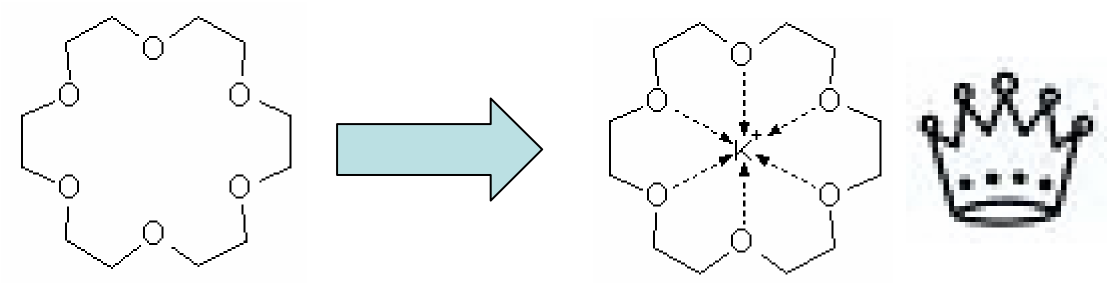
June 12, 2007@DBD07, Osaka

CAlcium fluoride for studies of Neutrinos and Dark matters by Low Energy Spectrometer

# Enrichment of $^{48}$Ca

## *~Separation with a crown ether~*



18-crown-6-ether

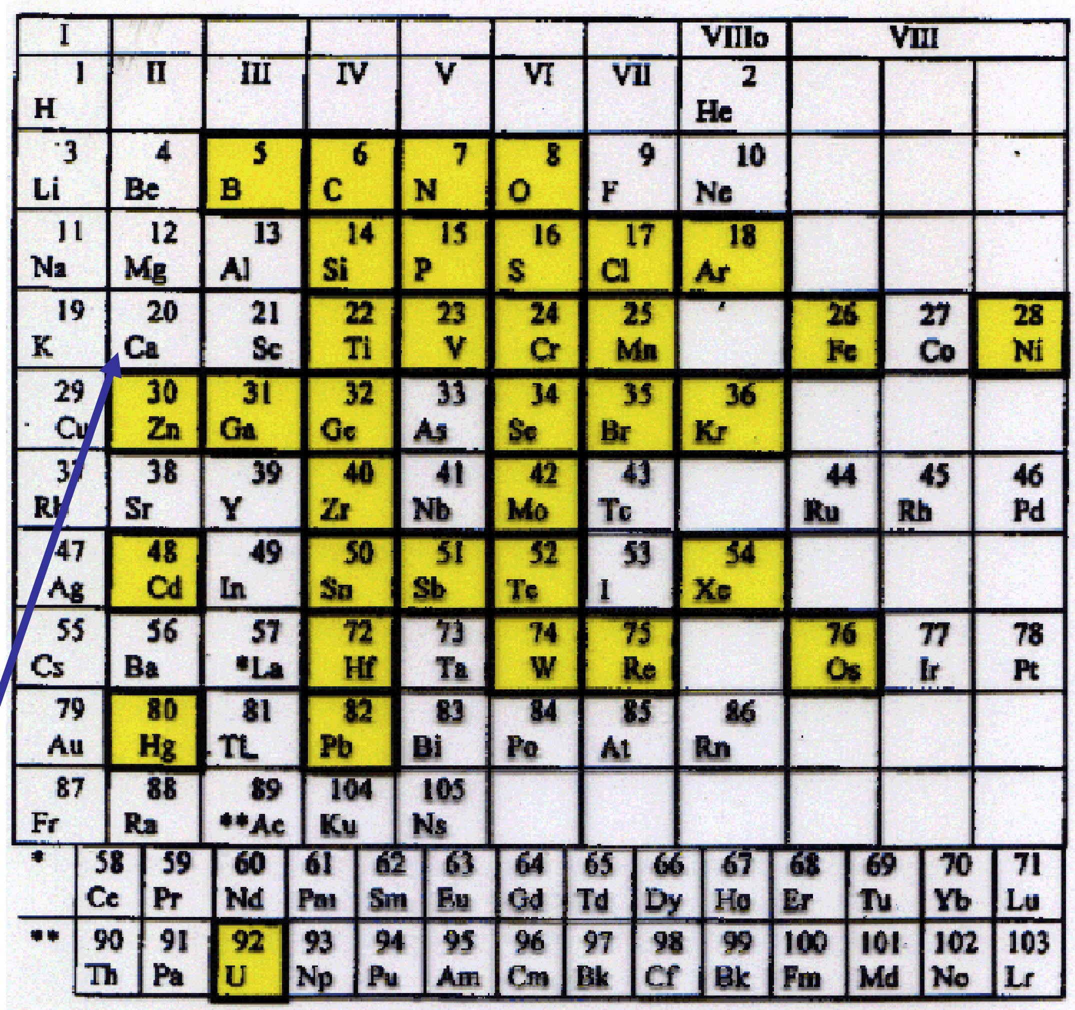
*Pedersen@1962*
*Cram&Lehn@1987*
*Molecular Recognition Technology*
*Nobel Prize*


Ryuta Hazama
Hiroshima University

広島大学
大阪大學

# $^{48}$Ca enrichment

- Natural abundance
  - → 0.187%
  - – Enriched isotope
  - → expensive
  - (elemag. ~~separator; Calutrons~~)~200K$/g
  - ~10g × 2 (in the world)
  - →no gaseous compounds
  - at room temp.
  - ~~Gas centrifuge~~




Elements separated into isotopes with gas centrifuges - □

A.I.Karchevski

ββ isotopes; $^{48}$Ca, $^{96}$Zr, $^{150}$Nd etc.

# Technologies for isotope production for Ca

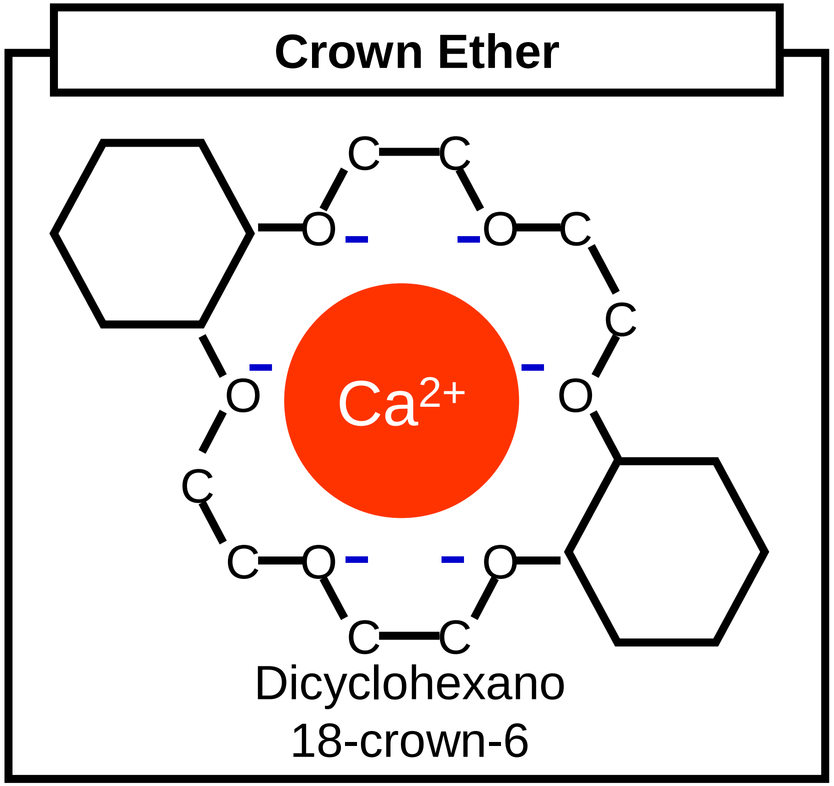
| *Separation technology* | *Field of use* | *Production per year* | *Cost* |
|---|---|---|---|
| Electromagnetic (mass-spectroscopy effect) | universal | tens of grams | high |
| Chemical & phys. processes (rectification, chem. exchange etc) | light elements | tons | low |
| Gas diffusion | elements forming gas compounds | thousands of tons | middle |
| Gas centrifuge | elements forming gas compounds | thousands of tons | low |
| Laser (optical) separation | elements having isotope shift of spectrum lines | kilograms | middle |
| Plasma ion-cyclotron effect (under developing – the USA, Russia) | universal | hundreds of kilograms | middle |

