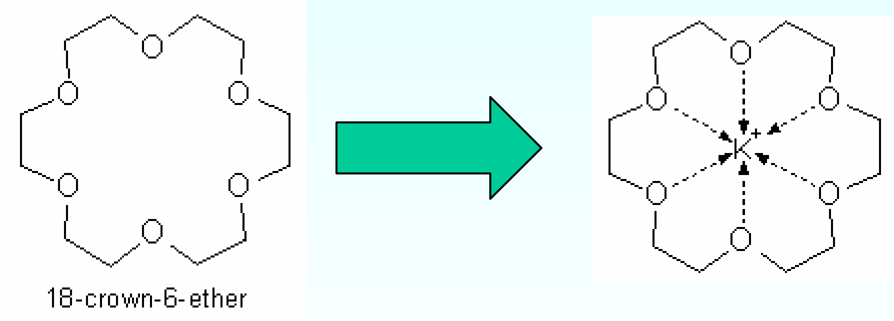
Sep 19,2005@US-Japan Seminar, Hawaii

Challenge on ^{48}Ca enrichment

Separation of Calcium Isotopes with a Crown Ether



Pedersen@1962
Cram&Lehn@1987

Ryuta Hazama
for the CANDLES Collaboration
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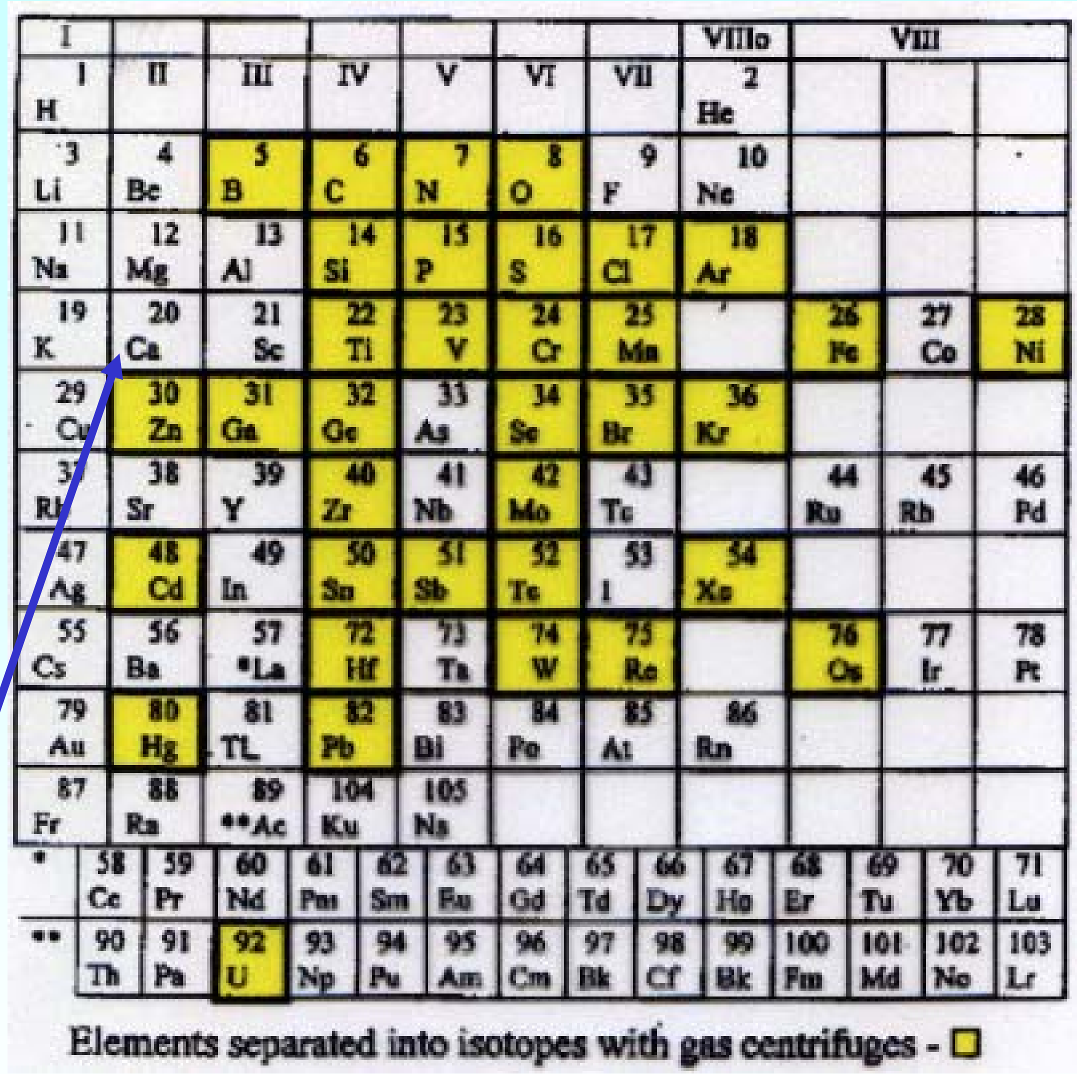
^{48}Ca enrichment

