Towards Rapid Radiochemical Analysis

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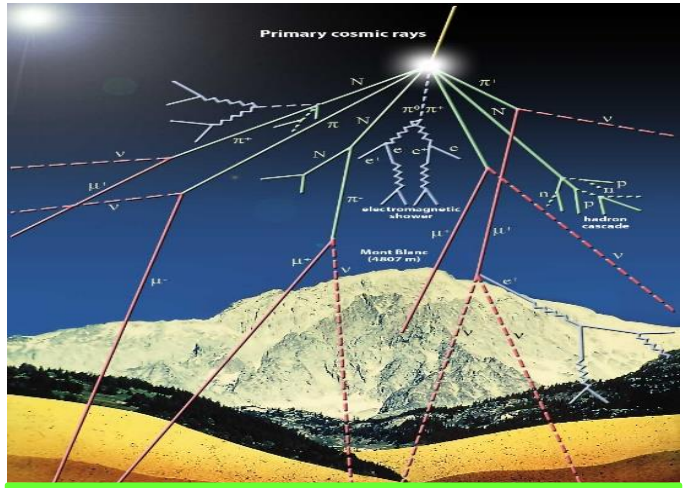
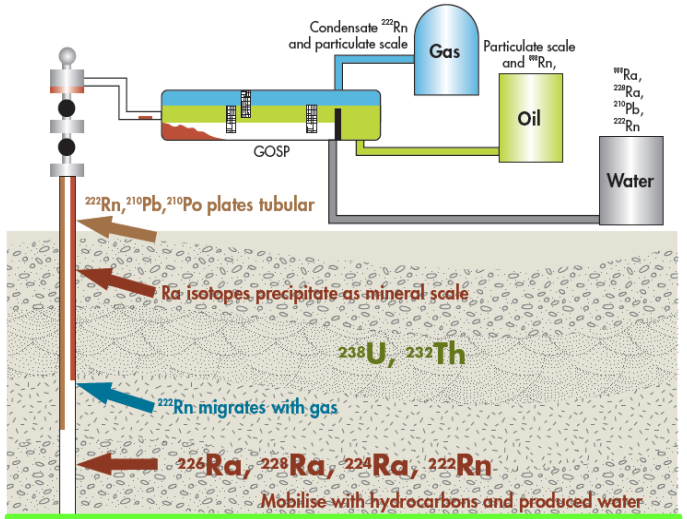
Source of radioactivity in the environment



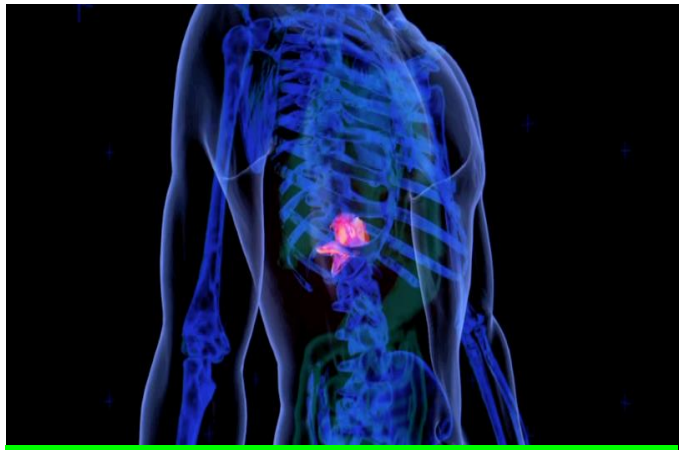
Nature (U/Th, cosmic ray reactions)



Technically enhanced natural radioactivity (oil/gas, mining, geothermal)

Nuclear weapons testing (atmosphere)