*Find a cost-effective & efficient way of enrichment!!!*

# Unique Property of Crown Ether

Complexing of cations(anions) by neutral molecules is an uncommon phenomenon.

Stability is ~$10^4$ × no-ring(crown)




DC18C6

Total # of atoms in the ring

# of oxygen atoms in the ring

- **Held by electrostatic attraction between negatively charged $O^-$ of the C-O dipoles & cation ($Ca^{2+}$)**
- **How well the cation fits into the crown ring**
- **Liquid(aq-salt)-liquid(org-crown) extraction in isotopic equilibrium**

# Ca Isotope effects～Separation Principle

$^{40}Ca^{2+}(aq)+^{48}CaL^{2+}($

↑ ⇓

$^{48}Ca^{2+}(aq)+^{40}CaL^{2+}($

$CaCl_2$ aqueous phase $^{48}Ca$

$^{40}Ca$ 0.07M

Crown-chloroform organic

DC18C6: Aldrich Chemical

$CHCl_3$:Nakarai Tesque, 99.0%

$CaCl_2$:Nakarai Tesque, 95.0%

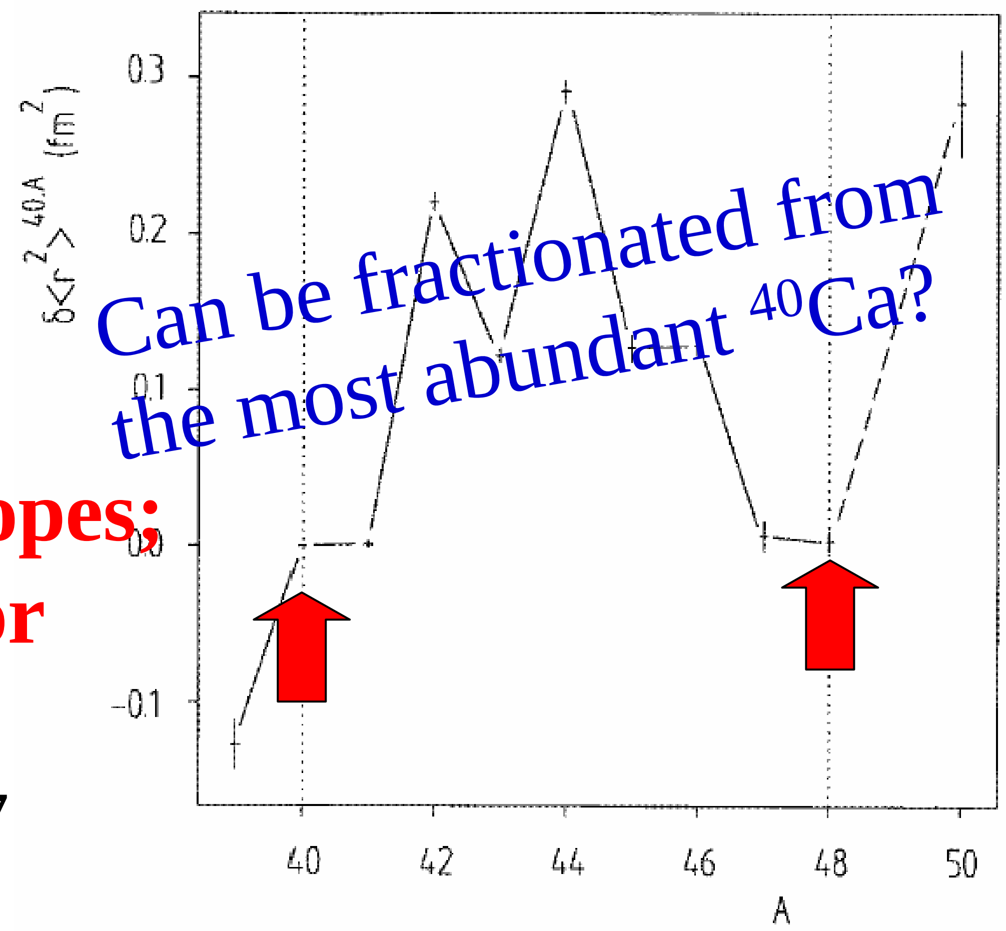
## Solvent Extraction process

1. vacant extraction to reduce impu.
2. mixed & stirred for 1 hour
3. standing for 1 hour @7°C
4. LLE iterated 6 times

Magnetic Stirrer

B.E.Jepson&R.Dewitt, J. Inorg.nucl.Chem38(1976)1175

# The mean square Nuclear charge radius of Ca




Can be fractionated from the most abundant $^{40}$Ca?

**Two doubly magic isotopes;**

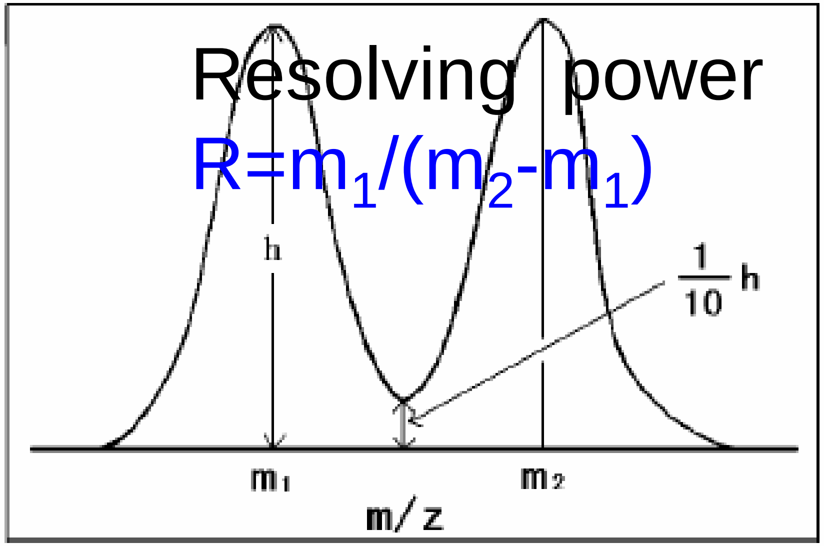
**A parabolic behavior**

L.Vermeeren et al., J.Phys.G,22(1996)1517

| Ca isotope | $^{40}$Ca | $^{42}$Ca | $^{43}$Ca | $^{44}$Ca | $^{46}$Ca | **$^{48}$Ca** |
|---|---|---|---|---|---|---|
| abundance（%） | 96.9 | 0.65 | 0.135 | 2.09 | 0.004 | **0.187** |