- 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~~



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

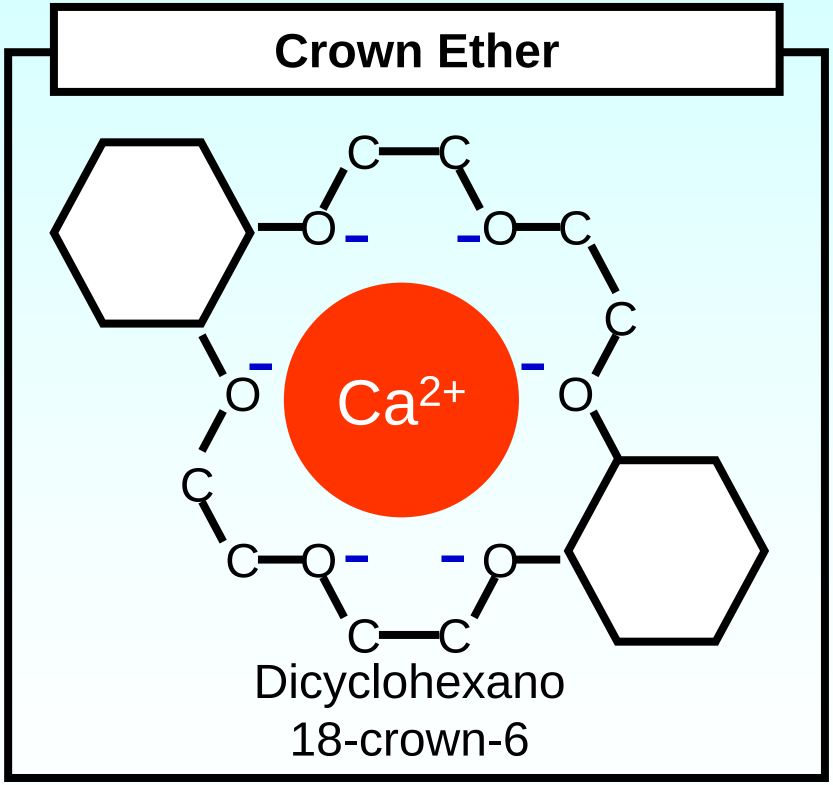
Liquid centrifuge? (mobility/viscosity with $CaCl_2$ solution & almina)

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)



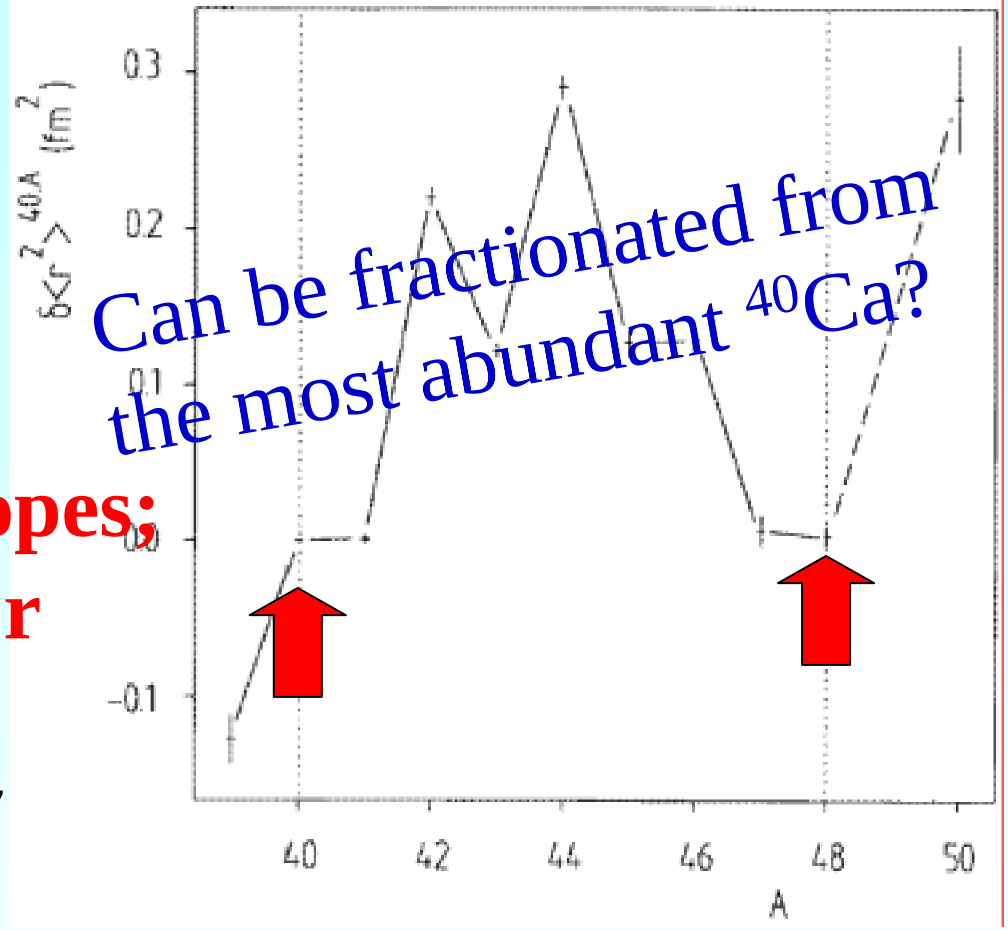
- **Held by electrostatic attraction between negatively charged O^- of the C-O dipoles & cation (Ca^{2+})**
- **How well the cation fits into the crown ring**
- **Liquid(aq-salt)-liquid(org-crown) extraction in isotopic equilibrium**

DC18C6

→ Total # of atoms in the ring

→ # of oxygen atoms in the ring

The mean square Nuclear charge radius of Ca



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

Two doubly magic isotopes;

