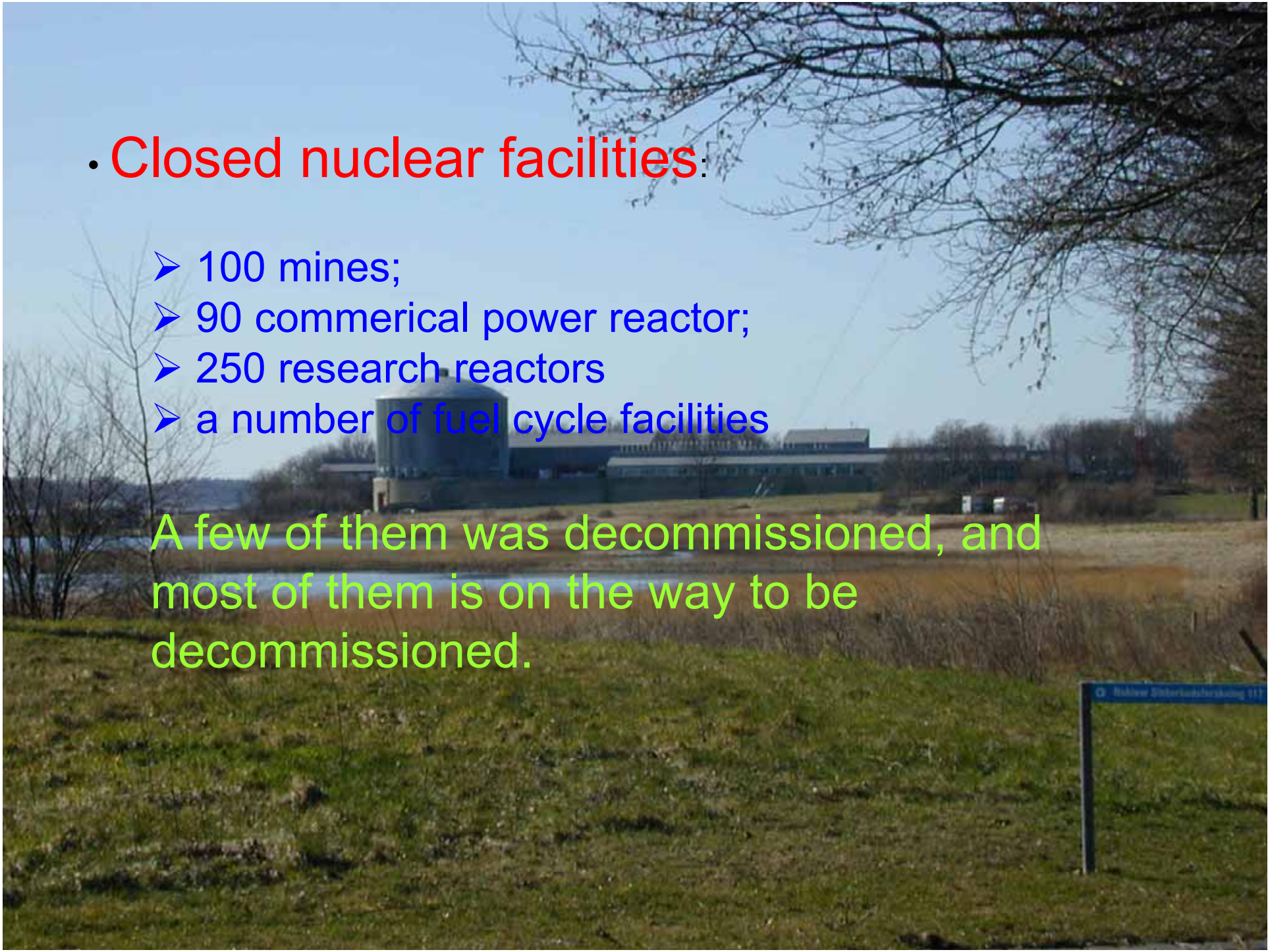
Radioanalytical Chemistry in Decommissioning of Nuclear Facilities

Xiaolin Hou

Technical University of Denmark

Center for Nuclear Technologies, Risø Campus, Roskilde, Denmark

DTU Nutech
Center for Nuclear Technologies



- Closed nuclear facilities:
  - 100 mines;
  - 90 commerical power reactor;
  - 250 research reactors
  - a number of fuel cycle facilities

A few of them was decommissioned, and most of them is on the way to be decommissioned.

Steps of decommissioning of nuclear facility

- Preparation (investigating the background radioactivity around NPP)
- Plant Cleanout
  - Removal of most radioactive component such as spend fuel elements, reactor internals, reactor vessel, etc. which is transferred for storage and disposal. (high level waste). (Evaluation of radioactivity before transferring)
- Decontamination
  - Removal of contamination from surfaces of facilities or equipment by chemical or mechanical methods, which can reduce the waste volume and active level in the waste. (Measurement of radioactivity to evaluation the decontamination, and estimation of radioactivity in the waste)
- Dismantling
  - Equipments within the facility are dismantled and classified by estimation of the radioactivity)
- Demolition and site clearance
  - Buildings demolished and radioactive wastes removed to storage or disposal facilities after estimation of the radioactivity in the waste.
- Release of the site to alternative use (measure the radioactivity level in the released area)

Production of main radionuclides in nuclear reactors

- Long-lived fission products

  $^{137, 135}Cs$, ^{106}Ru, **^{90}Sr, ^{99}Tc, ^{129}I**, etc.

- Neutron activation products (long-lived)

  $^{58,60}Co$, ^{133}Ba, ^{134}Cs, $^{152,154, 155}Eu$, **^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, $^{63, 69}Ni$**, ^{94}Nb, **$^{55,59}Fe$**, ^{93}Zr, ^{93}Mo, ^{54}Mn, ^{110m}Ag, $^{238\text{-}241}Pu$, ^{241}Am, $^{243,244}Cm$, ^{237}Np, etc.

Waste samples and the relevant critical radionuclides for decommissioning

- **Graphite (reactor)**
  - ^{3}H, ^{14}C, ^{55}Fe, $^{63,59}Ni$, ^{60}Co, ^{152}Eu
- **Concrete (normal or heavy)**
  - ^{41}Ca, ^{60}Co, ^{55}Fe, $^{63,59}Ni$, ^{133}Ba, ^{152}Eu
- **Steel/stainless steel**
  - ^{55}Fe, $^{63,59}Ni$, ^{36}Cl, ^{93}Zr, ^{93}Mo, ^{94}Nb, ^{60}Co, ^{152}Eu, transuranics
- **Aluminium**
  - ^{60}Co, ^{63}Ni, ^{55}Fe, ^{36}Cl
- **Lead**
  - ^{60}Co, ^{63}Ni, ^{55}Fe
- **Water**
  - ^{3}H, ^{14}C, ^{63}Ni, ^{99}Tc, ^{129}I, ^{90}Sr, ^{60}Co, ^{137}Cs, transuranics
- **Ion exchange resin**
  - ^{55}Fe, $^{63,59}Ni$, ^{14}C, ^{99}Tc, ^{36}Cl, ^{93}Zr, ^{93}Mo, ^{94}Nb ^{90}Sr, ^{129}I, ^{137}Cs, ^{60}Co, ^{135}Cs, transuranics

Main Radionuclides in the nuclear waste and used materials in the view of measurement

- Gamma radionuclides

  ^{60}Co, ^{133}Ba, ^{137}Cs, ^{134}Cs, ^{106}Ru, ^{152,154,155} Eu, ^{58}Co, ^{54}Mn,^{59}Fe, ^{110m}Ag, ^{94}Nb, etc.

  Easy to measure, No chemcial separation

- Beta Emitter

  ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63,59}Ni, ^{90}Sr, ^{99}Tc, ^{129}I,^{93}Zr, ^{93}Mo.

  Difficult to measure, **separation of individual radionuclide from matrix and all other radionuclides** is needed before measurement.

- Alpha emitter (actinides)

  $^{238\text{-}241}$Pu, ^{241}Am, ^{243,244}Cm, ^{237}Np, etc.

  High toxicity, difficult to measure, **separation of individual radionuclide from matrix and all other radionuclides** is needed.

Radioanalytical Chemistry of important radionculides for decommissioning

- ^{3}H and ^{14}C
- ^{41}Ca and ^{90}Sr
- ^{36}Cl and ^{129}I
- ^{99}Tc
- ^{55}Fe and ^{63}Ni
- Transuranics (Pu isotopes, ^{237}Np)

Determination of ^{3}H and ^{14}C in graphite, concrete, and other solid materials

- ***Production of ^{3}H in reactor***
  - $^{2}H\ (n, \gamma)^{3}H$
  - $^{6}Li(n, \alpha)^{3}H$
  - $^{3}He(n, p)^{3}H$

- ***Production of ^{14}C in reactor***
  - $^{13}C(n, \gamma)^{14}C$
  - $^{14}N(n, p)^{14}C$
  - $^{17}O(n, \alpha)^{14}C$

Properties of C-14 and H-3

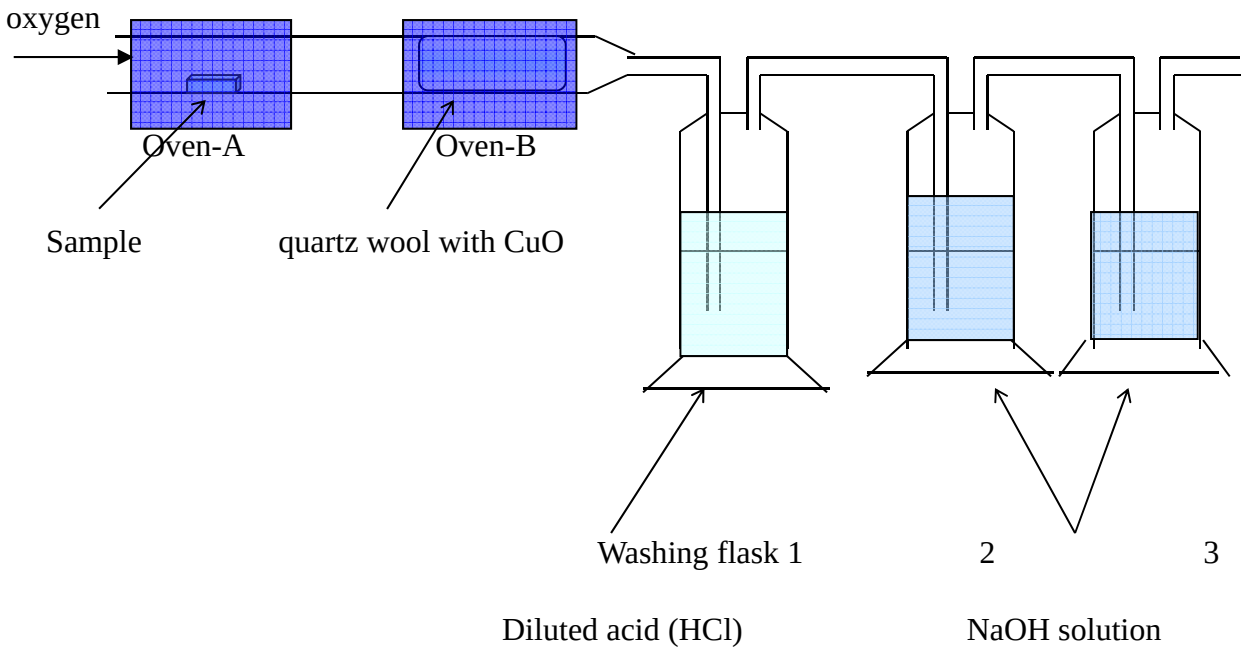
Nuclides	Half life	Decay	Energy, keV	Measurement
^{3}H	12.35 y	β	18.6	LSC
^{14}C	5736 y	β	156	LSC

Measurement of C-14 and H-3

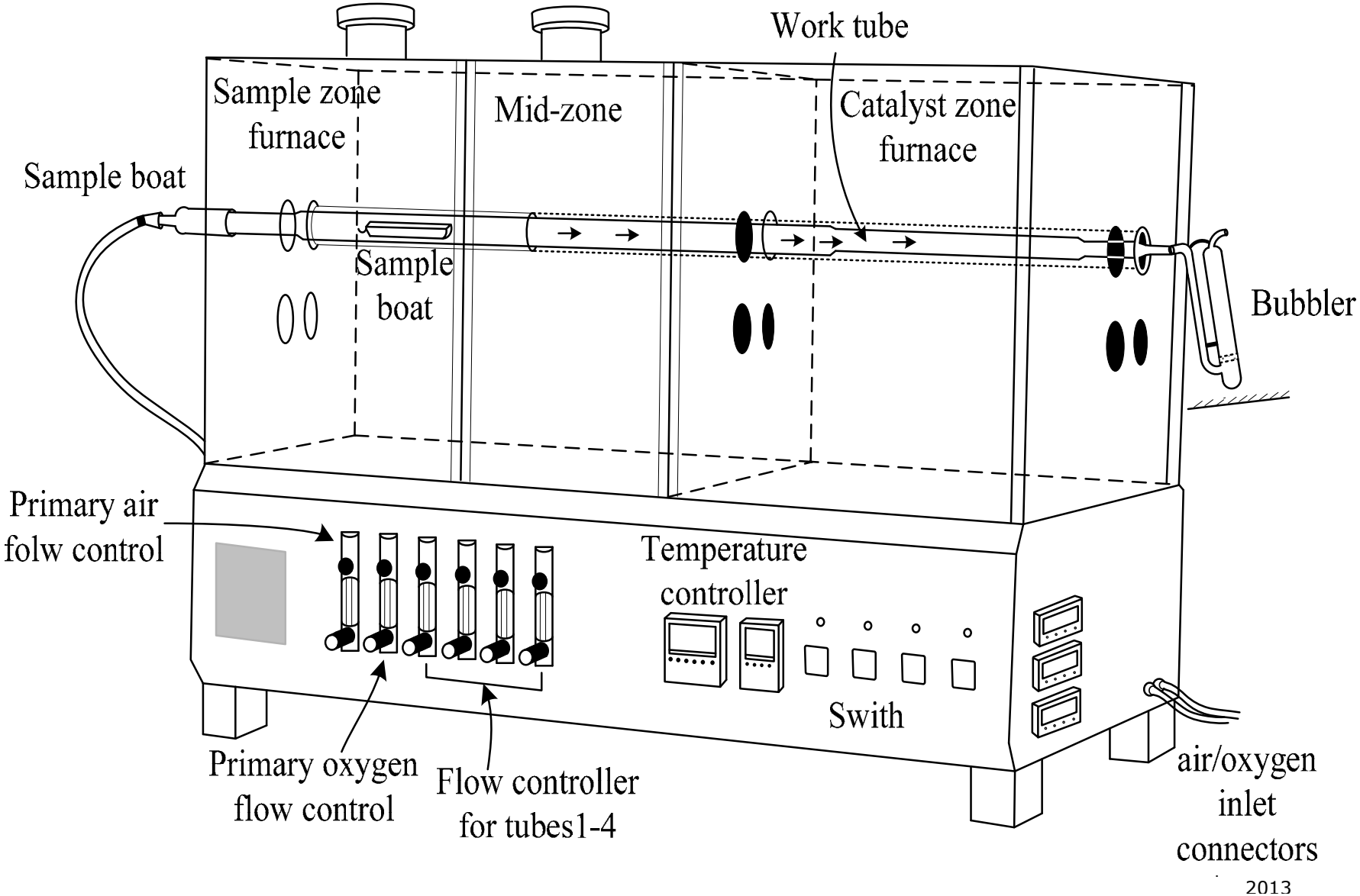
- Low energy
  Liquid Scintilation Counter
- Continueous epectrum
  Separation before measurement

