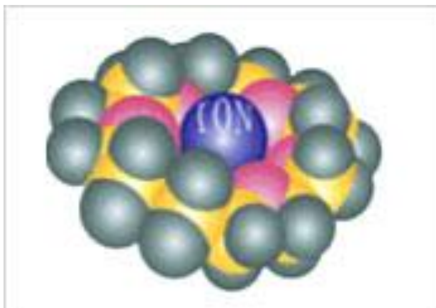
Candles

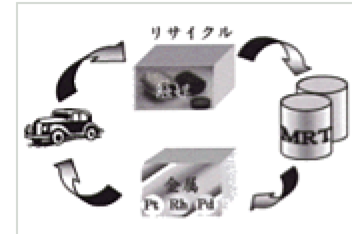
^{48}Ca enrichment

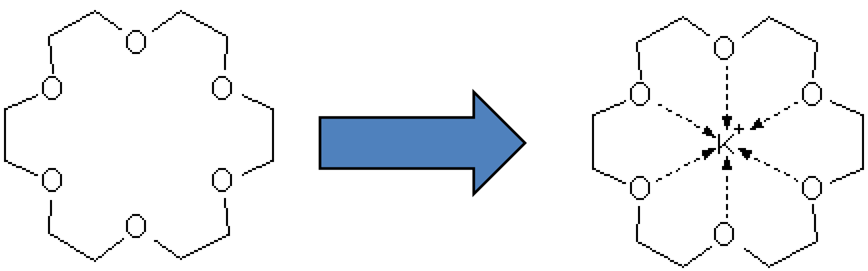
~liquid-liquid extraction~



SuperLig resin

IBC Advanced Technologies





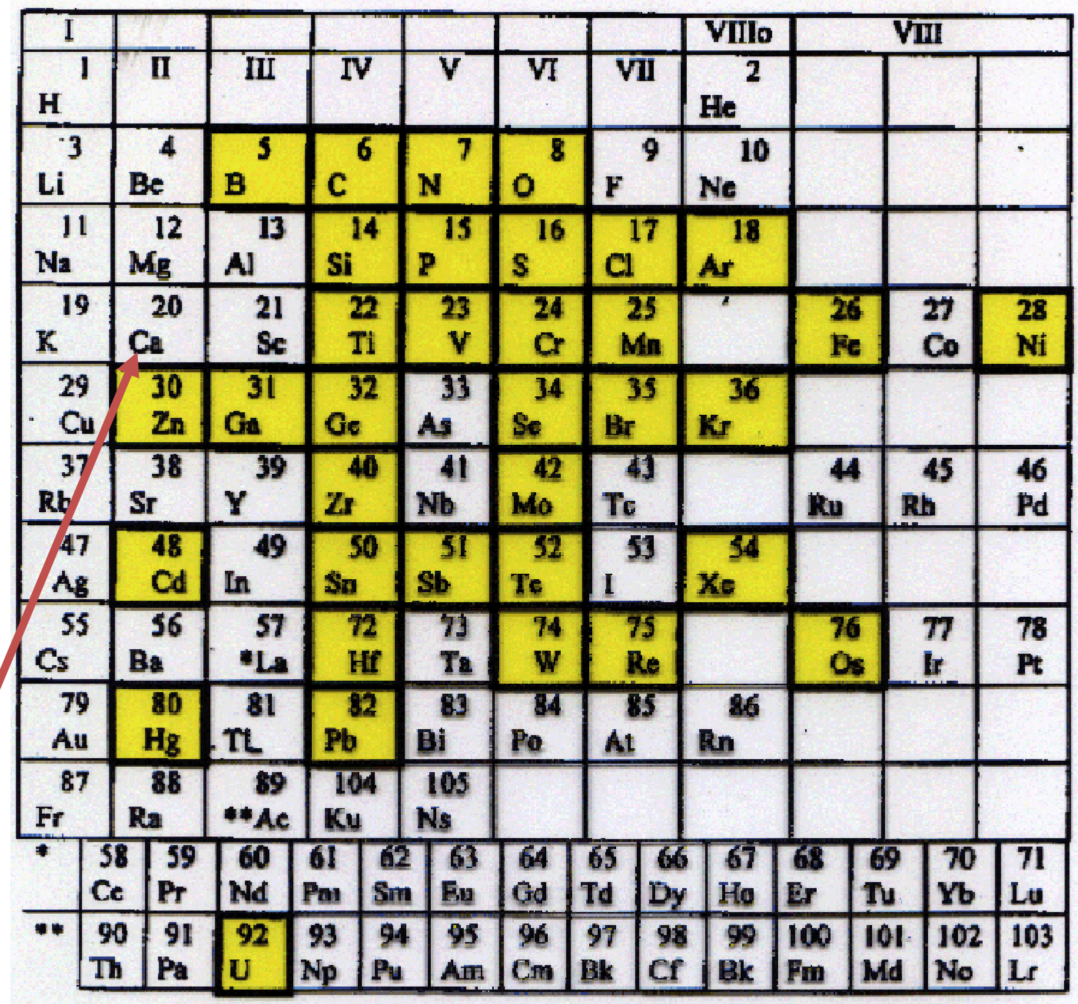
18-crown-6-ether

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

Ryuta Hazama
Hiroshima University

^{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.

for Ca Technologies for isotope production

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

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

- Liquid centrifuge? (mobility/viscosity with $CaCl_2$ solution & almina)
- Gel electrophoresis ($CaCl_2$ & HCl)
- Laser separation R&D (with Prof. Niki@Fukui Univ.)