Nuclear power plants and fuel cycle facilities operation



Medical use of radionuclides

Nuclear accidents

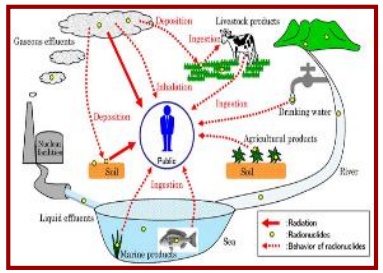
Radioactivity determination

Nuclear emergency prepardness

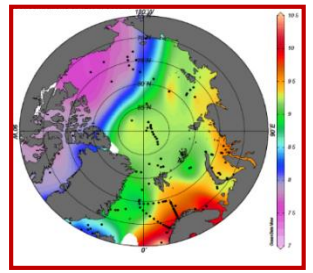
Nuclear decommissioning

Radioactivity determination

Environment monitoring

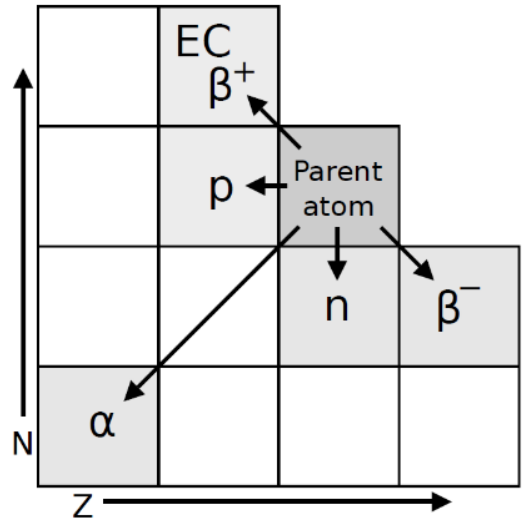


Radioecology and tracer studies

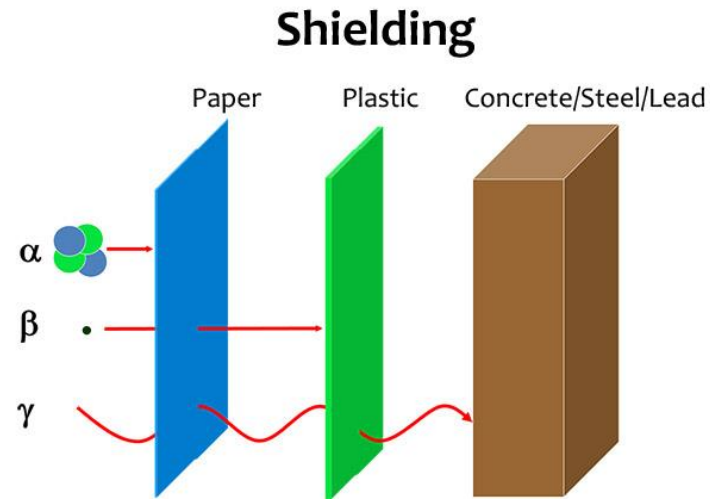


Why radiochemical analysis?

- There are three primary types of ionizing radiation: **alpha, beta and gamma radiation**.
- Alpha and beta radiation are particles.
- Gamma rays are electromagnetic waves.



Transition diagram for decay modes of a radionuclide, with neutron number N and atomic number Z (shown are α, $\beta^{\pm}$, p^{+}, and n^{0} emissions, EC denotes electron capture).



most gamma emitters

Easy-to-measure radionuclides

most alpha and beta emitters

Hard-to-measure radionuclides

↓

Radiochemical analysis

Radiochemical analysis

Samples

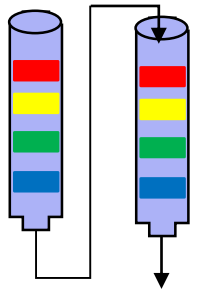
Pre-treatment

Most time-consuming processes

Radiochemical separation

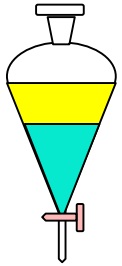
Purified radionuclides

Chromatography



or

Solvent extraction



Radiometric measurement

Alpha spectrometry
$^{238, 239,240}$Pu, ^{237}Np, ^{226}Ra, $^{234, 235, 238}$U, $^{228, 230, 232}$Th, ^{241}Am, ^{243}Cm

Liquid scintillation counting
^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63}Ni, ^{89,90}Sr, ^{93}Zr, ^{94}Nb, ^{93}Mo, ^{241}Pu