Separation of ^{3}H, ^{14}C by combustion

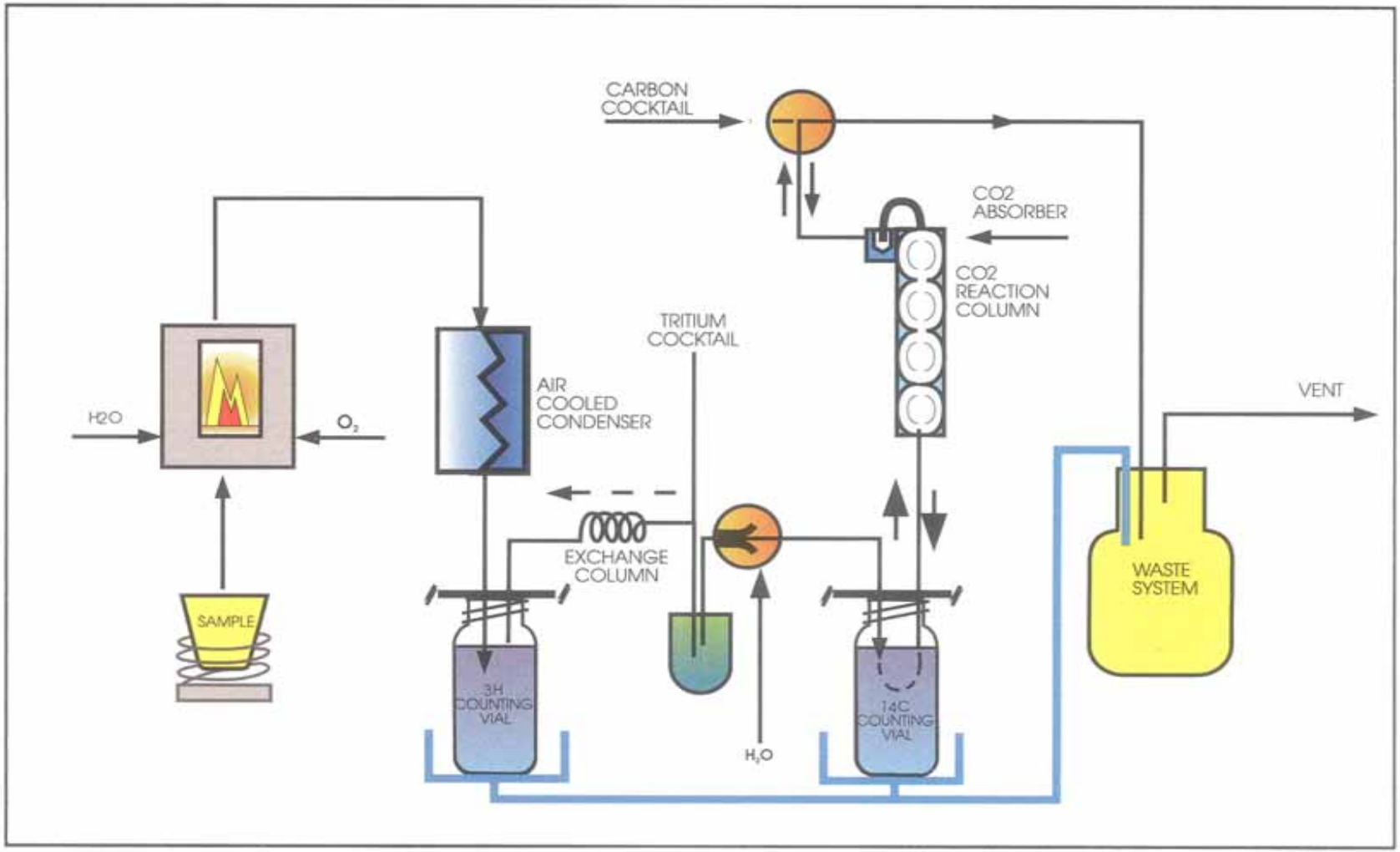
- Flask 1: ^{3}H, ^{129}I, ^{99}Tc
- Flask 2,3: ^{14}C, ^{129}I



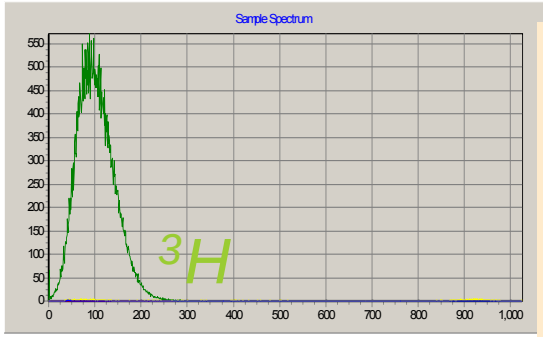
- Time consumming: (2-4 hours is needed for decomposition of sample.
- Large volume of absorption solution worsen the detection limit.

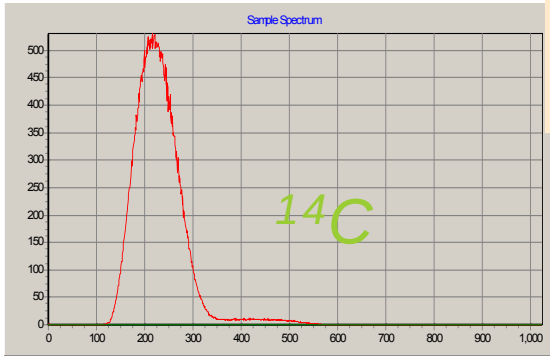

Work tube
Sample zone furnace
Mid-zone
Catalyst zone furnace
Sample boat
Sample boat
Bubbler
Primary air folw control
Temperature controller
Swith
Primary oxygen flow control
Flow controller for tubes1-4
air/oxygen inlet connectors

Rapid separation of ^{3}H and ^{14}C waste samples by combustion using Packard Oxidizer

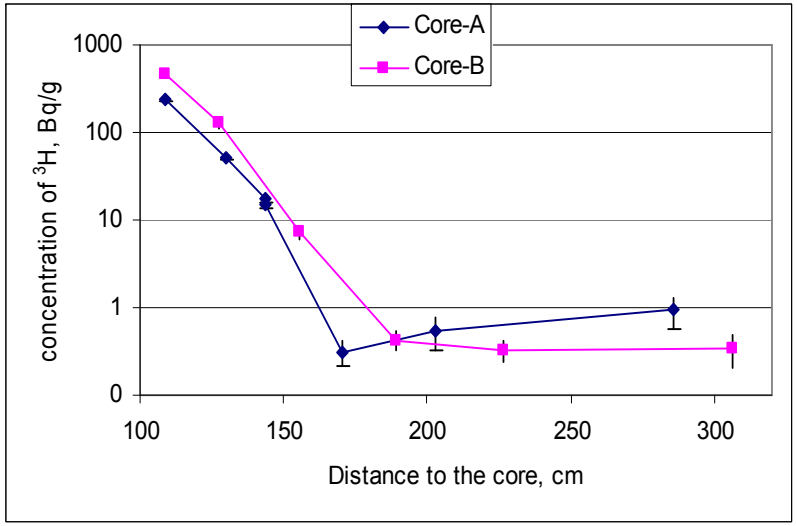


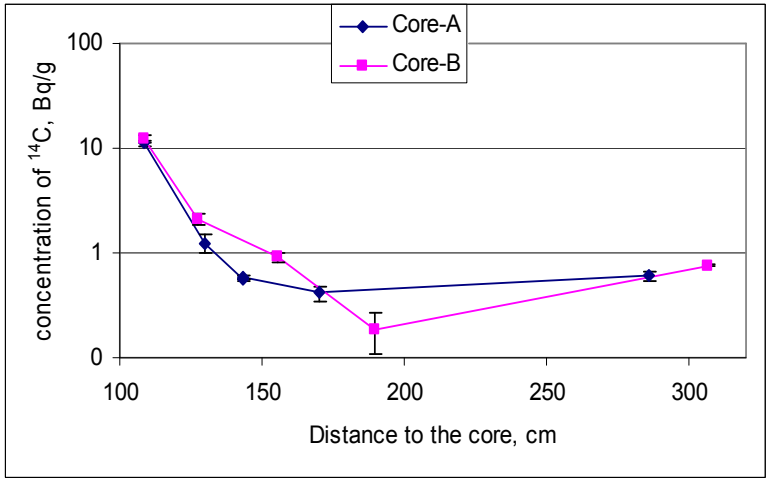
^{3}H and ^{14}C in concrete and graphite





No other impurity nuclides were seen in the H-3 and C-14 spectrum





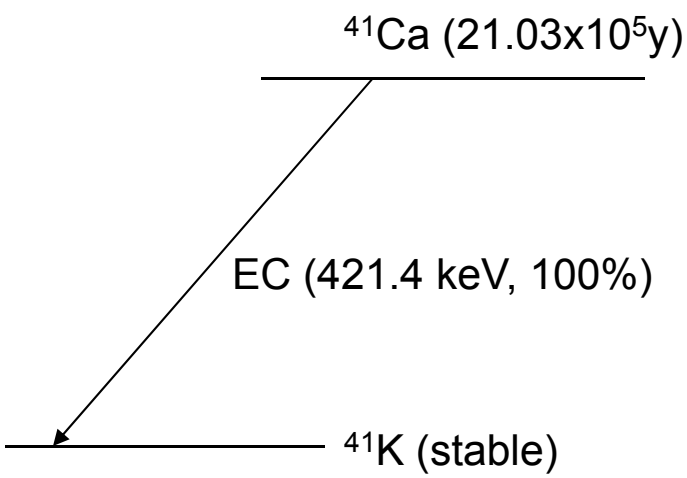
^{3}H and ^{14}C in graphite and their stability

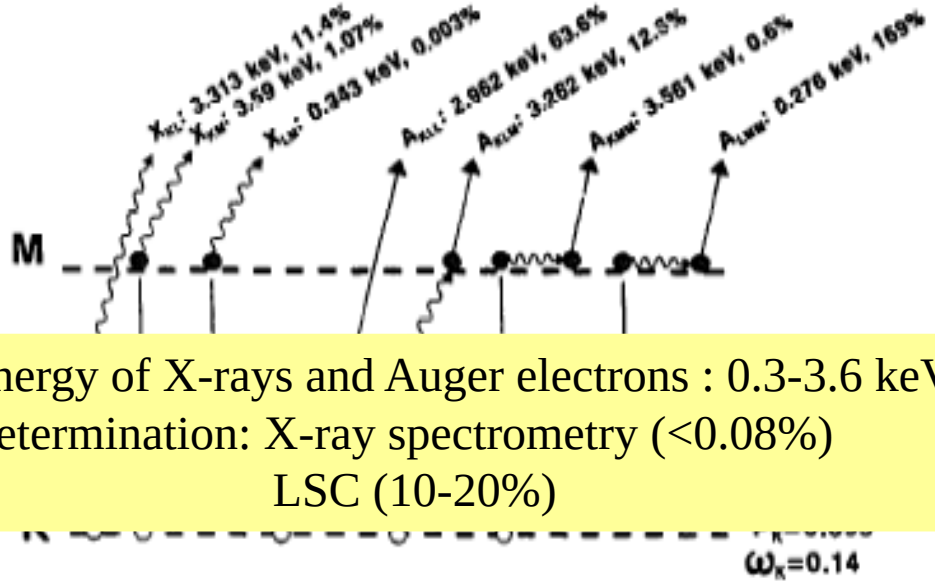
Nuclide	code	15-01-2003 (first measurement)		Room temperature 4 months		110 °C for 5 days	
		Average	SD %	Average	SD %	Average	SD %
C-14	TK5.5 Yi	2,12E+02	4,50	2,08E+02	5,2	2,17E+02	3,8
C-14	TK7.5 Yi	2,67E+04	2,19	2,54E+04	2,93	2,64E+04	4,27
H-3	TK5.5 Yi	4,70E+03	17,33	4,72E+03	3,74	4,66E+03	4,12
H-3	TK7.5 Yi	1,11E+06	3,39	1,05E+06	5,79	1,05E+06	4,8

^{41}Ca in concrete

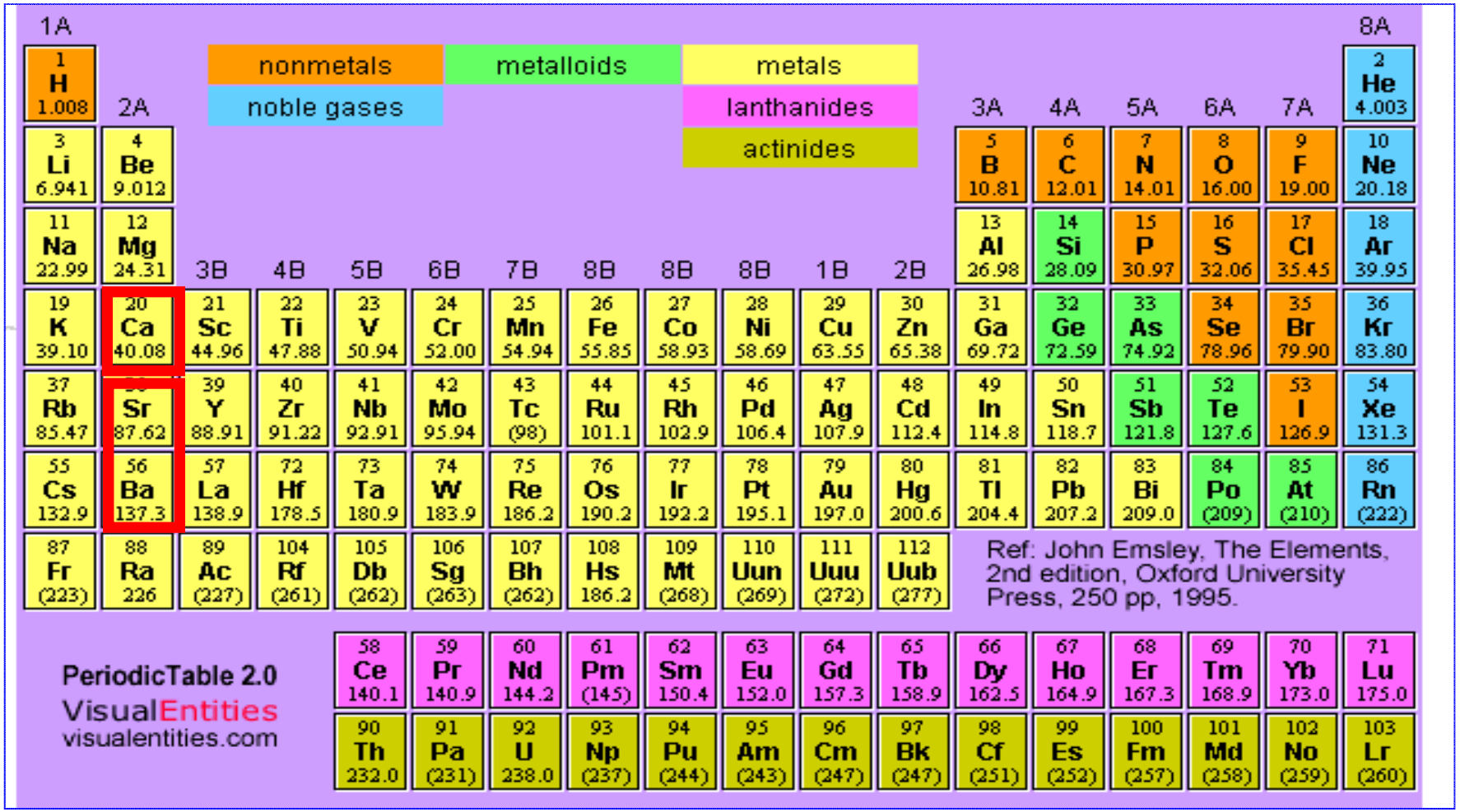
Activation products of calcium isotopes

Nuclide	Target isotope Aboundance %	Reaction	Cross section, bar	Half life	Decay
^{41}Ca	96.94	$^{40}Ca(n, \gamma)^{41}Ca$	0.41	1.03×10^5 y	EC
^{45}Ca	2.086	$^{44}Ca(n, \gamma)^{45}Ca$	0.84	162.7 d	β-
^{47}Ca	0.004	$^{46}Ca(n, \gamma)^{47}Ca$	0.7	4.54 d	β, γ
^{49}Ca	0.187	$^{48}Ca(n, \gamma)^{49}Ca$	1.0	8.72 min.	β, γ





