Radiochemcial Analysis for Characterization of Decommissioning waste

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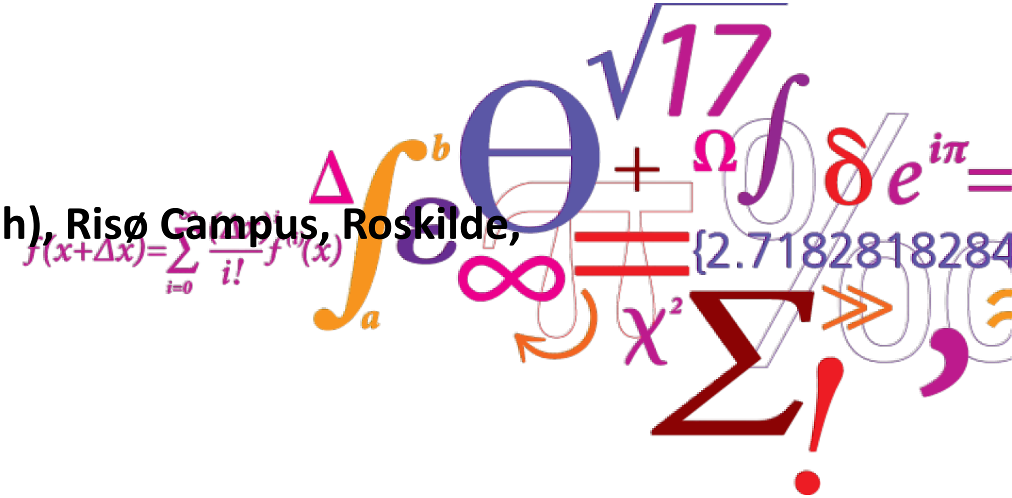
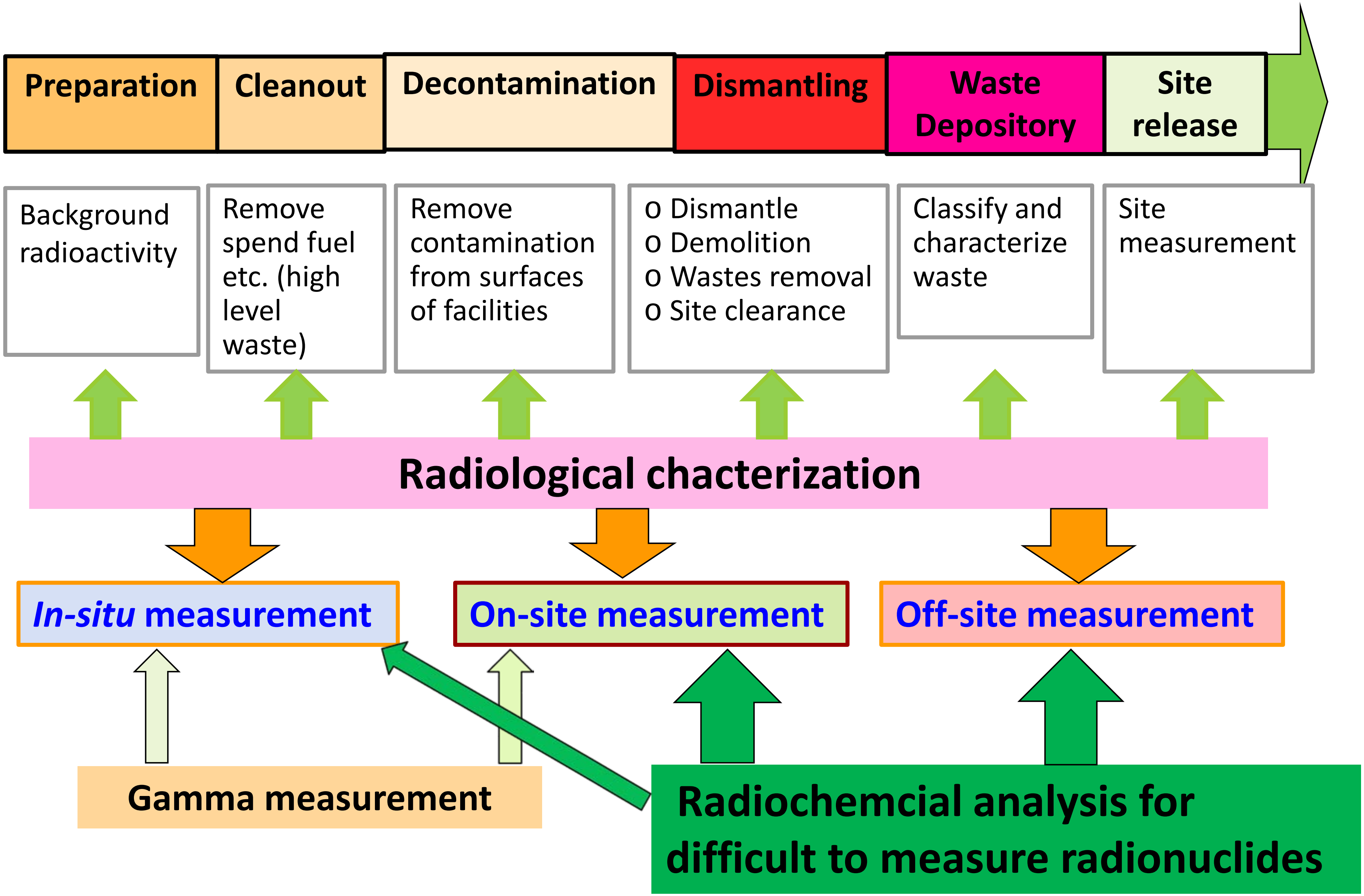


Process of decommissioning nuclear facilities



Preparation

Cleanout

Decontamination

Dismantling

Waste Depository

Site release

Background radioactivity

Remove spend fuel etc. (high level waste)

Remove contamination from surfaces of facilities

- o Dismantle
- o Demolition
- o Wastes removal
- o Site clearance

Classify and characterize waste

Site measurement

Radiological chacterization

***In-situ* measurement**

On-site measurement

Off-site measurement

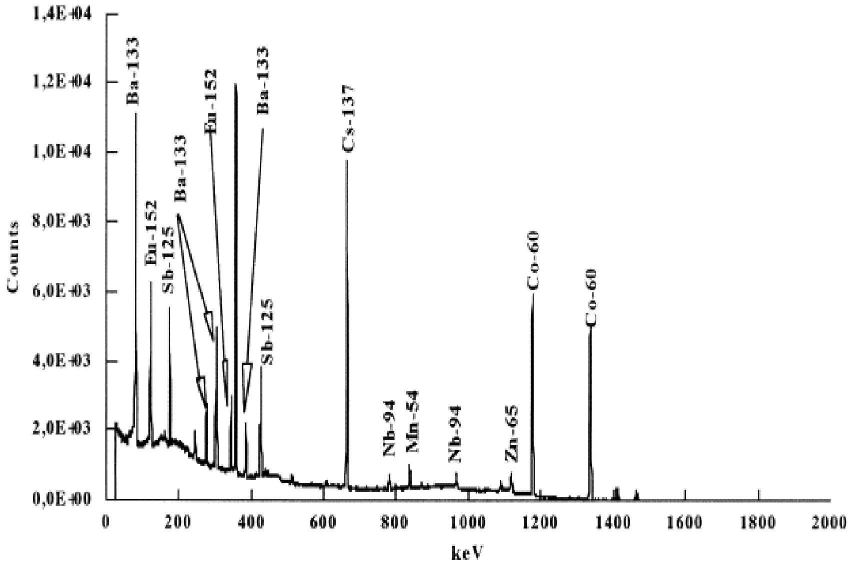
Gamma measurement

Radiochemcial analysis for difficult to measure radionuclides

Major Radionuclides in the nuclear waste

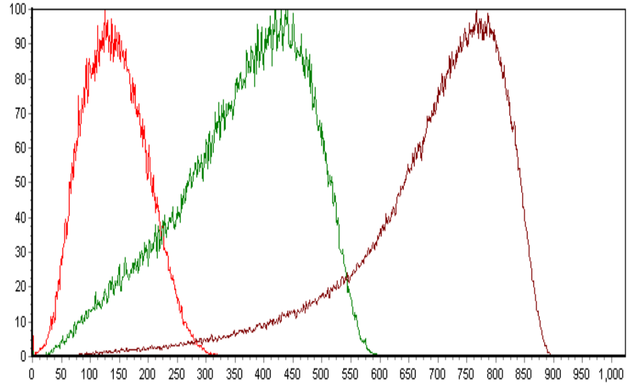
- **γ- radionuclides**

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



Difficult-to-measure radionuclides

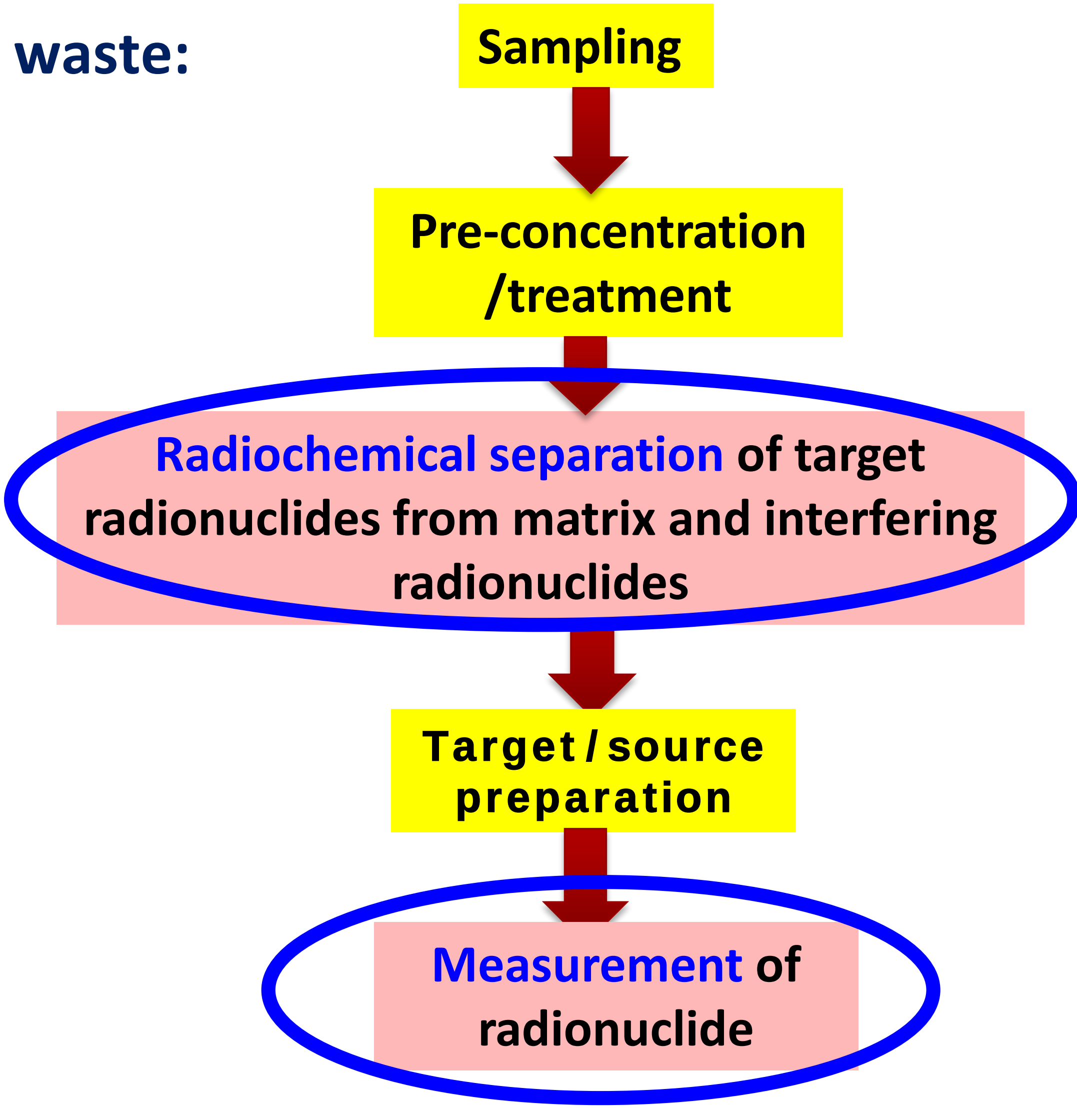
- **β- Emitter**
  - **^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63,59}Ni, ^{93}Zr, ^{93}Mo, ^{90}Sr, ^{99}Tc, ^{129}I, ^{241}Pu, etc.**
- **α- emitter (actinides)**
  - **$^{238-240}$Pu, ^{241}Am, ^{243,244}Cm, ^{237}Np, etc.**



Waste types in decommissioning of nuclear facilities

- **Large volume and common waste:**
  - **Concrete (normal or heavy)**
  - **Graphite (reactor)**
  - **Steel/stainless steel**
  - **Evaporator concentrate**
  - **Ion exchange resin**

- **Unconventional waste**
  - **Non-ferrous metals (Al, Pb, Cu)**
  - **Zirconium and its alloy**
  - **Mercury**
  - **Plastics (PCB, PE, etc.)**
  - **Oil**
  - **Desiccant (silica gel, CaO, etc.)**



Sampling

Pre-concentration /treatment

Radiochemical separation of target radionuclides from matrix and interfering radionuclides

Target / source preparation

Measurement of radionuclide

Challenges on radiological characterization of decommissioning waste

- Complicated and unknown components of sample matrix
- Instability of the volatile radionuclides in sampling, storage and pre-treatment
- Difficulties in decomposition and pretreatment of some sample matrix
- Different species of critical radionuclides related to their different mobility
- High radiation exposure and large number of samples
- Lack of reliable method for accurate determination of some radionuclides
- No standards for some radionuclides (e.g. ^{93}Zr, ^{93}Mo, etc.)