A parabolic behavior

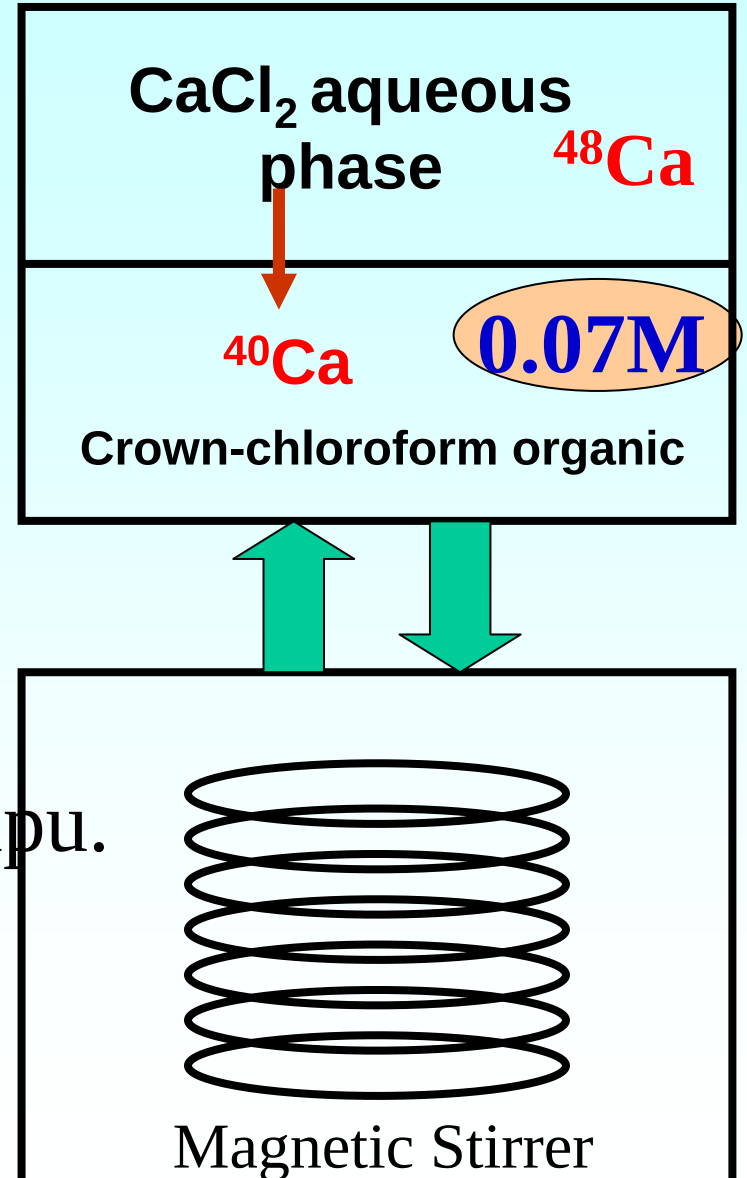
L.Vermeeren et al., J.Phys.G,22(1996)1517

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**

Ca Isotope effects～Separation Principle

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

DC18C6: Aldrich Chemical, 98.0%
$CHCl_3$:Nakarai Tesque, 99.0%
$CaCl_2$:Nakarai Tesque, 95.0%