Energy of X-rays and Auger electrons : 0.3-3.6 keV
Determination: X-ray spectrometry (<0.08%)
LSC (10-20%)



Ca, Sr and Ba: Alkline earth element

Determination ^{41}Ca in concrete

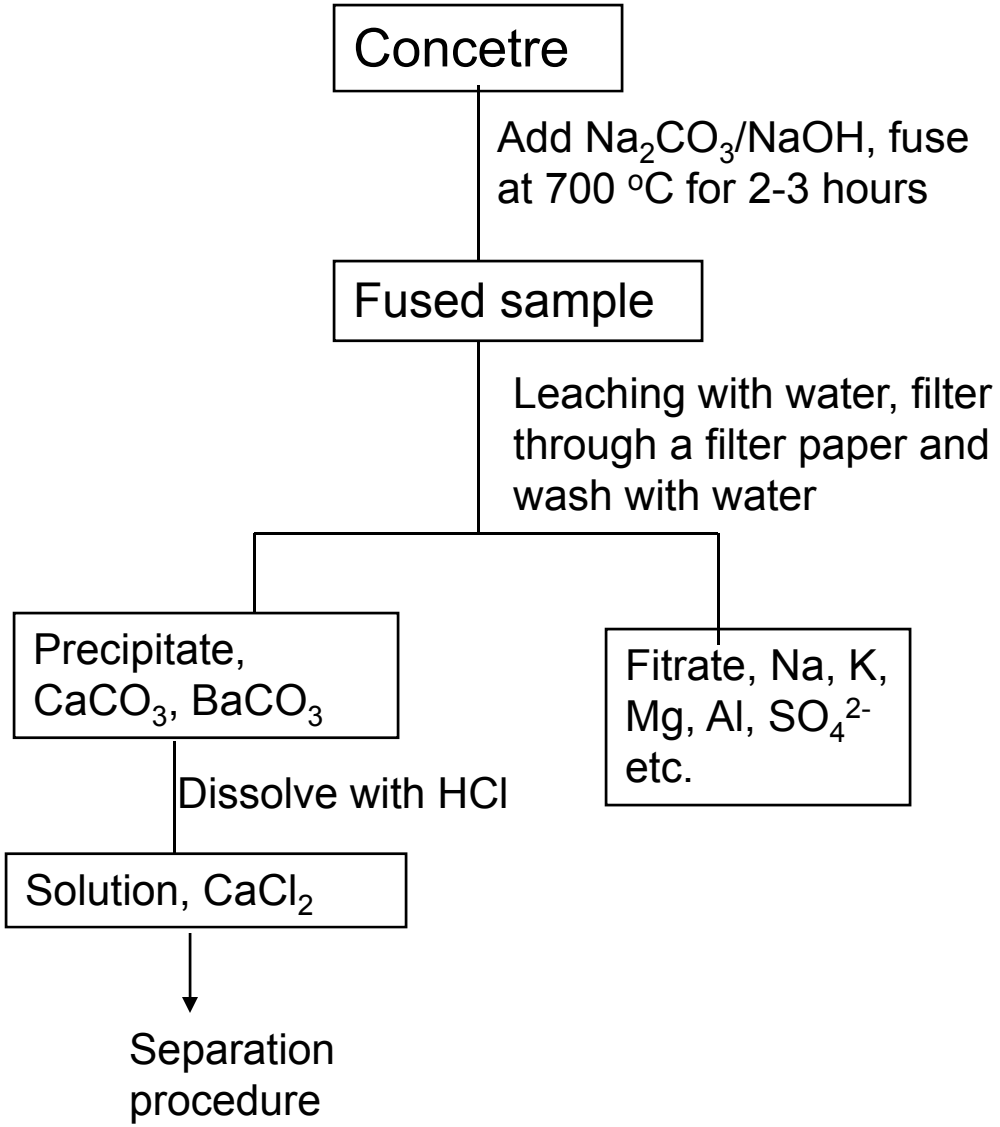
- **Separation fro matrix**
  - Decomposition of heavy concrete by alkali fussion
  - Leaching Ca by acids
- **Separation from active metals such as ^{60}Co, ^{152}Eu, ^{55}Fe, ^{63}Ni, ^{65}Zn, ^{54}Mn, ^{51}Cr,etc.**
  - Precipitation with $Fe(OH)_3$ by hydroxides at pH9
- **Separation from other alkaline metals, such as ^{133}Ba, ^{226}Ra and ^{90}Sr.**
  - $BaCrO_4$ and $SrCrO_4$ precipitation
  - $BaCl_2$ and $SrCl_2$ precipitation in HCl solution
  - $Ca(OH)_2$ precipitation in NaOH solution

Concrete in the reactor

- Ordinary concrete
- Heavy concrete (50-70% $BaSO_4$ was added)

Decomposition of concrete for ^{41}Ca and other radionuclides

- **For Ordinary concrete, silicates of calcium does not easily be decomposed by acids**
- **For heavy concrete, some calcium exists as $CaSO_4$, which does not dissolved by acid.**
- **Alkaline fusion have to be used for the decomposition of concrete for the determination of calcium isotopes.**

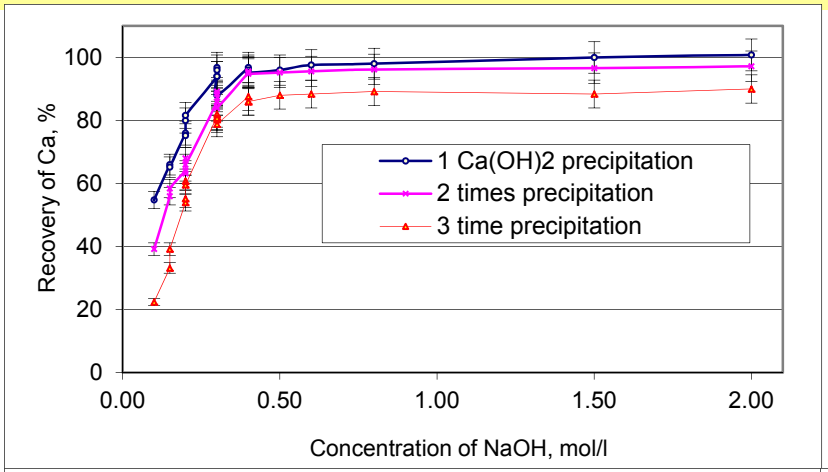


Separation of Ca and Sr from other metals by hydroxides precipitation

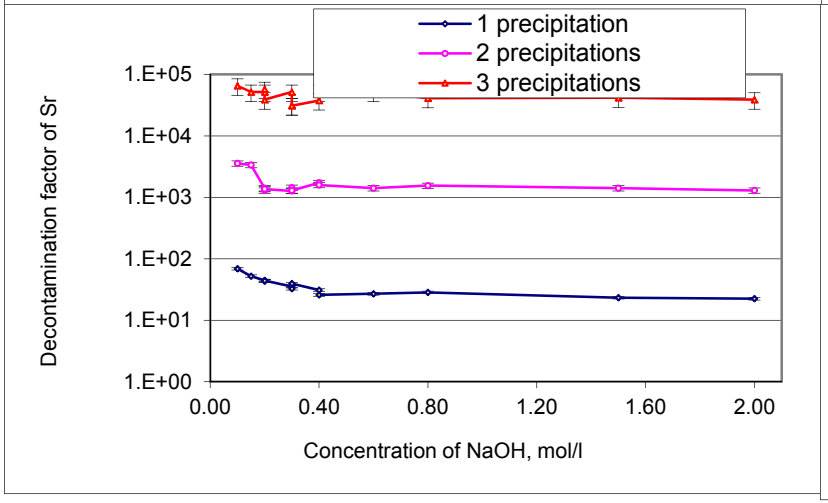
Element	Recovery, %	Element	Decontamination factor
Ca	97.7±3.9	^{137}Cs	(4.5±0.3)×10^{5}
^{85}Sr	97.9±2.1	^{60}Co	(1.2±0.4)×10^{5}
^{133}Ba	97.3±2.8	^{152}Eu	(8.5±0.5)×10^{5}
		^{59}Fe	(2.5±0.1)×10^{5}
		^{63}Ni	(2.5±0.2)×10^{5}

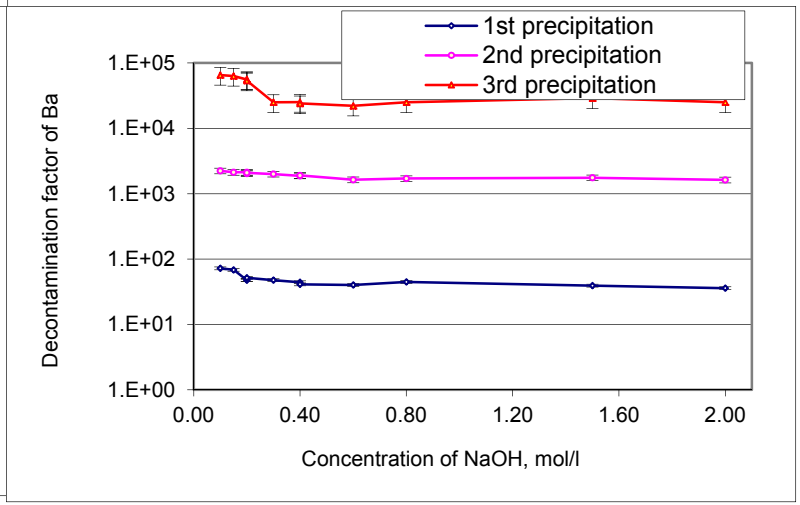
The new method for the separation of Ca from Sr and Ba

- Separation of Sr from Ca by $Ca(OH)_2$ precipitation
  - $Ca(OH)_2$: insoluble, Ksp = 5.2×10^{-6}
  - $Sr(OH)_2$ and $Ba(OH)_2$: Soluble in alkine solution



Precipitate Ca as $Ca(OH)_2$ at 0.5 – 0.8 mol/l NaOH, repeat 3 times, 85% Ca can be recovered, and the decontamination factor for Sr and Ba are higer than $5x10^4$