Beta counting
^{99}Tc, ^{89,90}Sr

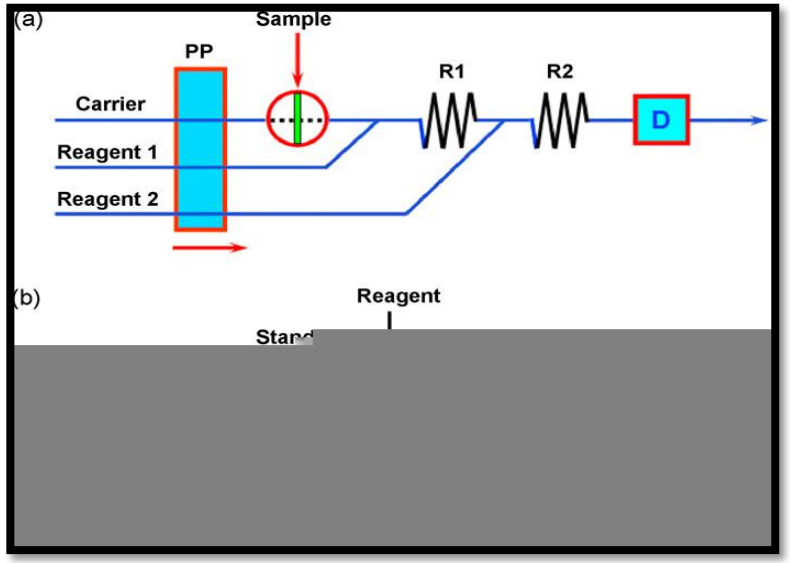
Mass spectrometric measurement

ICP-MS: ^{239}Pu, ^{240}Pu, ^{237}Np, ^{99}Tc, $^{234, 235, 238}$U, ^{232}Th,
AMS: ^{129}I, ^{36}Cl, ^{41}Ca, ^{236}U, ^{233}U
TIMS: ^{135}Cs, $^{239, 240}$Pu, $^{234, 235, 238}$U

ICP-MS: Inductively coupled plasma mass spectrometry
AMS: Accelerator mass spectrometry
TIMS: Thermal ionization mass spectrometry

Automation for radiochemical separation

Flow injection (FI)/sequential injection (SI)



Pros: Highly flexible, possibilities for sequential separation or multi-sample handling

Cons: High cost, high demands in technical support

High performance liquid chromatography (HPLC)

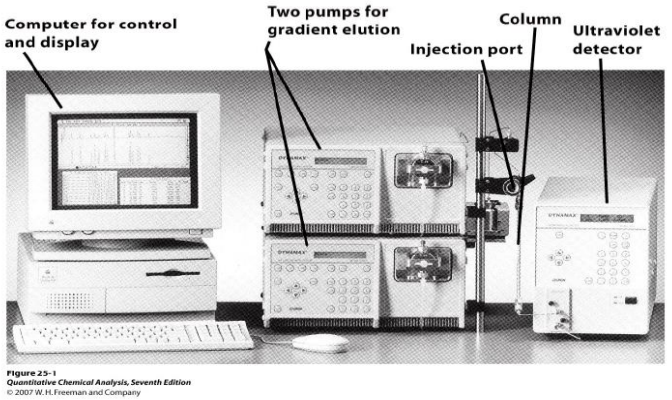
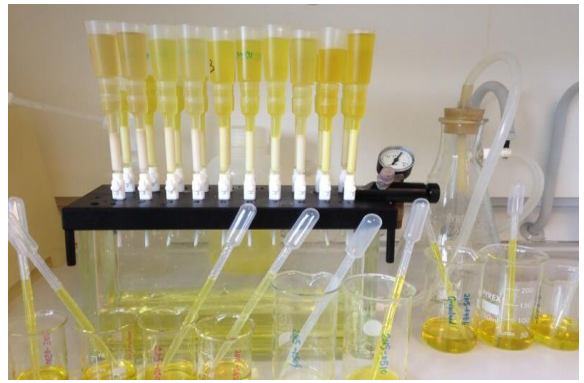


Figure 25-1
Quantitative Chemical Analysis, Seventh Edition
© 2007 W. H. Freeman and Company