Strategies on radiochemical analysis of decommissioning waste

- Reliable radiochemcial analytical methods for difficult to measure radionuclides (^{41}Ca,^{55}Fe, ^{63}Ni, ^{93}Mo, ^{93}Zr, actinides)
- Methods for accurate determination of volatile radionuclides (^{3}H, ^{14}C, ^{36}Cl, ^{99}Tc, ^{129}I)
- Rapid methods for separation and analysis of difficult to measure radionuclides --Automated approaches
- Sensitive measurement of low level and long-lived radionuclides using mass spectrometric techniques (ICP-MS & AMS)
- Speciation analysis of important radionuclides in view of depository of waste (mobile species, e.g. ^{3}H, ^{14}C, ^{99}Tc)

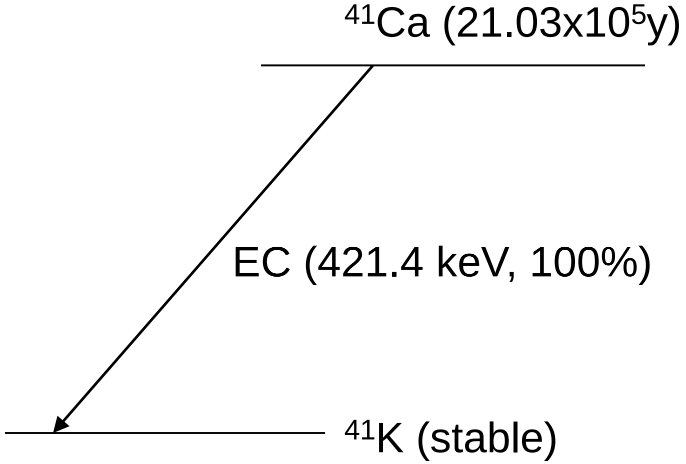
Radiochemcial analysis for difficult to measure radionuclides

- ^{41}Ca in concrete
- ^{55}Fe and ^{63}Ni in metals, concrete, graphite, etc.
- ^{90}Sr in exchange resin, sludge, metals, etc.
- Actinides ($^{238,\ 239,240,241}$Pu, ^{237}Np, ^{241}Am, $^{233,\ 234}$Cm)
- ^{93}Mo, ^{93}Zr in metals and exchange resin
- ^{135}Cs, ^{79}Se, ^{126}Sn, ^{147}Pm, ^{151}Sm in metal, ion exchange resin, etc.

^{41}Ca in the concrete

Activation products of calcium isotopes

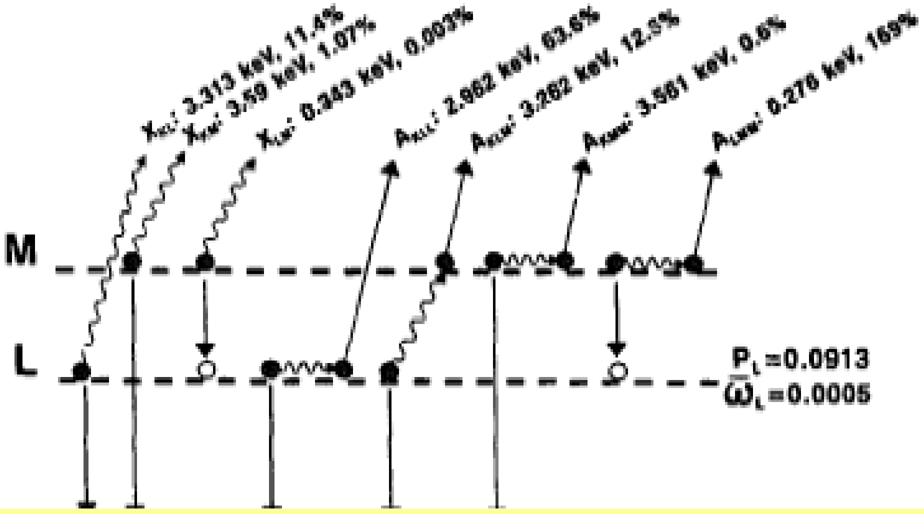
Nuclide	Target isotope Aboundance %	Reaction	Cross section, bar	Half life	Decay
^{41}Ca	96.94	^{40}Ca(n, γ)^{41}Ca	0.41	1.03×10^{5} y	EC
^{45}Ca	2.086	^{44}Ca(n, γ)^{45}Ca	0.84	162.7 d	β-
^{47}Ca	0.004	^{46}Ca(n, γ)^{47}Ca	0.7	4.54 d	β, γ
^{49}Ca	0.187	^{48}Ca(n, γ)^{49}Ca	1.0	8.72 min.	β, γ



^{41}Ca (21.03x10^{5}y)

EC (421.4 keV, 100%)

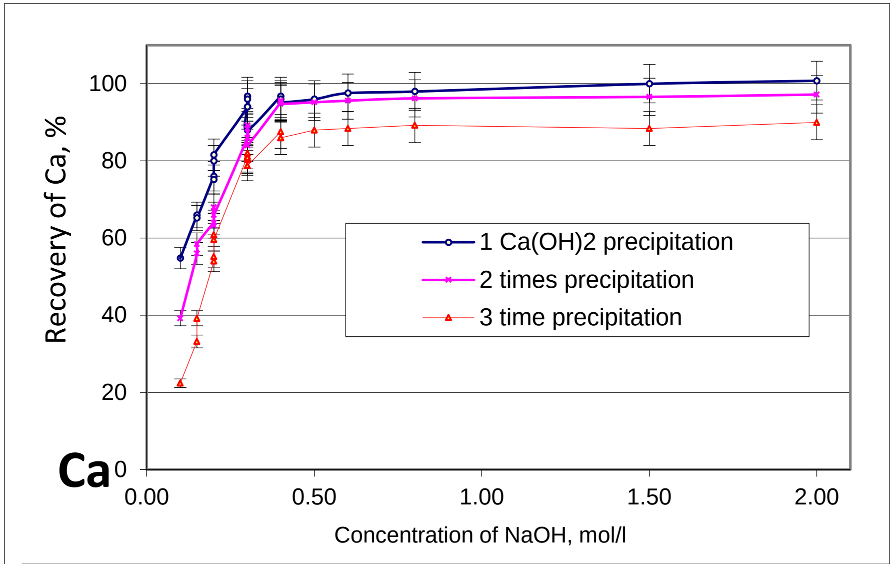
^{41}K (stable)



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

Separation of Ca from Ba, Sr, Ra by hydroxide

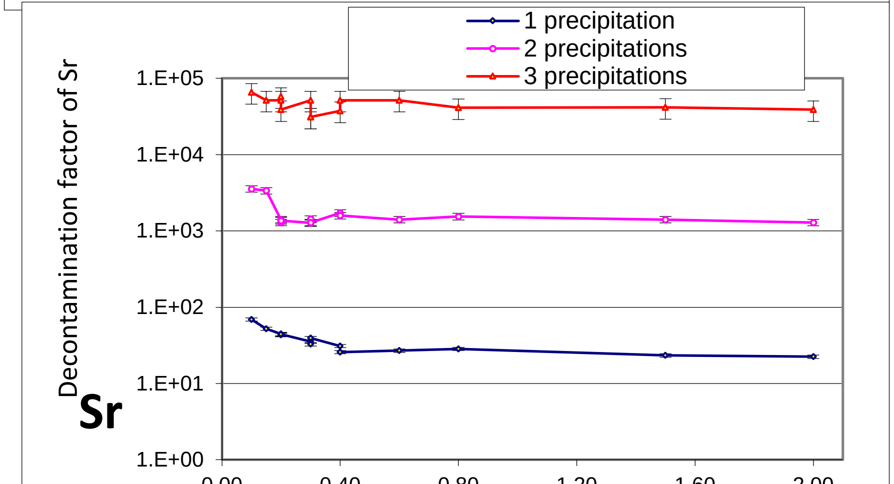
- **Separation of Sr from Ca by $Ca(OH)_2$ precipitation**
  - **$Ca(OH)_2$: insoluble, Ksp = 5.2×10^{-6}**
  - **$Sr(OH)_2$ and $Ba(OH)_2$: Soluble in alkine solution**

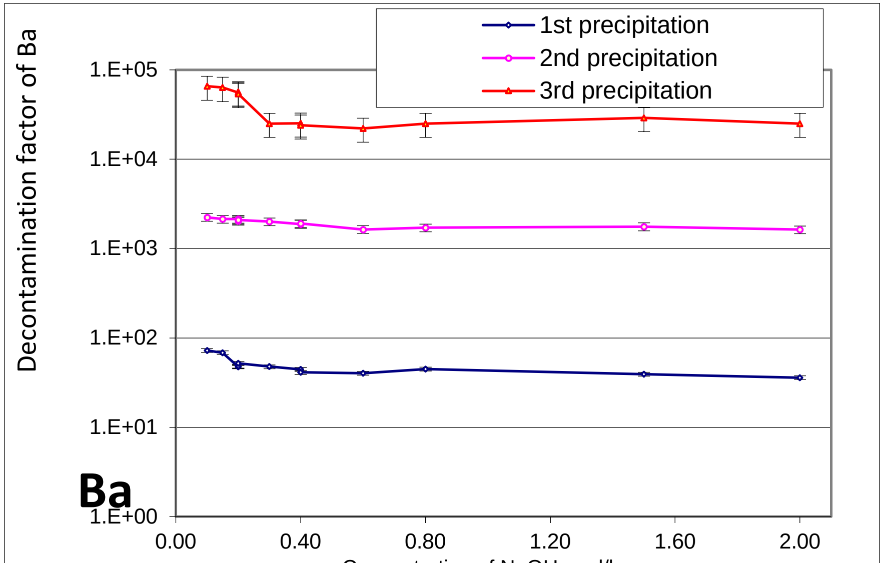


Precipitate Ca as $Ca(OH)_2$ at 0.5 –0.8 M NaOH, repeat 3 times

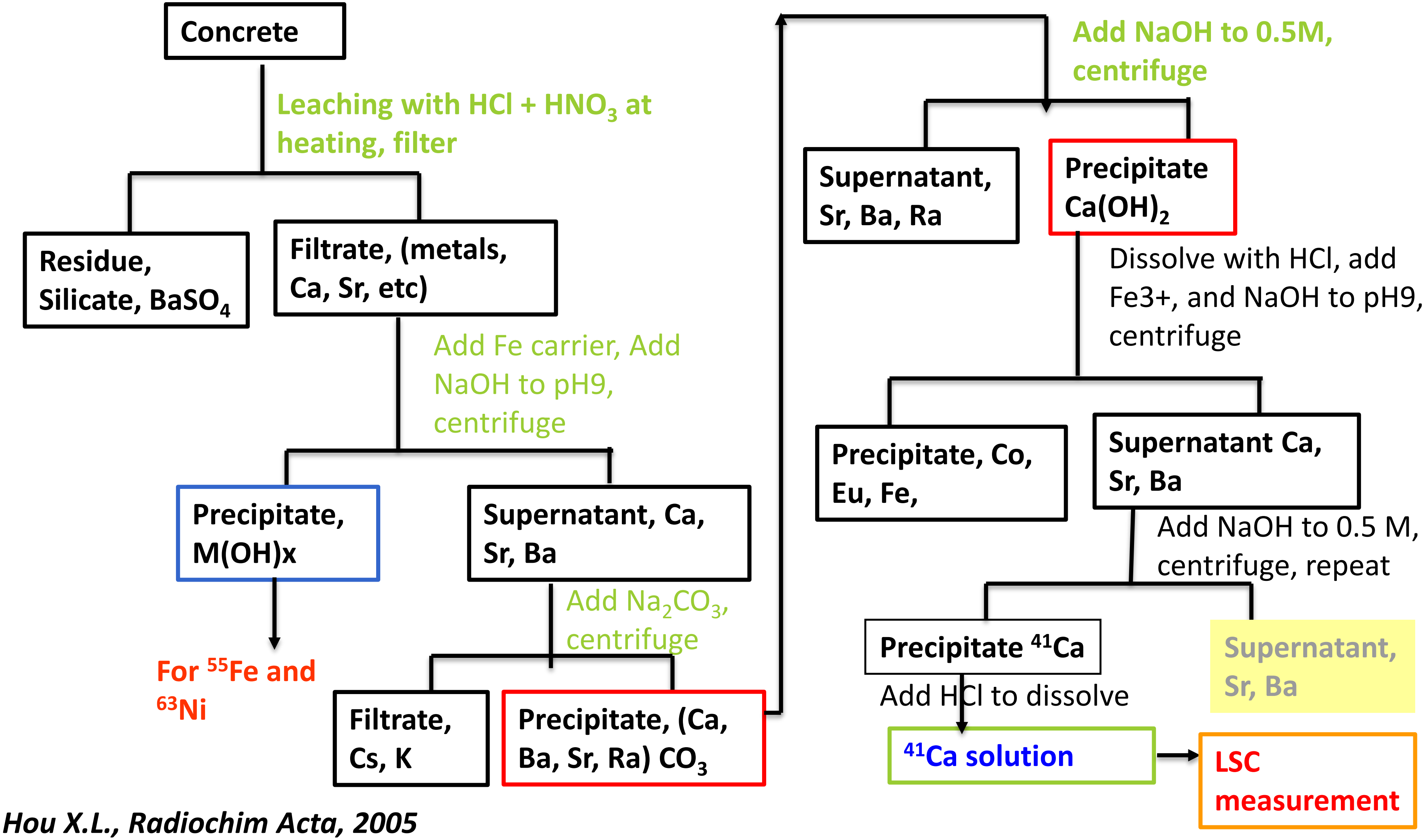
✓ Ca recovery: 85%

✓ Decontamination factors for Sr and Ba: > $5x10^4$





Procedure for determination of ^{41}Ca



Concrete

Leaching with HCl + HNO_3 at heating, filter

Residue, Silicate, $BaSO_4$

Filtrate, (metals, Ca, Sr, etc)