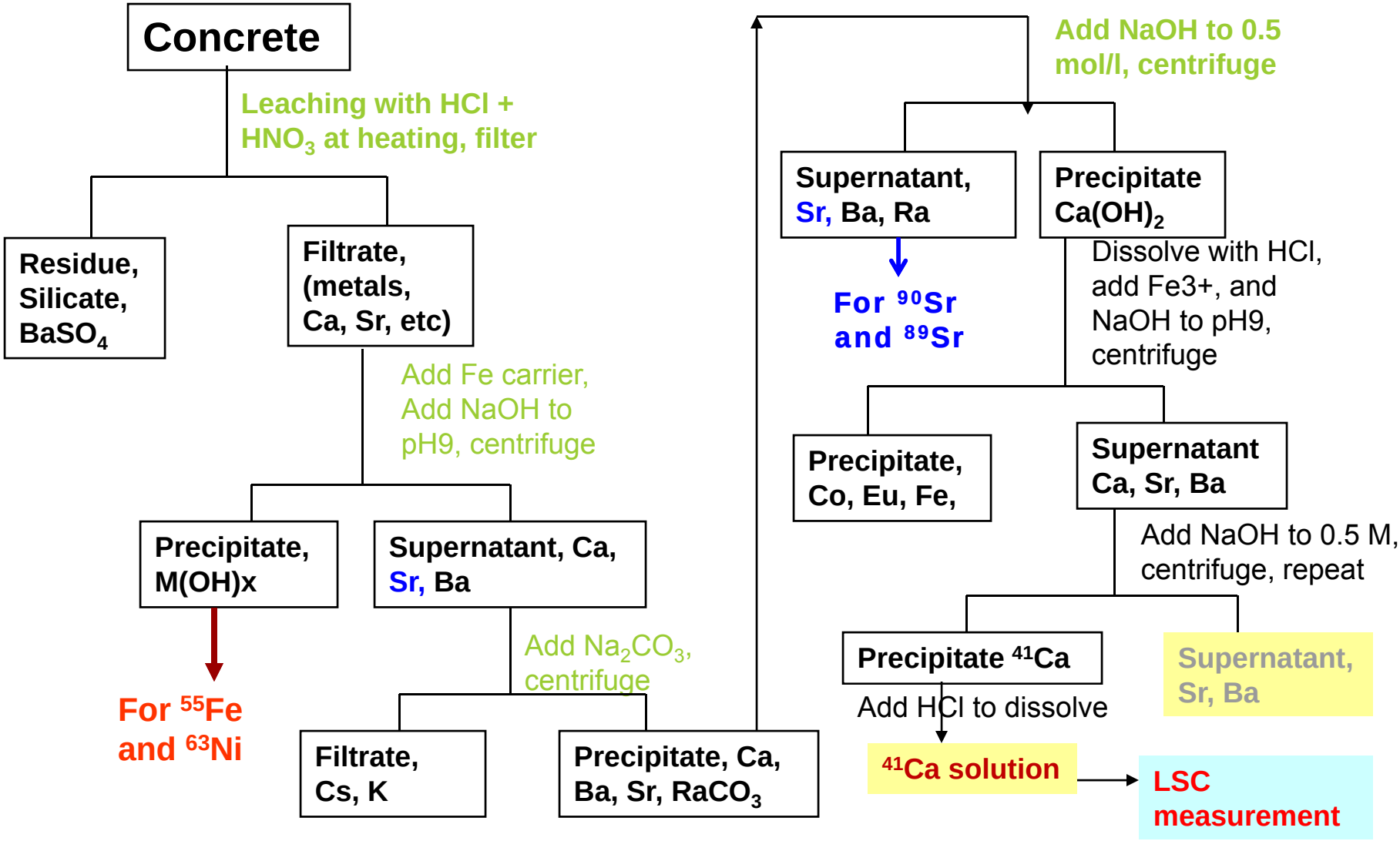




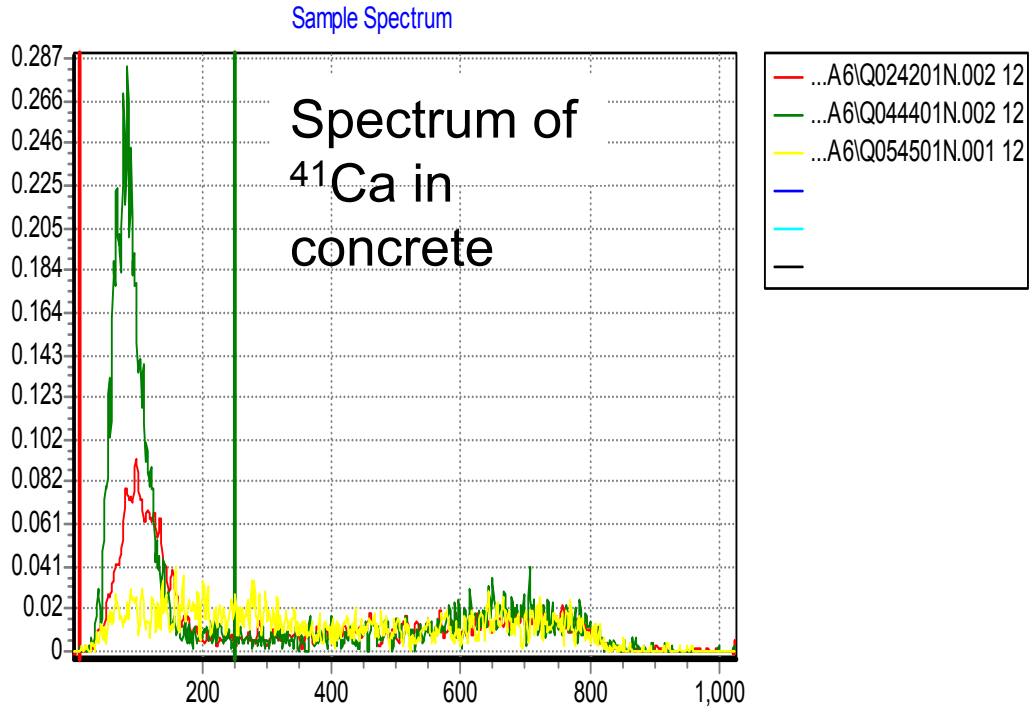
Separation of Ca from Sr and Ba by 3 repeated steps of $Ca(OH)_2$ precipitations at different NaOH concentrations

[NaOH]	Decontamination factor, 3 precipitations		Recovery of Ca, %		
mol/l	Ba	Sr	1 prec.	2 prec	3 prec
0.10	6.54×10^4	6.54×10^4	54.80	39.20	22.40
0.15	6.33×10^4	5.17×10^4	66.00	56.00	33.20
0.20	5.37×10^4	4.97×10^4	76.00	64.00	54.00
0.30	5.01×10^4	4.57×10^4	94.00	86.00	81.20
0.40	4.62×10^4	4.47×10^4	95.20	94.80	86.00
0.50	4.71×10^4	4.42×10^4	98.00	95.20	88.00
0.60	4.71×10^4	4.37×10^4	97.60	95.60	88.40
0.80	4.51×10^4	4.10×10^4	98.00	96.20	89.20
1.50	4.19×10^4	3.77×10^4	99.94	96.60	88.40
2.00	3.81×10^4	3.18×10^4	99.35	97.20	90.00

Procedure for simultaneous Fe, Ni, Sr and determination of ^{41}Ca



^{41}Ca in heavy concrete from DR-2

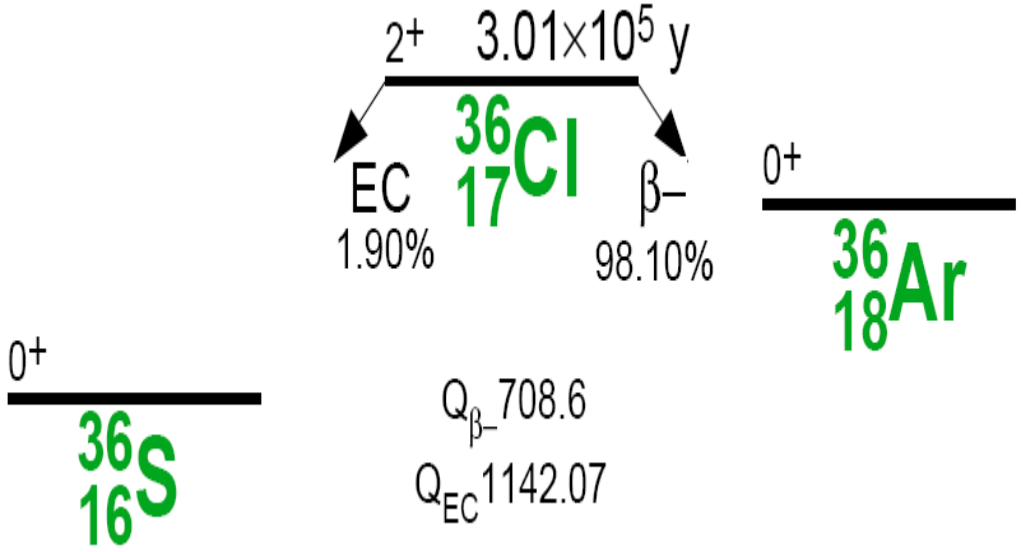


Features of Method for ^{41}Ca

- A separation of ^{41}Ca from concrete is **easy to operate**
- **Good decontamination** from interferring radionuclides (>10^4)
- The **chemical yields** of the separation procedures for ^{41}Ca is **80-90%.**
- The detection limits for ^{41}Ca is **0.020 Bq**.

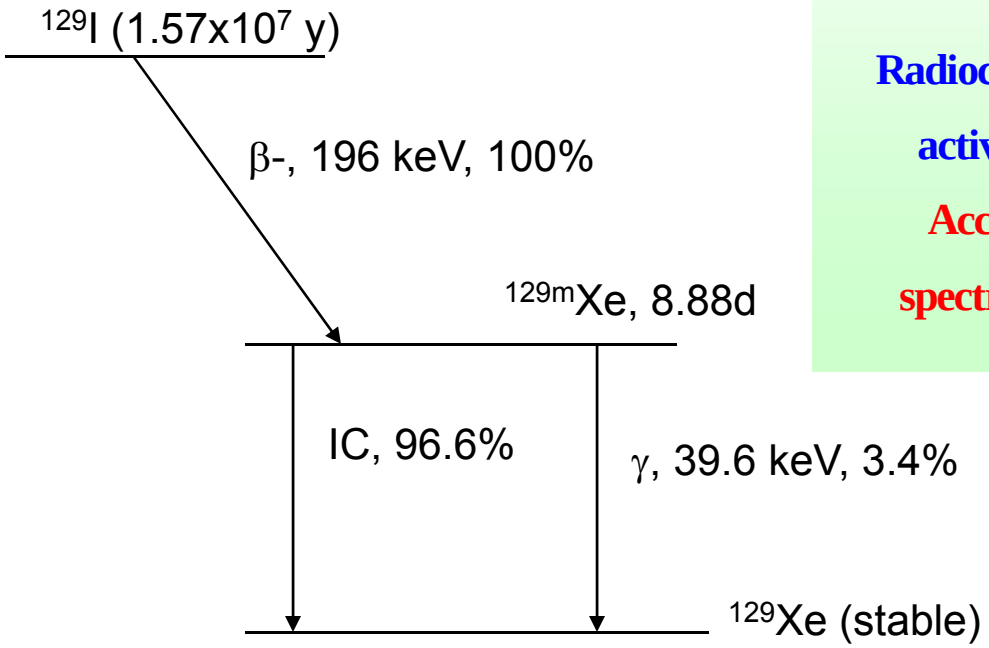
Hou X.L., Radiochim Acta, 2005

Determination of ^{36}Cl



- ^{36}Cl is long-lived radionuclides ($3x10^5$ yrs)
- ^{36}Cl decays mainly by pure beta emission of Emax=708.6 keV.
- ^{36}Cl measurement is normally carried out by LSC and AMS

Determination of ^{129}I



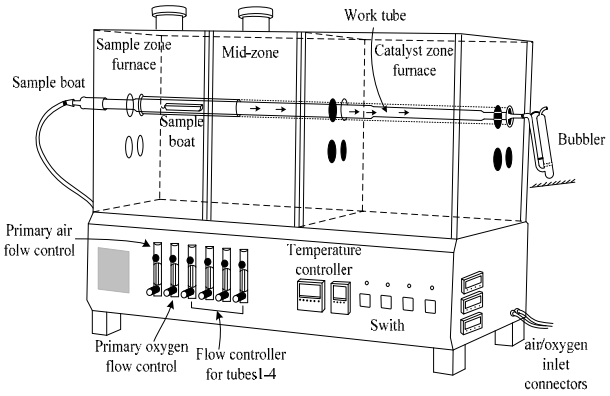
Method	Detection limit (atoms)
Liquid scintillation	10^{12} (1 mBq)
γ-spectrometry	10^{14} (0.1 Bq)
ICP-MS	5×10^{11}
Radiochemical neutron activation analysis	10^{8}
Accelerator mass spectrometry (AMS)	10^{6}

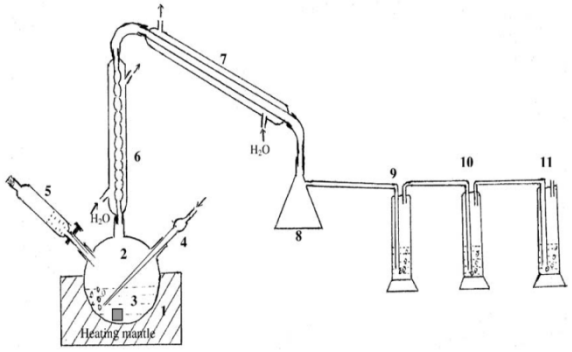
Analytical procedure of ^{36}Cl and ^{129}I

- Decomposition of sample to release Chlorine and iodine
- Separation of iodine from solution
- Purification of Cl from other radionuclides
- Measurement of ^{36}Cl and ^{129}I by LSC or other methods

Determination of ^{36}Cl and ^{129}I in graphite --- Sample decomposition

- Ashing at 900˚C: ---iodine and part of Cl are lost.
- Decomposition at 900˚C with O_2 and trapping iodine in NaOH solution: ---good recovery for iodine, but not good for chlorine
- Leaching with acid (HNO_3) at heating: --- not complete remove iodine and Cl from graphite, and loss of the leached iodine.
- Digestion with HNO_3 and trapping iodine and chlorine with NaOH: ---- Not complete removal of iodine and chlorine
- How to Do?





Determination of ^{36}Cl and ^{129}I in graphite --- Sample decomposition

- Graphite can be completely dissolved in a mixture of acids: HNO_3+H_2SO_4 +$HClO_4$

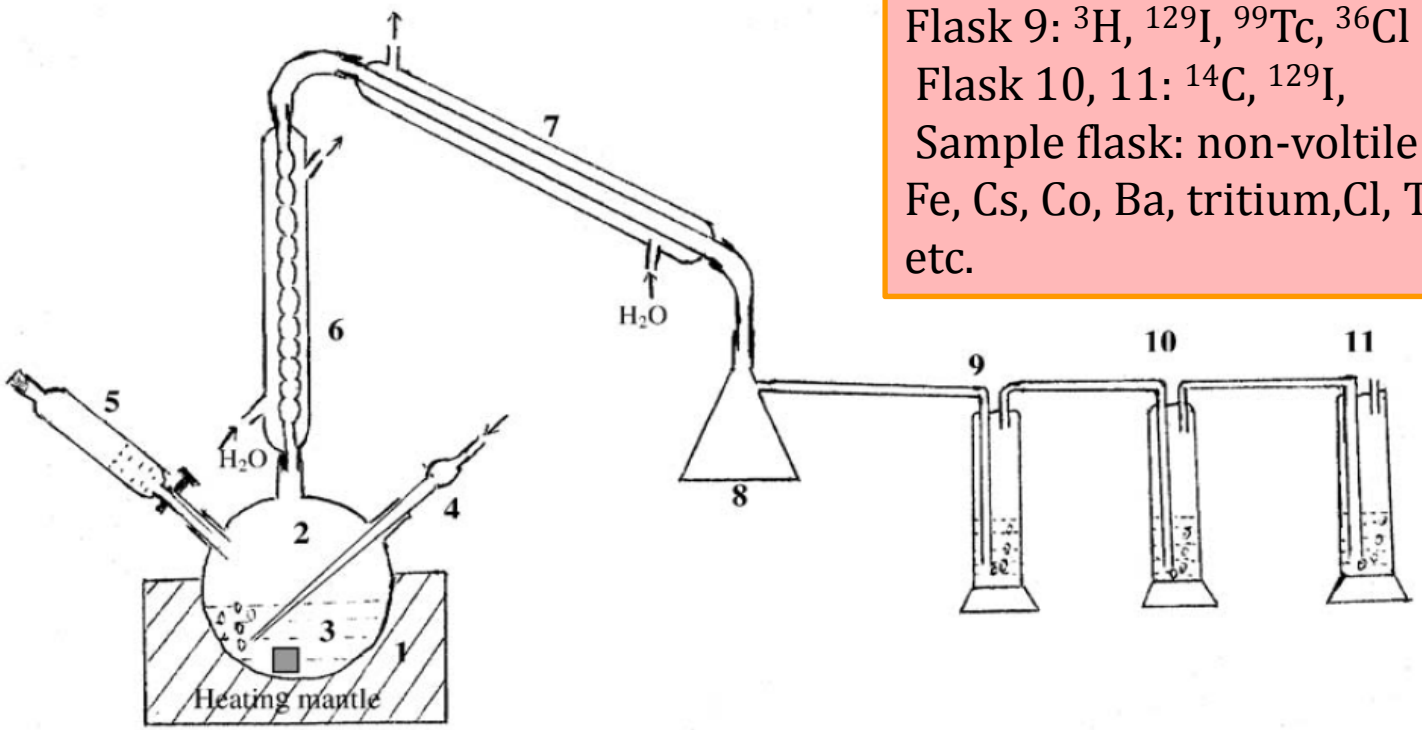
- The optimal ratio of mixture is:

H_2SO_4:HNO_3:$HClO_4$ =15:4.1

- A closed dissolution system is used for dissolve graphite in heating, Cl on the condenser tube and trap solution, while iodine mainly in the trap solution.

Decomposition of sample to release chlorine and iodine

- Acid digestion (graphite, steel, Al, Pb,)
  - ✓ Graphite (H_2SO_4:HNO_3:$HClO_4$=15:4:1)
  - ✓ Steel, aluminum (8 mol/l H_2SO_4)
  - ✓ Lead (8 mol/l HNO_3)



Flask 9: ^{3}H, ^{129}I, ^{99}Tc, ^{36}Cl
Flask 10, 11: ^{14}C, ^{129}I,
Sample flask: non-voltile elements, Ca, Ni, Fe, Cs, Co, Ba, tritium,Cl, Tc, transuranics, etc.

Determination of ^{36}Cl and ^{129}I in concrete --- Sample decomposition

- Leaching with acid (HNO_3) at heating: --- not complete remove iodine and Cl from graphite, and loss of the leached iodine.