Pros: Fully automated, Direct connection to MS

Cons: Only handle small samples, Single sample processing, High cost

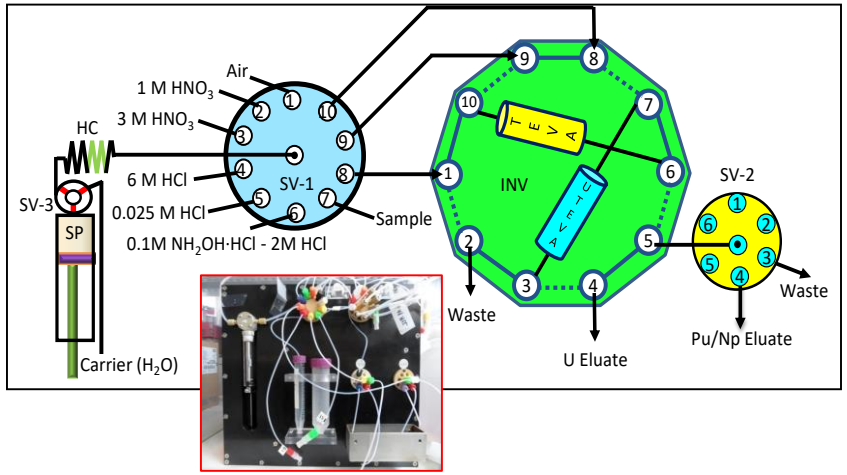
Vacuum box

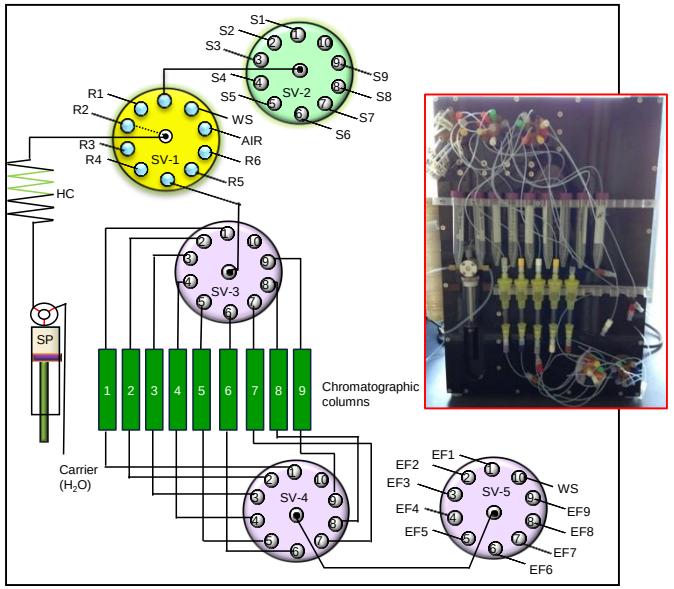


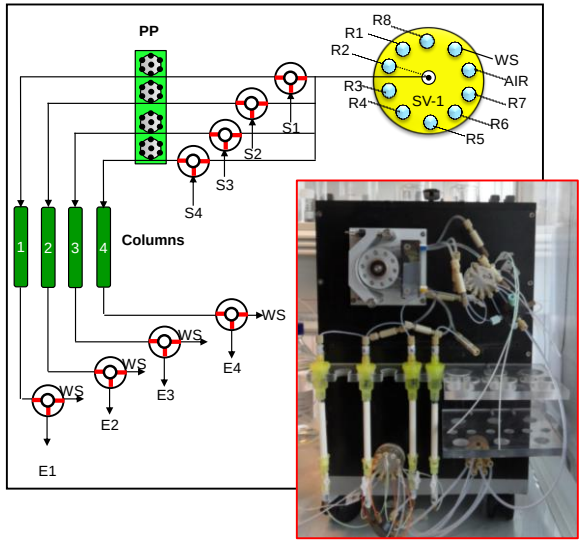
Pros: Multi-sample processing, Easy operation, Low cost, Flexible