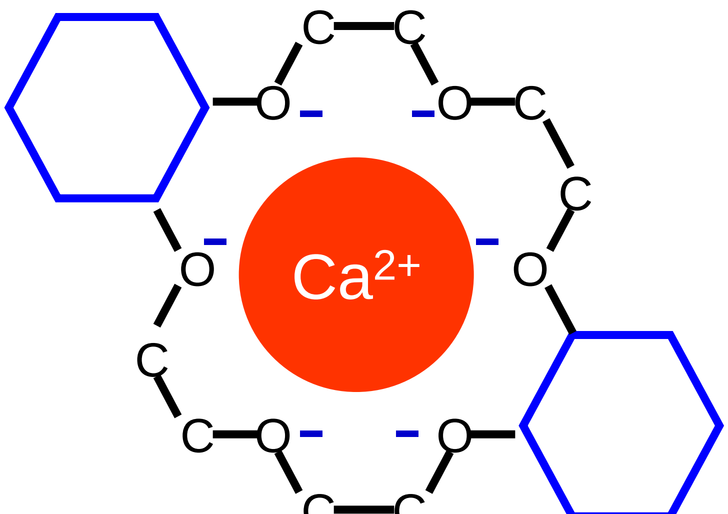
Crown Ether

Benzo or Di-benzo
or
Di-cyclo or bare-18C6

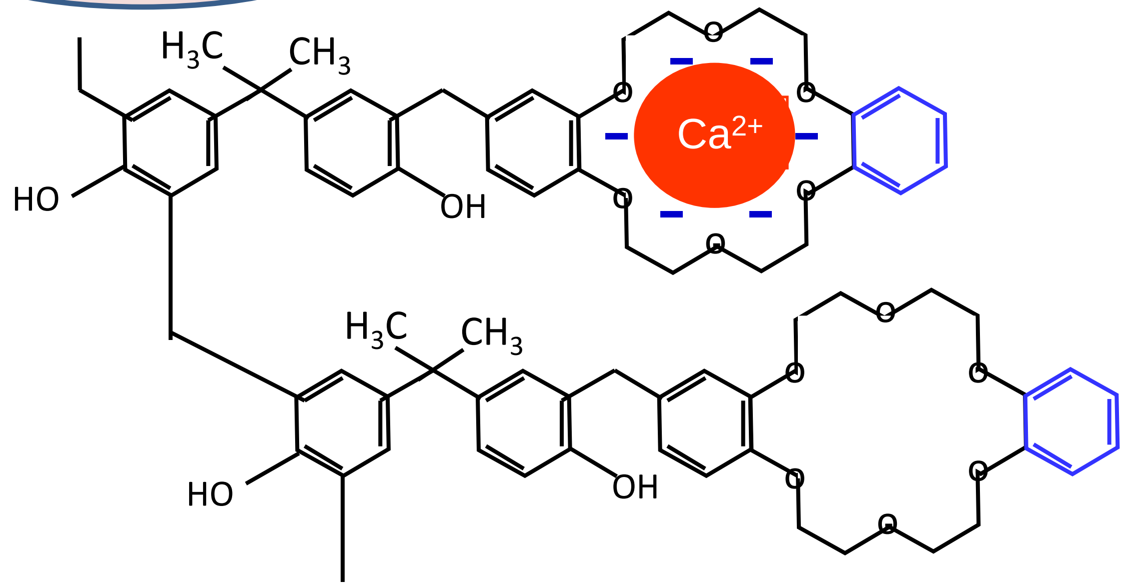
Liquid

Microchip

Soild Resin



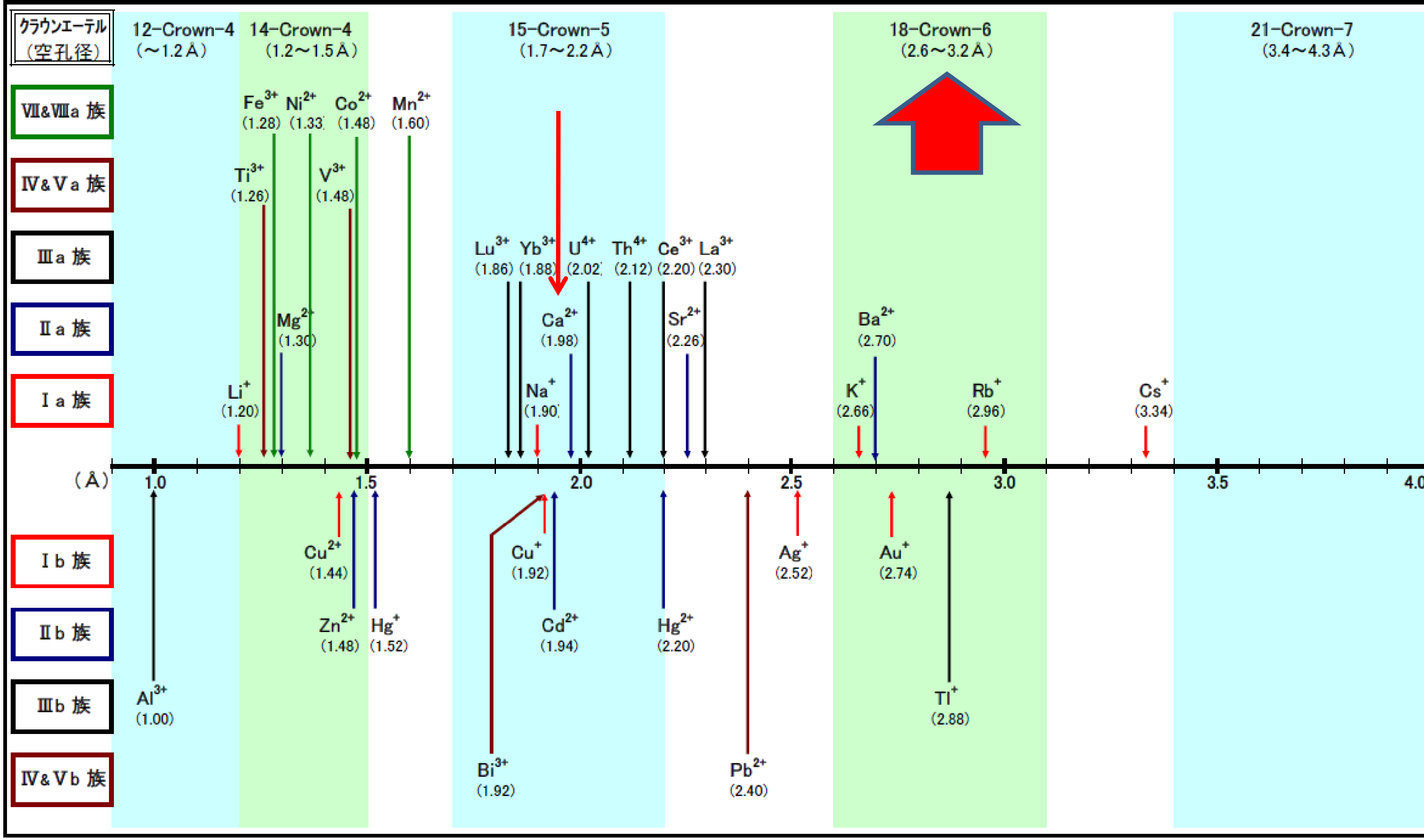
Dicyclohexano
18-crown-6



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)/solid(resin) extraction in isotopic equilibrium**



Ca isotope	^{40}Ca	^{42}Ca	^{43}Ca	^{44}Ca	^{46}Ca	^{48}Ca
abundance（%）	96.94	0.65	0.135	2.09	0.004	**0.187**

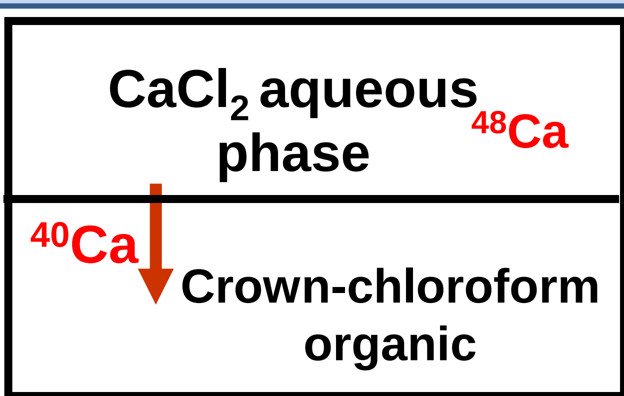
Prospect for Mass production

Liq./Liq. Extraction

LLE by Microchannel/reactor

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

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



Solid/Liq.