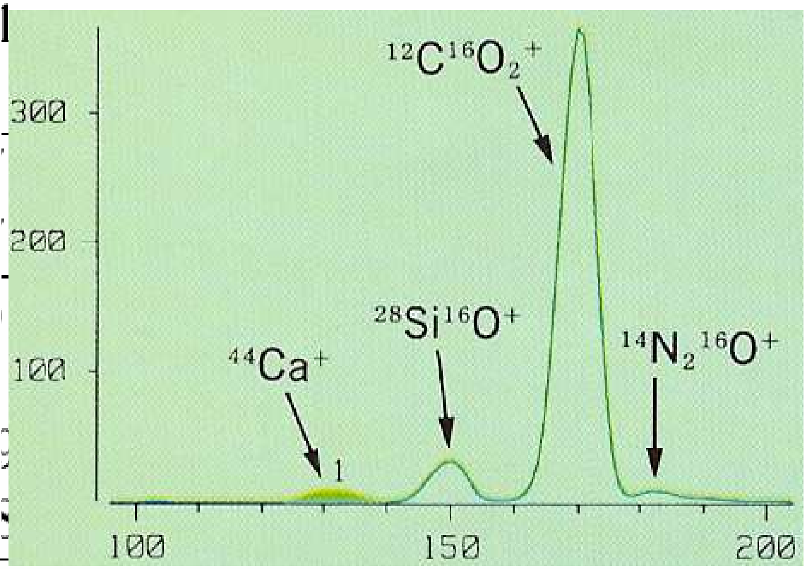
# Major background molecular ions formed from the Ar Plasma, nebulized water and dissolved/contained air.

**m/z=**




Resolving power

$R = m_1/(m_2 - m_1)$




| Mass | Molecular ion | isotopic ratio(%) | required resolution |
|---|---|---|---|
| 44 | $^{44}Ca$ | 2.086 | - |
| 44 | $^{88}Sr^{2+}$ | 82.58 | 16448 ✕ |
| 44 | $CO_2$ | 98.43 | 1280 |
| 44 | $^{14}N_2^{16}O$ | | |
| 48 | $^{48}Ca$ | 0.187 | - |
| 48 | $^{48}Ti$ | 73.8 | 10457 |
| 48 | $^{36}Ar^{12}C$ | 0.333 | 2447 ← Enemy |

# How to measure $^{40}Ca$?

1. TIMS(TRITON Thermo Electron)

   No-Ar *Only four TRITONs in Japan*

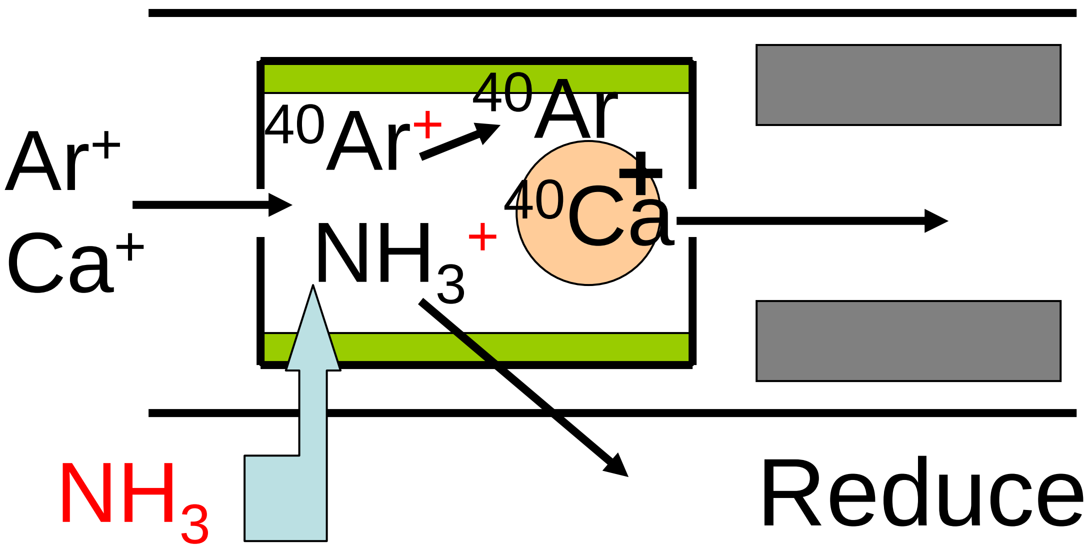
2. Reaction(collision)-cell ICPMS

   *Perkin Elmer ELAN-DRCII@Kochi Univ.*

Q inside reaction-cell allows use of ammonia

→ can avoid interference of Ar by reaction-gas

*Simple collision-cell must use simple gas($H_2$, He) to limit adverse side reaction products*