- Digestion with HNO_3 and trapping iodine and chlorine with NaOH: ---- Not complete removal of iodine and chlorine

- Alklinal fussion using NaOH and Na_2CO_3, dissolution of fused cake in water, the supernatant is used for ^{129}I and ^{36}Cl: ---- sample is completely decomposed and iodine and Cl are released. Iodine and Cl are not lost in alkaline medium.

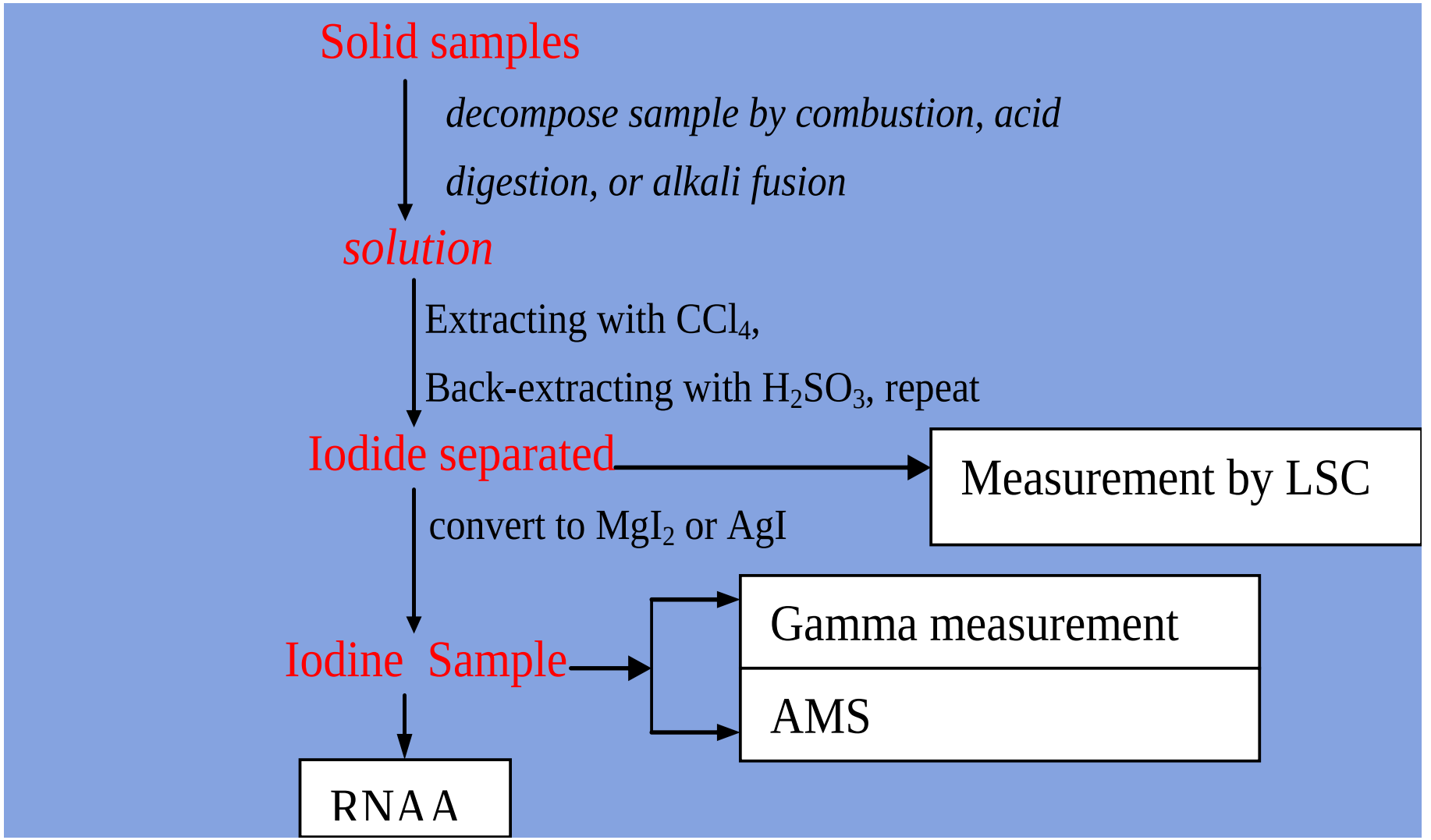
Determination of ^{36}Cl and ^{129}I in stainless steel --- Sample decomposition

- Stainless steel is normally dissolved with HCl or HCl+HNO3: --- could not be used for ^{36}Cl because of too much Cl in HCl is introduced.

- Single acid, HNO_3, could not dissolve stainless steel.

- 10M H_2SO_4 with H_3PO_4 is sucessfully used for dissolve stainless steel for ^{129}I and ^{36}Cl: ---- sample is completely decomposed and iodine and Cl are released.

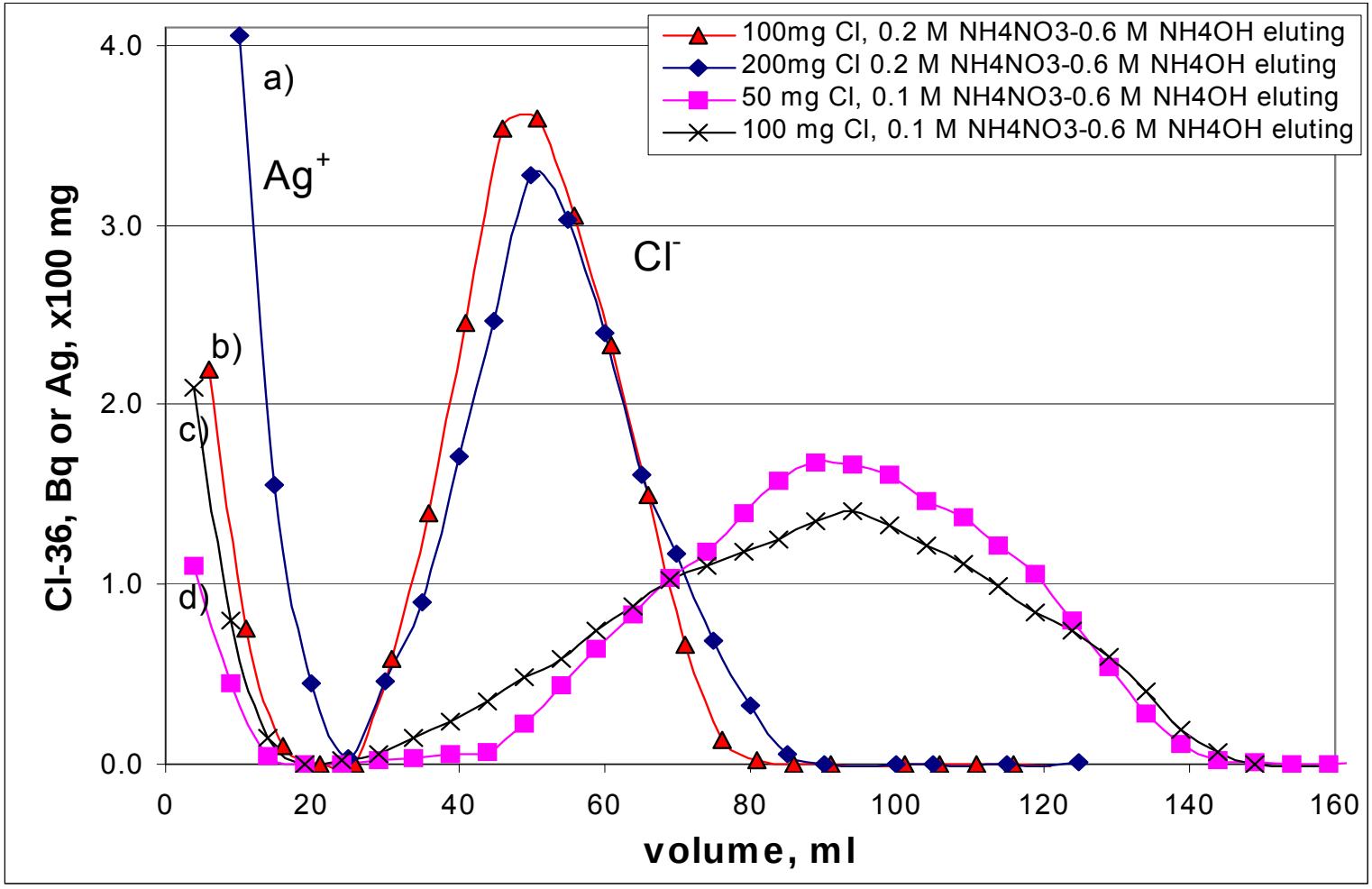
Separation procedure of iodine



Separation of Chlorine and iodine from matrices and other radionuclides

- ✓ Specific precipitation of Cl^- with Ag^+ (AgCl) can be used to selectively separation of Cl from matrix and other radionuclides (except iodine and bromine).
- ✓ Iodine (^{129}I) should be first separated from the solution before AgCl precipitation.
- ✓ ^{129}I can be separated by solvent extraction using $CHCl_3$
- ✓ No need to separate Br, since no long-lived radioisotopes of Br in the waste and environmental samples.
- ✓ The separated AgCl can be dissolved in NH_4OH and mixed with scintillation cocktail for LSC: But less AgCl can be used and high quench effect. How to improve?

Separation of Ag^+ and Cl^- in anion exchange chromatography



Combined Analytical procedure for ^{36}Cl and ^{129}I

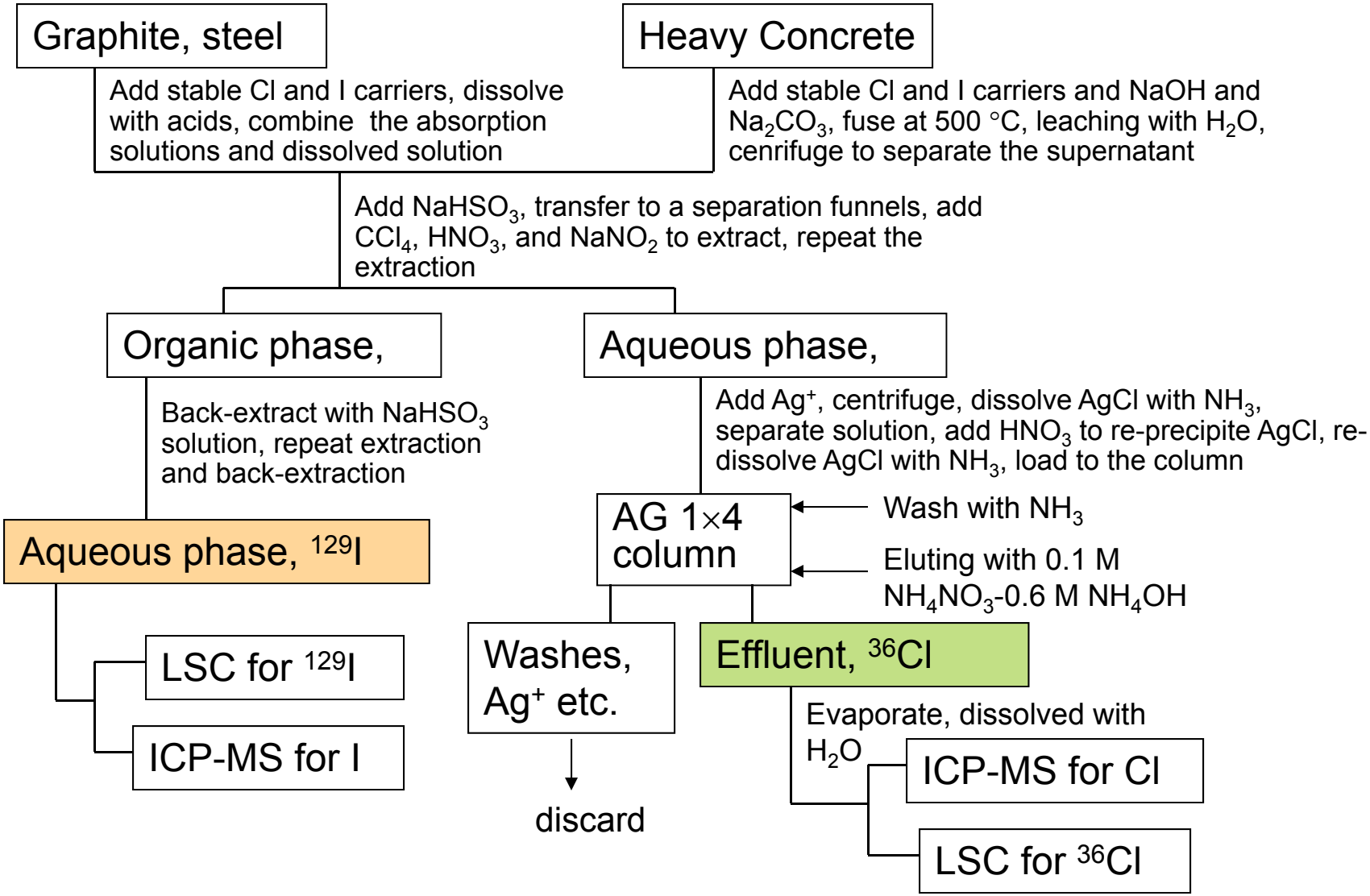


Table Recovery of Cl and decontamination factors o other elements in the chemical separation procedure

Element	AgCl precipitation	Anion exchange	Whole procedure
Cl (recovery, %)	96.5	98.3	**94.7±3.2**
I (^{125}I)	1.4×10^3	1.4×10^3	**8.9×10^5**
S	1.5×10^3		**5.6×10^5**
tritium	2.1×10^3		**4.8×10^6**
^{14}C (CO_3^{2-})	1.5×10^3		**2.8×10^6**
Co (^{60}Co)	1.9×10^3	2.5×10^3	**1.5×10^6**
Eu (^{152}Eu)	4.7×10^3	6.5×10^3	**8.9×10^6**
Cs (^{137}Cs)	3.8×10^3	5.1×10^3	**7.9×10^6**
Ba (^{133}Ba)	6.7×10^3	4.9×10^3	**5.6×10^6**
Sr (^{85}Sr)	4.7×10^3	3.3×10^3	**6.7×10^6**
Ni (^{63}Ni)	5.9×10^3	3.8×10^3	**4.8×10^6**
Fe (^{55}Fe)	1.9×10^3	2.8×10^3	**2.1×10^6**

Recovery of chlorine in the chemical separation procedure measured from stable chlorine and ^{36}Cl tracer

Stable chlorine					^{36}Cl tracer		
Graphite g	form	Cl mg	measured, mg	Recovery %	Added Bq	measured Bq	Recovery %
0.210	NaCl	50	315.5	87.4	2.50	2.17	86.8
0.255	NaCl	50	368.9	92.3	2.50	2.13	91.2
0.195	$NaClO_3$	50	297.2	89.8	2.50	2.18	89.2
0.301	$NaClO_3$	50	305.7	96.5	2.50	2.20	97.0