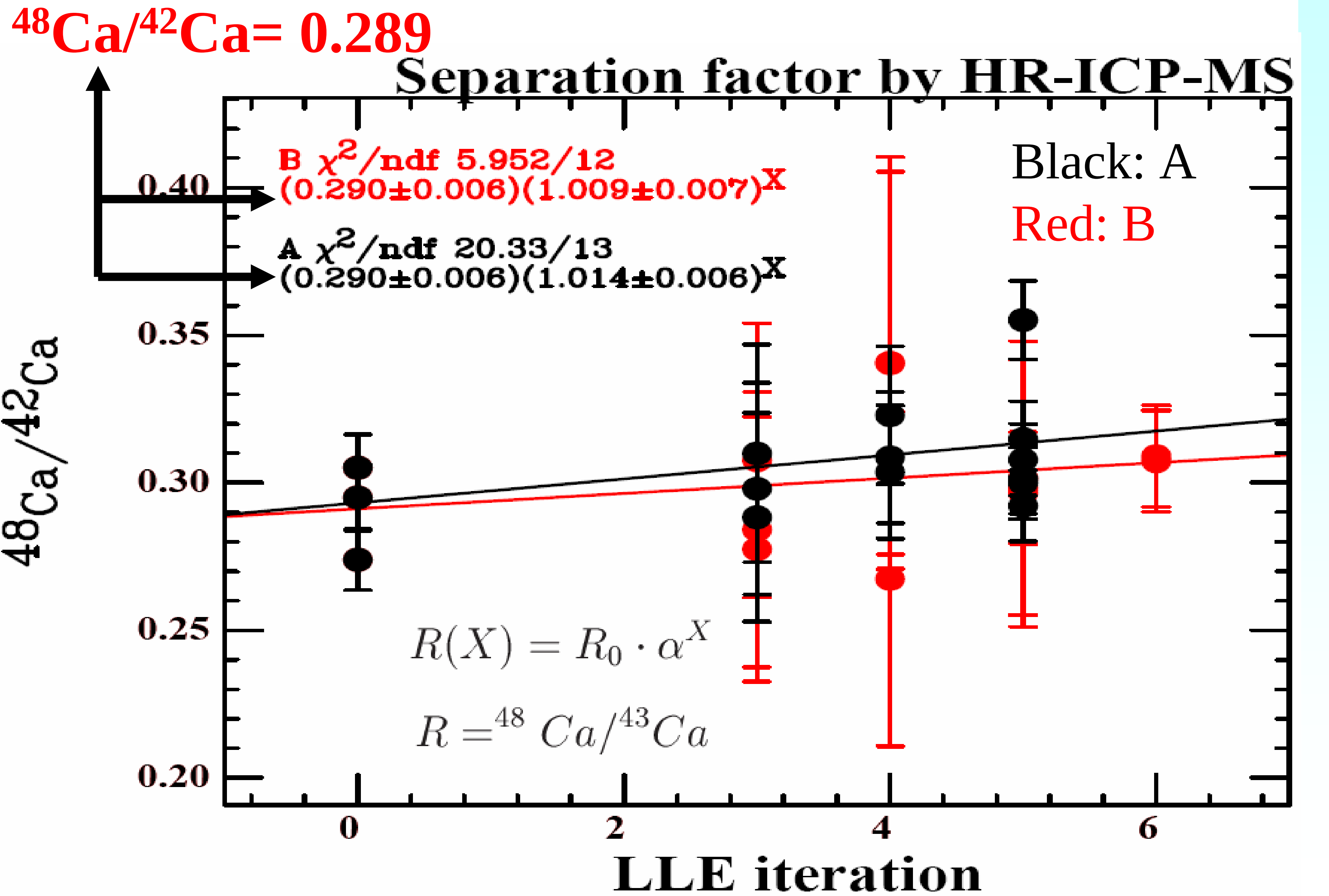


Solvent Extraction process

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

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

Isotopic Analysis by HR-ICP-MS@WERC



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±0.005 (α^{48}_{42})	LLC(DC18C6)	Osaka RI-center and WERC
1.0028	1.014±0.006 (α^{48}_{43})	LLC(DC18C6)	Osaka RI-center and WERC
1.0010	1.0080±0.0016† (α^{48}_{40})	LLC(DC18C6)	[1]
1.0007	1.0029±0.0006 (α^{48}_{44})	LLC(HDEHP)	[2]
	1.0013±0.0003	LLC(amalgam(Hg))	[3]
	1.000043~1.000034	SLC(ion-exchange)	[4]resin(Dowex)
	1.00026 (α^{47}_{40})	SLC(ion-exchange)	[5]resin(Dowex)
	1.00021 (α^{44}_{40})	SLC(ion-exchange)	[6]resin(Dowex)
	1.00087±0.00008 (α^{48}_{40})	SLC(ion-exchange)	[7]NH_4α-hydroxyisobutyrate&(Dowex)
1.0010	1.0041±0.0004 (α^{44}_{40})	SLC(ion-exchange)	[8] iminodiacetate&resin(ANKB-50)
	1.00013~1.00087‡	SLC(ion-exchange)	[9](TIT)resin(PK-1),Counter-Current
	1.00016~1.00037 (α^{48}_{40})	SLC(ion-exchange)	[10](Sophia) resin(Asahi LS-6)
	1.00018 (α^{48}_{40})	SLC(ion-exchange)	[11]resin(AG50WX4)
	1.00049~1.00013 (α^{44}_{40})	SLC(ion-exchange)18C6	[12]resin(AG50WX4)
1.0010	1.0039±0.0002 (α^{44}_{40})	SLC(cyptand2$_B$.2.2)	[13]
1.0006	1.0025±0.0003 (α^{44}_{40})	SLC(18C6)	[13]
	1.00011±0.00003 (α^{44}_{40})	SLC(iminodiacetate)	[13]
1.0009	1.0035±0.0003 (α^{44}_{40})	SLC(18C6+dimethylsulfoxide)	[14]
1.0006~1.0013	1.0045~1.0104(α^{48}_{40})§	SLC(cryptand2$_B$.2.2)	[15]
	-	LIS(LLNL)	a few $/mg(¥1M/kg) for ^{48}Ca [16]
	20%	MCIRI	5kg/day→10g/day(0.7K$/g)* [17]
	65.3~95.7%	carbonate or oxide	TRACE Science Int. [18]
	6%% (α^{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%

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

m/z=

Mass	Molecular ion	isotopic ratio(%)	required resolution
40	$^{40}Ca^{+}$	99.941	-
40	$^{40}Ar^{+}$	99.6	192498 ✗
42	^{42}Ca	0.647	
42	$H_2^{40}Ar$	99.57	2162
43	^{43}Ca	0.135	-
43	$^{86}Sr^{2+}$	9.86	10392
43	$^{42}CaH^{+}$	0.6469	5597
43	$^{40}Ar3H$	0.0298	1683
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

Max resolution=12000

Enemy

How to measure ^{40}Ca?