Add Fe carrier, Add NaOH to pH9, centrifuge

Precipitate, M(OH)x

For ^{55}Fe and ^{63}Ni

Supernatant, Ca, Sr, Ba

Add Na_2CO_3, centrifuge

Filtrate, Cs, K

Precipitate, (Ca, Ba, Sr, Ra) CO_3

Add NaOH to 0.5M, centrifuge

Supernatant, Sr, Ba, Ra

Precipitate $Ca(OH)_2$

Dissolve with HCl, add Fe3+, and NaOH to pH9, centrifuge

Precipitate, Co, Eu, Fe,

Supernatant Ca, Sr, Ba

Add NaOH to 0.5 M, centrifuge, repeat

Precipitate ^{41}Ca

Supernatant, Sr, Ba

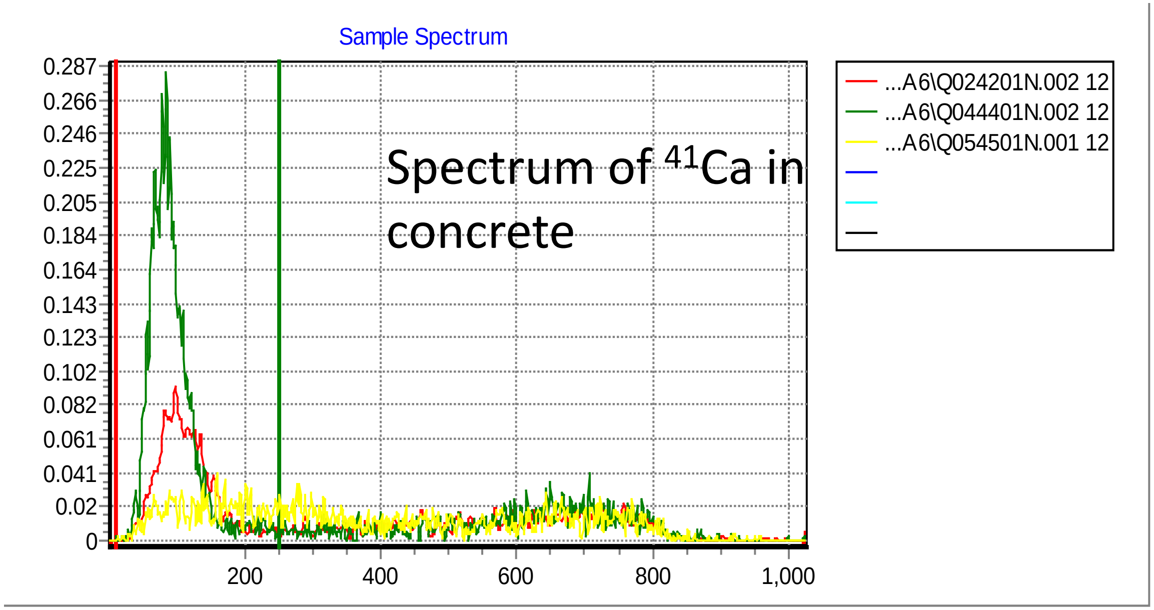
Add HCl to dissolve

^{41}Ca solution

LSC measurement

Hou X.L., Radiochim Acta, 2005

^{41}Ca in heavy concrete

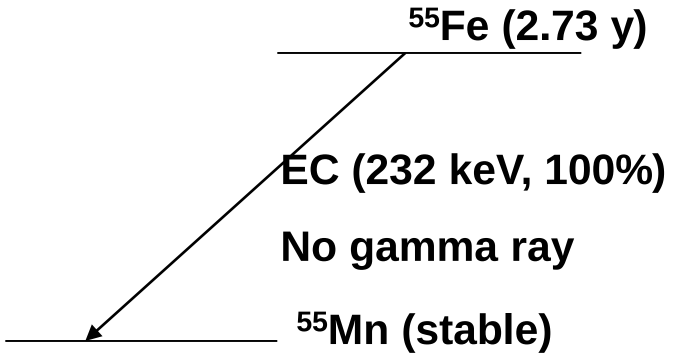


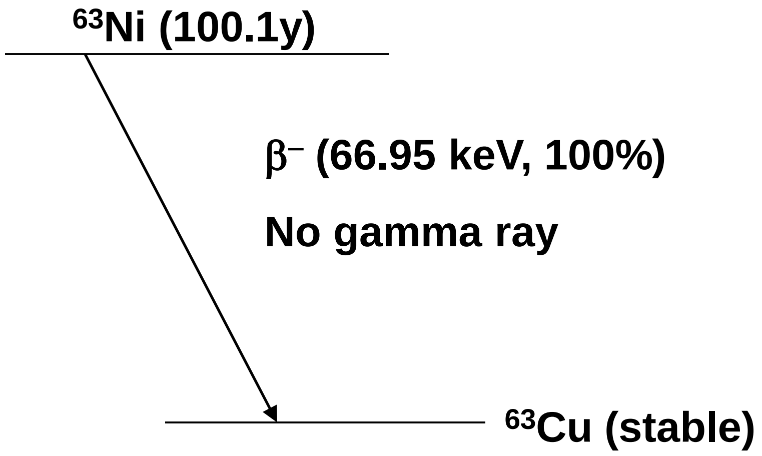
Spectrum of ^{41}Ca in concrete

- **Good decontamination for interferences: >10^5**
- **Good chemical yields for ^{41}Ca: 80-90%**
- **Good detection limit for ^{41}Ca: 0.020 Bq**

Hou X.L., Radiochim. Acta, 2005

^{63}Ni and ^{55}Fe

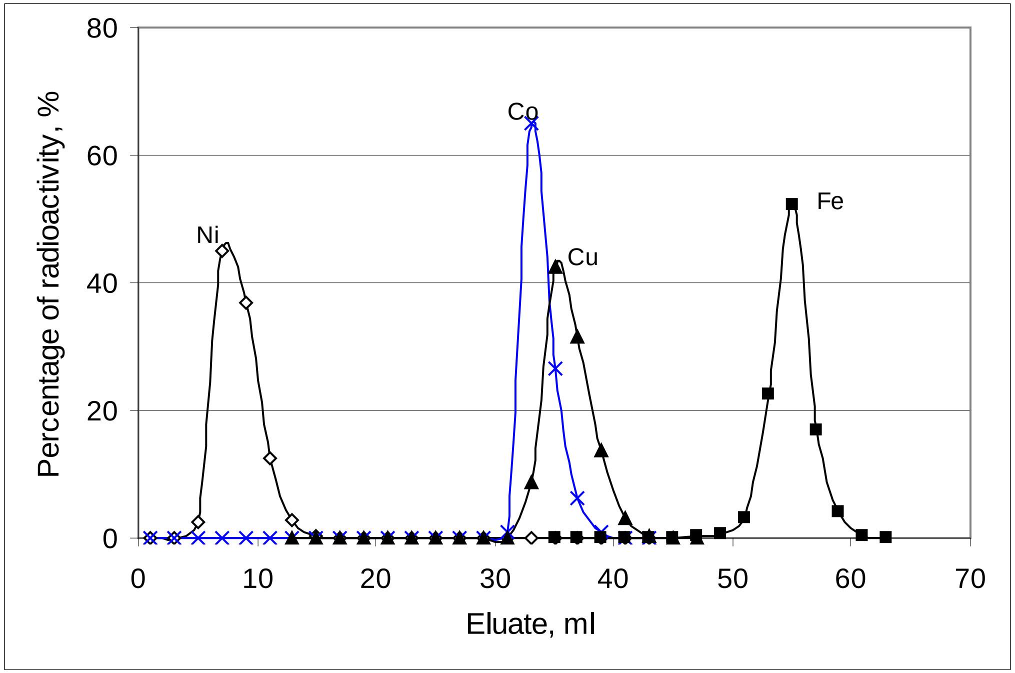




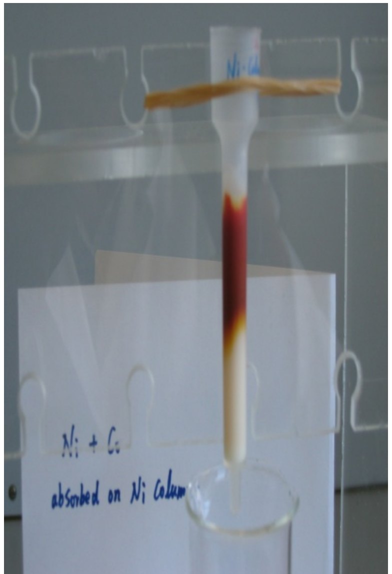
- ^{55}Fe:
  - ^{54}Fe(n, g)^{55}Fe (s=2.3 b; h_{54Fe}=5.85%)
  - ^{56}Fe(n, 2n)^{55}Fe, (h_{56Fe}=91.75%)
- ^{63}Ni:
  - ^{62}Ni(n, γ)^{63}Ni (s=14.5 b; h_{62Ni}=3.63%)
  - ^{63}Cu(n, p)^{63}Ni, (h_{63Cu}=69.17%)

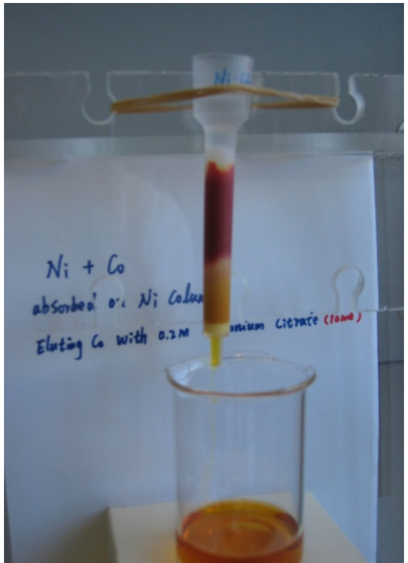
Major Challenge:
High ^{60}Co and ^{58}Co activity in most samples

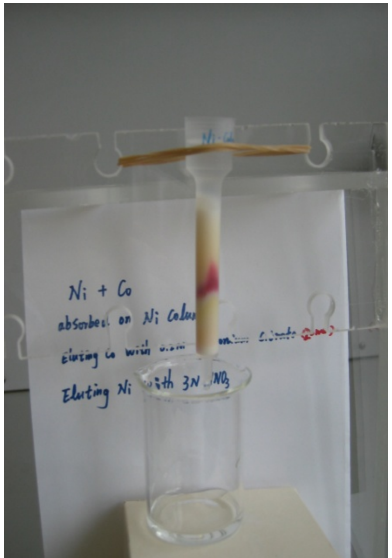
Separation of Ni from Co, Eu, etc. using ion exchange chromatography and Ni column (DMG)

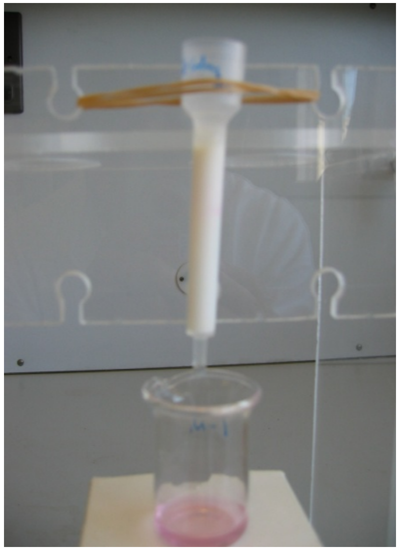


Element	Recovery or decontamination factor
Ni^{2+}	> 98.5%
Fe^{3+}	$>10^6$
Co^{2+}	$>10^6$
Ba^{2+}	$>10^6$
Eu^{3+}	$>10^6$
Cs^{+}	$>10^6$
Sr^{2+}	$>10^6$

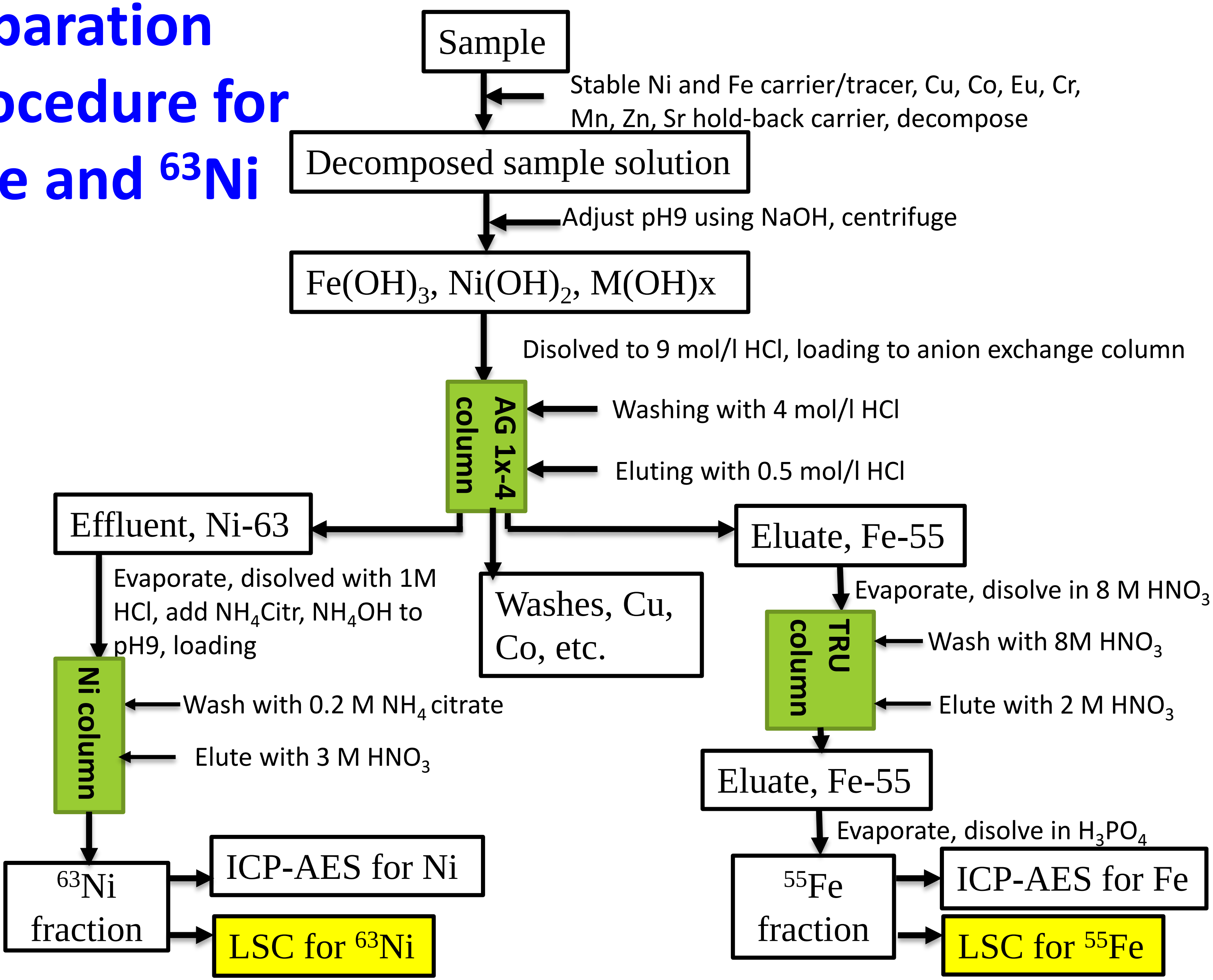








Separation procedure for ^{55}Fe and ^{63}Ni



Sample

Stable Ni and Fe carrier/tracer, Cu, Co, Eu, Cr, Mn, Zn, Sr hold-back carrier, decompose

Decomposed sample solution

Adjust pH9 using NaOH, centrifuge

$Fe(OH)_3$, $Ni(OH)_2$, $M(OH)x$

Disolved to 9 mol/l HCl, loading to anion exchange column

AG 1x-4 column

Washing with 4 mol/l HCl

Eluting with 0.5 mol/l HCl

Effluent, Ni-63

Evaporate, disolved with 1M HCl, add NH_4Citr, NH_4OH to pH9, loading

Ni column

Wash with 0.2 M NH_4 citrate

Elute with 3 M HNO_3

^{63}Ni fraction

ICP-AES for Ni

LSC for ^{63}Ni

Washes, Cu, Co, etc.