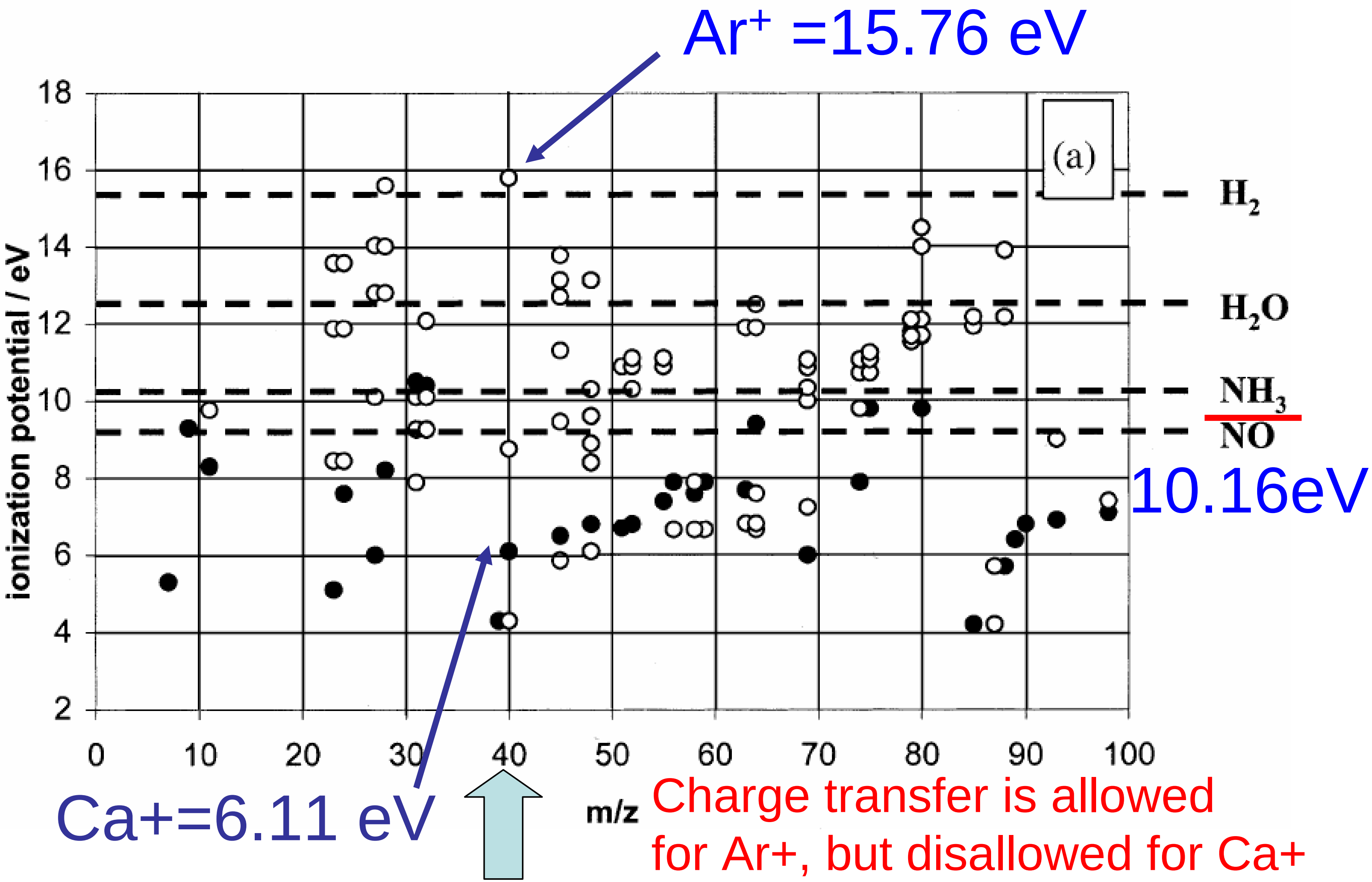



$Ar^+ + NH_3$

$\rightarrow NH_3^+ + Ar$

Reduce $Ar^+ \rightarrow 10^9 > 10^3$

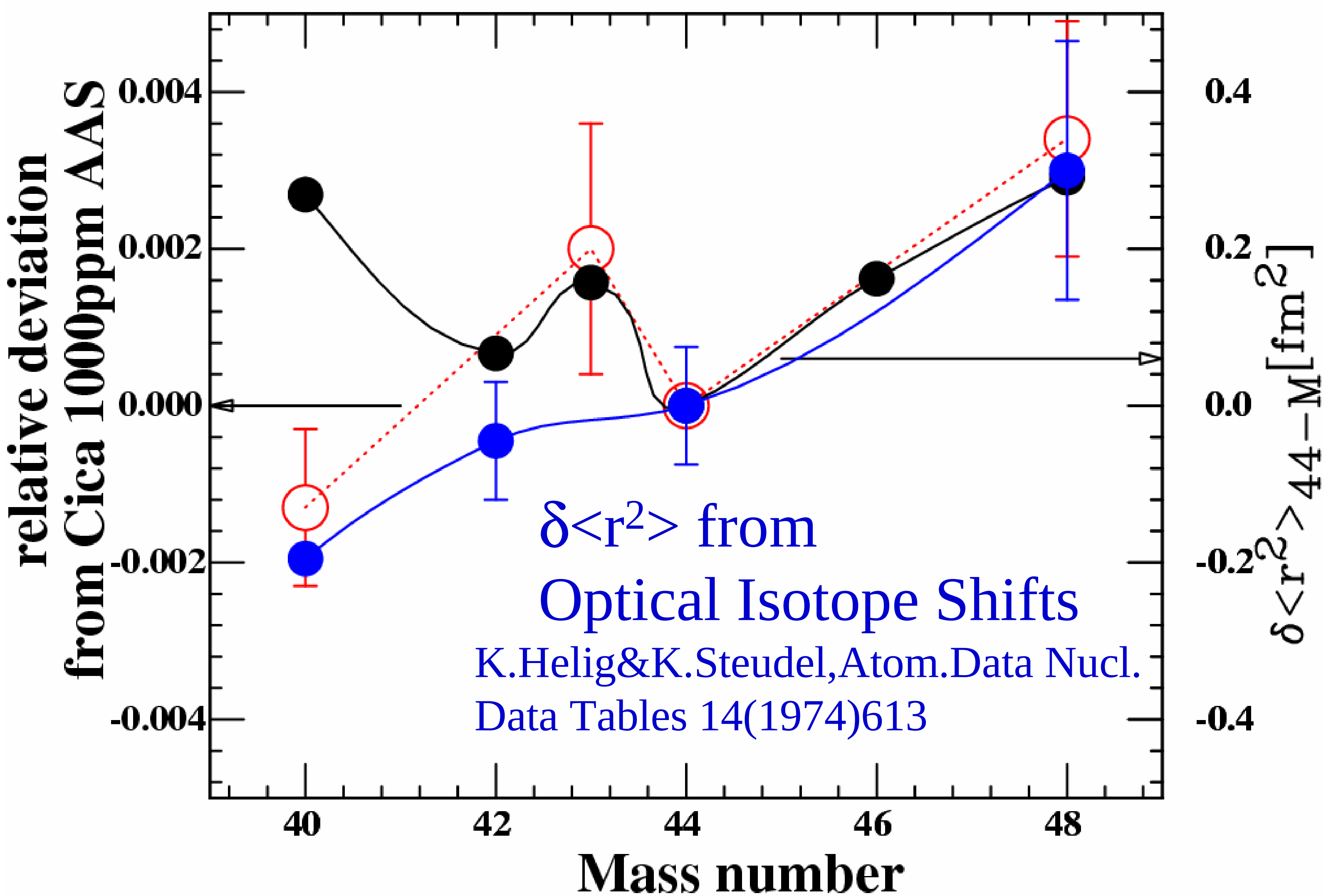
S.D. Tanner et al. / Spectrochimica Acta Part B 57 (2002) 1361–1452




Charge transfer is allowed for Ar+, but disallowed for Ca+

Ca(6.11eV)<NH3(10.16eV)<Ar(15.76eV)

# $^{40}$Ca, $^{48}$Ca are doubly magic → **A parabolic behavior**




Nuclear mass effect > Nuclear size&shape effect!!!