1. TIMS(TRITON Thermo Electron)

No-Ar *Only four TRITONs in Japan*

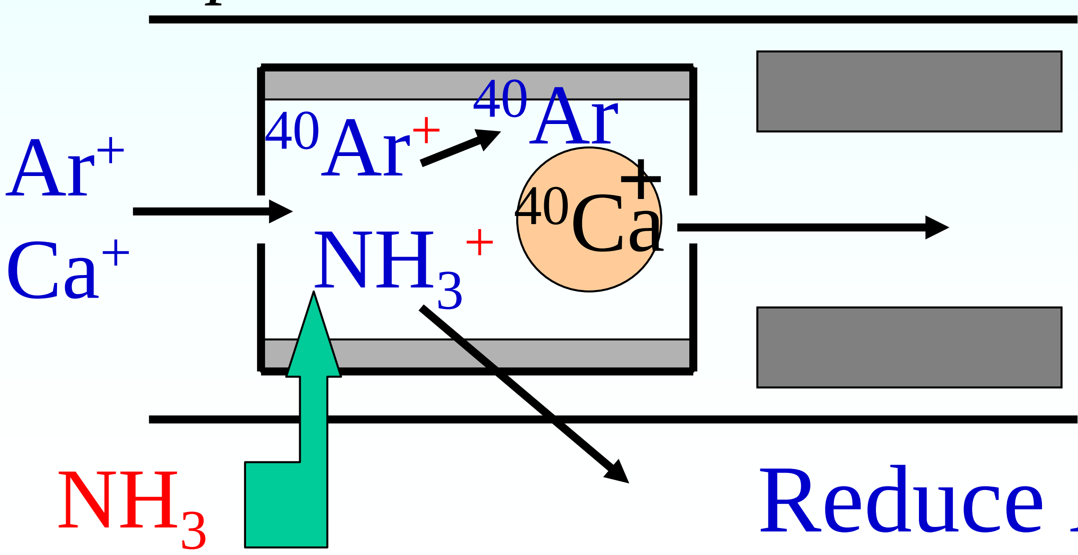
2. Reaction(collision)-cell ICPMS

Perkin Elmer ELAN-DRCII@Kochi Univ.

Q inside reaction-cell allows use of ammonia

→ can avoid interference of Ar by reaction-gas

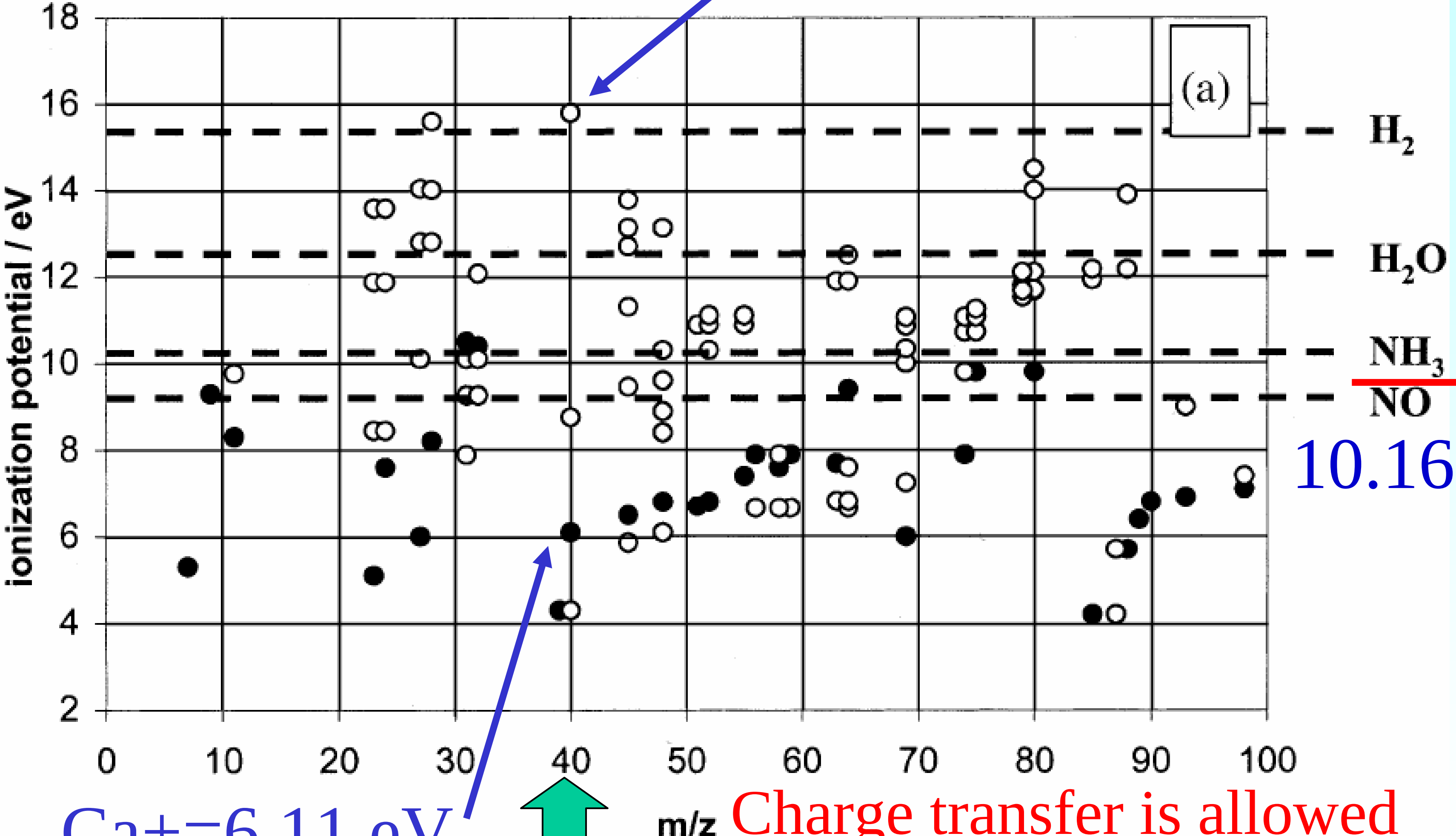
Simple collision-cell must use simple gas(H_2, He) to limit adverse side reaction products