Eluate, Fe-55

Evaporate, disolve in 8 M HNO_3

TRU column

Wash with 8M HNO_3

Elute with 2 M HNO_3

Eluate, Fe-55

Evaporate, disolve in H_3PO_4

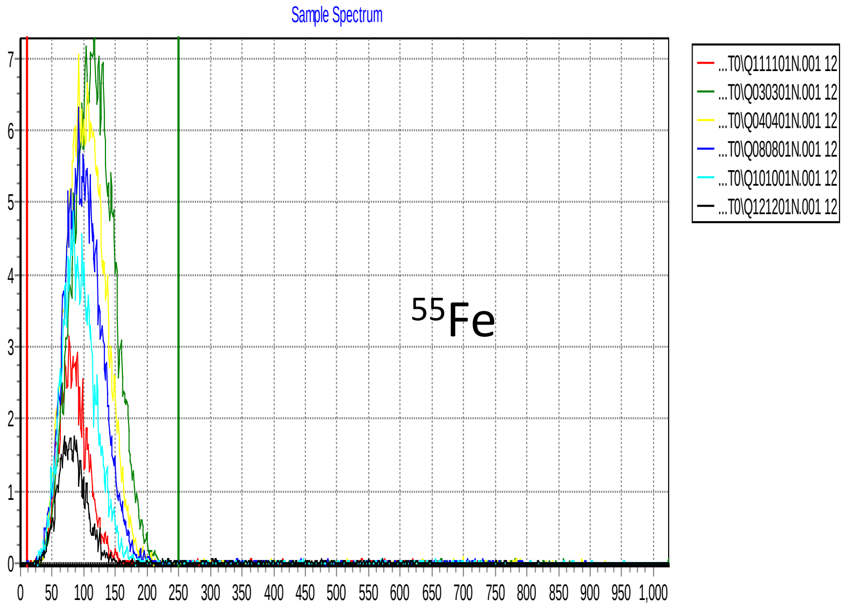
^{55}Fe fraction

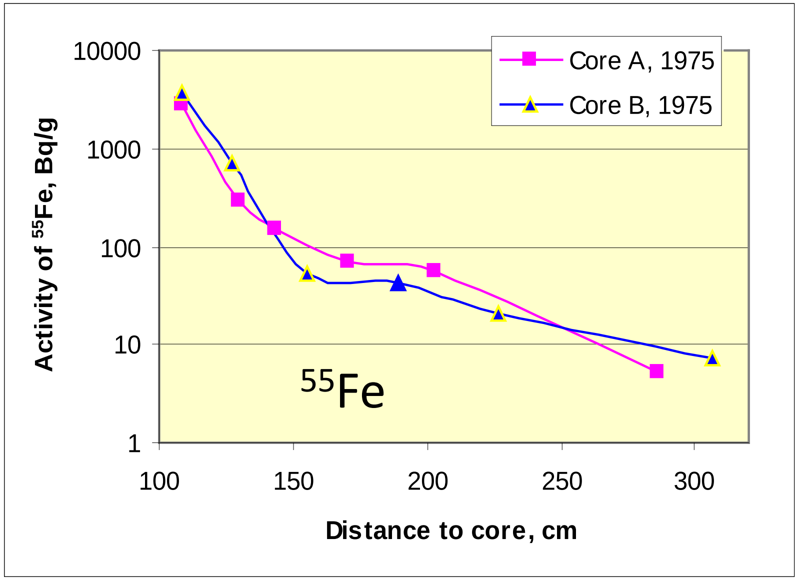
ICP-AES for Fe

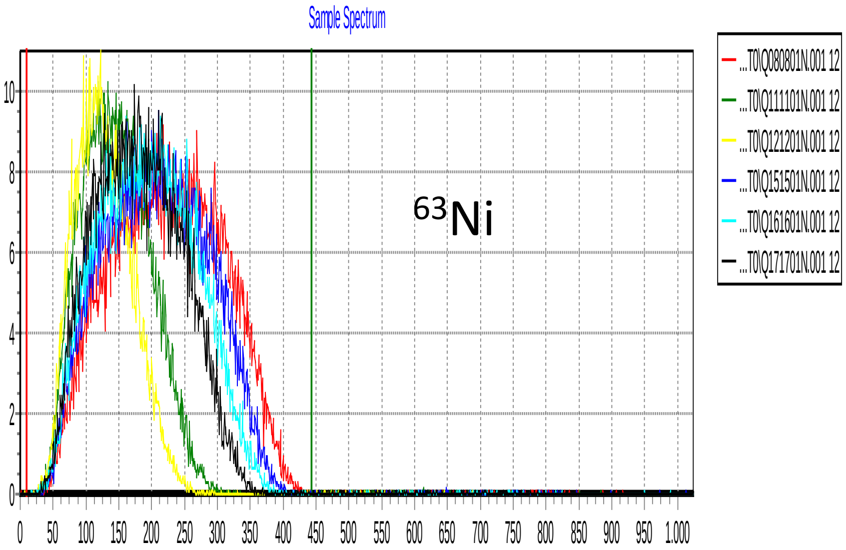
LSC for ^{55}Fe

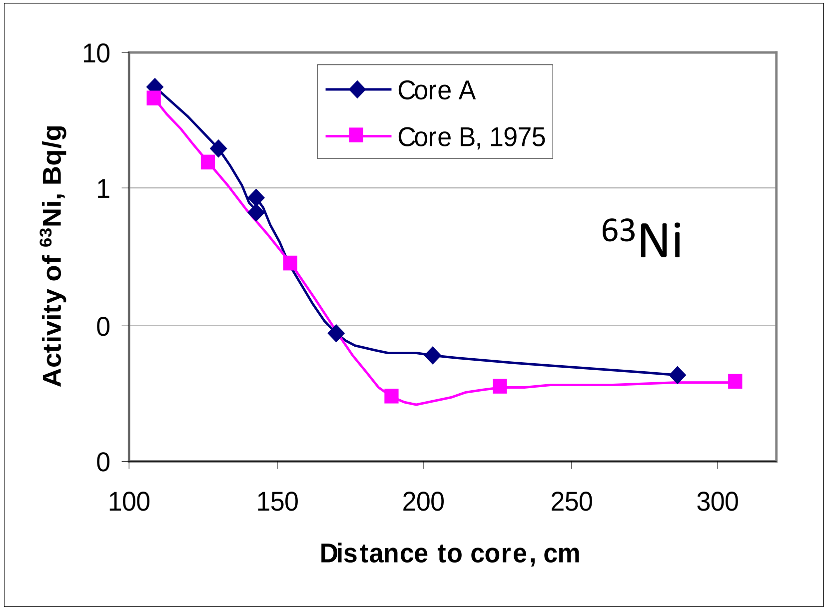
Hou, et al. Anal. Chim. Acta, 2005

^{55}Fe and ^{63}Ni in concrete core from DR-3









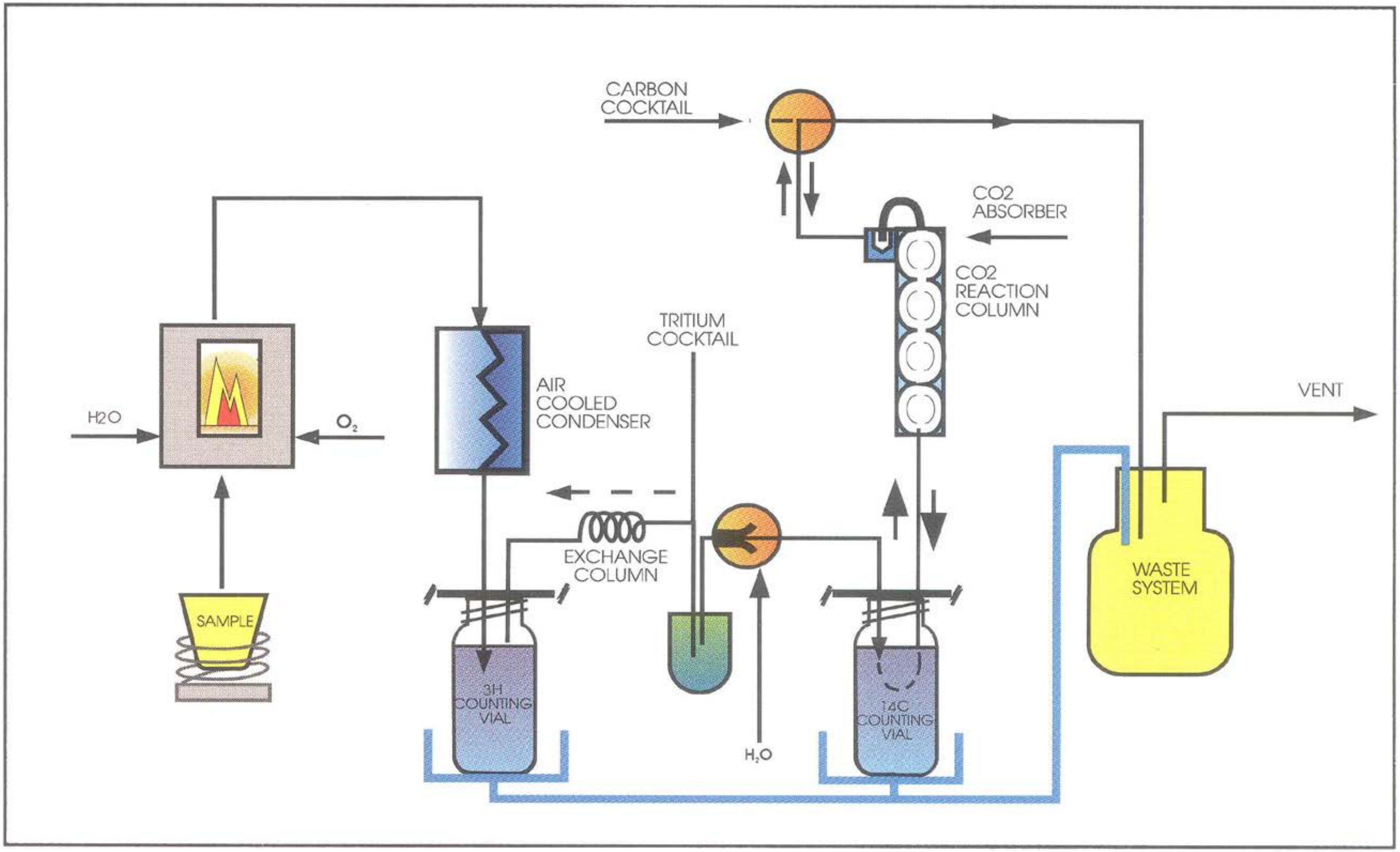
Radiochemcial analysis of volatile radionuclides

- ^{3}H and ^{14}C in solid waste (metals, concrete, graphite, etc.)
- ^{36}Cl in metals, graphite, concrete, etc.
- ^{129}I in solid waste (exchange resin, evaporator, etc.)
- ^{99}Tc in liquid and solid waste
- $^{103, 106}$Ru, ^{210}Po, etc.

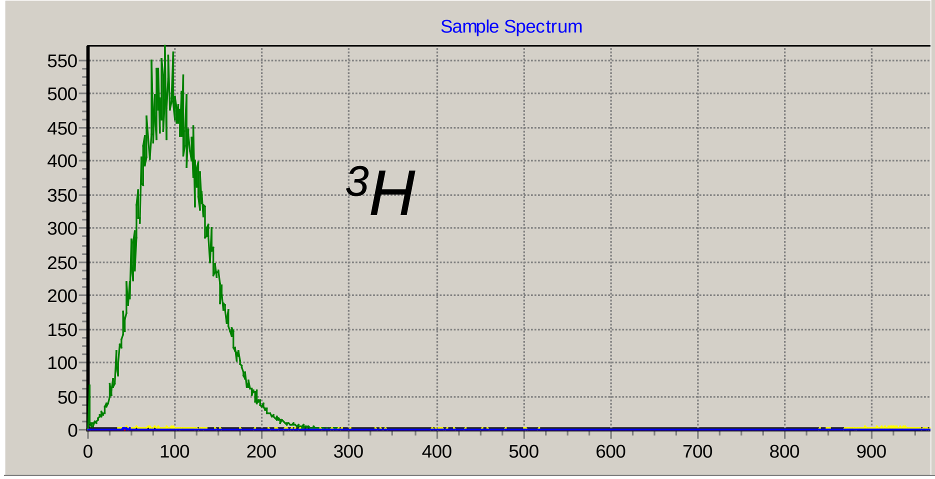
Main challenge: loss of radionuclides during sampling, pre-tratement and separation.

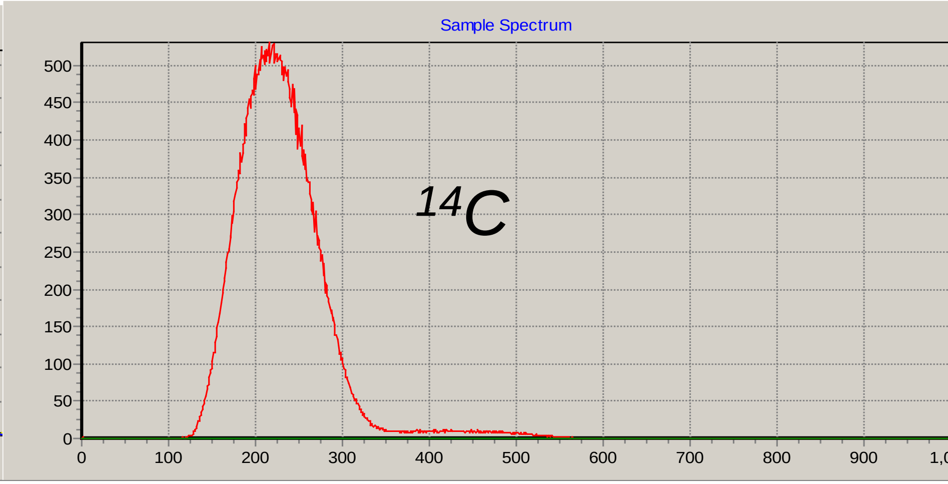
Stratege: Application of combustion for their separation