This is crucial asset to realize $^{48}$Ca enrichment (from $^{40}$Ca)

# Comparison

Table 1: Summary of previously achieved(measured:known) calcium enrichment. LLC(liquid-liquid chromatography), DC18C6((polyether) dicyclohexyl 18-crown-6), HDEHP(di(2-ethylhexyl) orthophosphoric acid), SLC(solid-liquid-chromatography), LIS(laser isotope separation), MCIRI(Magnetic Cyclotron Ion Resonance of Isotopes)

| | separation factor | process | ref.(manufacturer) |
|---|---|---|---|
| **1.0020** | $1.012\pm0.005$ ($\alpha^{48}_{42}$) | LLC(DC18C6) | Osaka RI-center and WERC |
| **1.0028** | $1.014\pm0.006$ ($\alpha^{48}_{43}$) | LLC(DC18C6) | Osaka RI-center and WERC |
| **1.0010** | $1.0080\pm0.0016^{\dagger}$ ($\alpha^{48}_{40}$) | LLC(DC18C6) | [1] |
| **1.0007** | $1.0029\pm0.0006$ ($\alpha^{48}_{44}$) | LLC(HDEHP) | [2] |
| | $1.0013\pm0.0003$ | LLC(amalgam(Hg)) | [3] |
| | 1.000043~1.000034 | SLC(ion-exchange) | [4]resin(Dowex) |
| | 1.00026 ($\alpha^{47}_{40}$) | SLC(ion-exchange) | [5]resin(Dowex) |
| | 1.00021 ($\alpha^{44}_{40}$) | SLC(ion-exchange) | [6]resin(Dowex) |
| | $1.00087\pm0.00008$ ($\alpha^{48}_{40}$) | SLC(ion-exchange) | [7]$NH_4$$\alpha$-hydroxyisobutyrate&(Dowex) |
| **1.0010** | $1.0041\pm0.0004$ ($\alpha^{44}_{40}$) | SLC(ion-exchange) | [8] iminodiacetate&resin(ANKB-50) |
| | $1.00013\sim1.00087^{\sharp}$ | SLC(ion-exchange) | [9](TIT)resin(PK-1),Counter-Current |
| | 1.00016~1.00037 ($\alpha^{48}_{40}$) | SLC(ion-exchange) | [10](Sophia) resin(Asahi LS-6) |
| | 1.00018 ($\alpha^{48}_{40}$) | SLC(ion-exchange) | [11]resin(AG50WX4) |
| | 1.00049~1.00013 ($\alpha^{44}_{40}$) | SLC(ion-exchange)18C6 | [12]resin(AG50WX4) |
| **1.0010** | $1.0039\pm0.0002$ ($\alpha^{44}_{40}$) | SLC(cyptand$2_B$.2.2) | [13] |
| **1.0006** | $1.0025\pm0.0003$ ($\alpha^{44}_{40}$) | SLC(18C6) | [13] |
| | $1.00011\pm0.00003$ ($\alpha^{44}_{40}$) | SLC(iminodiacetate) | [13] |
| **1.0009** | $1.0035\pm0.0003$ ($\alpha^{44}_{40}$) | SLC(18C6+dimethylsulfoxide) | [14] |
| **1.0006~1.0013** | 1.0045~1.0104($\alpha^{48}_{40}$)§ | SLC(cryptand$2_B$.2.2) | [15] |
| | - | LIS(LLNL) | a few \$/mg(¥1M/kg) for $^{43}$Ca [16] |
| | 20% | MCIRI | 5kg/day→10g/day(0.7K\$/g)* [17] |
| | 65.3~95.7% | carbonate or oxide | TRACE Science Int. [18] |
| | 6%% ($\alpha^{44}_{40}$) | chemical diffusion‡ | [19] |

† 0.185% →10% for 1kg/yr by Counter current distribution method.
♯ 0.185% →0.226%♯ after 5 weeks, yielding 144mg of the enriched calcium(1.4g/yr).
§ In a preliminary experiment, they could isolate 30mg of calcium in which $^{48}$Ca was enriched by 3.3 % at 0°C from 210mg of natural abundant calcium.
* This corresponds to 3.7kg/yr(¥0.7M/kg). Current cost of product at "electromagnetic"(aka calutrons at ORNL) separation ~200K\$/g(¥200M/kg) .

Preliminary

**Need to verify by precise TIMS & More iterate LLE**

~800 iteration

0.187→ 2.0%

# Prospect for Mass production

**LLE by Microchannel/reactor**

- Fast & Highest conversion synthesis
- Aqueous-organic multi-phase flow

**Column chromatography using crown ether resins**

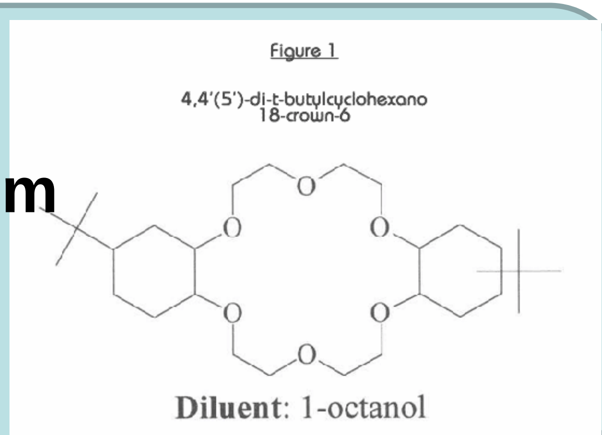
- Multi-stage process
- Slow & low conversion

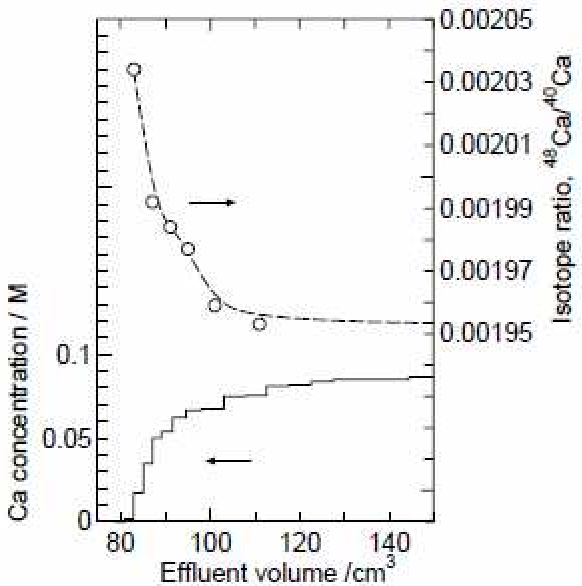
Ca solution: Analyte(mobile phase)

Packed column (stationary phase)

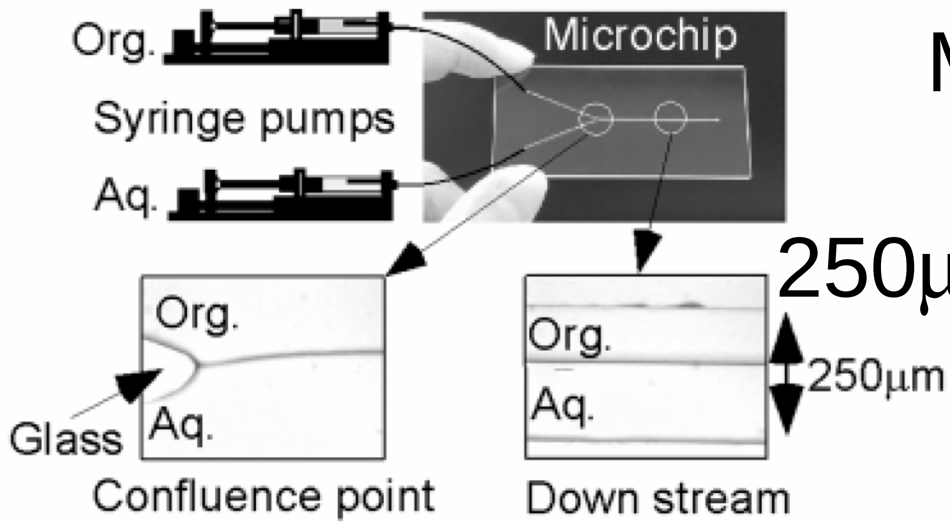
II

**Eichrom or IBC Resin**




Prof. Y. Fujii@TIT Frontal development: $\alpha_{40}^{48} \sim 1.0028$




Macro)10cm cube
S/V~0.6/cm
250μm wide,100μm deep,
and 3cm length
S/V~80/cm

**Fig. 1** Photographs showing glass microchip and liquid–liquid interface formed inside the microchannel.

No-stirring,Fast!!