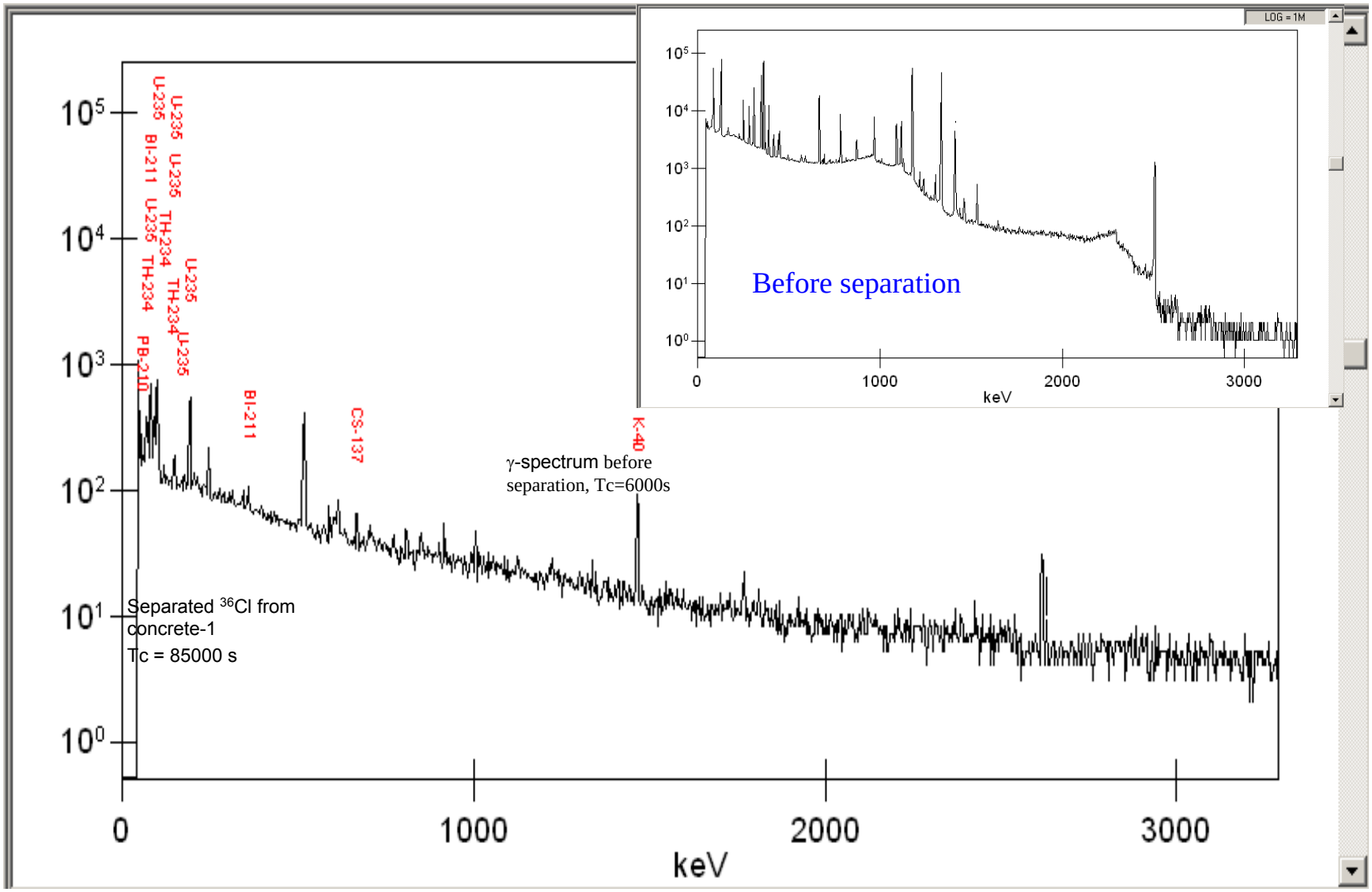
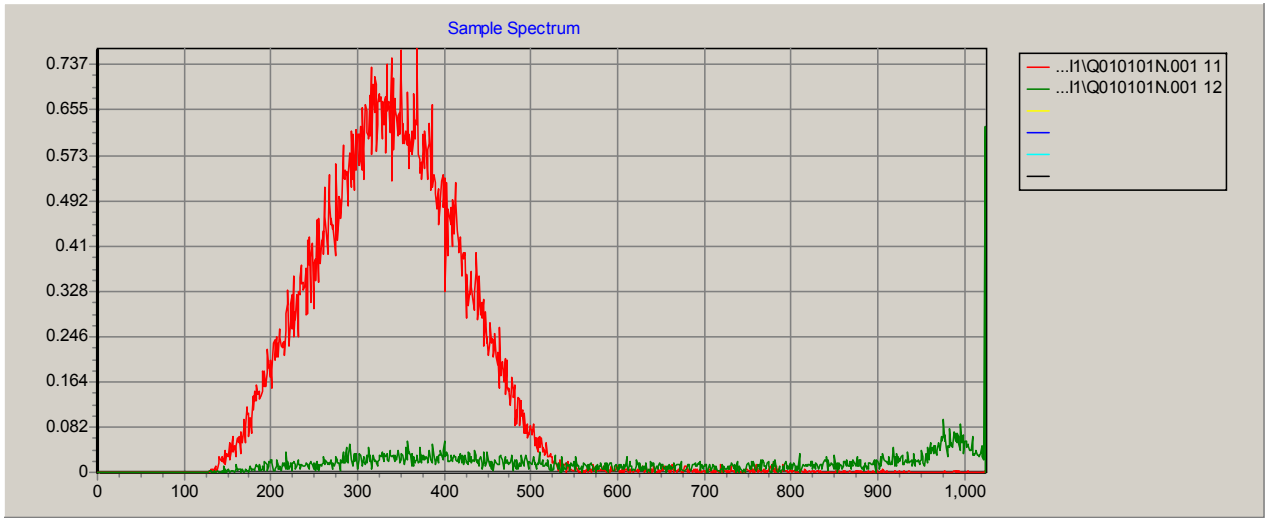
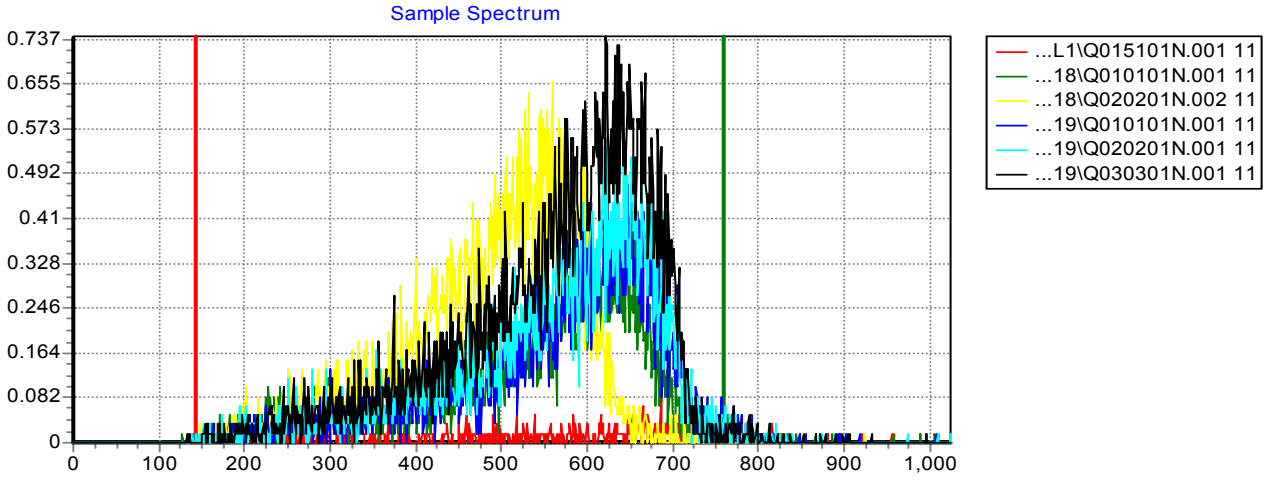


Fig. Gamma spectra of sample (graphite) before and after chemical separation of ^{36}Cl

LSC spectrum of ^{129}I and 36Cl in waste samples

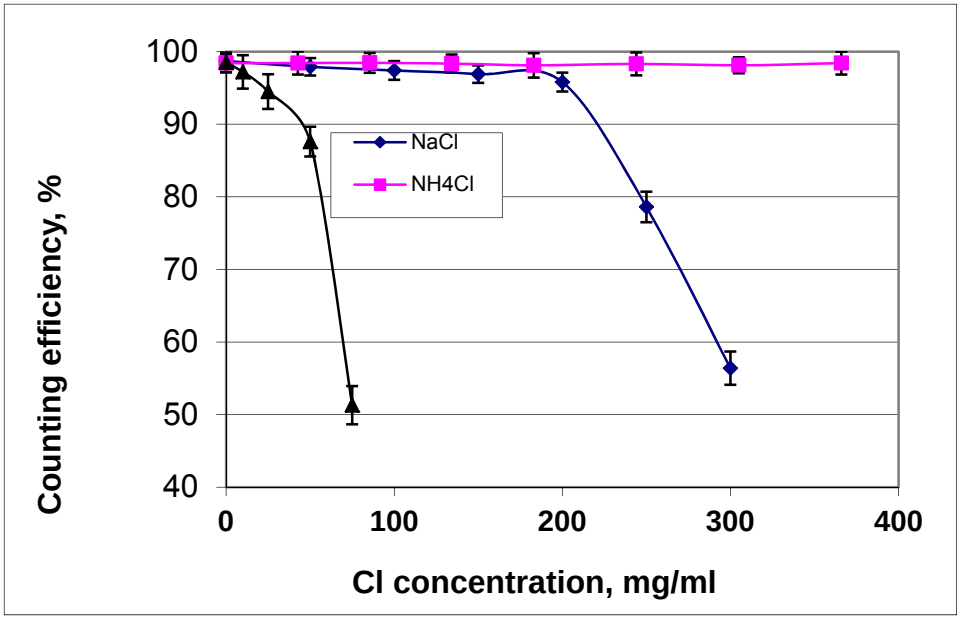


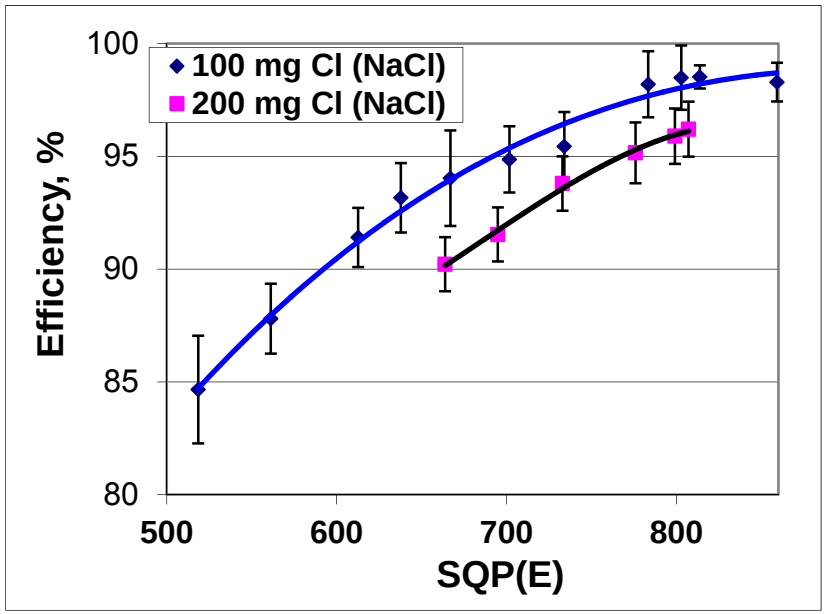
^{129}I in swip from Ignalina NPP

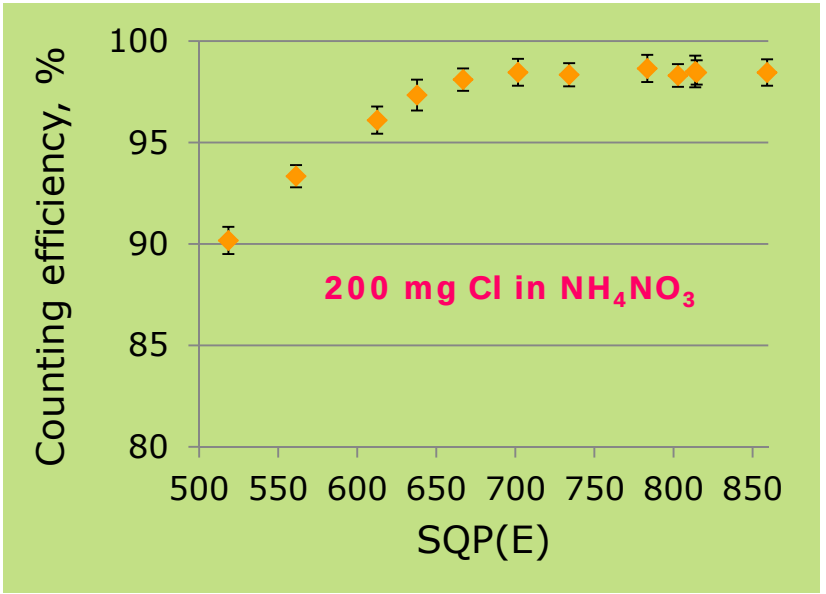


^{36}Cl in Steel and graphite from DR-2

Effect of the medium of measurement solution to counting efficiency by LSC



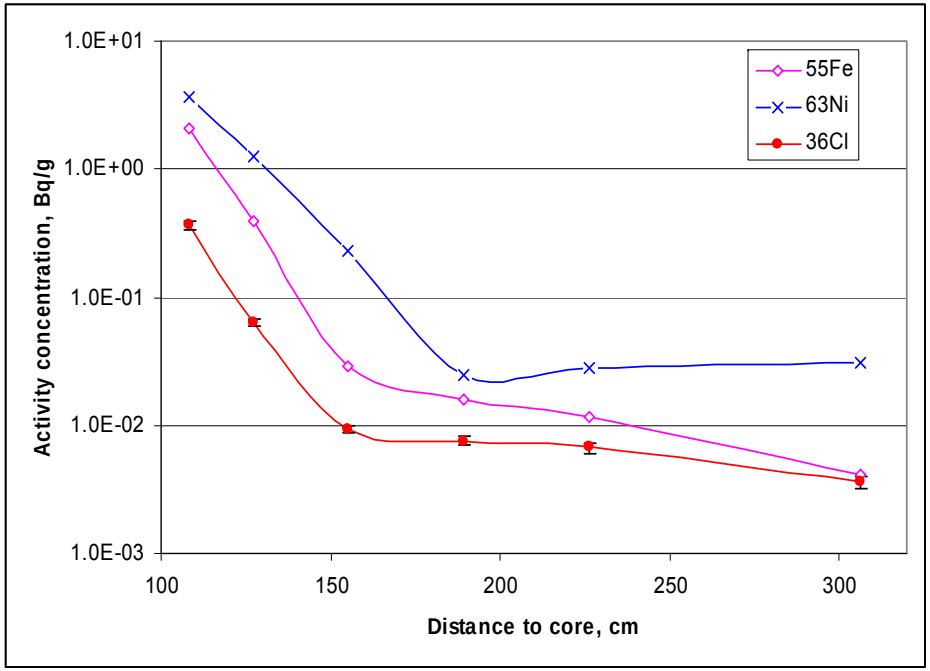




Performance of the procedure for ^{36}Cl

- Recovery of Cl: >70%
- Decontamination factors for most of radionculides: $>10^6$
- Detection limit using LSC : 14 mBq
- Decommissioing samples, concrete, graphite, stainless steel, aluminum, lead, have been sucessfully analysed for ^{36}Cl.