Column chromatography using crown ether resins

- Multi-stage process
- Slow & low conversion

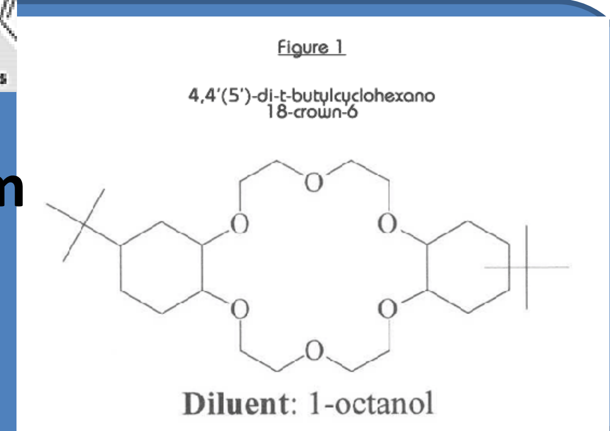
Ca solution: Analyte(mobile phase)

Packed column (stationary phase)

SuperLig樹脂

II

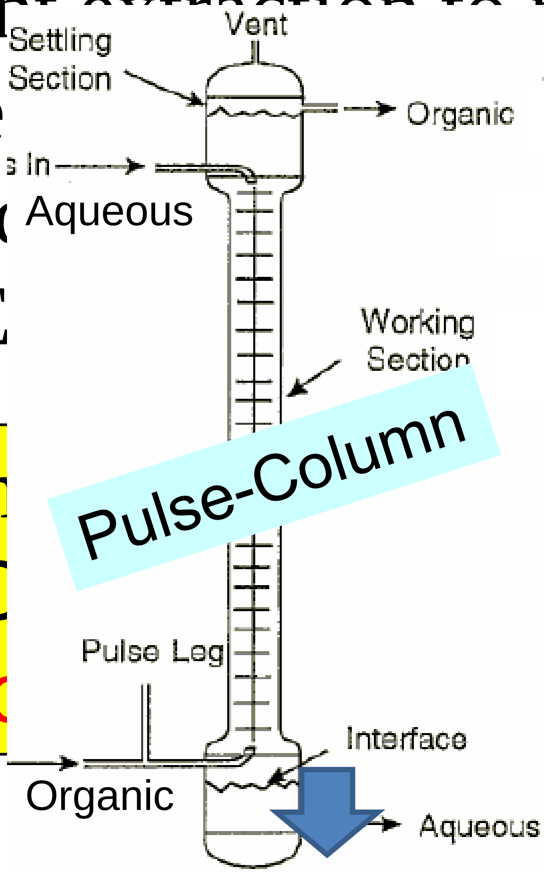
Eichrom or IBC Resin

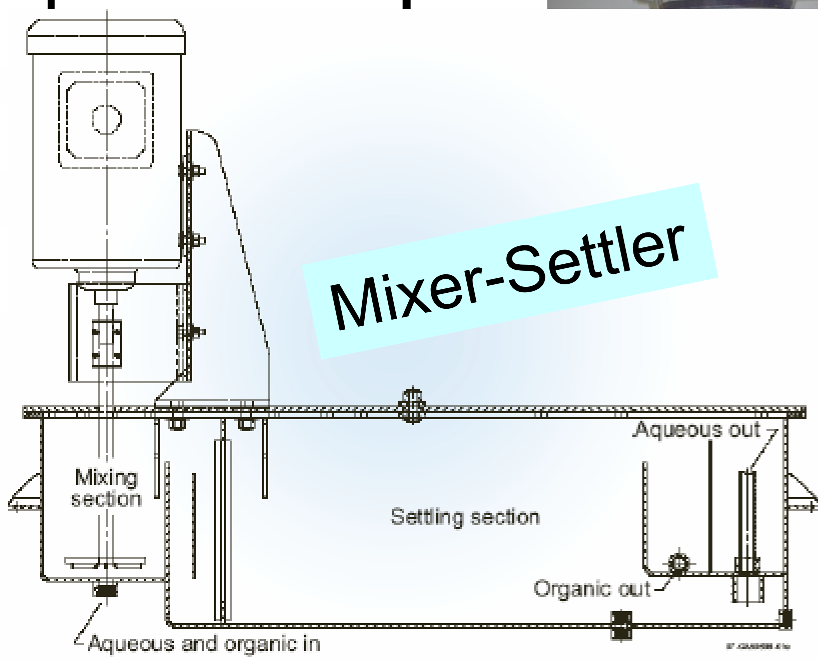


Batch (Macroscale reaction) Liq./Liq. etraction

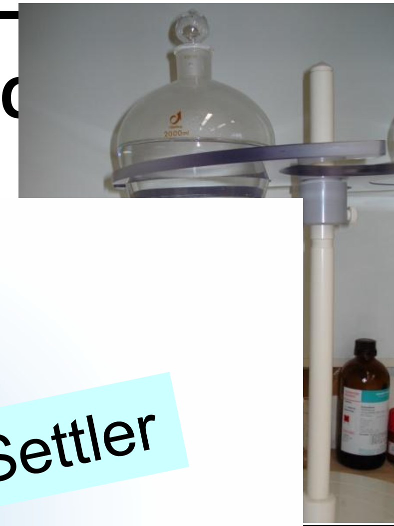
Solvent Extraction process

1.vacant extraction to reduce impu.
2.mixe
3. stan
4. LLE



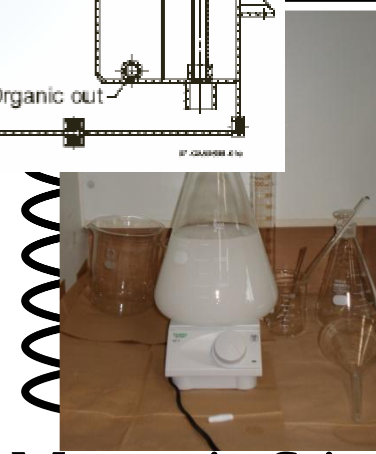


CaC... ase
Ca



07M
ganic

•Tem
•18C
Di-c



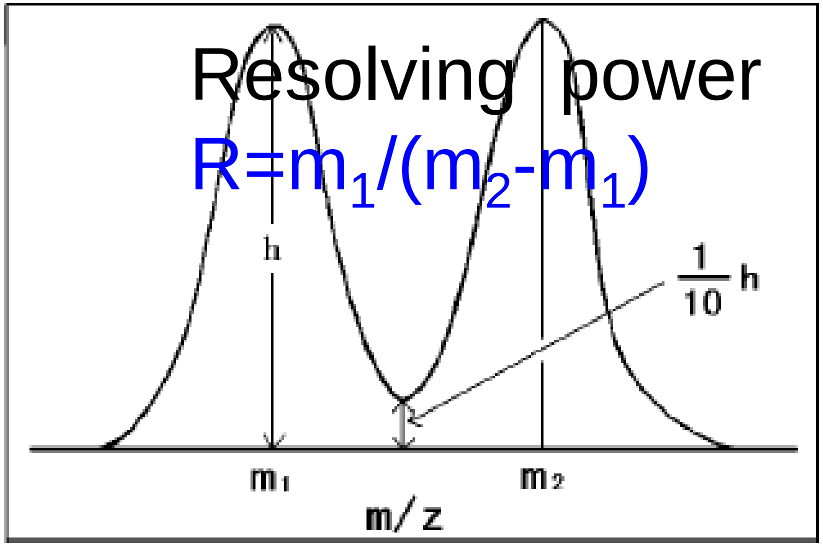
Magnetic Stirrer

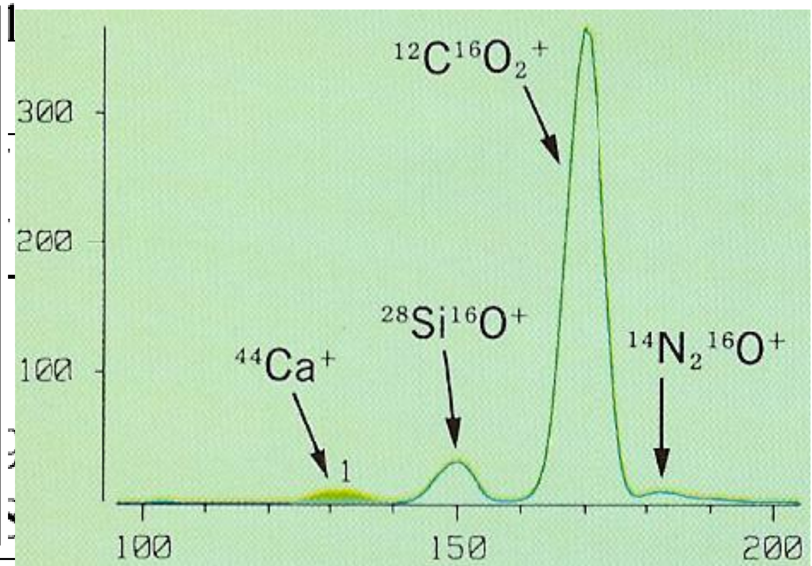
•Ca content for each LLE by ICP-OES
