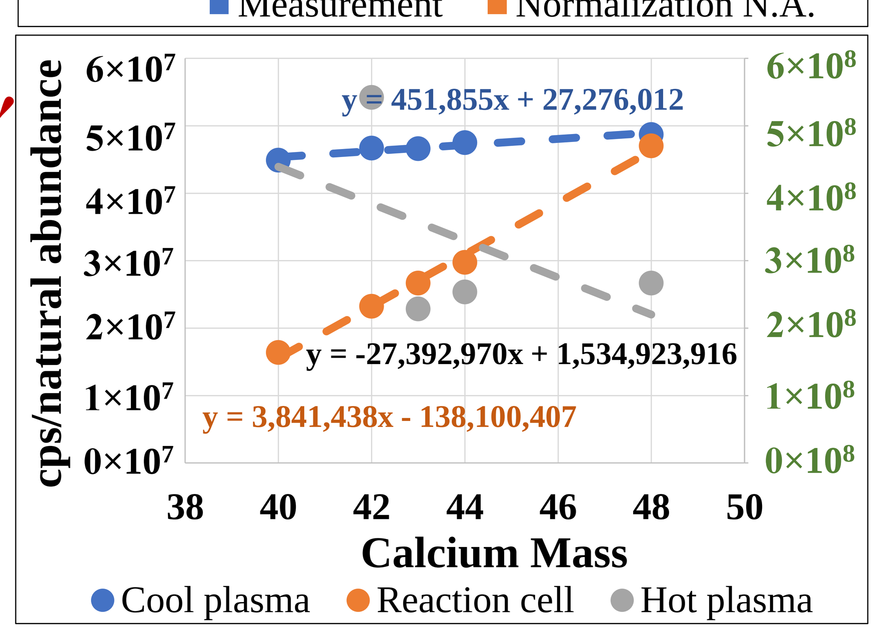
Inductively coupled plasma mass spectrometry (ICP-MS)

❖ The comparison chart of natural abundance and sample counts









❑ Sample: standard calcium at 1 ppm

$$\text{Normalization N.A. of }{}^{x}Ca = \sum_{i=40}^{48} {}^{i}Ca\ cps \times \text{N.A. of }{}^{x}Ca$$

- The natural abundance of each calcium isotope and the sample count
- The difference in count per second (cps) between the natural abundance and the sample count of each Ca isotope (number in the Figure) decreases when using cool plasma

Natural abundance refer to the smaller in mass bias

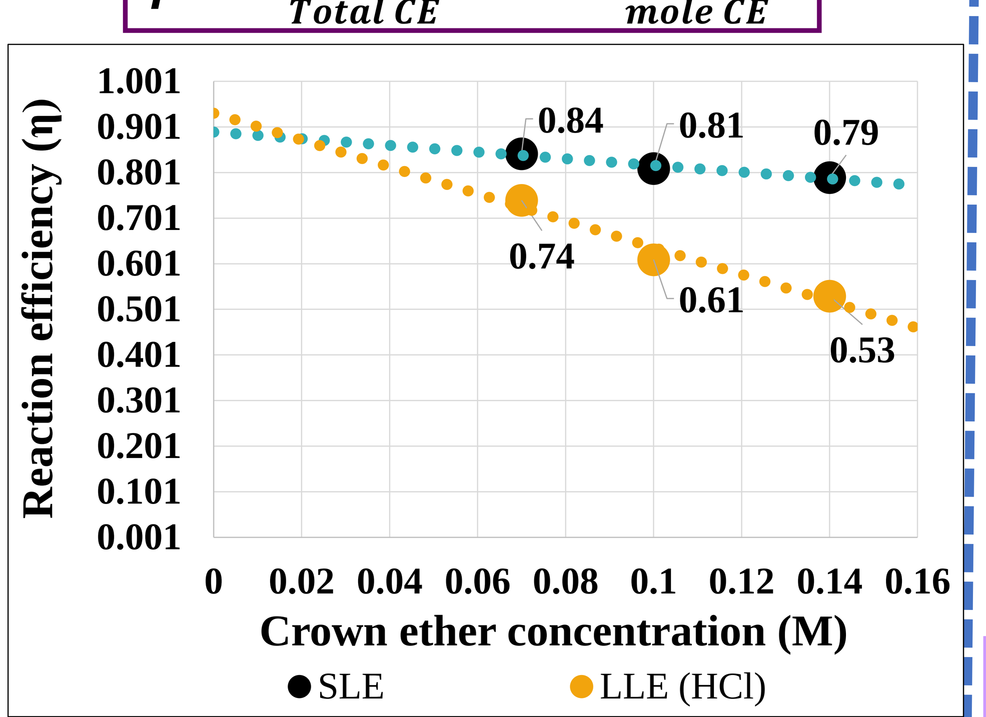
- Mass bias is smaller when using cool plasma