Hou et al., Anal. Chem., 2007

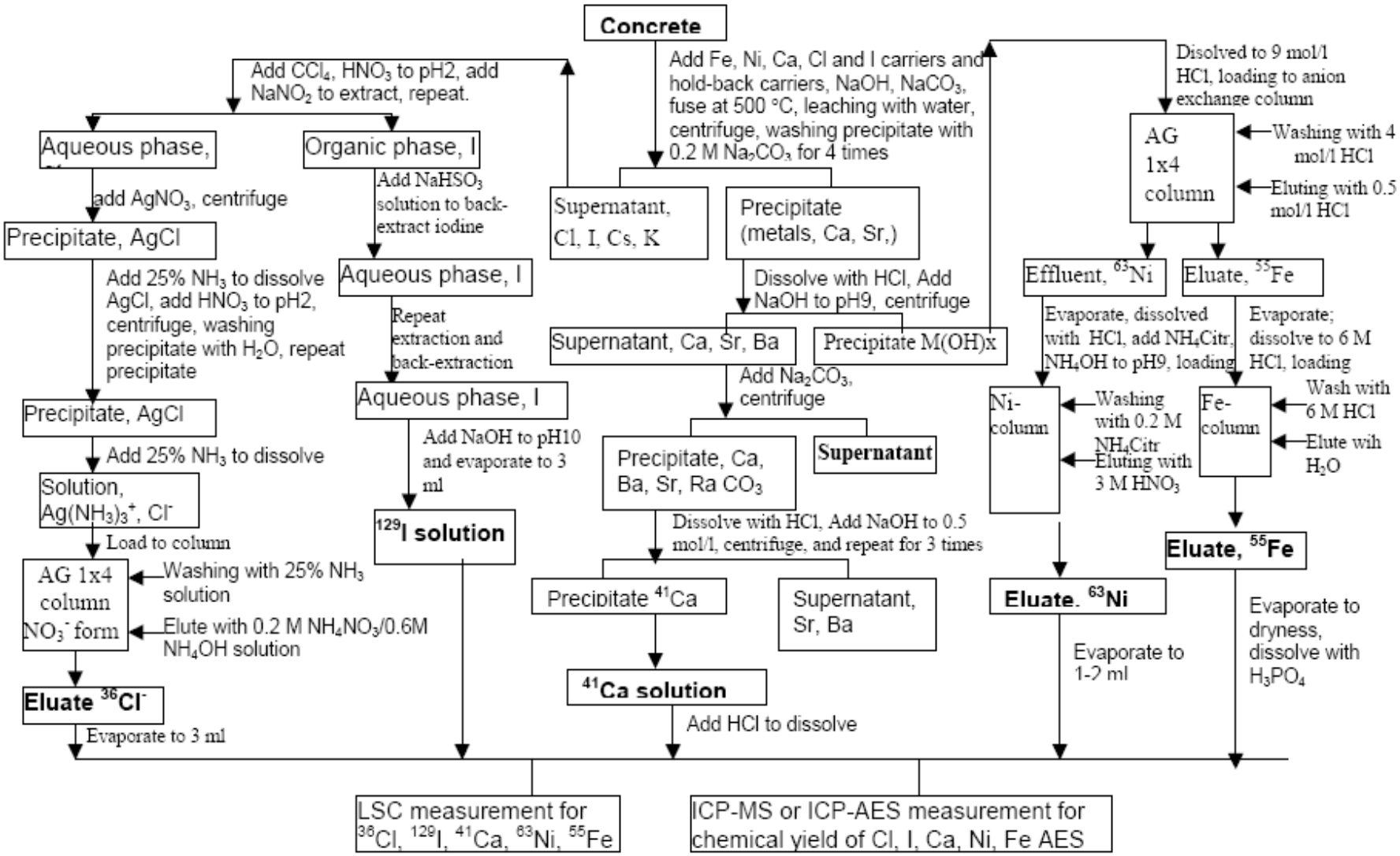


Distribution of ^{36}Cl in the concrete core from DR-2 with comparison to ^{55}Fe, and ^{63}Ni

^{36}Cl in 2 swip samples from Ignalina NPP

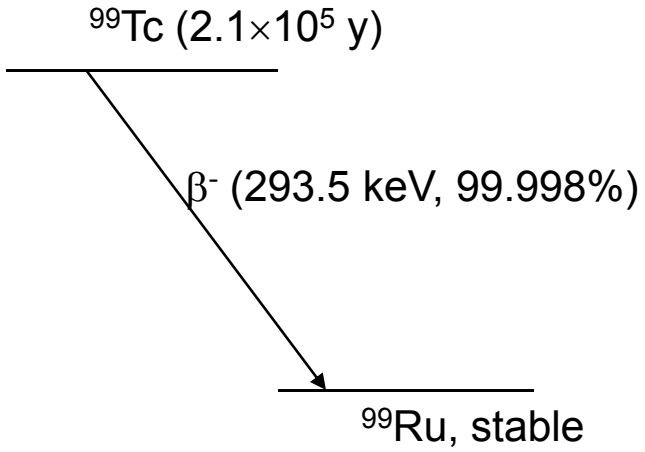
Sample	Count rate, CPM					^{36}Cl measured, Bq	
	No.1	No.2	No.3	Average	SD, %	Value	Uncertainty
SWIPE-111-2	117.05	120.83	118.57	119.47	1.41	**2.14**	**0.18**
SWIPE-111-1	112.20	114.83	115.57	114.24	2.50	**2.04**	**0.19**
^{36}Cl-SWIPE-2-ST	226.90	227.51	223.76	226.06	0.89		
BK	3.05	2.98	3.13	3.05	2.41		

Combined analytical procedure for ^{36}Cl, ^{129}I, ^{41}Ca, ^{90}Sr ^{63}Ni, and ^{55}Fe

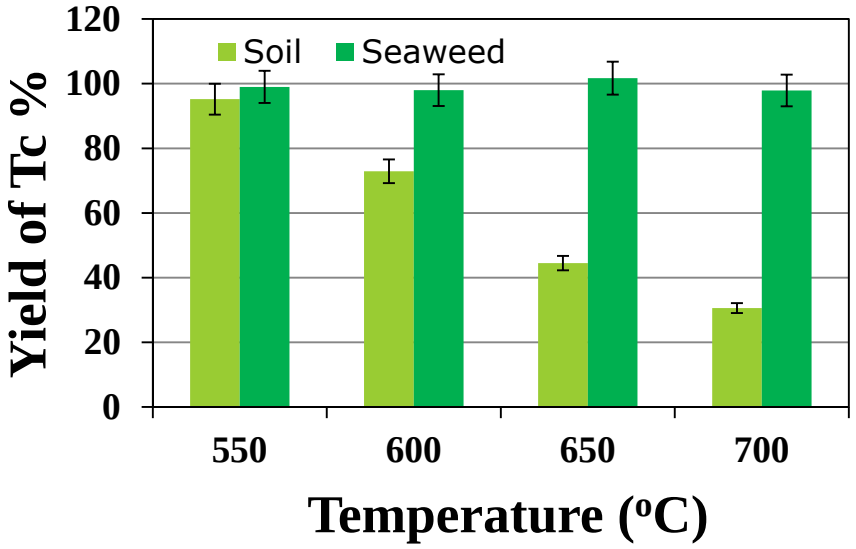


^{99}Tc analysis

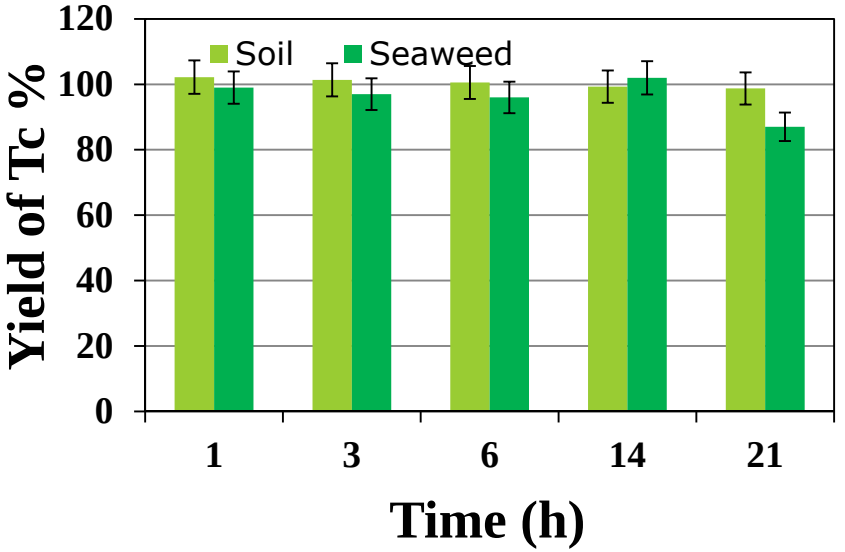
- **Long half-life (2.1×10^5 y)**
- **High mobility (TcO_4^-)**
- **High fission yield (about 6 %)**
- **Tc is a volatile element, and easily to be loss at high temperature.**
- **A pure beta emitter**
- **Measured by GM counter, LSC, and ICP-MS.**
- **It has to be separated from other radionuclides before measurement by beta counting, especially ^{106}Ru and ^{93}Mo**
- **Completely Removal of Ru (^{99}Ru) and Mo ($^1H^{98}$Mo) for ICP-MS.**



Loss of ^{99}Tc in Solid sample in dry ashing



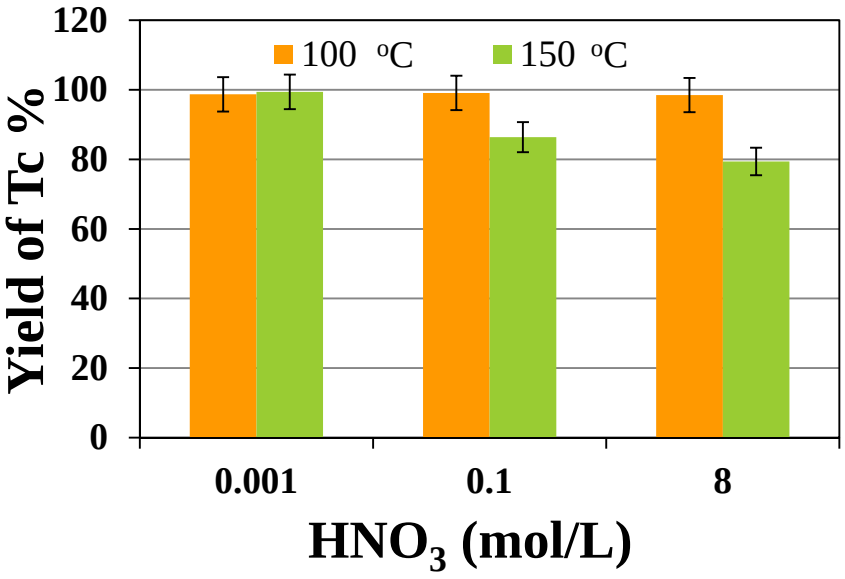
(samples ashed at different temperature for 6 h)

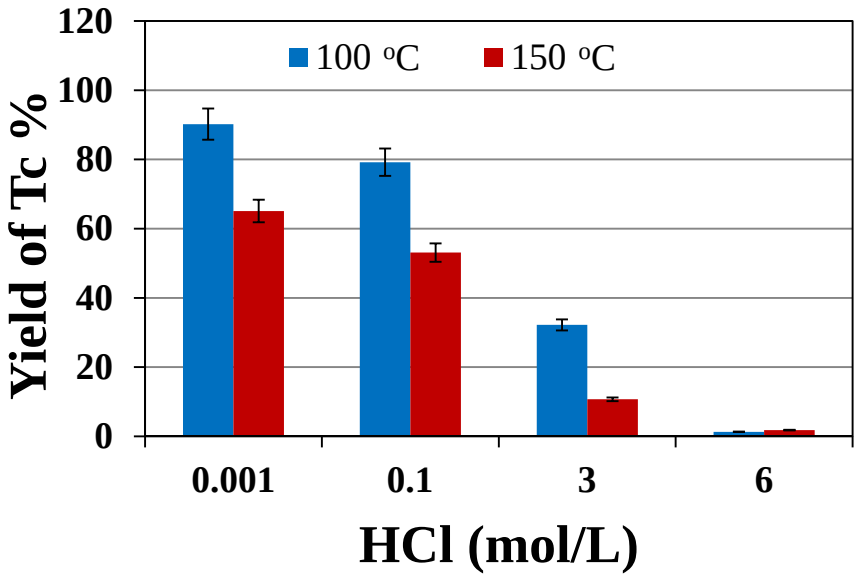


(seaweed ashed at 700 °C; soil ashed at 550 °C)

- In seaweed, Tc is relatively stable when ashed at 700 °C for ≤ 14 h
- In soil, Tc starts to lost when ashed at > 550 °C

Loss of ^{99}Tc in Solution evaporation



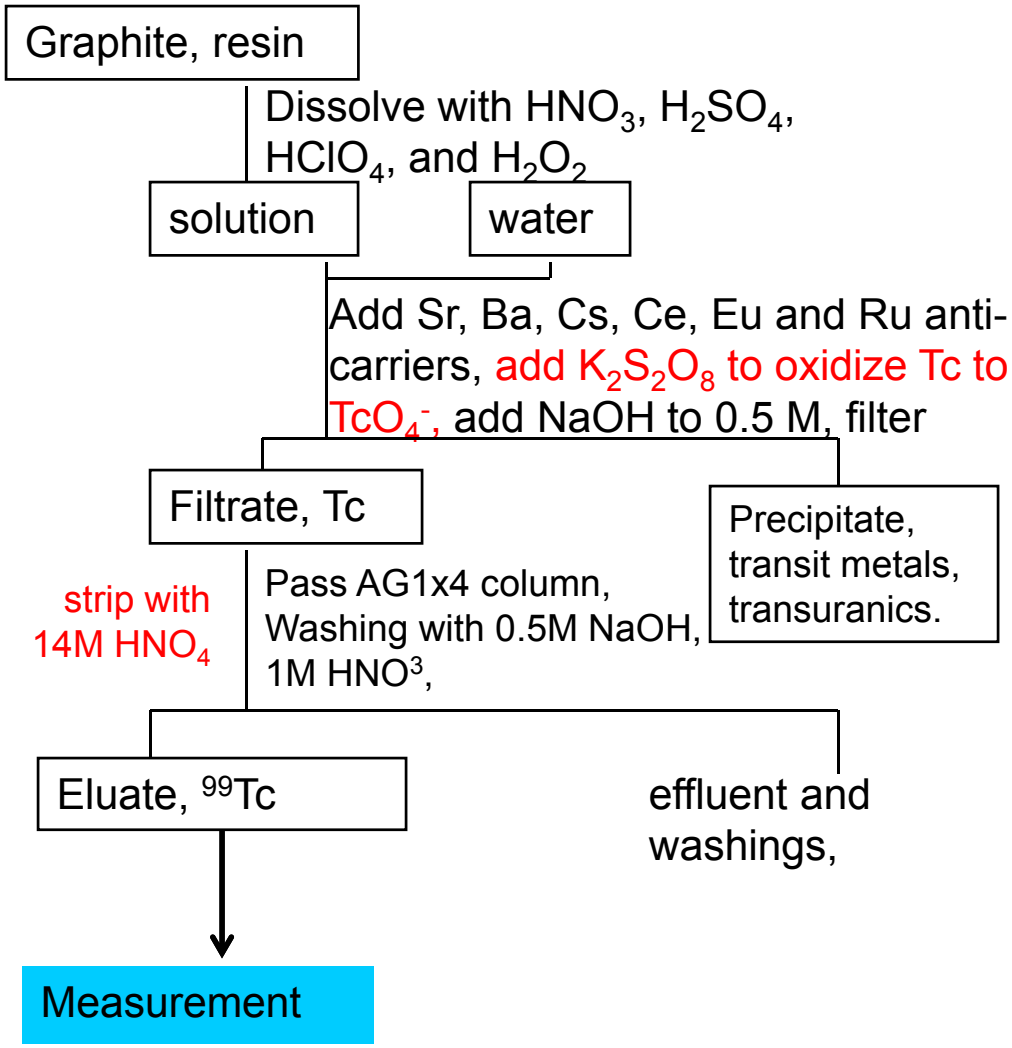


Solution media	Yield of Tc after evaporation at different temperature (%)		
	100 °C	150 °C	200 °C
25% $NH_3 \cdot H_2O$	97.0 ± 2.1	94.6 ± 1.9	71.1 ± 2.6
0.1 M NaOH	98.0 ± 0.8	99.1 ± 1.5	101.3 ± 1.2
0.01 M NaOH	98.4 ± 1.6	97.8 ± 2.3	98.9 ± 2.7