•Isotope ratio(ε) by Reac.-ICP or TIMS

B.E.Jepson&R.Dewitt, J. Inorg.nucl.Chem38(1976)1175 & R. Hazama et al., arXiv:0710.3840

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

m/z=





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

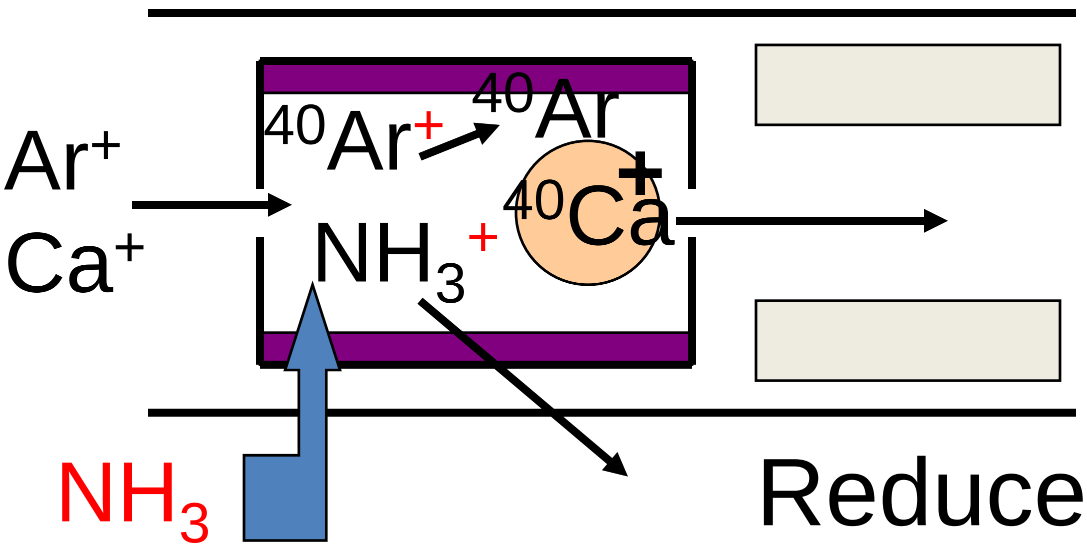
2. Reaction(collision)-cell ICPMS

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

Solid./Liq.

Increase Ca content → ε doesn't change

		A-type		FH-type
		)	Run (3)	
Co[illegible] in the			0.25	0.088
		6	0.00211	0.0034
		45	0.00026375	0.000425
l[illegible]		2	−3.5788	-3.3716

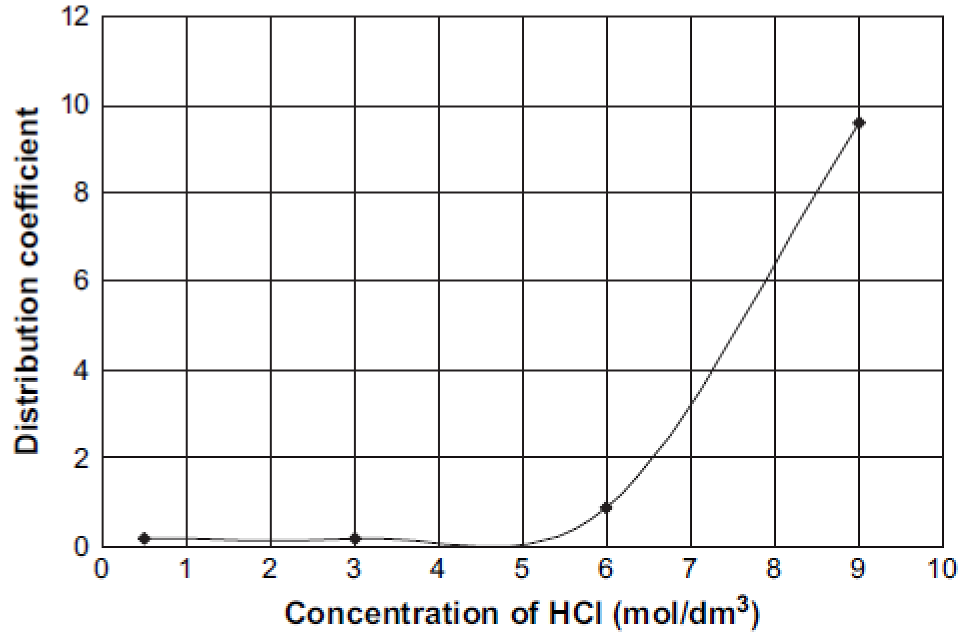


Fig. 4. Distribution coefficient of calcium between benzo-18-crown-6 resin and HCl aqueous solution.

Liq./Liq.