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



^{3}H and ^{14}C measurement



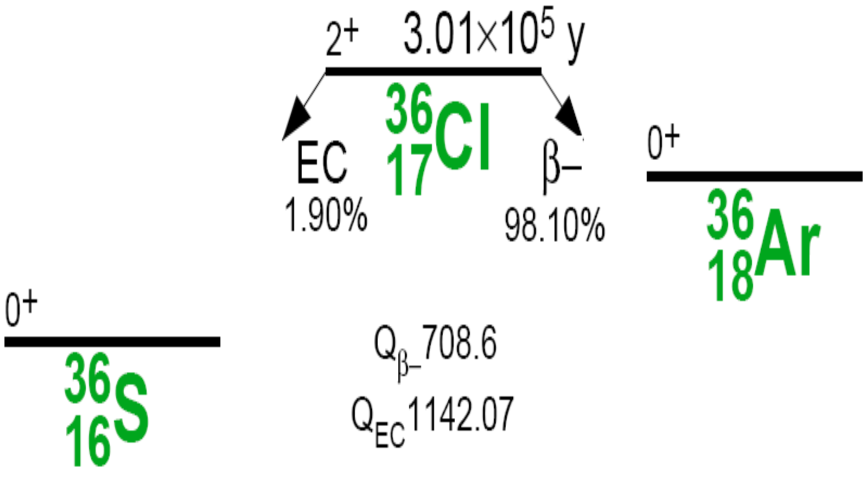


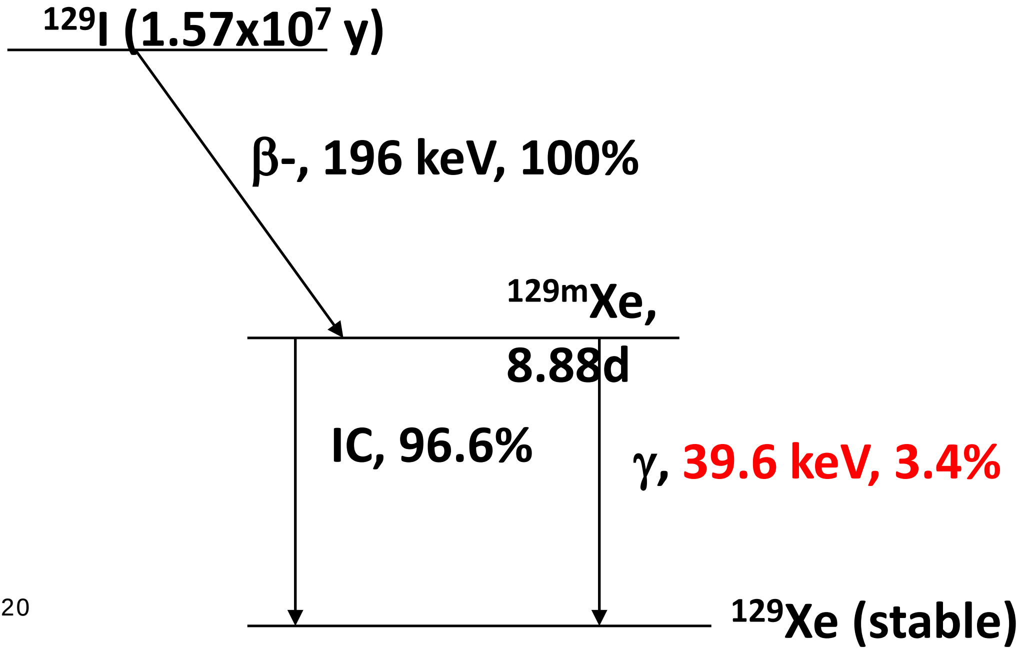
No other impurity nuclides, no cross contamination.

- **Analytical time: 2 min/sample + counting time**
- **Detection limits:**
  - **^{14}C: 0.1 Bq**
  - **^{3}H: 0.15 Bq**

Hou., Appl. Rad. Iso., 2005
Hou, JRNC, 2008

^{36}Cl and ^{129}I

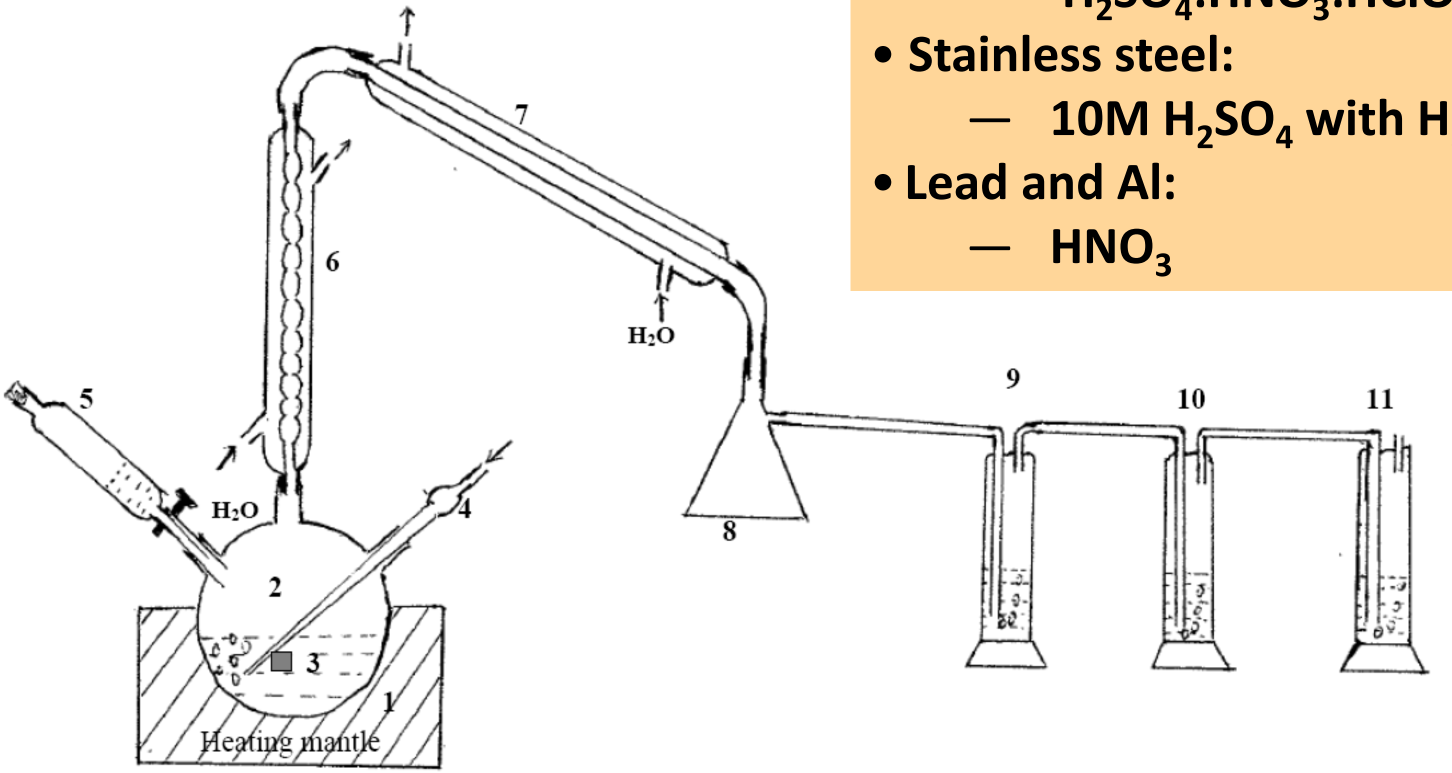




- Iodine and chlorine are volatile, easy to be lost during heating or by oxidizing.
- ^{36}Cl and ^{129}I are long-lived radionuclides (0.3 My, and 15.7 My)
- Iodine and chlorine are high mobile in environment.
- Iodine and chlorine are biophilic.

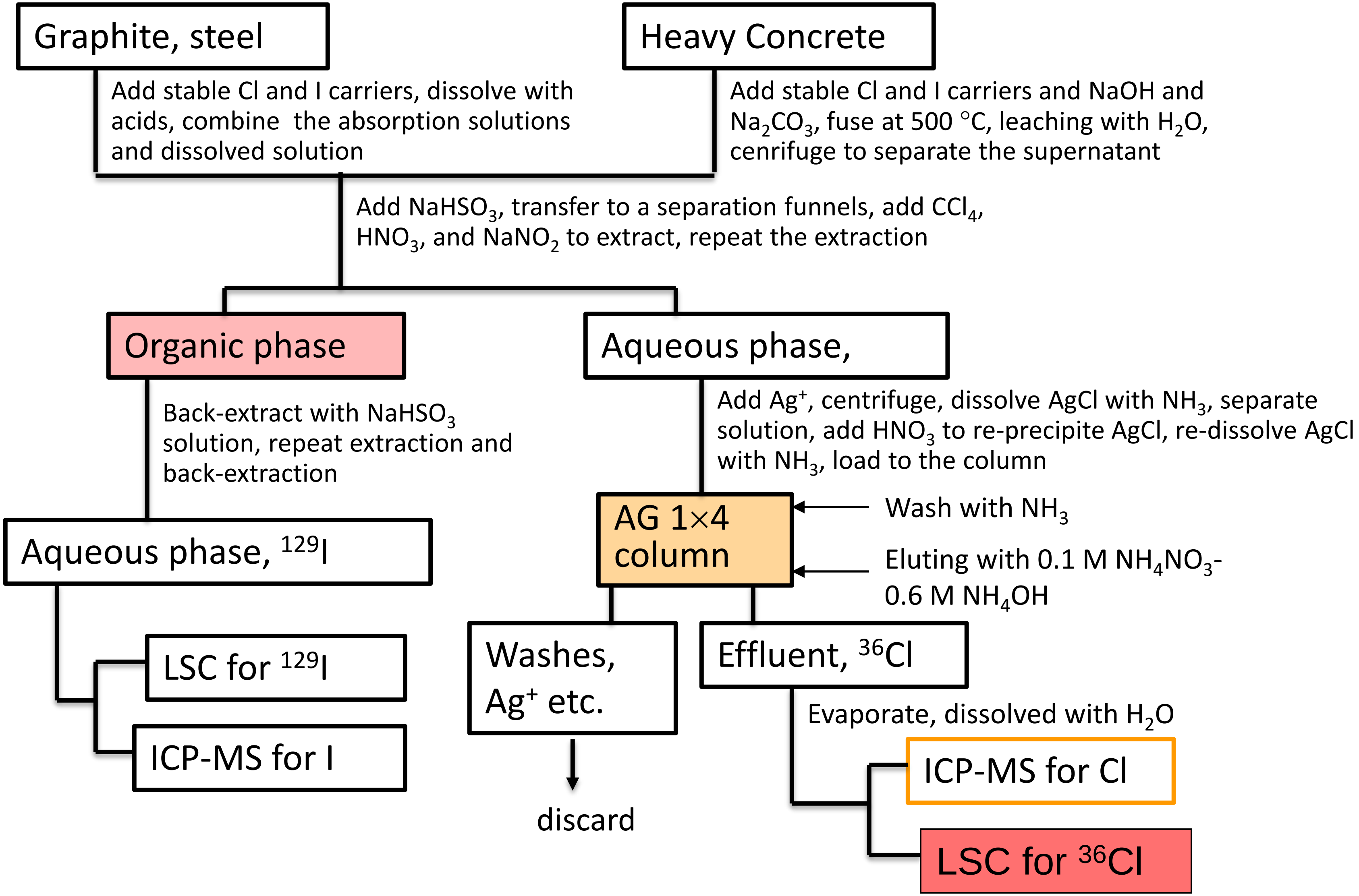
Acid digestion system of for separation of ^{36}Cl and ^{129}I

- Graphite: mixed acids,
  - H_2SO_4:HNO_3:$HClO_4$ =15:4:1
- Stainless steel:
  - 10M H_2SO_4 with H_3PO_4
- Lead and Al:
  - HNO_3



1-Heating mantle; 2-three-necked flask; 3-sample in acid mixture; 4-bubbling tube; 5-separating funnel for adding acids; 6,7-reflux condenser; 8- receiver; 9-wash bottle containing water; 10, 11-absorption bottles containing 0.4 mol/l NaOH

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



Graphite, steel

Add stable Cl and I carriers, dissolve with acids, combine the absorption solutions and dissolved solution

Heavy Concrete

Add stable Cl and I carriers and NaOH and Na_2CO_3, fuse at 500 °C, leaching with H_2O, cenrifuge to separate the supernatant

Add $NaHSO_3$, transfer to a separation funnels, add CCl_4, HNO_3, and $NaNO_2$ to extract, repeat the extraction

Organic phase

Back-extract with $NaHSO_3$ solution, repeat extraction and back-extraction

Aqueous phase, ^{129}I

LSC for ^{129}I

ICP-MS for I

Aqueous phase,

Add Ag^+, centrifuge, dissolve AgCl with NH_3, separate solution, add HNO_3 to re-precipite AgCl, re-dissolve AgCl with NH_3, load to the column

AG 1×4 column

Wash with NH_3

Eluting with 0.1 M NH_4NO_3-0.6 M NH_4OH

Washes, Ag^+ etc.

discard

Effluent, ^{36}Cl

Evaporate, dissolved with H_2O

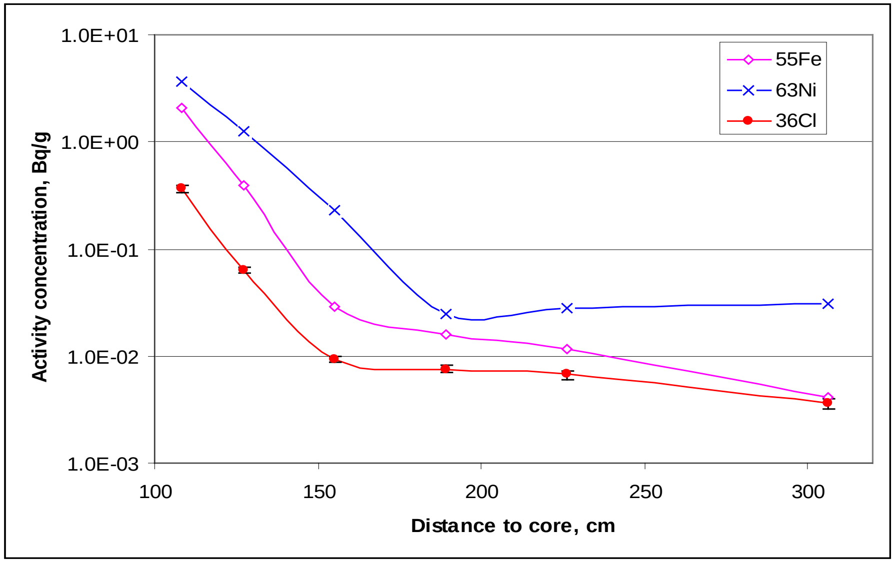
ICP-MS for Cl

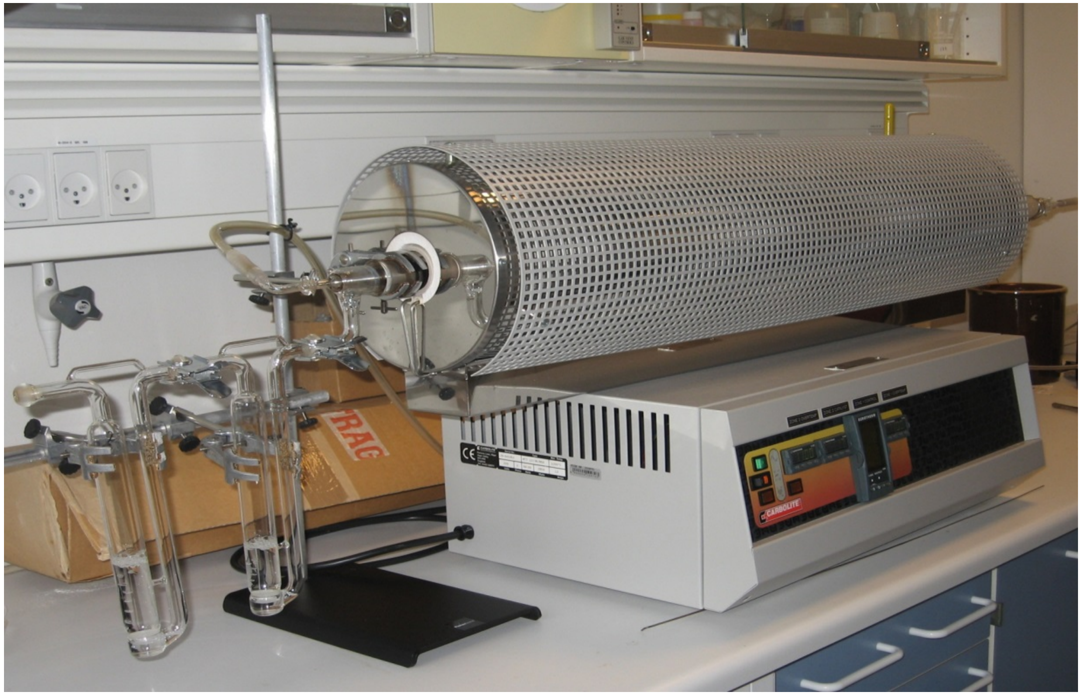
LSC for ^{36}Cl

Hou et al., Anal. Chem., 2007

Determination of ^{36}Cl

- Recovery of Cl: >70%
- Decontamination factors for most of radionculides: >10^6
- Detection limit using LSC : 14 mBq