$Ar^+ + NH_3 \rightarrow NH_3^+ + Ar$

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

Ar^{+} =15.76 eV



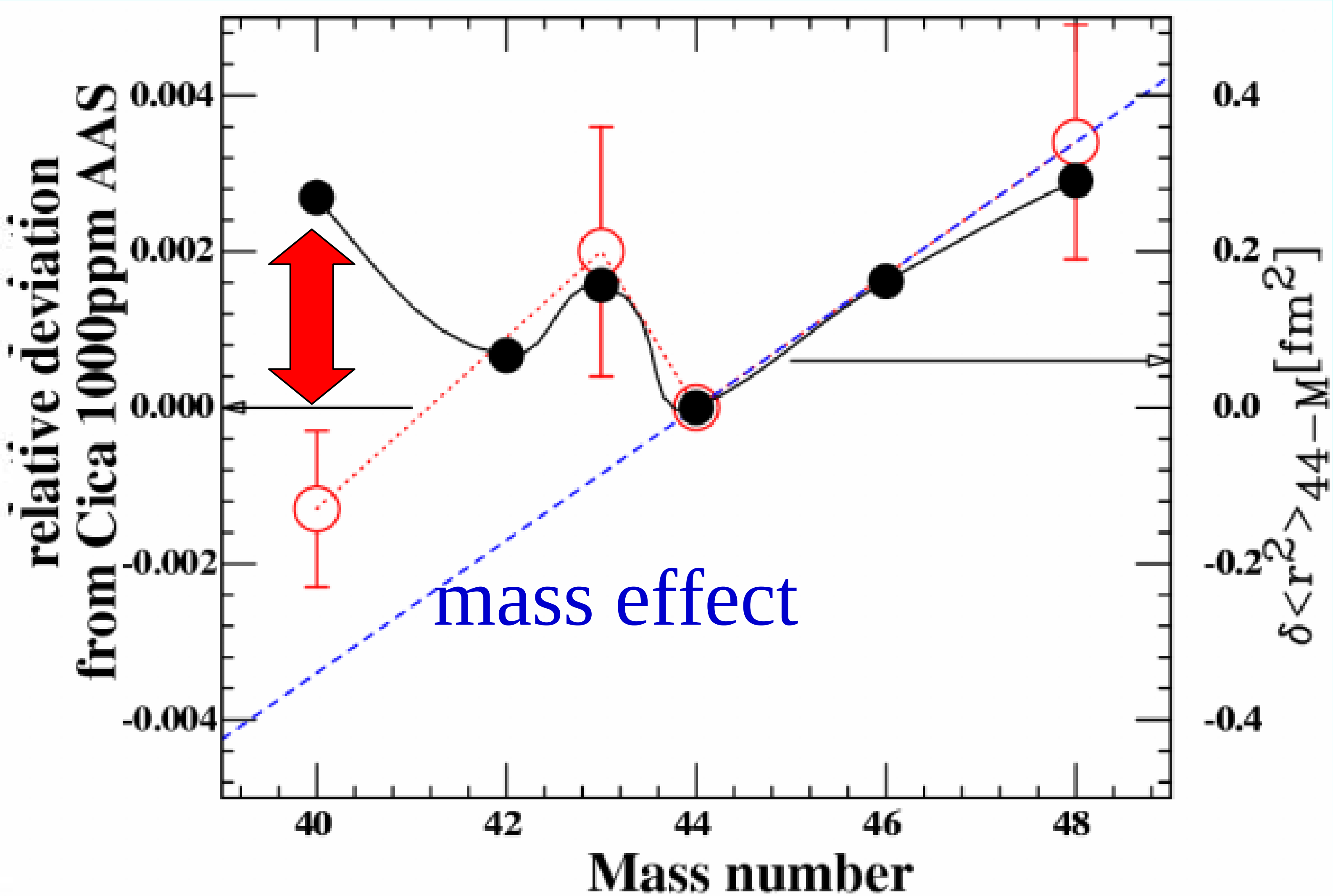
10.16eV

Ca+=6.11 eV

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

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

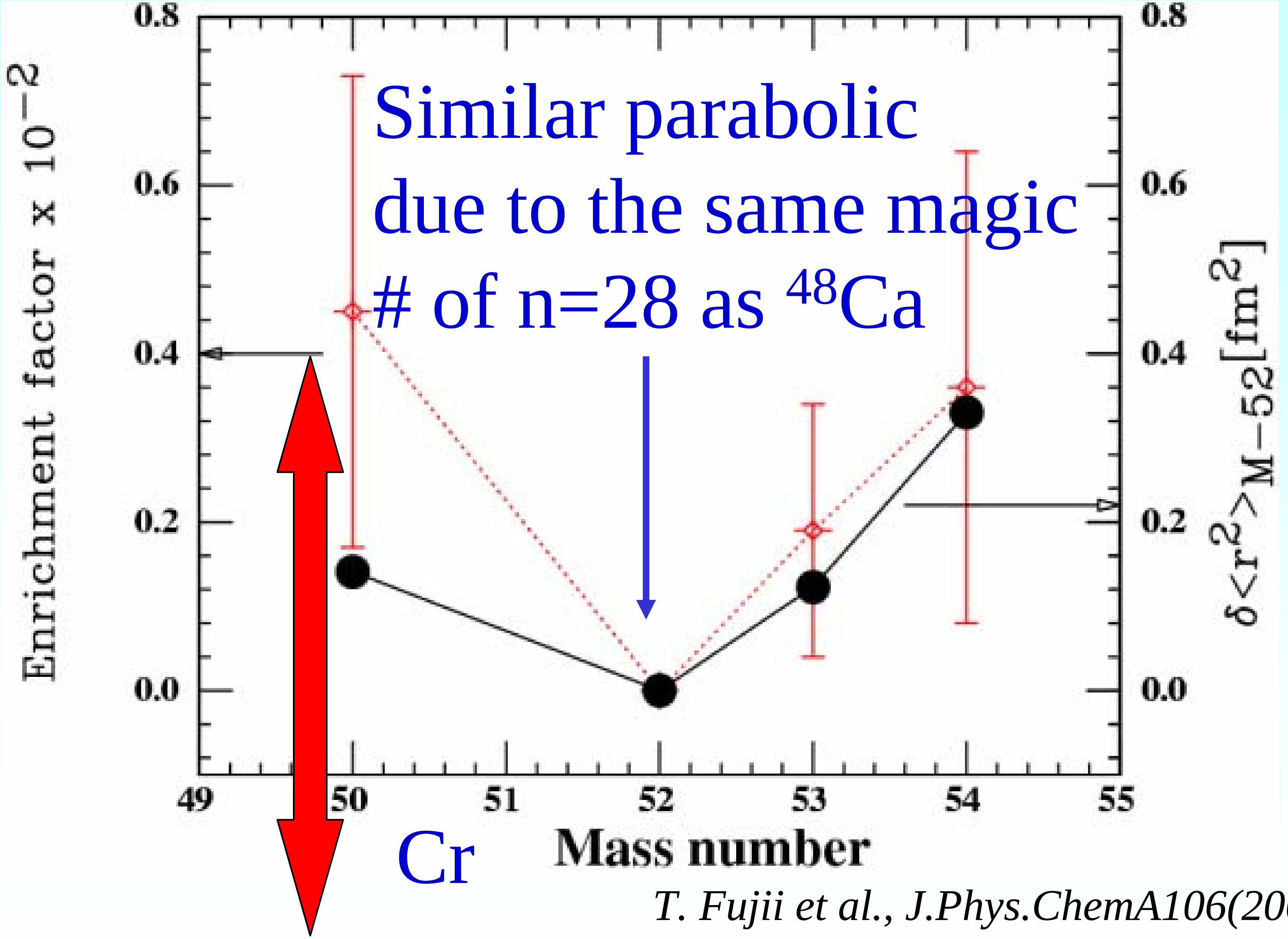
^{40}Ca, ^{48}Ca are doubly magic→ **A parabolic behavior**