× ~ 10

$\varepsilon(\alpha_{40}^{48})$= 0.016 ~0.022

~800 iteration

0.187→ 2.0%

樹脂法～7000 iteration

α_{40}^{48} ~1.0028
(~1.00035)

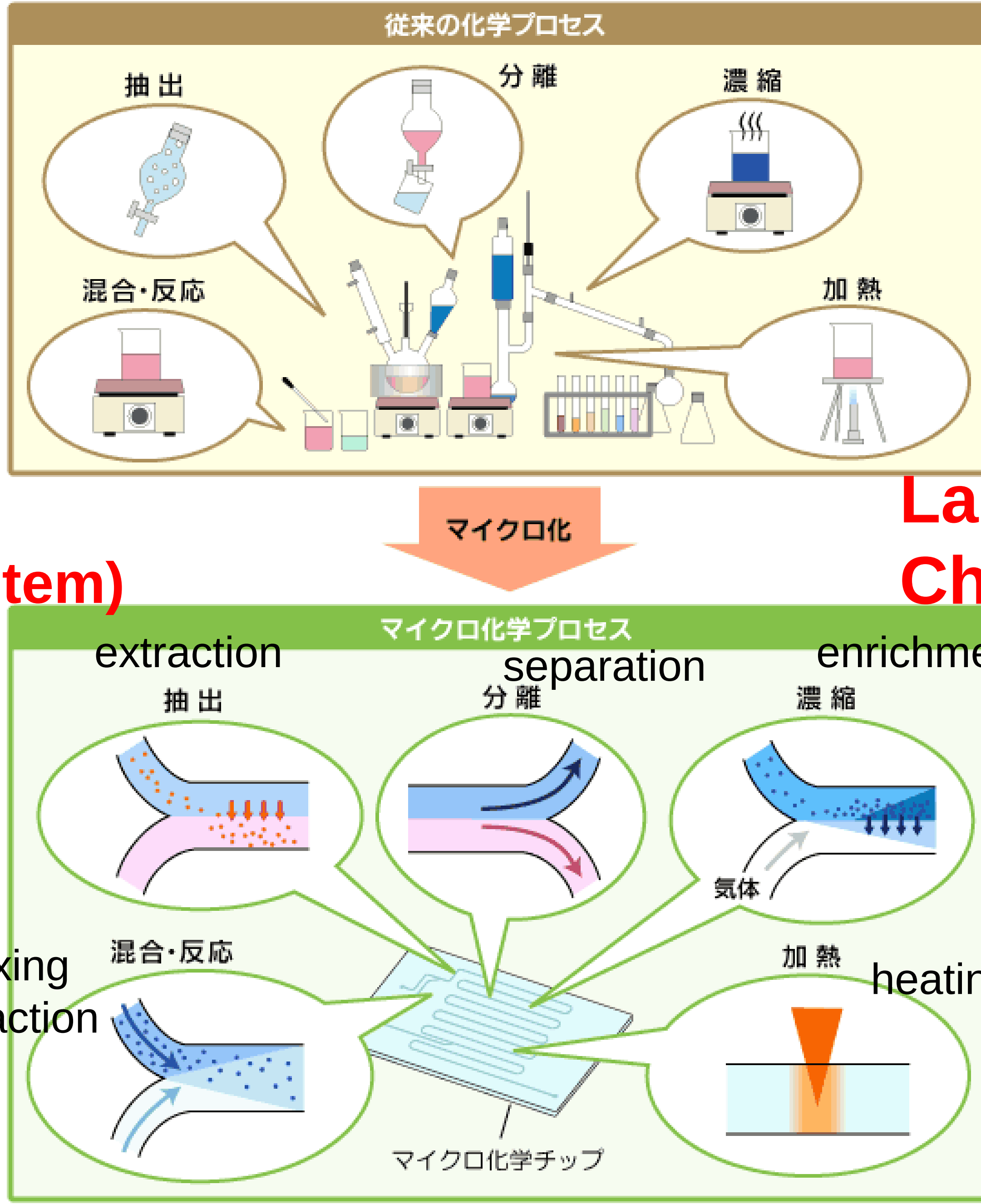
$$R(X) = R_0 \cdot \alpha^X$$

Conventional Chemical Process

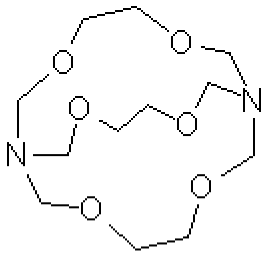
μ TAS (Micro Total Analysis System)

Lab-on-a-chip Chemistry

Microchemical Process



Microreactor’s features



cryptand[2,2,2]

Advantages

（1）multi-phase flow→ideal reaction/extraction field

（2）Large interfacial area→**>10^2**xstirring high conv.

（3）short diffusion distance→**fast** reaction speed

（4）small heat capacity→uniform/fast temp.control

（5）small flow output→toxic manage・fast heating

（6）piling-up technology→easy to scale-up

Disadvantage **→small output/1 chip→piling-up**

（1）cheap microreactor → plastic vs. glass

（2）piling-up technology & stable flow technology

Liq./Liq. extracion → two keywords

Specific interfacial area
(surface to volume ratio:S/V)

S/V = dL/(wdL/2)= 2/ **w**

W=100μm → S/V=**200** !

Diffusion time

T= **W²** /D
(D=10^{-9} m^2/s
typical # for molecular in water)

W=100μm → T=**10s** !