Combustion method for solid samples: concrete, graphite, metals, resin, sludge, etc.

- ✓ ^{3}H
- ✓ ^{14}C
- ✓ ^{129}I
- ✓ ^{36}Cl
- ✓ ^{99}Tc

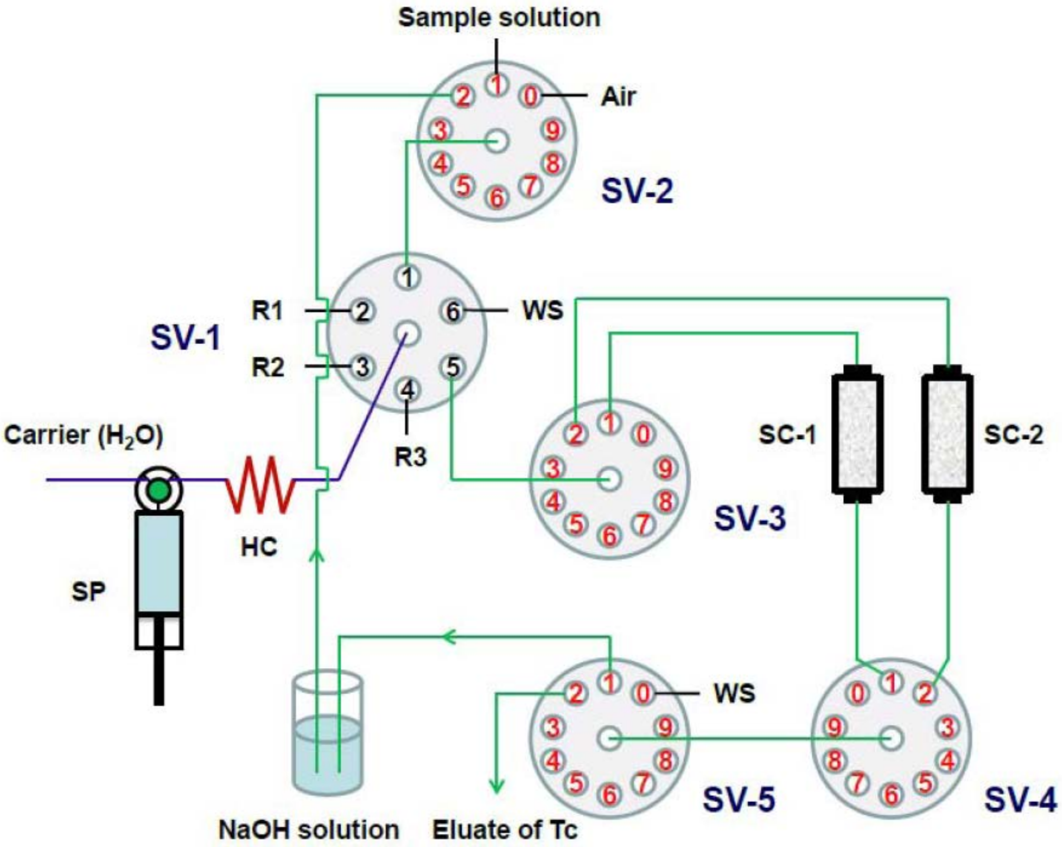
Hou et al., Anal. Chem., 2010

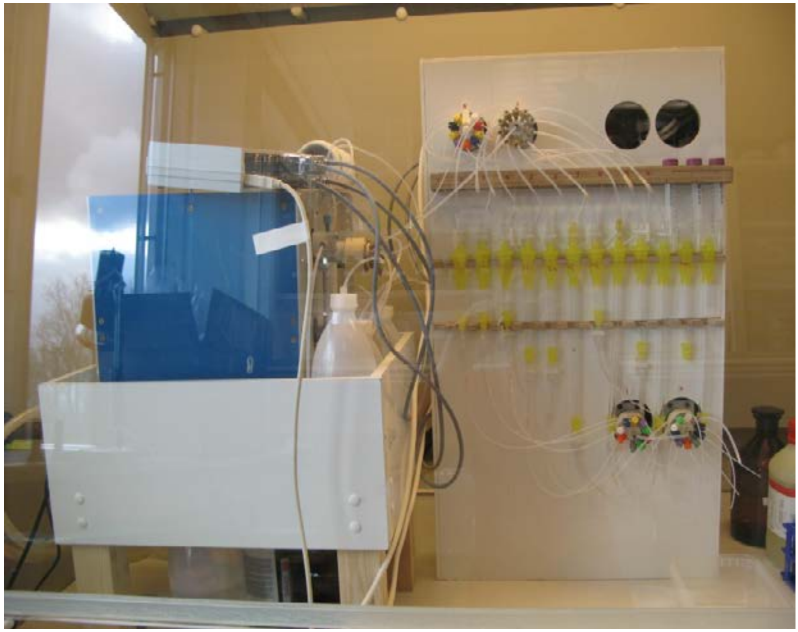
Hou, et al. JAAS, 2016

Rapid separation and analysis of difficult to measure radionuclides by Automatation approach

- **Reduce the radiation exposure for high radioactive samples**
- **Quick analysis of large number of samples**
- **Reduce the cost of analysis**
- **Apply for on-line analysis in site**

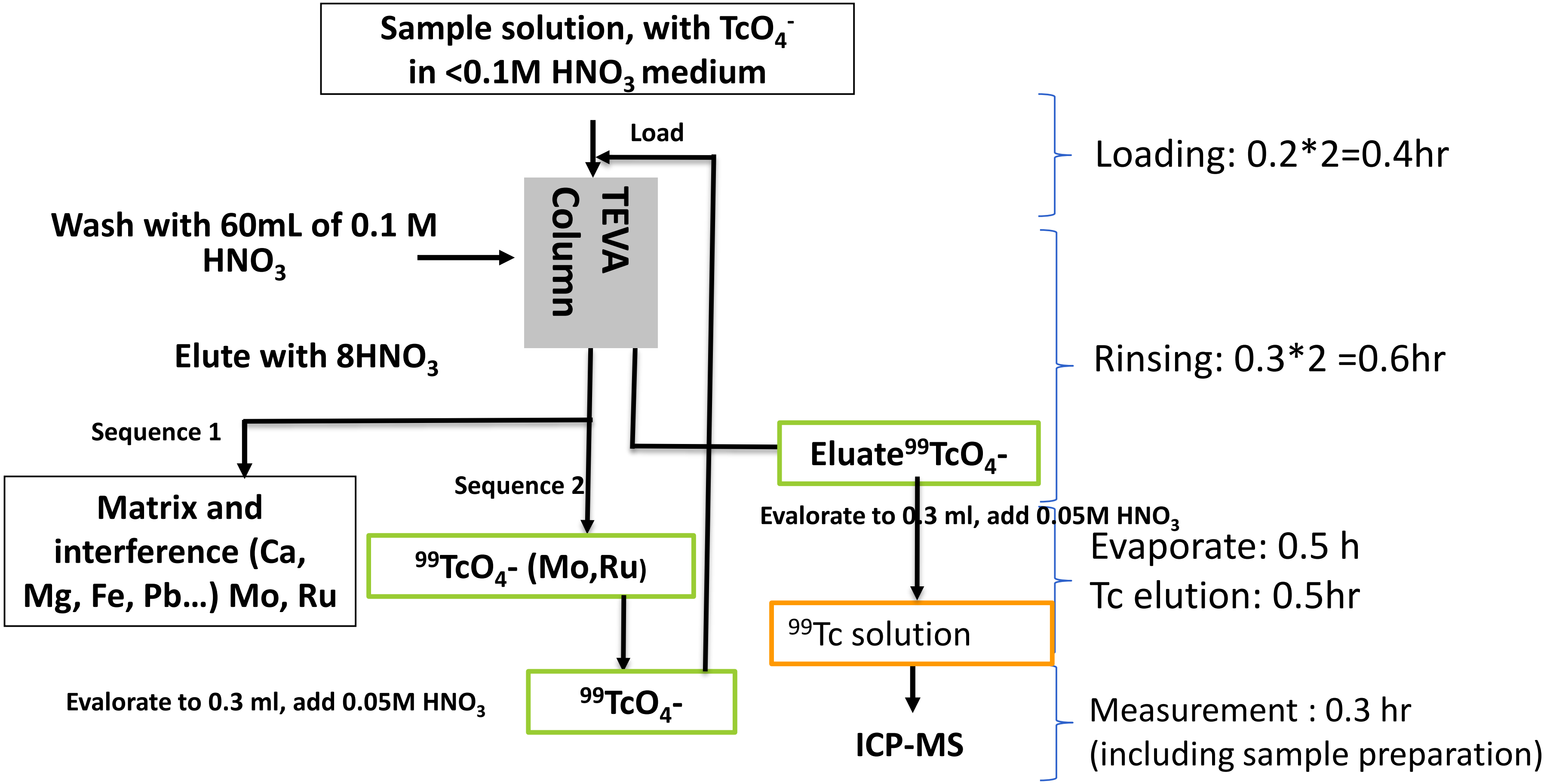
Sequentical injection approach for automated separation of radionuclides





Qiao, Hou, et al., Anal. Chem., 2009

Determination of ^{99}Tc by on-column separation sequential injection approach



Sample solution, with TcO_4^- in <0.1M HNO_3 medium

Load

TEVA Column

Wash with 60mL of 0.1 M HNO_3

Elute with $8HNO_3$

Sequence 1

Matrix and interference (Ca, Mg, Fe, Pb…) Mo, Ru

Sequence 2

$^{99}TcO_4$- (Mo,Ru)

$^{99}TcO_4$-

Evalorate to 0.3 ml, add 0.05M HNO_3

Eluate $^{99}TcO_4$-

Evalorate to 0.3 ml, add 0.05M HNO_3

^{99}Tc solution

ICP-MS

Loading: 0.2*2=0.4hr

Rinsing: 0.3*2 =0.6hr

Evaporate: 0.5 h

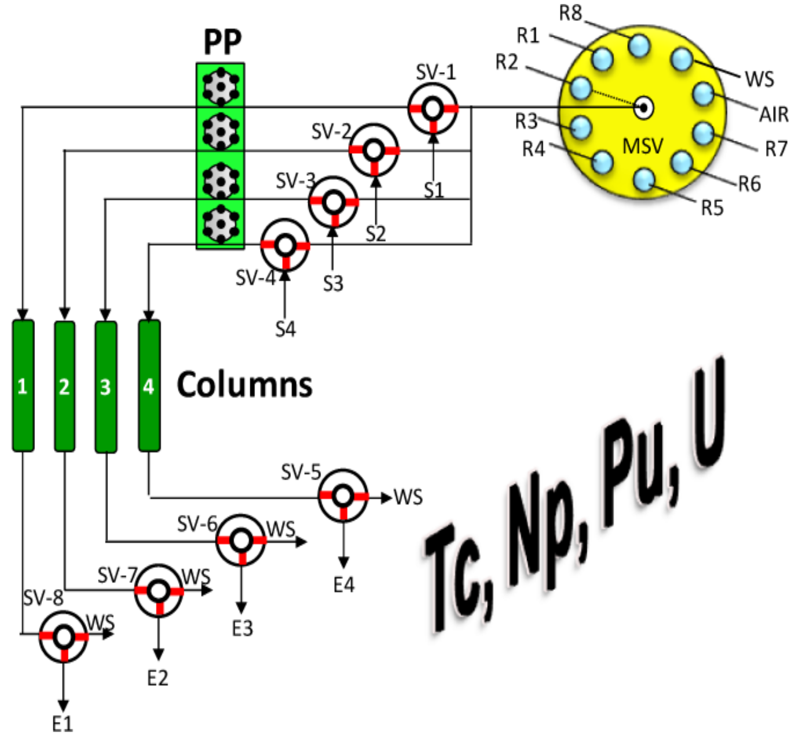
Tc elution: 0.5hr

Measurement : 0.3 hr (including sample preparation)