Hot plasma > Reaction cell > Cool plasma

Solid-liquid extraction

❖ Comparison the reaction efficiency (η) between SLE without HCl and LLE with HCl

$$\eta = \frac{CE\ reacted\ with\ Ca}{Total\ CE} = \frac{mole\ Ca_{org}}{mole\ CE}$$

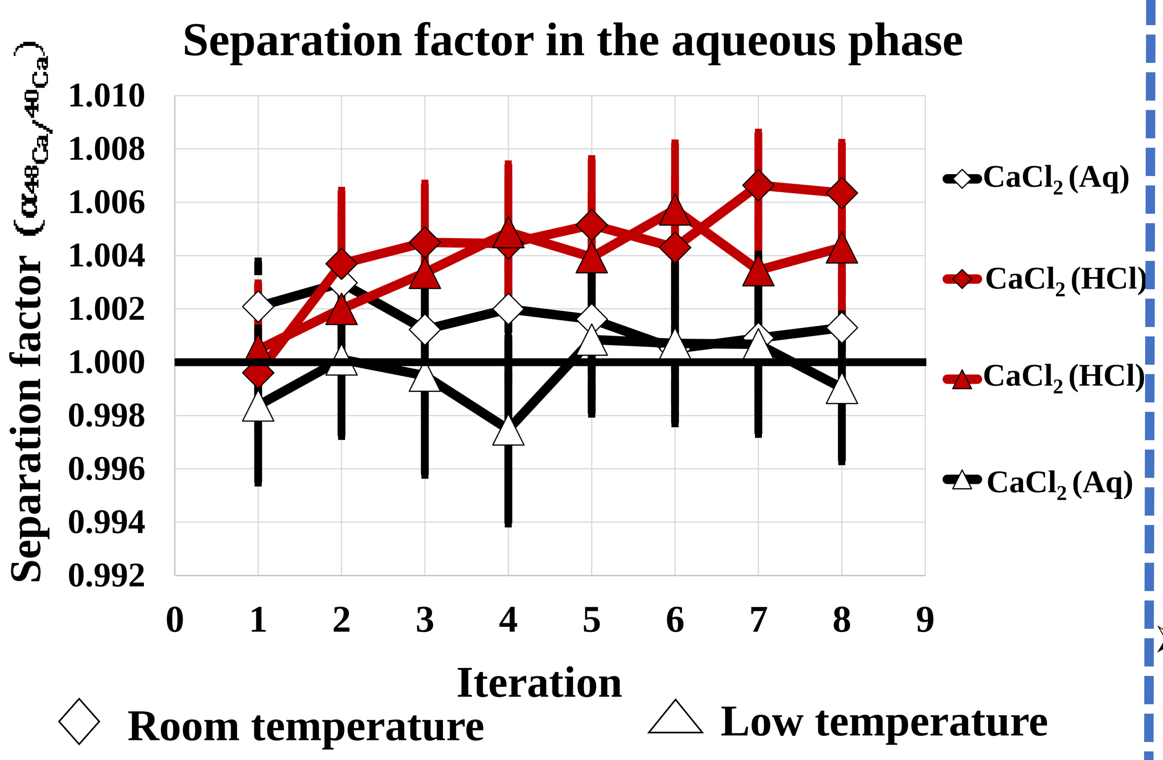


- The reaction efficiency (η) was larger in SLE than in LLE

- LLE: $CaCl_2$ (HCl) + 100 mL DC18C6
- SLE: $CaCl_2 \cdot 2H_2O$ (s) + 10 mL DC18C6