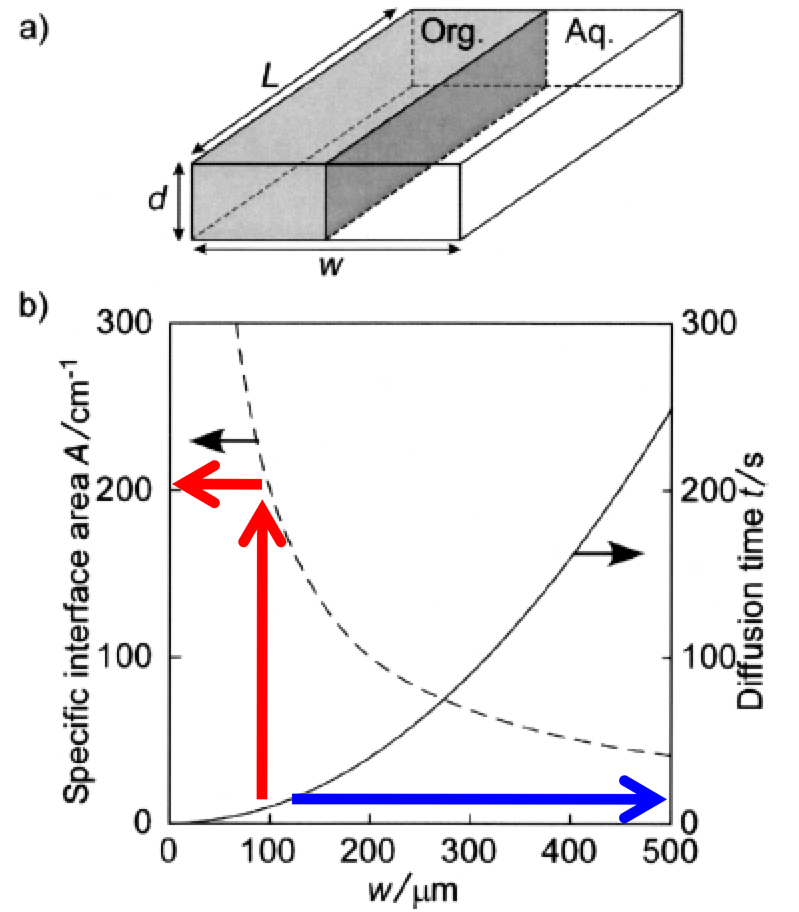
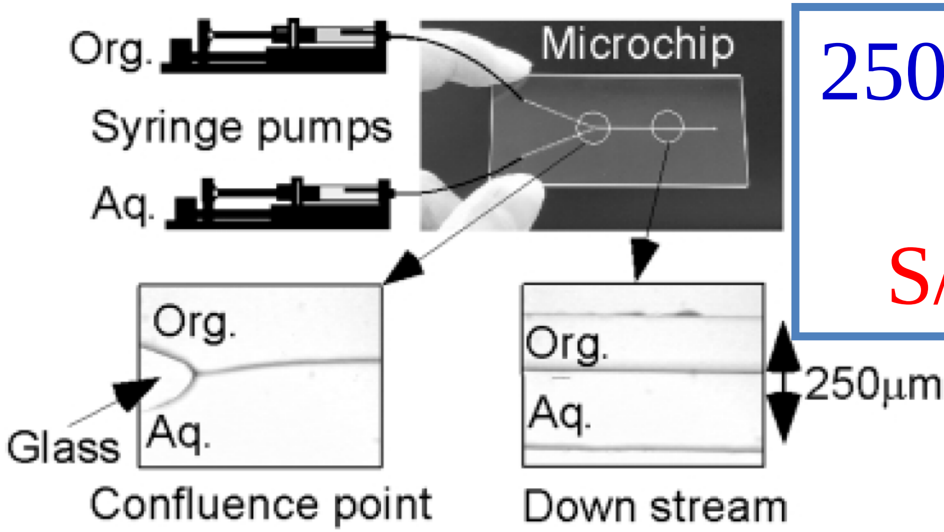


Fig. 2 (a) Illustration of a model of a liquid-liquid interface between the aqueous and organic phases, (b) Specific interface area and diffusion time dependence on the microchannel width



250μm wide,100μm deep, and 3cm length

S/V~80/cm^{-1} T~63sec

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

No-stirring,Fast!!

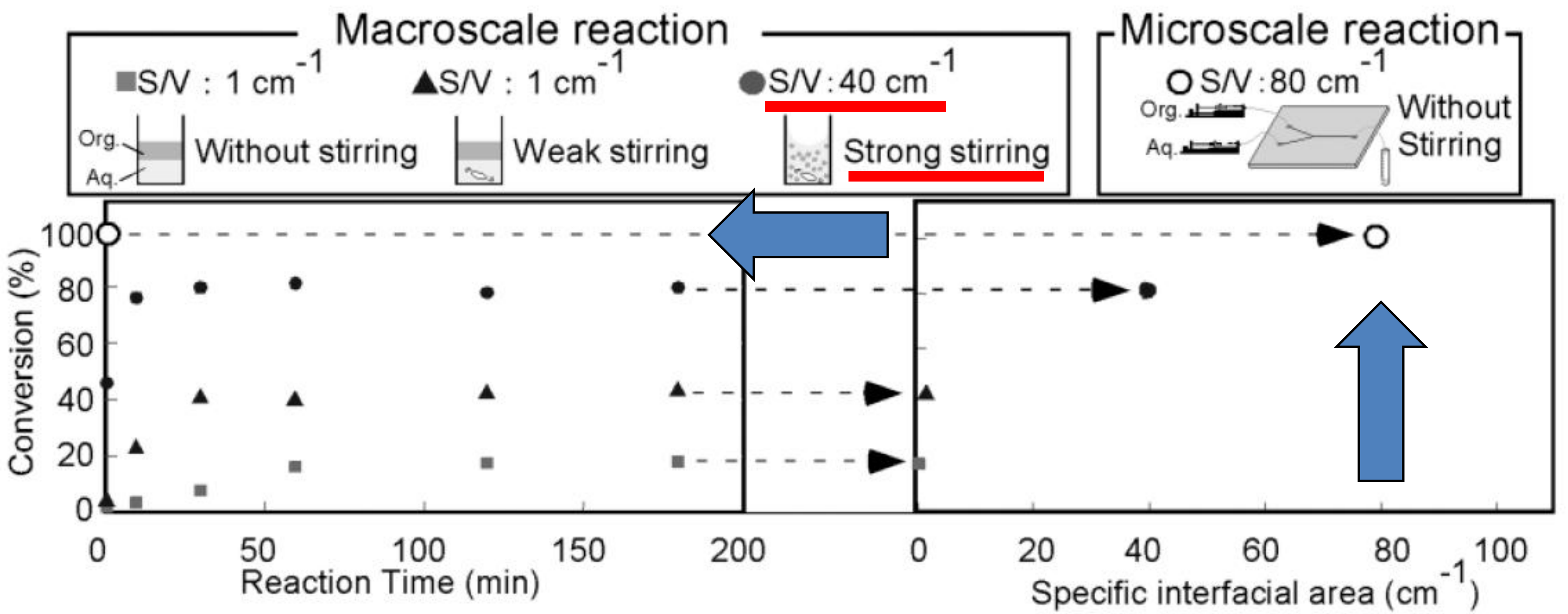
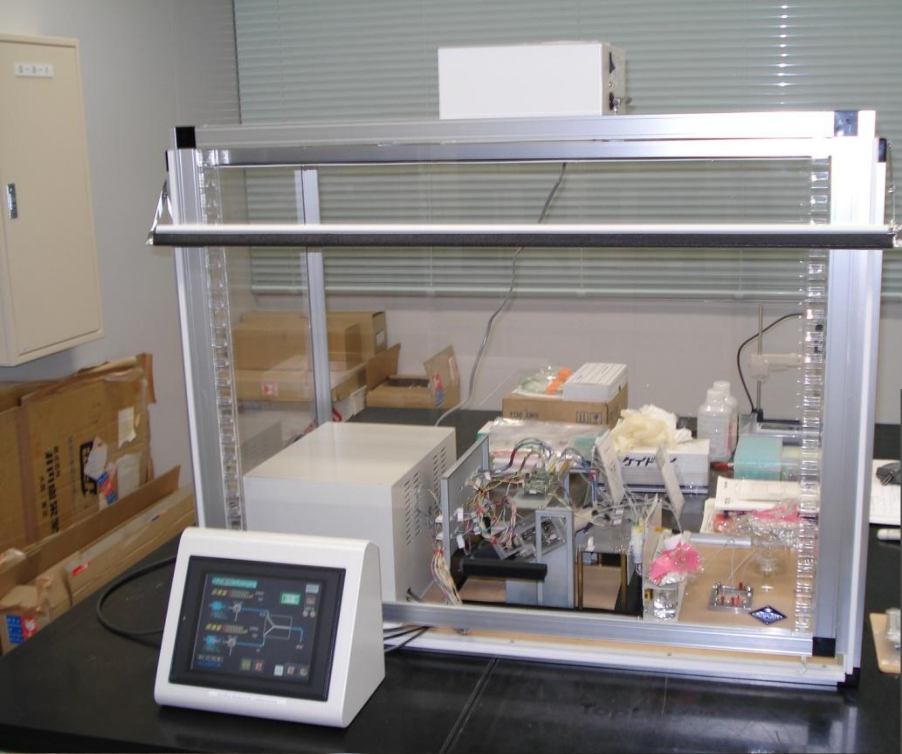
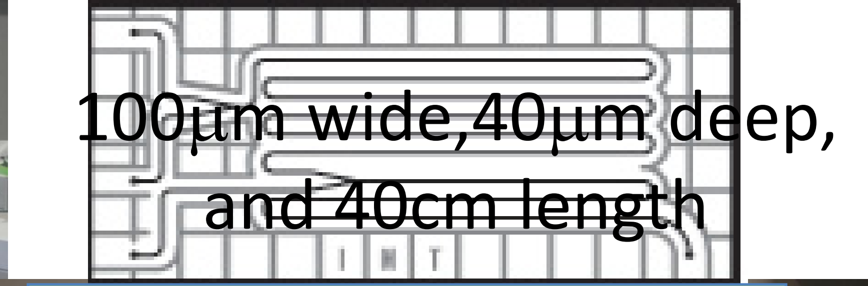