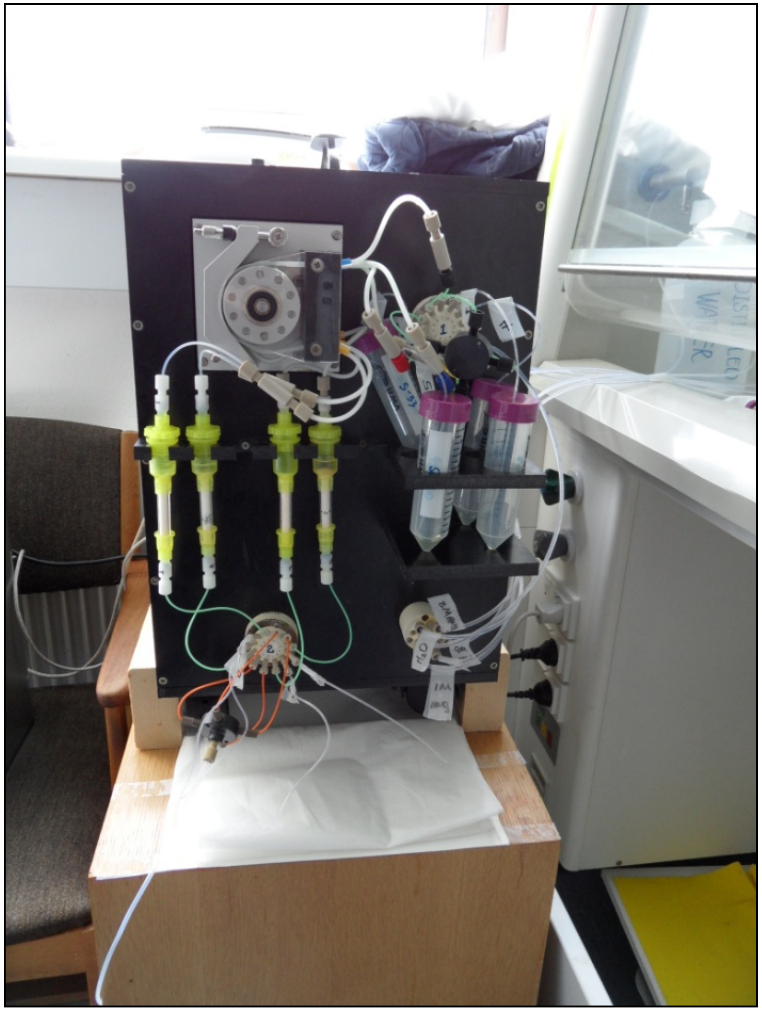
Total: 2.3 hr/batch

Shi, Hou, et al. Anal. Chem. 2012

Flow injection approach for automated separation of multi-radionuclides separation in multi-samples

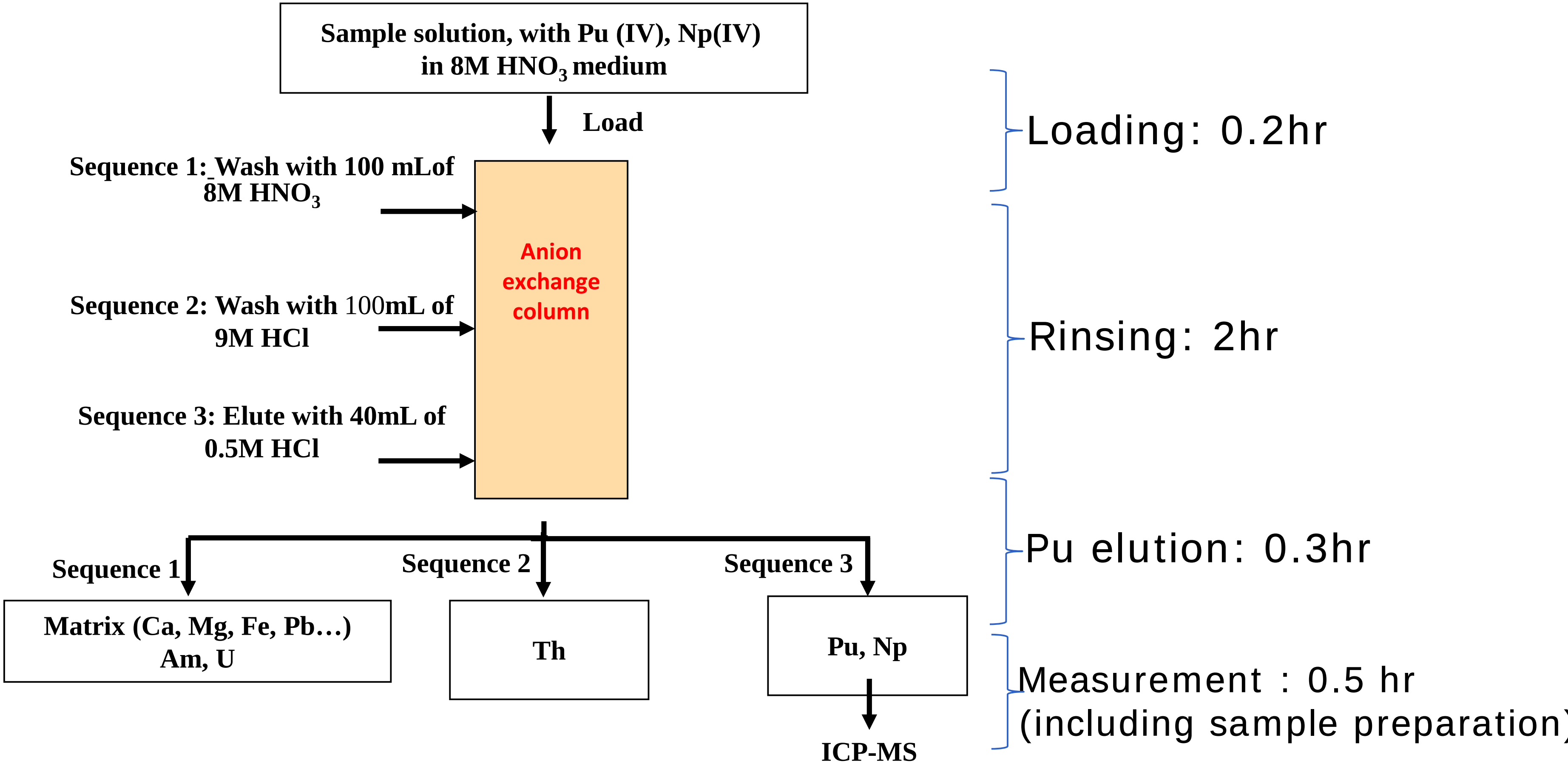


Tc, Np, Pu, U



Qiao, Shi, Hou, et al. ES&T 2014

Determination of ^{239}Pu, ^{240}Pu, ^{237}Np by On-column separation using sequential injection approach



Sample solution, with Pu (IV), Np(IV) in 8M HNO_3 medium

Load

Anion exchange column

Sequence 1:_Wash with 100 mLof 8M HNO_3

Sequence 2: Wash with 100mL of 9M HCl

Sequence 3: Elute with 40mL of 0.5M HCl

Sequence 1 → Matrix (Ca, Mg, Fe, Pb…) Am, U

Sequence 2 → Th

Sequence 3 → Pu, Np → ICP-MS

Loading: 0.2hr

Rinsing: 2hr

Pu elution: 0.3hr

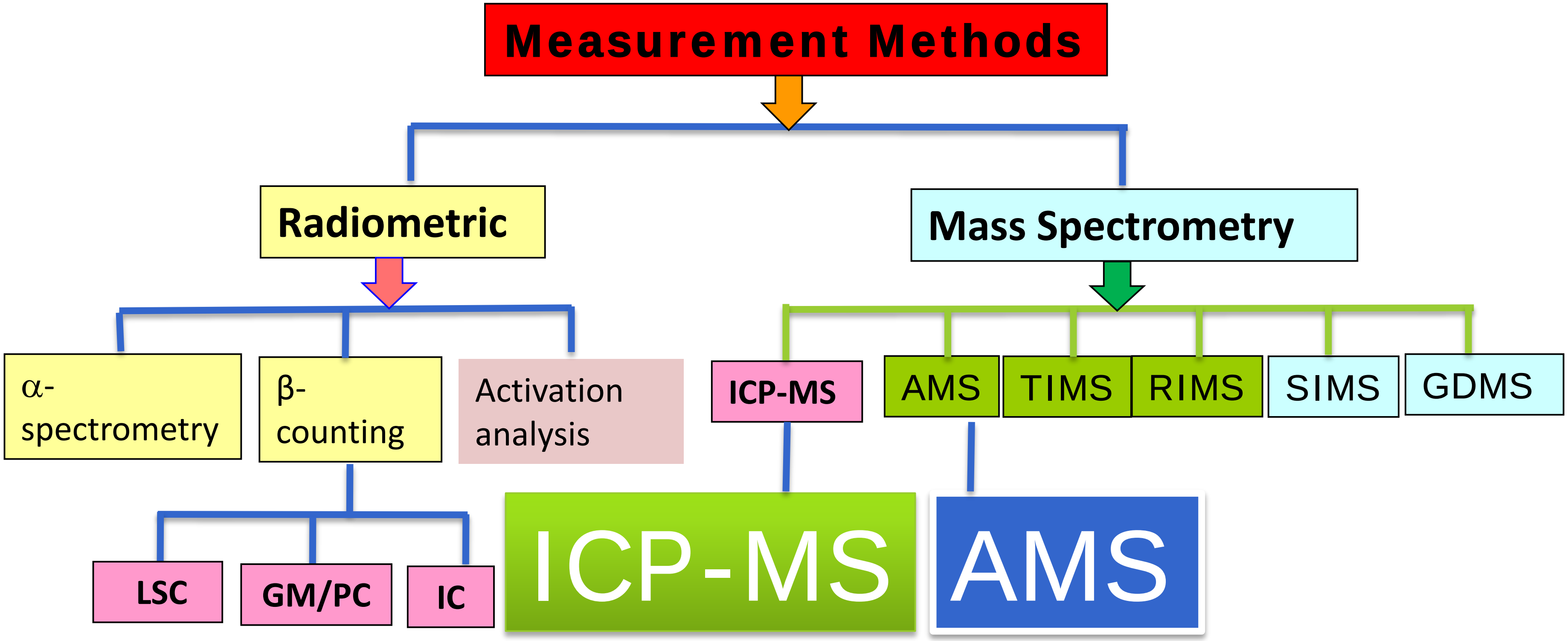
Measurement : 0.5 hr
(including sample preparation

Comparison: 2-3 days using traditional method

Total: 2.5 + 0.5 = 3hr

Qiao, Hou, et al. Anal. Chem. 2011

Sensitive measurement of radionucides



- Measurement Methods
  - Radiometric
    - α-spectrometry
    - β-counting
      - LSC
      - GM/PC
      - IC
    - Activation analysis
  - Mass Spectrometry
    - ICP-MS
      - ICP-MS
    - AMS
      - AMS
    - TIMS
    - RIMS
    - SIMS
    - GDMS

ICP-MS: Inductively coupled plasma mass spectrometry

AMS: Accelerator mass spectrometry

TIMS: Thermal ionization mass spectrometry

RIMS: Resonance ionization mass spectrometry

SIMS: Secondary ion mass spectrometry

GDMS: Glow discharge mass spectrometry

Present progress on measurement of radionuclides by mass spectrometry

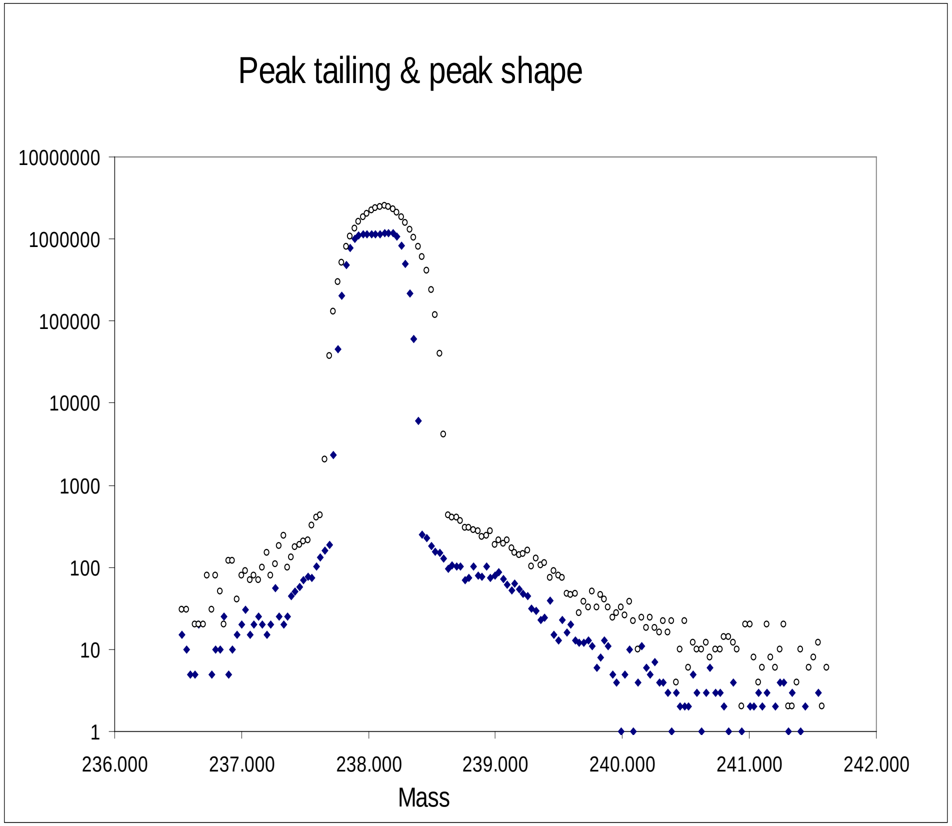
- ICP-MS is becoming a popular and often used technique for measurement of long-lived radionuclides.
  - ^{239}Pu, ^{240}Pu, ^{237}Np, ^{99}Tc, ^{226}Ra, ^{90}Sr, ^{135}Cs
  - Increased sensitivity and improved detection limit down to ppq or fg level measurement
  - Improved abundance sensitivity (10^{-10}) and double reaction/collision cells for tailing and isobar elimination.
- Increasing application of AMS for measurement of long-lived radionuclides
  - ^{14}C, ^{10}Be, ^{26}Al, ^{129}I, **^{36}Cl, ^{236}U, ^{239}Pu, ^{240}Pu, ^{237}Np, ^{243}Cm, ^{244}Cm, etc.**
  - Table-top AMS for ^{14}C
  - AMS with reaction cell for remove the interference

Improved detection limit in ICP-MS

- Increased sensitivity
- **Spectral interferences**
  - ✓Isobar (^{135}Ba-^{135}Cs, ^{99}Ru-^{99}Tc, ^{129}Xe-^{129}I)
  - ✓Molecular ions (argides, hydride, oxides, etc.)
- Instrumental limitation
  - ✓ **Abundance sensitivity** (tailing)

Nuclide	Detection limit, Bq			
	Radiometric	AMS	ICP-MS	New ICP-MS
^{129}I	17 mBq	10^{-6} mBq	0.1 mBq	0.01 mBq
^{99}Tc	5 mBq	--	1.5 mBq	0.2 mBq
^{135}Cs	--	--		0.5 mBq
^{237}Np	0.1 mBq	$3\text{x}10^{-5}$ mBq	$2\text{x}10^{-4}$ mBq	
^{239}Pu	0.1 mBq	0.003 mBq	0.017 mBq	$0.7\text{x}10^{-3}$ mBq
^{240}Pu	0.1 mBq	0.010 mBq	0.063 mBq	$2.5\text{x}10^{-3}$ mBq