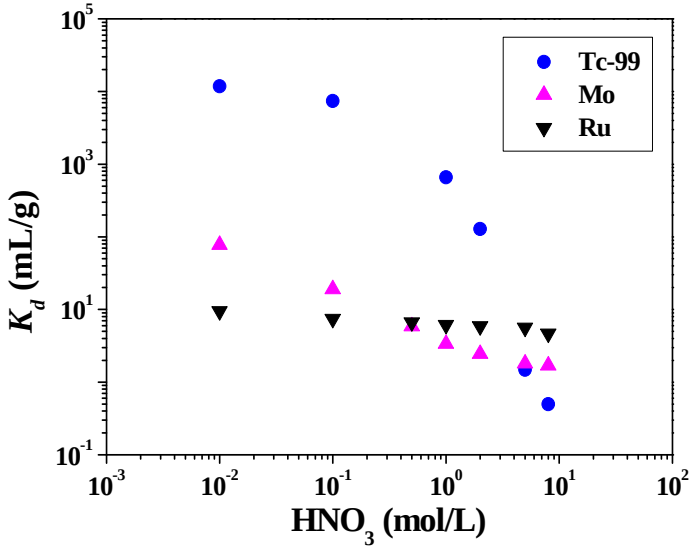
(The sample solutions were evaporated to dryness and then prepared for measurement)

Tc 的化学分离

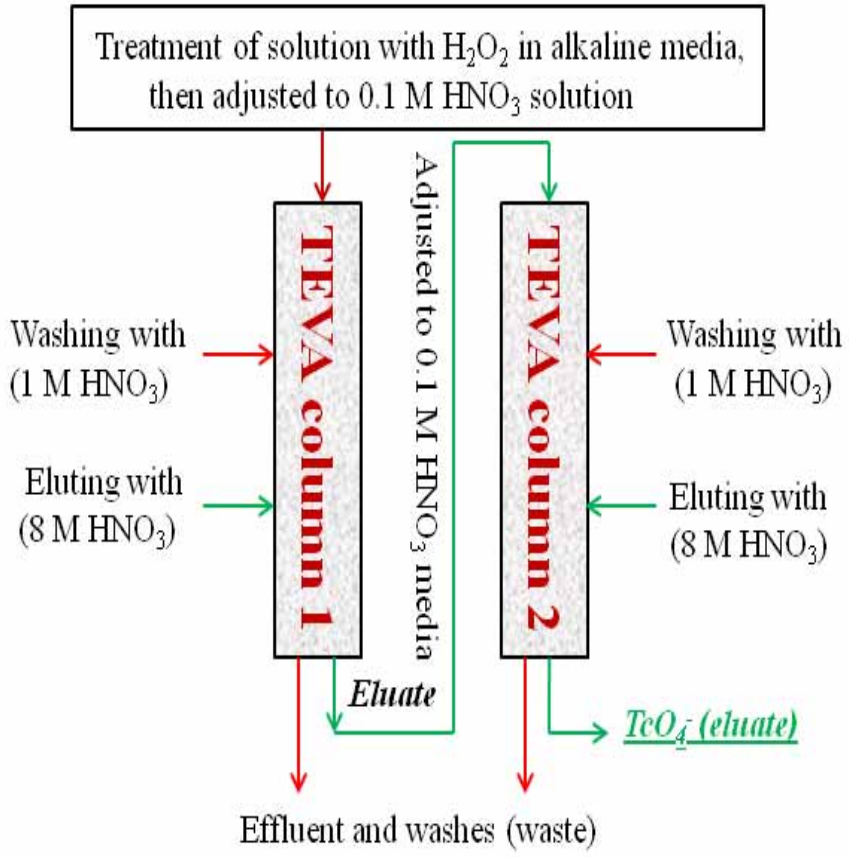
- Adjust Tc to TcO_4^- by $K_2S_2O_8$
- Separate Tc from transition metals, transuranics, Po etc by hydroxides, because TcO_4^- can not be precipitate at high pH.
- TcO_4^- can be tightly absorbed by anion exchange column,washing with NaOH and HNO_3 can remove most of interferring nuclides.
- Not satisfactory for removal Ru, and Mo



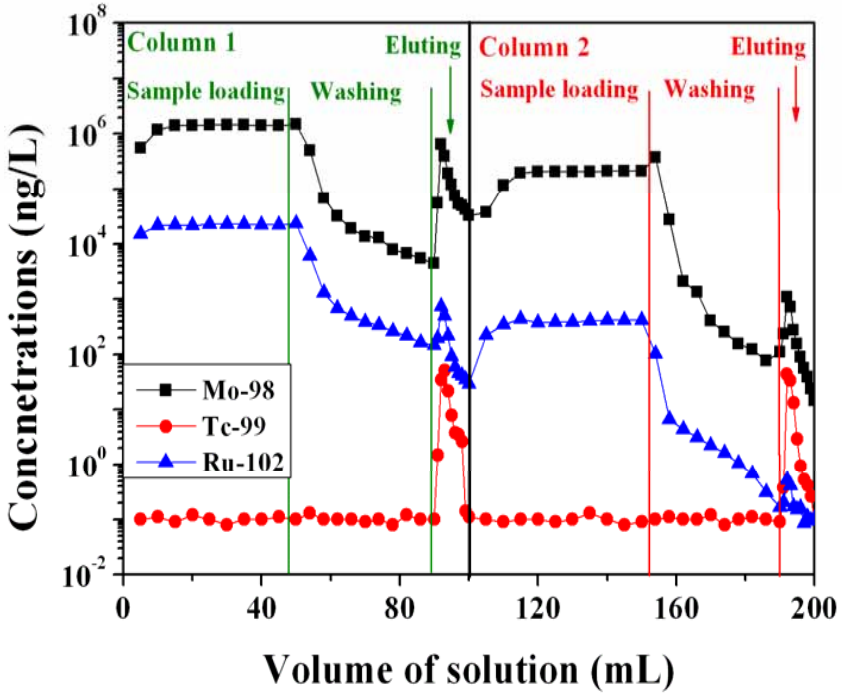
Two TEVA columns separation



- K_d of TcO_4^- decreased with increase of $[HNO_3]$
- Relatively high K_d of MoO_4^{2-} in low $[HNO_3]$ (<1 M)
- RuO_4^{2-} is insensitive with the variation of $[HNO_3]$



Decontamination of Mo and Ru



- One column is not enough
- Two TEVA columns
  1) High chemical yield of Tc
  2) Sufficient removal of Mo and Ru

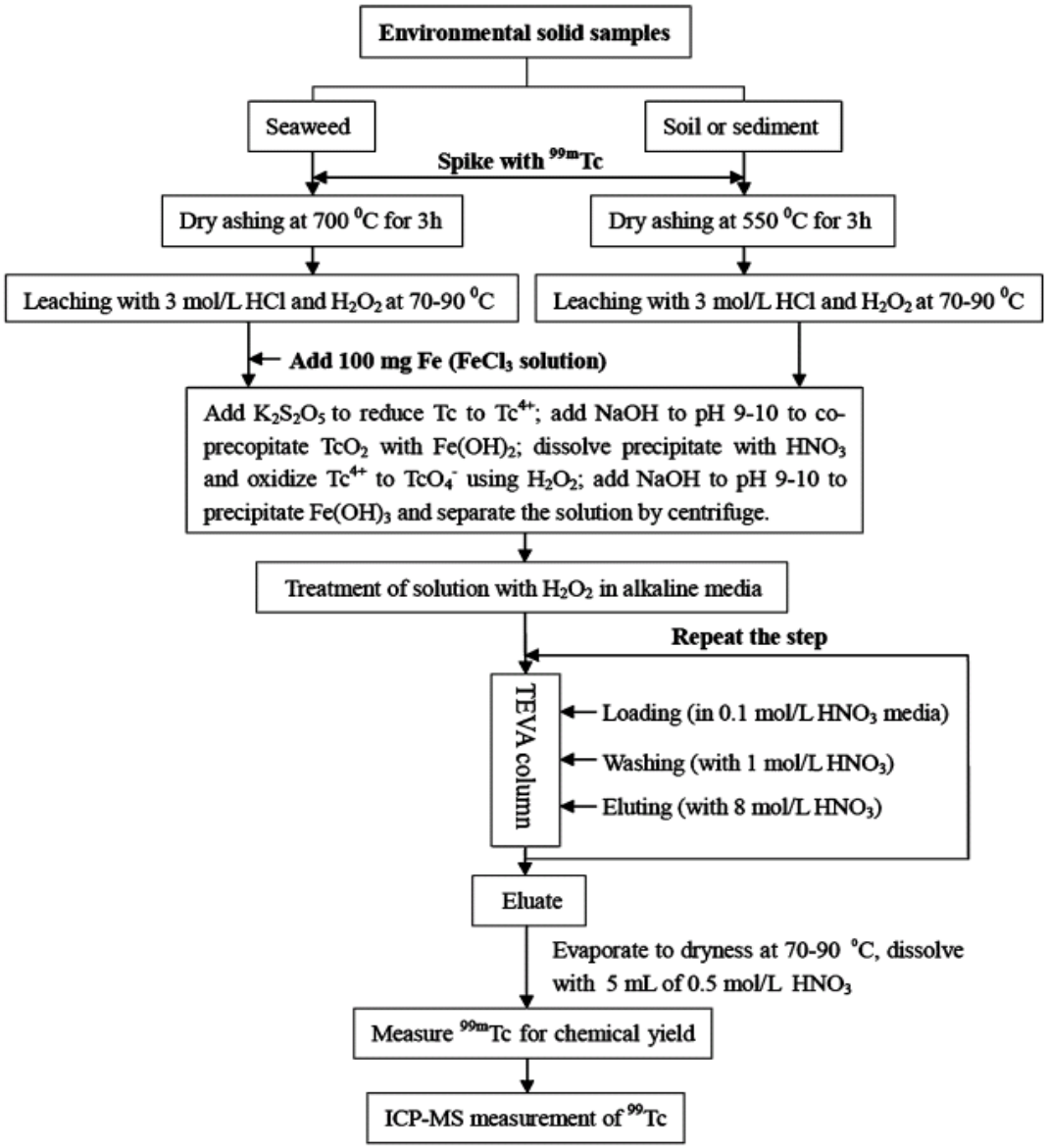
Sample	Size	Chemical yield %	Decontamination factors	
			Mo	Ru
Danish soil	10 g	78-85	$(4.4 \pm 0.3) \times 10^4$	$(1.0 \pm 0.2) \times 10^5$
Danish soil	100 g	65-75	$(2.5 \pm 0.2) \times 10^5$	$(1.1 \pm 0.1) \times 10^5$
Danish soil	500 g	60-68	$(1.2 \pm 0.1) \times 10^6$	$(5.1 \pm 0.3) \times 10^5$

H_2O_2 对Ru在 TEAV柱上吸附的影响

	Volume (mL)	Pre-treatment with H_2O_2 1M NaOH	Pre-treatment with H_2O_2 H_2O	No H_2O_2 0.1M HNO_3
		Ru (ppb)		
Sample loading	4	0.131	0.102	0.07
	8	0.197	0.150	0.091
	12	0.197	0.159	0.089
	16	0.196	0.154	0.092
	20	0.195	0.154	0.089
Washing	4	0.067	0.054	0.045
	8	< 0.001	0.004	0.003
	12	< 0.001	0.004	0.002
	16	< 0.001	0.005	0.002
	20	< 0.001	0.005	0.003
Removal (%)		**98**	**79**	**49**

*** Washing with 0.1 M HNO_3**

Procedure for solid sample analysis



Sample pre-treatment

Tc concentration

Separation and purification

Source preparation

Measurement

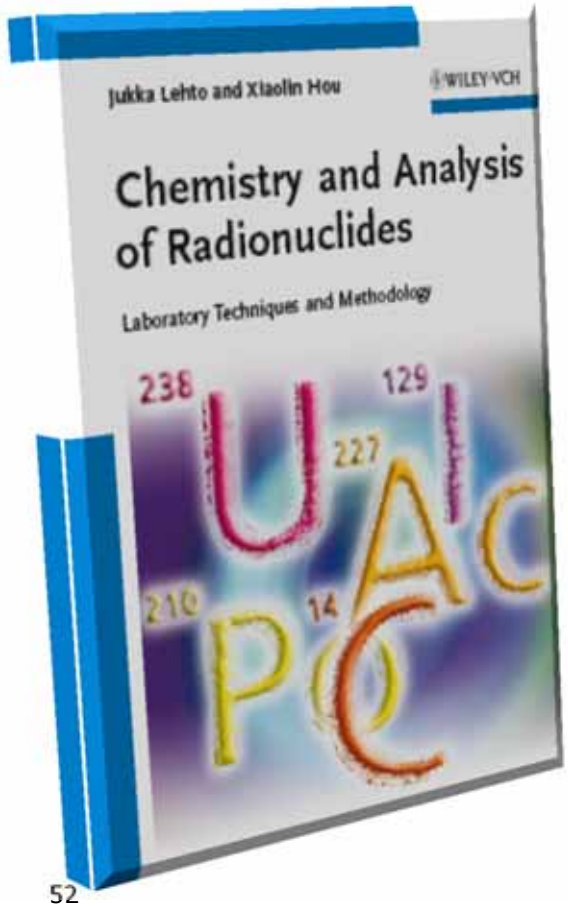
Achievement

	Developed methods	Reported methods
Decontamination factor for Mo	**$4 \times 10^4 \sim 1 \times 10^6$**	$< 5 \times 10^3$
Decontamination factor for Ru	**$1 \times 10^5 \sim 7 \times 10^6$**	$< 1 \times 10^4$
Analytical time (h)	**< 24**	> 30
Recovery (%)	**60-95**	60-90

Chemistry and Analysis of Radionuclides

—Laboratory Techniques and Methodology

Jukka Lehto & Xiaolin Hou



- The comprehensive guide to radioactive elements, written by chemists for chemists
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- Introduces readers to the important laboratory techniques and methodologies in the field
- Includes details on how to determine radionuclides in nuclear waste and in the environment
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