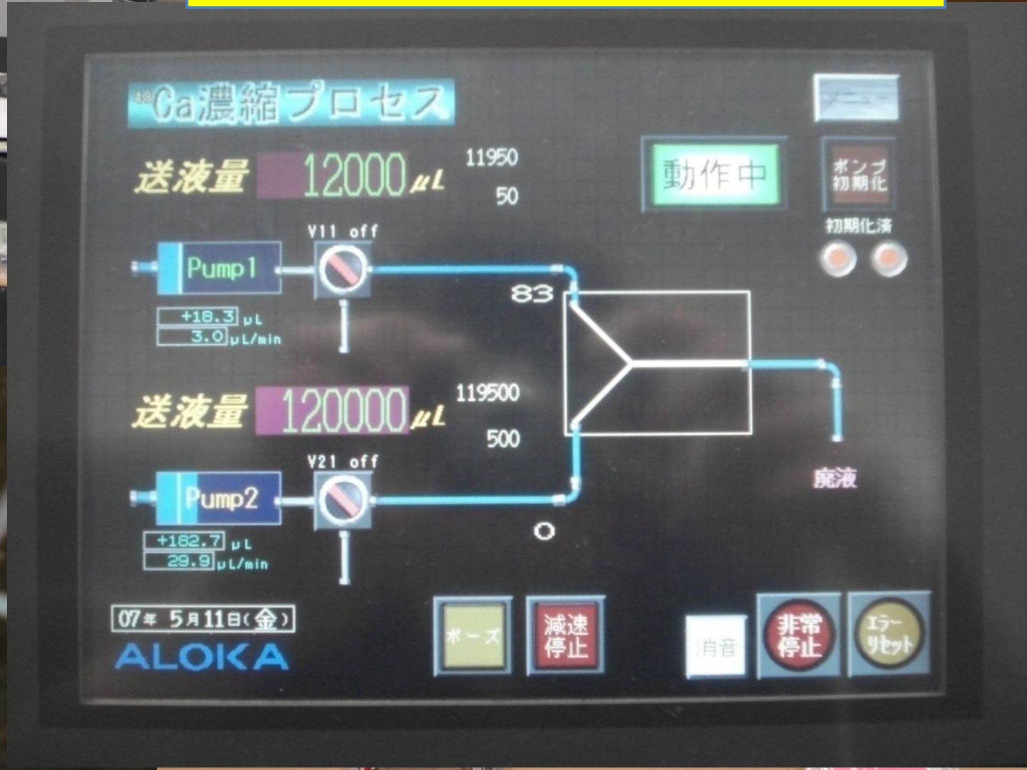
Fig. 3 Reaction conditions and results obtained with phase transfer diazocoupling reaction under microscale and macroscale conditions.