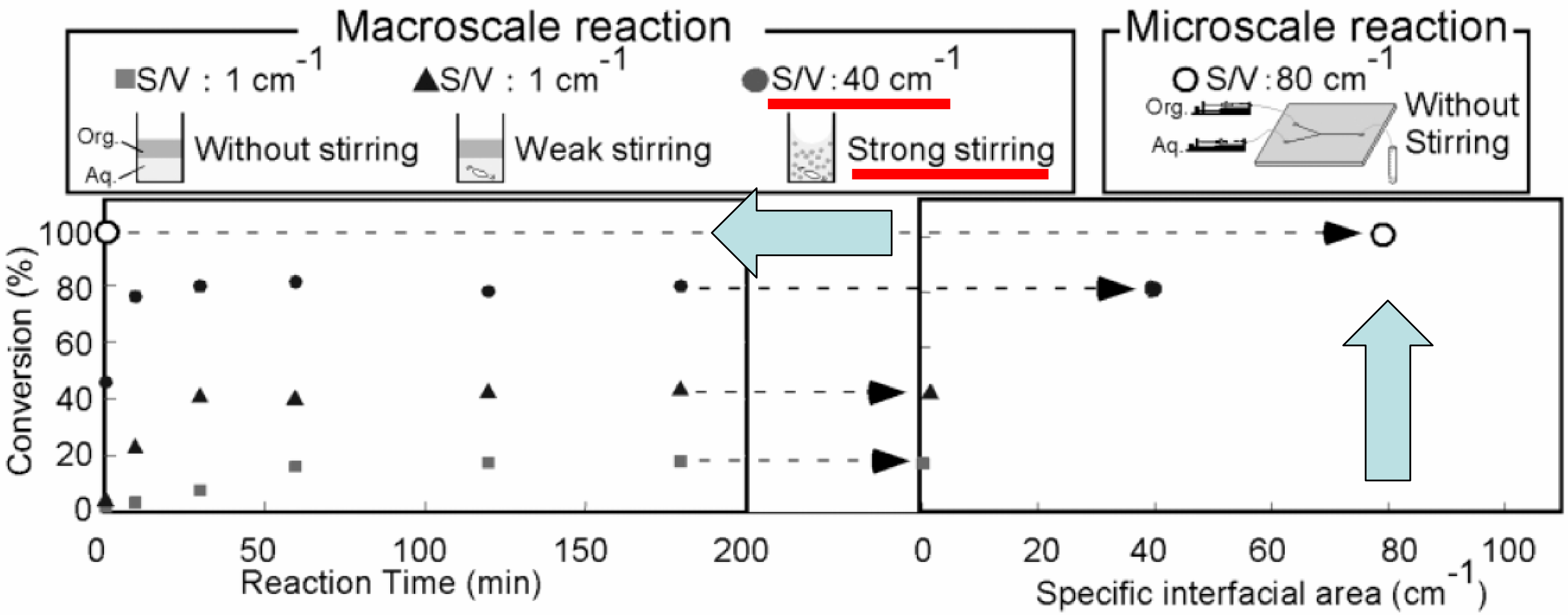
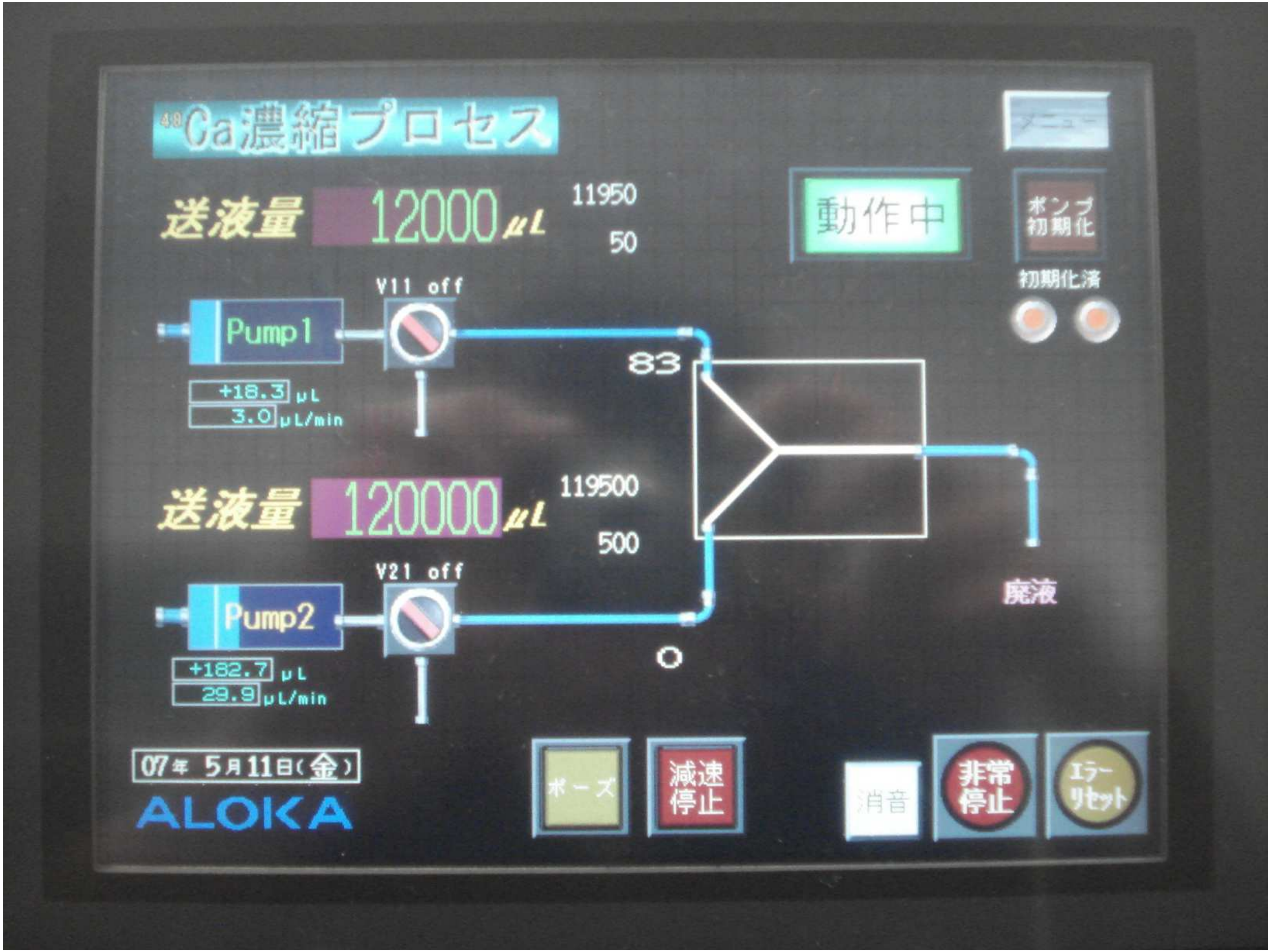
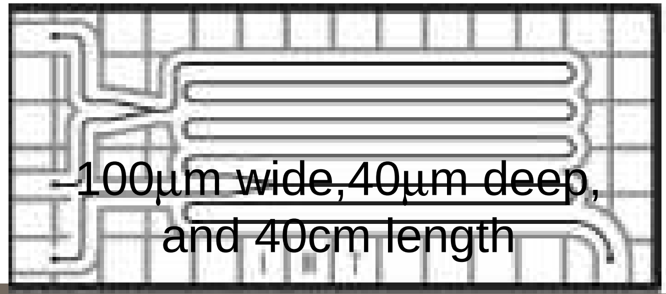