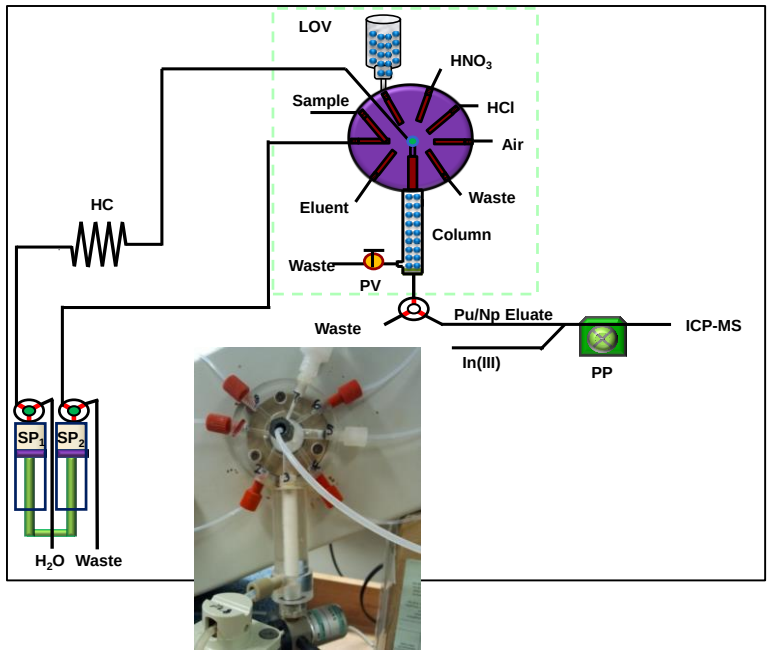
Cons: Need human attention

Automated radiochemical separation system









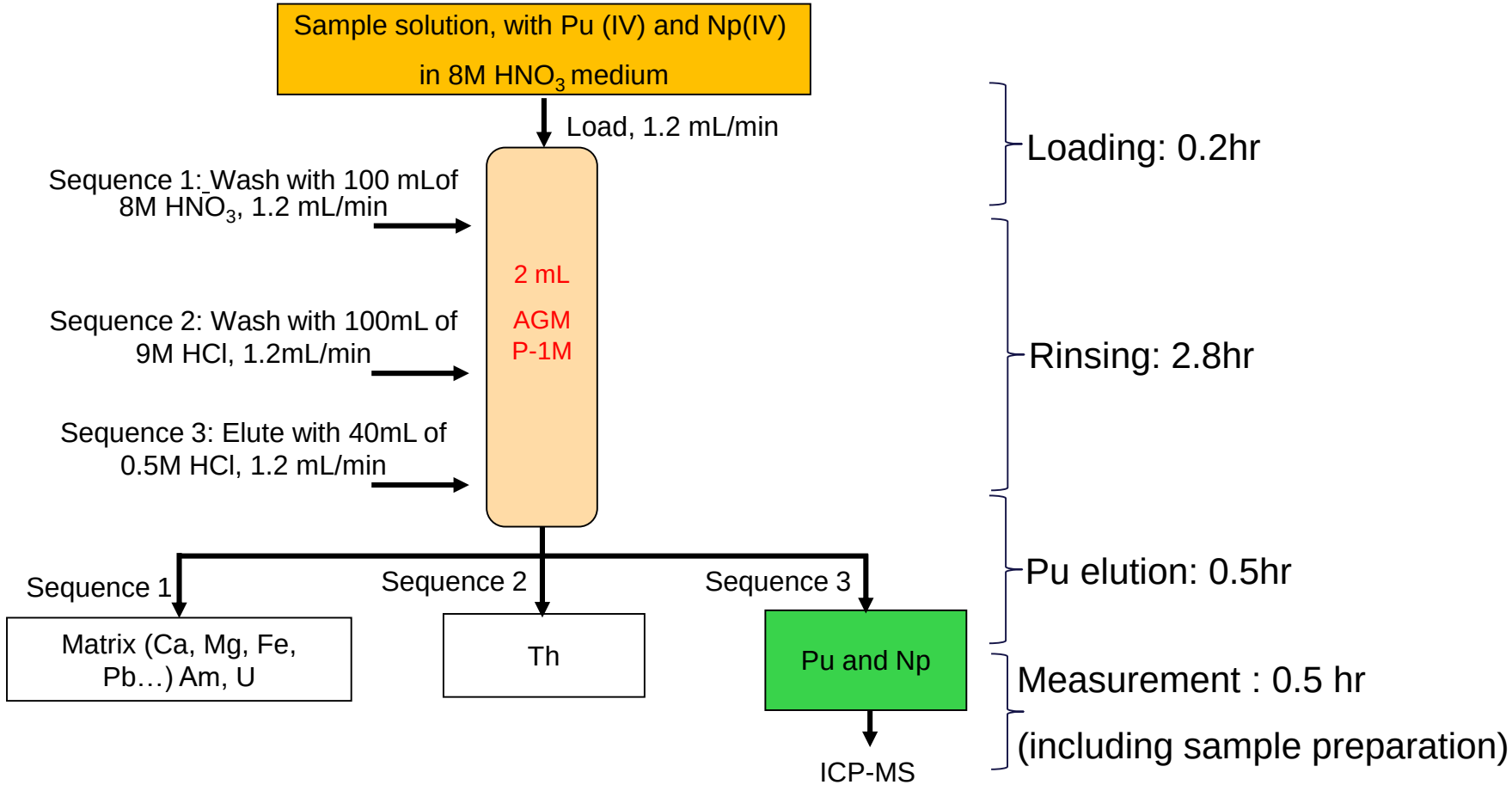
Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytica Chimic Acta. 2011, 685, 111-119.