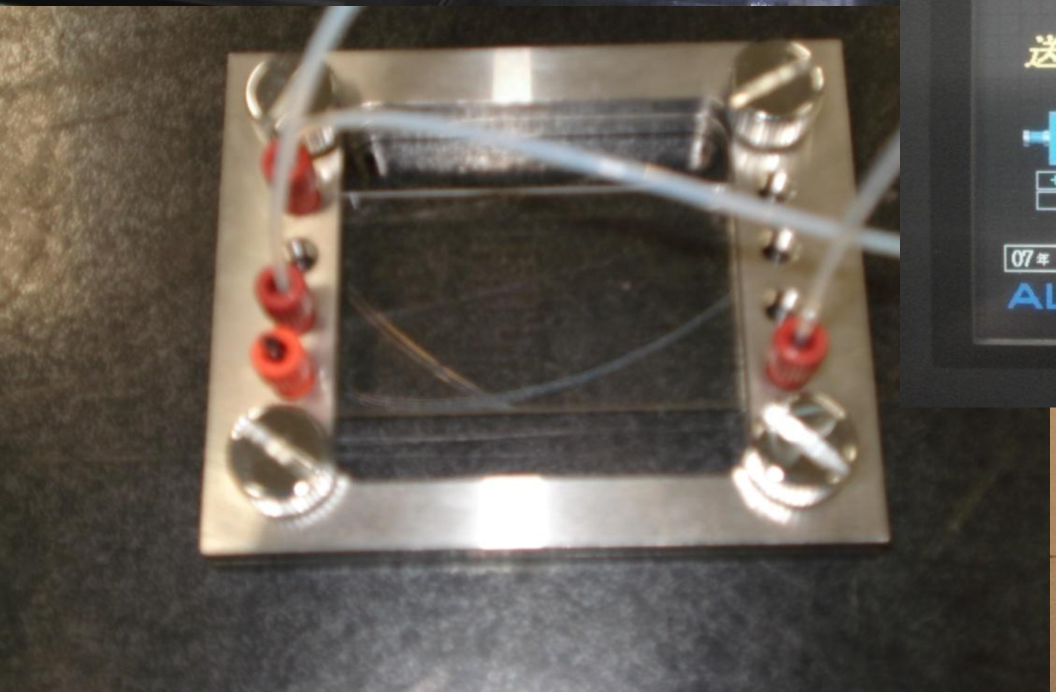


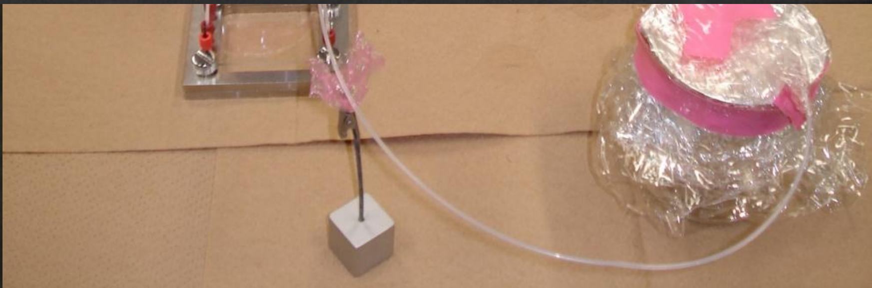


100μm wide,40μm deep,
and 40cm length

S/V~200/cm^{-1} T~10sec







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

TOSOH
The Chemistry of Innovation

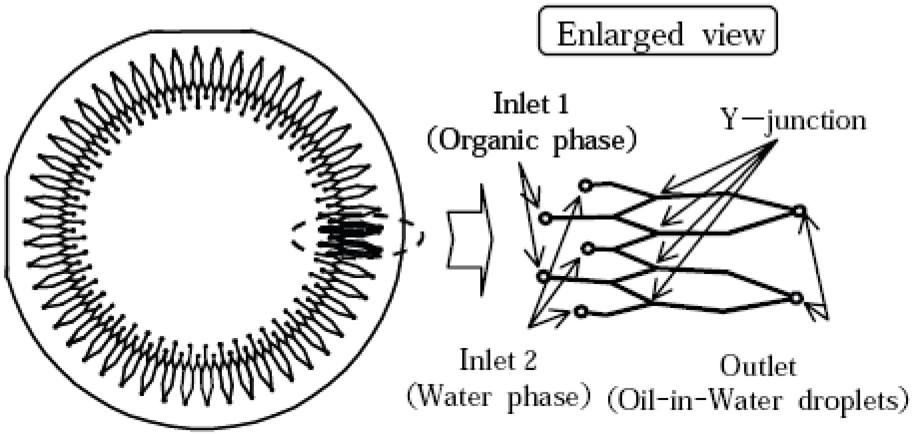
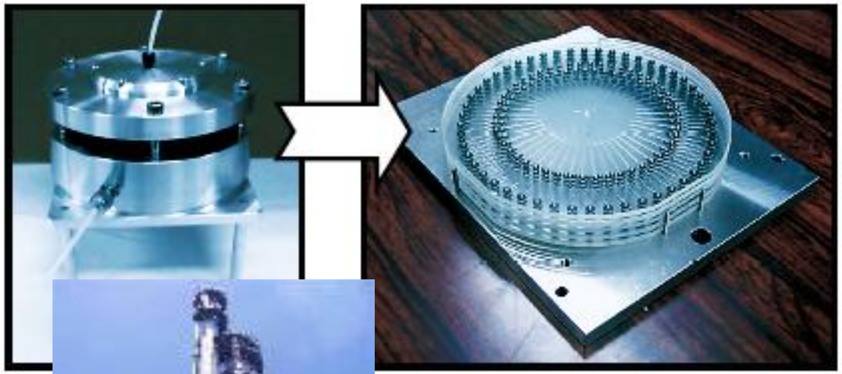
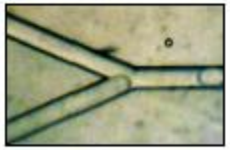


Fig. 7 The circular microchip having 100 Y-junction microchannel.



…chips block with piled up …ular microchips



~2L/h

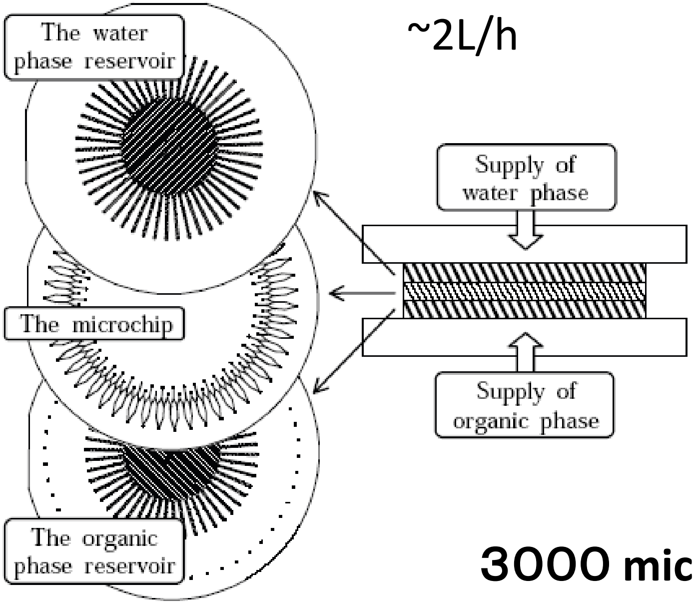
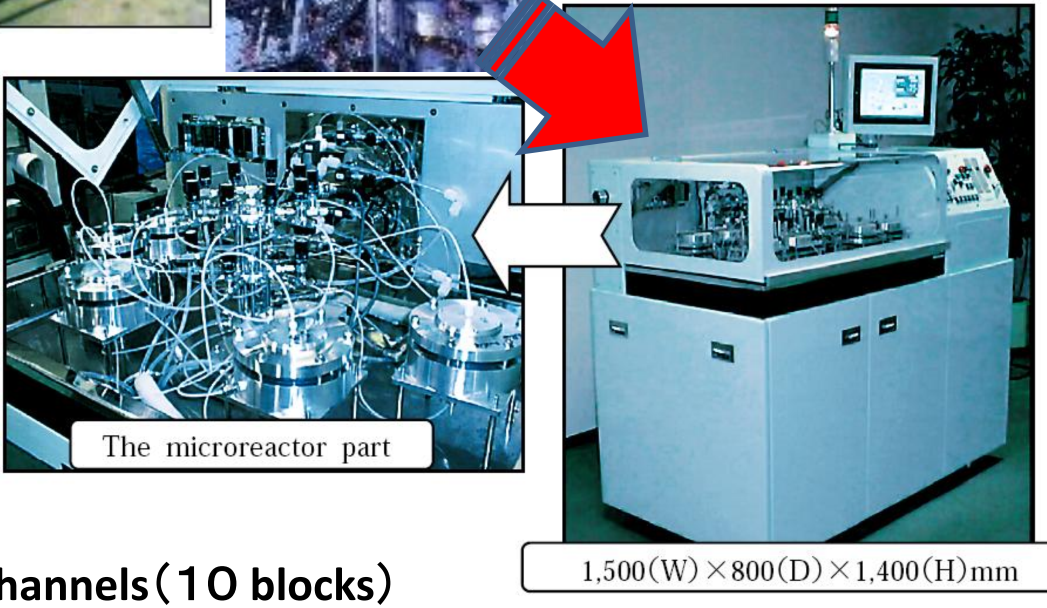


Fig. 8 The uniform liquid flow method to the microchip.



3000 microchannels (10 blocks)

Fig.11 Constitution of the prototype sysem.

80μ gel particles