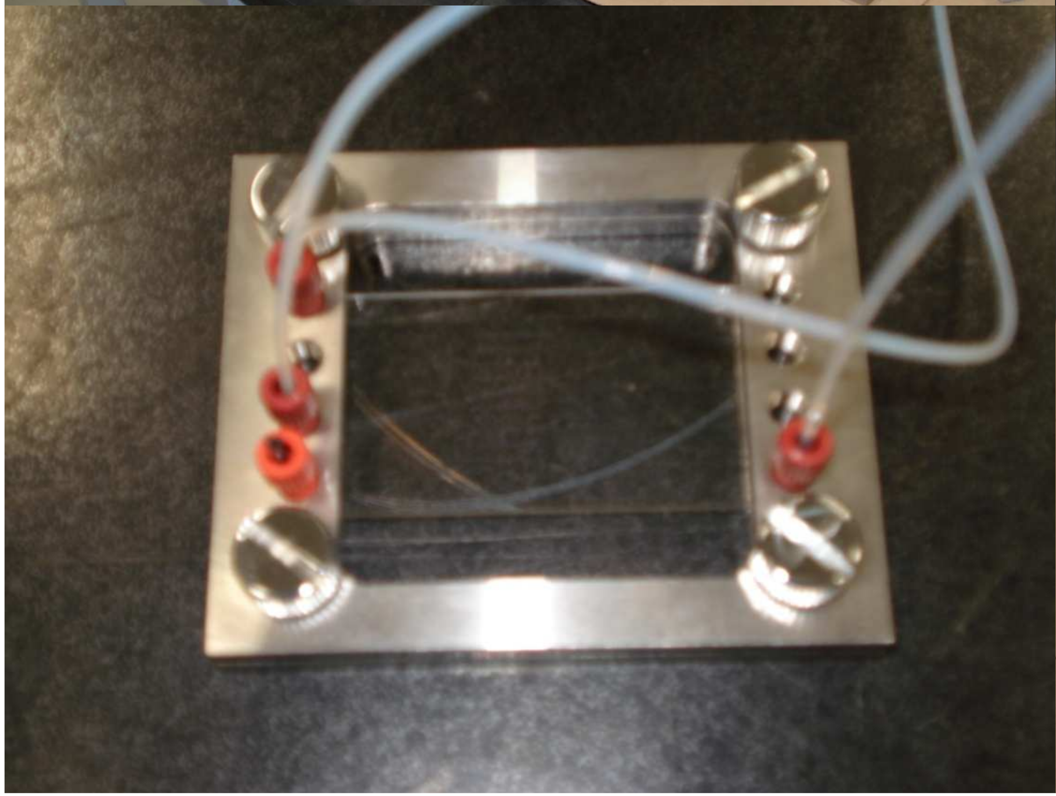

**Fig. 3** Reaction conditions and results obtained with phase transfer diazocoupling reaction under microscale and macroscale conditions.

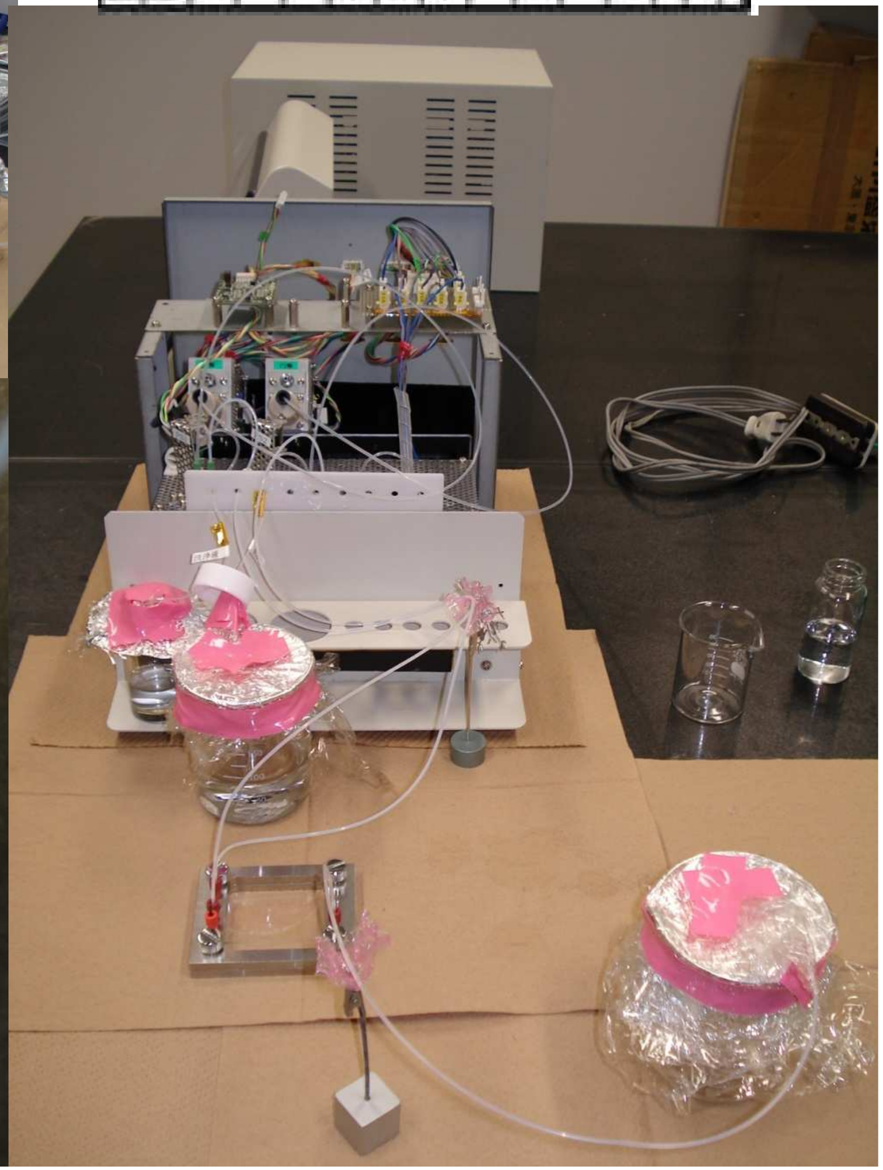


48Ca濃縮プロセス
メニュー
送液量 12000 μL
11950
50
動作中
ポンプ初期化
初期化済
V11 off
Pump1
83
+18.3 μL
3.0 μL/min
送液量 120000 μL
119500
500
V21 off
Pump2
廃液
0
+182.7 μL
29.9 μL/min
07年 5月11日(金)
ALOKA
ポーズ
減速停止
消音
非常停止
エラーリセット