Qiao, J. X., Hou, X. L., Steier, P., Golser, R. Analytical Chemistry. 2013, 85, 11026-11030.

Qiao, J. X., Shi, K. L., Hou, X. L., Nielsen, S., Roos, P. Environmental Science & Technology. 2014, 48, 3935-3942.

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry. 2013, 85, 2853-2859.

Automated method for Pu and Np determination



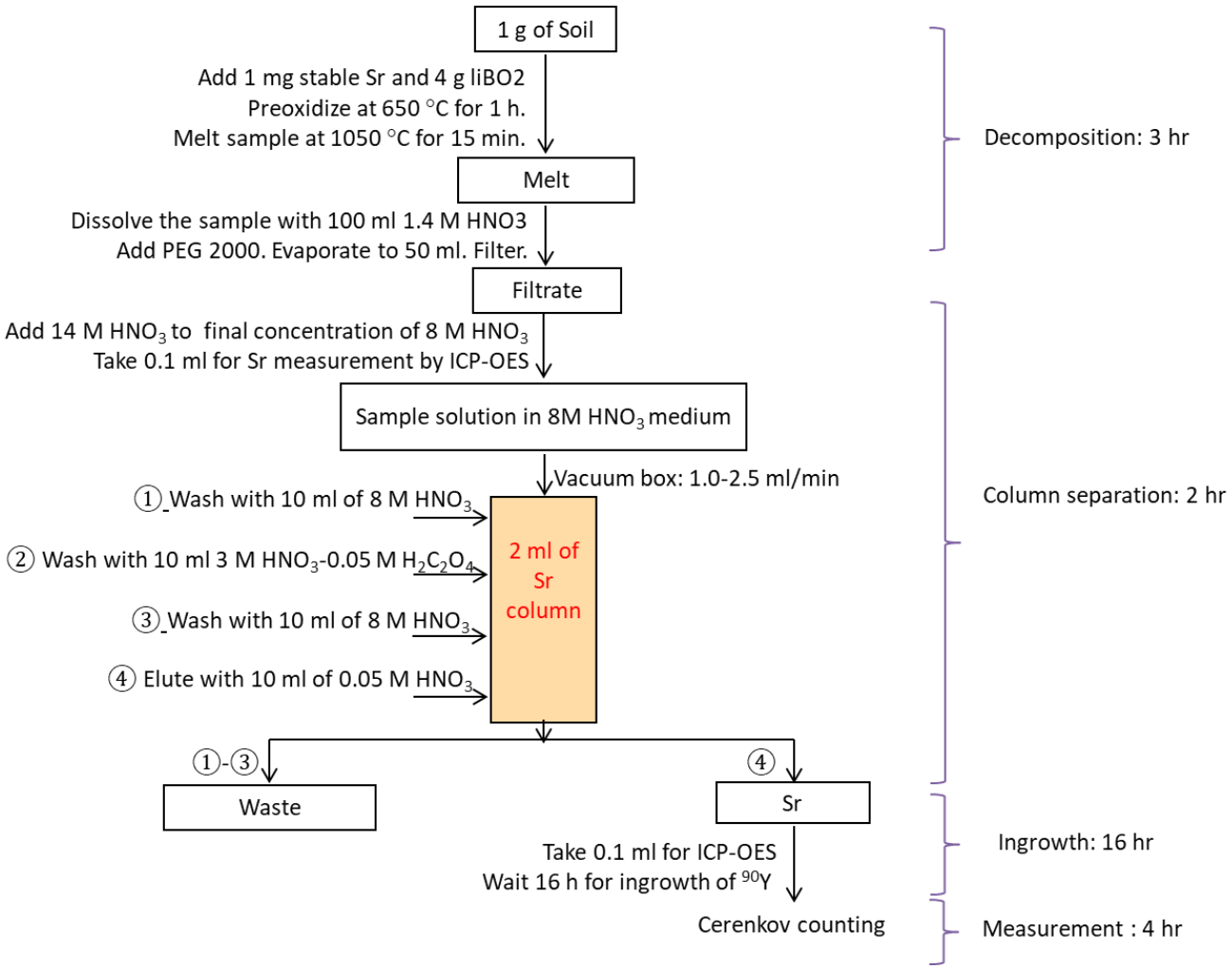
Comparison: 2-13 days using traditional method

Total: 3.5 + 0.5 = 4hr

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry. 2011, 83, 374-381.