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

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

cf. Chromium-crown(DC18C6)



T. Fujii et al., J.Phys.ChemA106(2002)6911

Nuclear mass effect < Nuclear size&shape effect!!!

How small?

Evaluate each isotope effects by 3 measured ε(=1−α)

Bigeleisen theory

$\varepsilon_{40\text{-}48}$, $\varepsilon_{43\text{-}48}$, $\varepsilon_{44\text{-}48}$

$$\varepsilon_{43\text{-}48} = a(\Delta M/MM')_{43\text{-}48} + b\delta\langle r^2\rangle_{43\text{-}48} + (\ln K_{hf})_{43}$$

Nuclear mass effect Nuclear size&shape effect Hyperfine splitting(spin)

	$CaLCl_2$ SrLCl₂ $CrLCl_3$	
	$b\delta < r^2 > /[a(\Delta M/MM')]$	$lnK_{hf}/[a(\Delta M/MM')]$
$^{40}Ca-^{48}Ca$	0.02 ± 0.48	
$^{44}Ca-^{48}Ca$	0.62 ± 1.31	-
$^{43}Ca-^{48}Ca$	0.22 ± 0.88	0.64 ± 1.35
$^{50}Cr-^{52}Cr$	1.12 ± 2.79	
$^{54}Cr-^{52}Cr$	-2.81 ± 5.97	-
$^{53}Cr-^{52}Cr$	-2.05 ± 8.94	-0.83 ± 6.17

field shift effect is small!

almost identical effect

~~***If the field shift effect is dominat, this method is not effective for Ca.***~~

Summary

- The **preliminary** largest separation factor of Ca by LLE using DC18C6 is suggested.
- 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 the current evolving cutting-edge tech. of microchannel chip.

See the details on

R. Hazama et al.,J. of Nucl. Sci.&Tech(2005)

http://wwwkm.phys.sci.osaka-u.ac.jp/~hazama/iso-wsp/workshop.html

Workshop on

Double Beta Decay and Isotope Science/Engineering

???-??? 2005 Osaka, Japan

大阪大學

~ October(Nov.), 2005

Top Annoucement Program Workshop site Organizer Contact

- August 8: 1st announcement, update program pages

Motivation and scope

Neutrino mass is a key issue of current neutrino physics. Double beta decay may be the only probe presently able to access small neutrino masses with sensitivity down to ~0.03 eV, inferred from neutrino oscillation experiments. Actually, observation of neutrinoless double beta decay would identify a Majorana-type electron neutrino with a non-zero effective mass. Now the widest variety of stable isotopes are mainly produced at electromagnetic separators and gas centrifuges. Flexible highly efficient centrifugal technology is only possible for those elements (about 20) which have gaseous compounds at room temperature. Therefore, these methods cannot meet the production of some double beta decay isotopes such as ^{48}Ca, ^{96}Zr and ^{150}Nd etc. The workshop will provide wide ranging opportunities for scientists and engineers in various fields working not only on isotope effects in physics, chemistry, and engineering but also applications of isotopes in various fields in order to exchange new ideas, share current knowledge and present new results.

Topics included are :

- Double beta decays
- Isotope Science/Engineering
- Mass Spectroscopy, etc.