All multi-stage liquid-liquid extraction

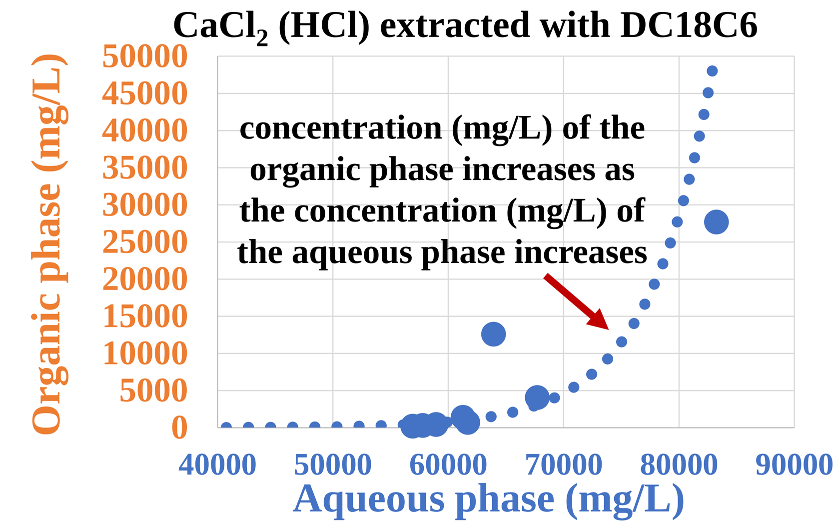
❖Comparison of all multi-stage LLE



ID	Separation Factor	To get 2% ^{48}Ca (iterations)
◇$CaCl_2$ (Aq)	1.001±0.002	10690
◆$CaCl_2$ (HCl)	1.006±0.002	1781
▲$CaCl_2$ (HCl)	1.004±0.002	2673
△$CaCl_2$ (Aq)	0.999±0.003	10690

Increasing mass product

❖ Changing the ratio between calcium and crown ether

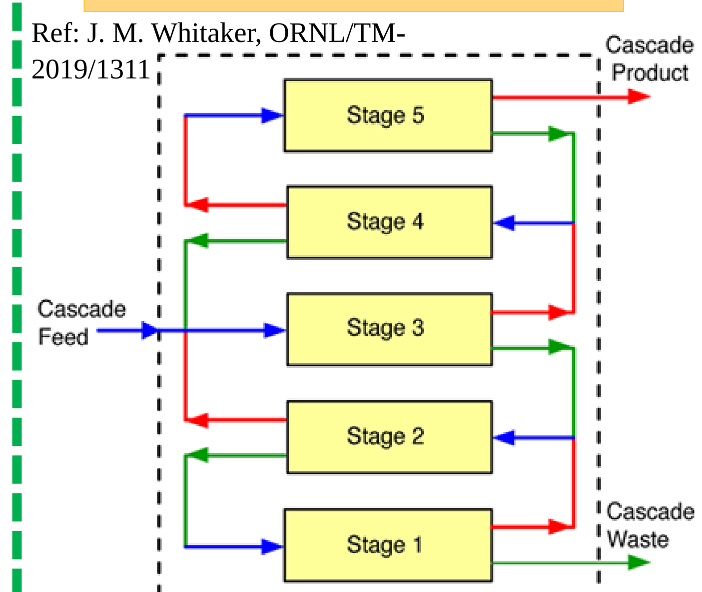


$$D = \frac{concentration\ (mg/L)\ of\ Ca\ in\ the\ organic\ phase}{concentration\ (mg/L)\ of\ Ca\ in\ the\ aqueous\ phase}$$

- Large D value denotes the large quantities of calcium products (mass product) in the organic phase
- To increase mass product, the concentration of the aqueous phase must be increased to get gram order

To achieve 2% of ^{48}Ca

Ref: J. M. Whitaker, ORNL/TM-2019/1311



Cascade separation element

- To increase the concentration of the ^{48}Ca in the material being processed
- Separation elements are connected in parallel to form stages in order to achieve 1781 iterations.

Conclusion

- Mass bias was reduced with cool-plasma ICP-MS
- The separation factor in aqueous phase at room temperature increased from 1.001±0.002 to 1.006±0.002
- Studying via the SLE method shows a higher reaction efficiency (η) than LLE