NKS Rapid-tech project

NKS-336
ISBN 978-87-7893-418-5



Application of Rapid and Automated Techniques in Radiochemical Analysis

Conclusions:

For ^{239,240}Pu determination, it is apparent that ICP-MS technique provides advantages of shortening the measurement time and reducing the LOD. Determination of ^{90}Sr through its daughter ^{90}Y requires sufficient ingrowth time for ^{90}Y. Gas flow proportional counting has a lower LOD except for Quantalus ultra low level LSC and can measure a batch of samples simultaneously. However, in this work, LSC measurement for ^{90}Sr works more effectively compared to beta counting. Rapid techniques including sequential injection and vacuum-box-assisted chromatographic separation were applied in this work, which are advantageous when aiming to improve the analytical efficiency.

Jixin Qiao [1]
Iisa Outola [2]
Petra Lagerkvist [3]
Rajdeep Singh Sidhu [4]
Kai Xu [1]
Sofia Josson [3]
Pia Vesterbacka [2]
Stina Holmgren [3]
Kaisa Vaaramaa [2]

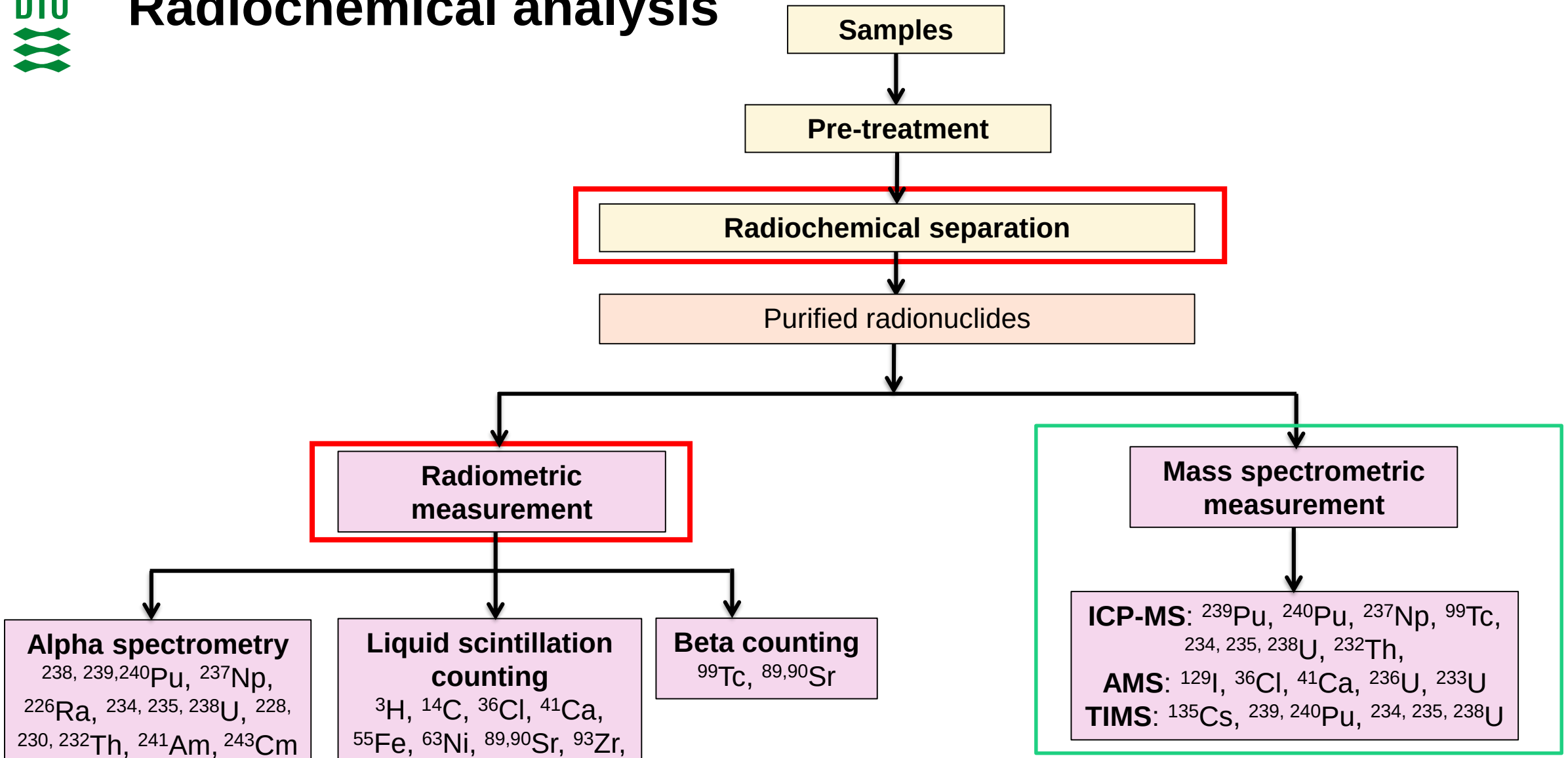
J Radioanal Nucl Chem (2017) 314:813–826
DOI 10.1007/s10967-017-5385-9