Abundance sensitivity in ICP-MS

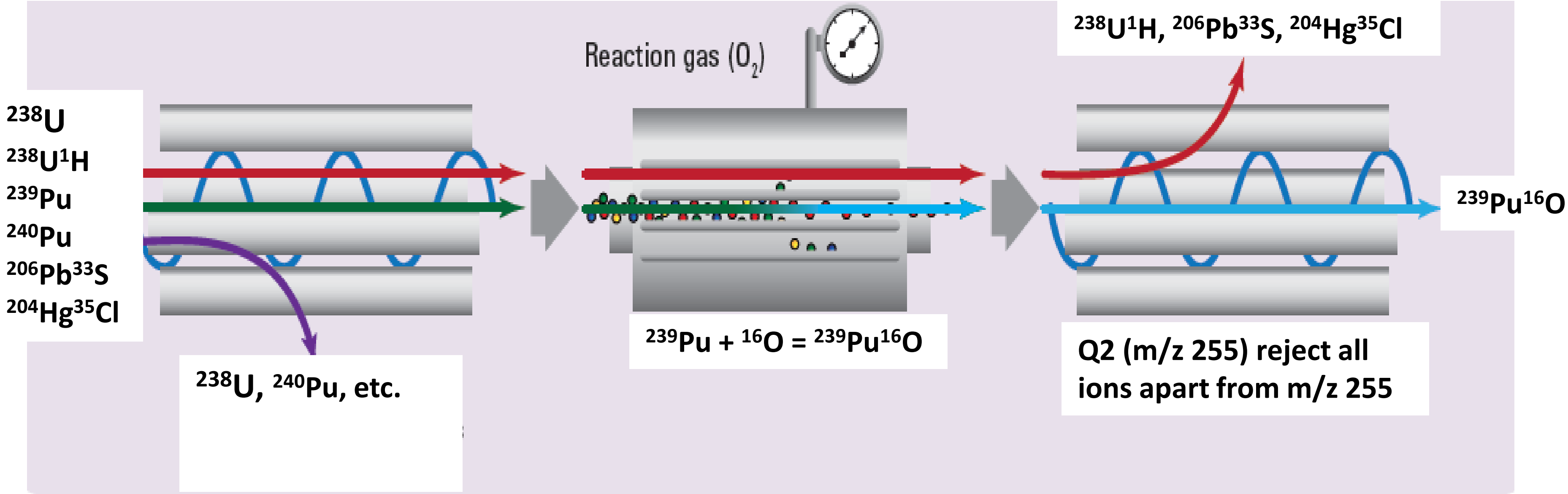


Nuclide	Abundance sensitivity	Requirement /limitation
^{239}Pu	**$239/^{238}U = 1x10^{-5}$**	**$<10^{-4}$**
^{236}U	$236/^{235}U = 1x10^{-5}$	$<1x10^{-4}$
^{129}I	$129/^{127}I = 1x10^{-7}$	$>1x10^{-6}$
^{135}Cs	$135/^{133}Cs = 1x10^{-7}$	$>1x10^{-6}$

- **Aboundance sensitivity is the ability of the instrument to detect a weak signal direct adjacent to a strong neighbouring peak.**
- **Defined as: $S = S_{m-1}/S_m$ or $S = S_{m+1}/S_{m,}$ Normally ranges in 10^{-7}-10^{-4}**

Improvement of abundance sensitivity and interference removal in ICP-MS

Agilent 3Q ICP-MS (or MS/MS technique)



^{238}U

$^{238}U^{1}H$

^{239}Pu

^{240}Pu

$^{206}Pb^{33}S$

$^{204}Hg^{35}Cl$

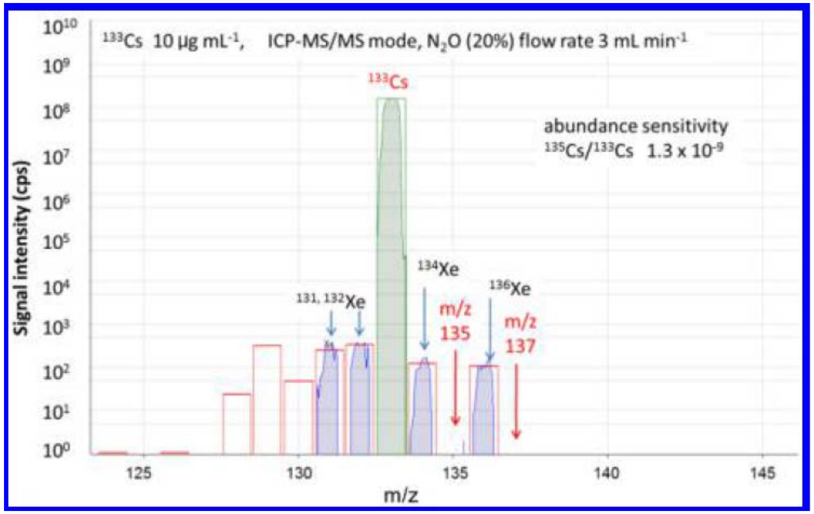
^{238}U, ^{240}Pu, etc.

$^{239}Pu + ^{16}O = ^{239}Pu^{16}O$

$^{238}U^{1}H$, $^{206}Pb^{33}S$, $^{204}Hg^{35}Cl$

Q2 (m/z 255) reject all ions apart from m/z 255

$^{239}Pu^{16}O$



Zheng, et al. Anal. Chem. 2014

Achievement:

$^{239}U/^{238}U = 2x10^{-8}$

For a solution of 1ppb U:

^{239}Pu: 10^{-16}g/g

Xing, Hou, et al. Talanta, 2018

2. filter
mass analysis (low-energy end)

3. filter
molecule destruction

$AB^- \longrightarrow A^+$
$ B^+$

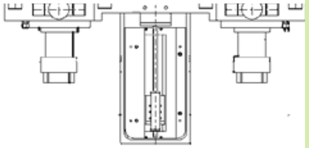
4. filter
mass analysis
(high-energy

Molecular interferences → Stripping process (Breaking up bindings)

AMS

Isobaric interferences → Negative ion formation Particle identification

ector



No abundance sensitivity/tailing problem

$^{14}C/^{12}C < 10^{-16}$

1. filter
negative ion formation

particle identification
dE/dx

Measurement of atom level radionuclides by Accelerator Mass Spectrometer (AMS)

- ^{14}C
- ^{3}H
- ^{10}Be
- ^{26}Al
- ^{36}Cl,
- ^{41}Ca
- ^{99}Tc
- ^{59}Ni,
- ^{79}Se,
- ^{126}Sn
- ^{129}I
- ^{236}U
- ^{239}Pu
- ^{240}Pu
- ^{237}Np
- ^{243}Cm
- ^{244}Cm

Measurement Method for ^{129}I and their detection limits

Method	Detection limit		
	^{129}I, atoms	^{129}I, mBq	^{129}I/^{127}I Ratio
Liquid scintillation	10^{13}	10 mBq	
γ-spectrometry	10^{13}	10 mBq	
ICP-MS	2×10^{11}	0.4 mBq	10^{-6}
Radiochemical neutron activation analysis	10^{8}	**0.2 mBq**	10^{-10}
Accelerator mass spectrometry (AMS)	10^{5}	**0.1 nBq**	10^{-14}

Hou, et al. Anal. Chim. Acta, 2009

Analytcial procedure of ^{129}I and ^{127}I in solid samples

Plants/solid sample

Dry, grind to powder

Dried plant powder

Separation of iodine

Trap/leaching solution

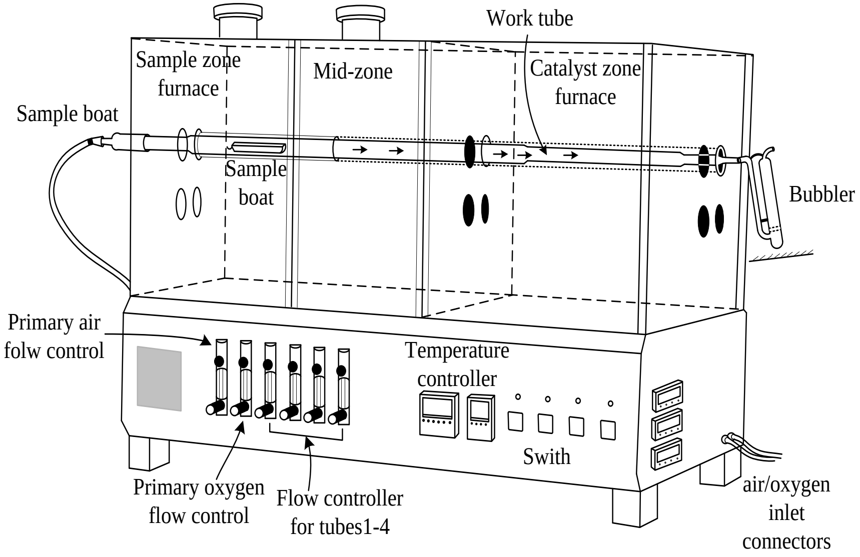
ICP-MS for ^{127}I

Add ^{127}I carrier, $AgNO_3$, and centrifuge

AgI target

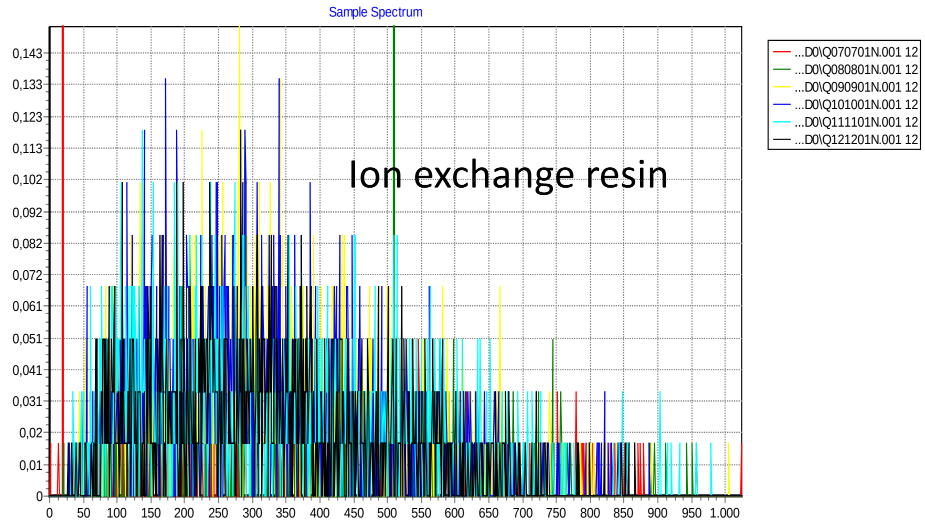
AMS for ^{129}I

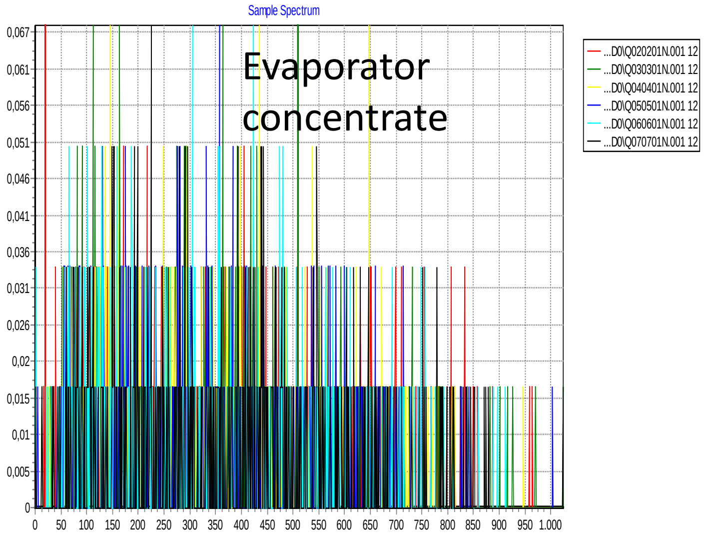
^{129}I/^{127}I

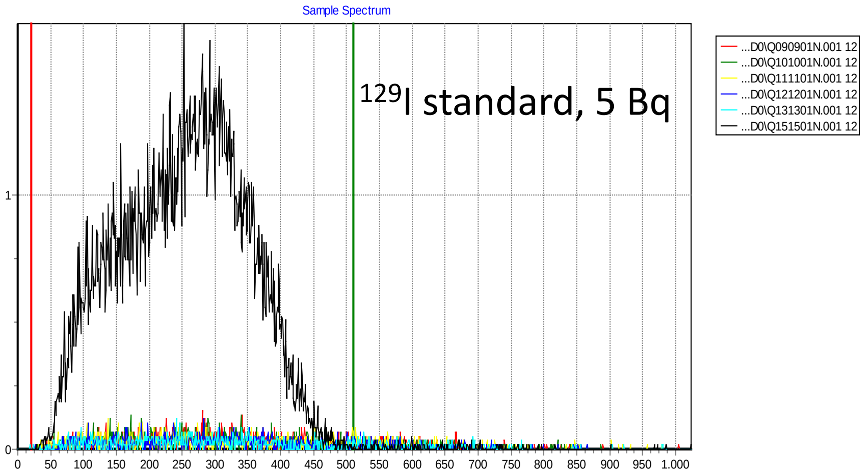


Hou, et al. JAAS, 2016
Hou, et al. JRNC, 2018

Determination of ^{129}I in evaporation concentrate and anion exchange resin using LSC







- 5 g samples was used for analysis
- ^{129}I is not measureable in evaporator concentrate samples,
- ^{129}I in ion exchange resin is measred by high uncertainty (<10 mBq/g)

Determination of ^{129}I in evaporation concentrate and anion exchange resin using AMS

Sample	Sample ID	^{129}I concentration, mBq/g	
		Value	Unc.
Evaporator concentrate	EC-1	0.0110	0.0012
Evaporator concentrate	EC-2	0.0070	0.0008
Evaporator concentrate	EC-3	0.0122	0.0014
Evaporator concentrate	EC-4	0.0128	0.0014
ion exchange resin	ICR-1	0.0083	0.0012
ion exchange resin	ICR-2	3.318	0.301
ion exchange resin	ICR-3	3.860	0.352
ion exchange resin	ICR-4	4.179	0.376

- <0.1 g sample was used for analysis
- Ld =0.00001 mBq/g

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Thank you for your attention !