ケイドライ


100µm wide,40µm deep,
and 40cm length





# World's 1st 30 ton/yr production Microchip Chemical Plant

TOSOH
The Chemistry of Innovation

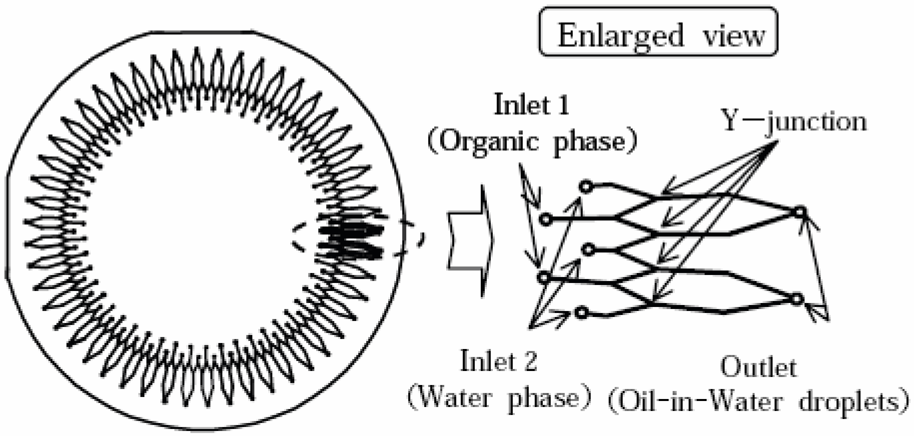
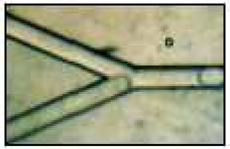
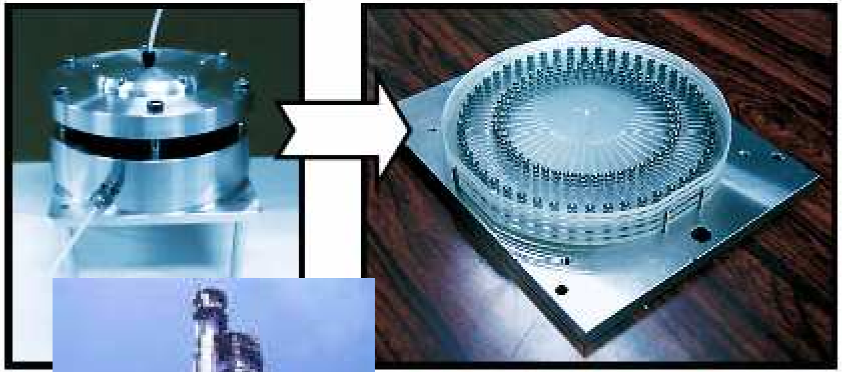



Fig. 7 The circular microchip having 100 Y-junction microchannel.





…hips block with piled up
…lar microchips

~2L/h

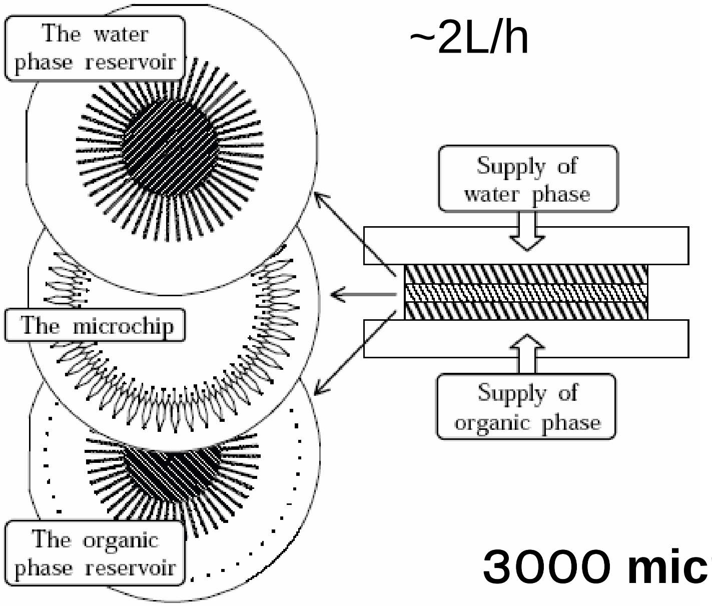
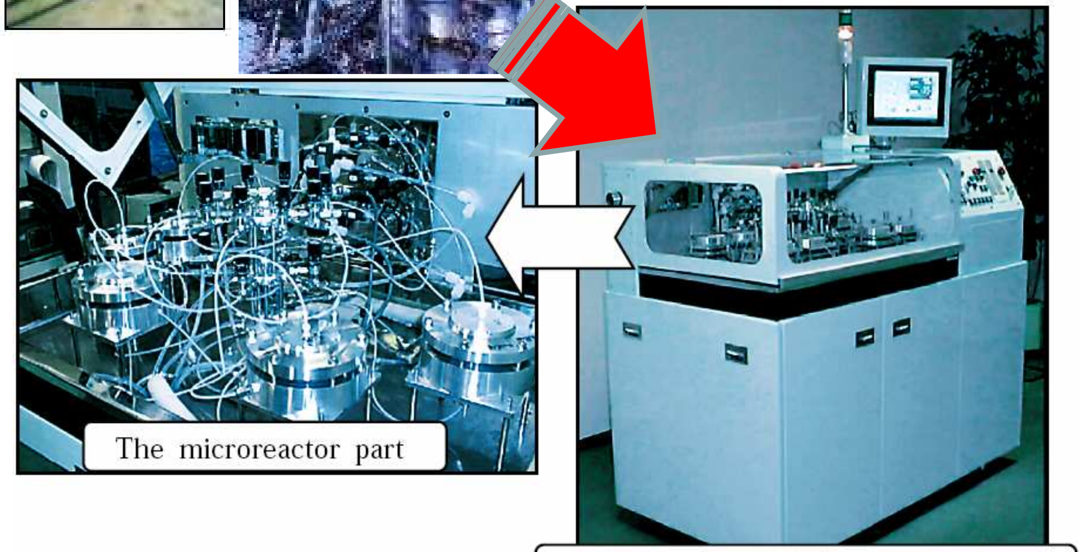



Fig. 8 The uniform liquid flow method to the microchip.




1,500(W)×800(D)×1,400(H)mm

**3000 microchannels (10 blocks)**

Fig.11 Constitution of the prototype sysem.

**80μ gel particles**

# Summary

- The **preliminary** largest separation factor of Ca by LLE using DC18C6 is suggested**.This still needs to be checked** by TIMS, temp.& concentration dependence.
- We evaluated each contribution ratio of the field shift/hyperfine splitting shift effect to the mass effect of Ca for the 1st time.

  The contributon of the field shift effect is small, especially for $^{40}Ca$-$^{48}Ca$, compared with Cr.
- These indications are promissing towards the mass production of enriched $^{48}Ca$ by the chemical separation method with the help of resins and/or microchannel chip.

*Many Thanks to Prof. Fujii, Y. Sakuma, M. Tanimizu, M. Tokeshi & Y. Shibahara*