Please contact R. Hazama
or Prof. T. Kishimoto

Microchip Technology(synthetic chemistry)
Microreactor

CHEMCOMM
Communication
www.rsc.org/chemcomm

Fast and high conversion phase-transfer synthesis exploiting the liquid–liquid interface formed in a microchannel chip

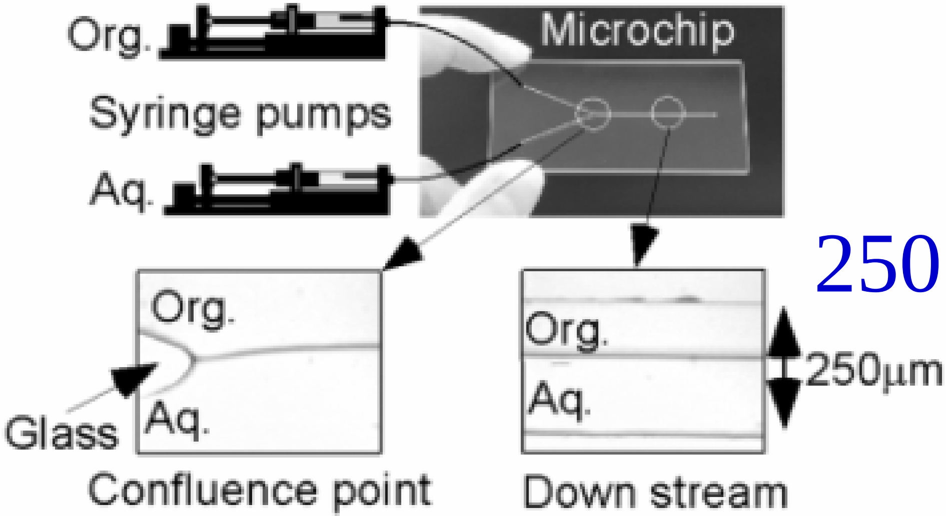
Hideaki Hisamoto,[a] Takumi Saito,[a] Manabu Tokeshi,[b] Akihide Hibara[a] and Takehiko Kitamori[ab]

[a] *Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: hisamoto@appchem.t.u-tokyo.ac.jp; Fax: +81-3-5841-6039; Tel: +81-3-5841-7233*

[b] *Integrated Chemistry Project, Kanagawa Academy of Science and Technology, Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan. E-mail: tokeshi@pop12.odn.ne.jp; Fax: +81-44-819-2092; Tel: +81-44-819-2037*

Chem. Commun. 2001, 2662

The large specific interfacial areas and short molecular diffusion distances provided by glass microchips play important roles not only for effective phase-transfer synthetic reaction, but also for avoiding an undesirable side reaction.



Macro)10cm cube

S/V~0.6/cm

250µm wide,100µm deep, and 3cm length

S/V~80/cm

No-stirring,Fast!!

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

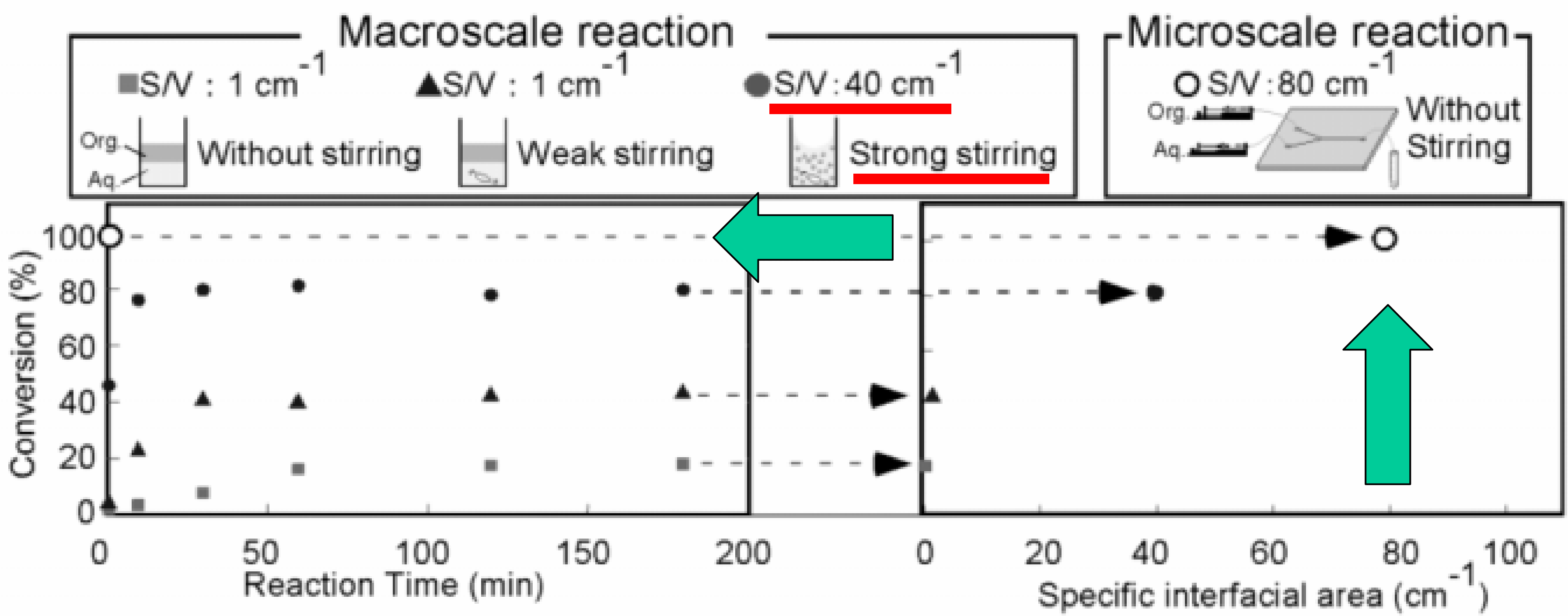


Fig. 3 Reaction conditions and results obtained with phase transfer diazocoupling reaction under microscale and macroscale conditions.