CrossMark

Inter-laboratory exercise with an aim to compare methods for ^{90}Sr and ^{239,240}Pu determination in environmental soil samples

Jixin Qiao[1] · Susanna Salminen-Paatero[2] · Stina Holmgren Rondahl[3] · Marie Bourgeaux-Goget[4] · Per Roos[1] · Petra Lagerkvist[3] · Elisabeth Strålberg[4] · Henrik Ramebäck[3,5]

Radiochemical analysis



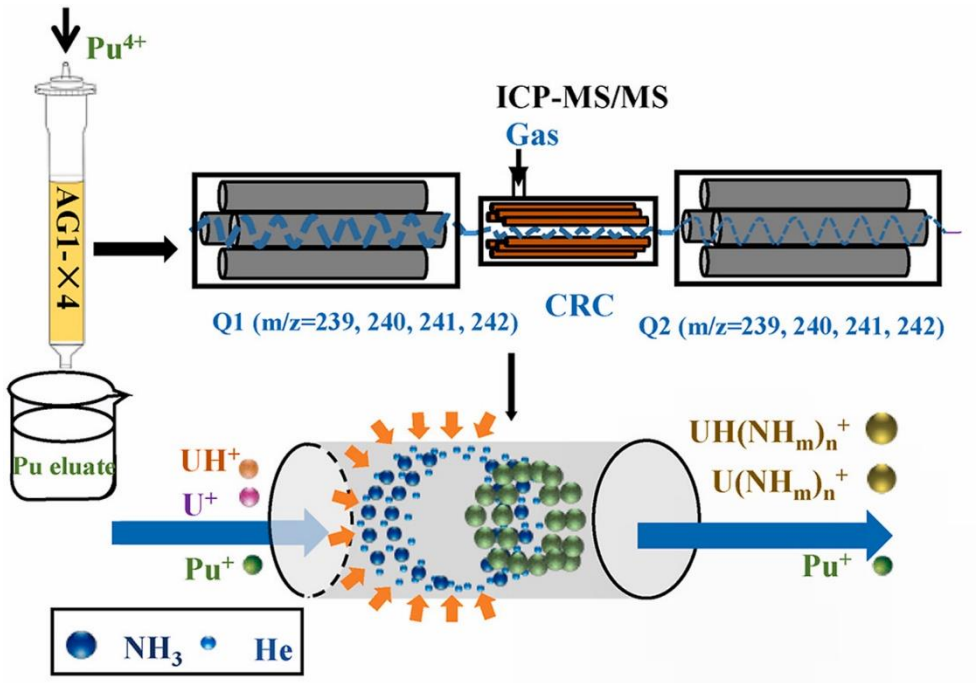
ICP-MS: Inductively coupled plasma mass spectrometry
AMS: Accelerator mass spectrometry
TIMS: Thermal ionization mass spectrometry

Measurement of radionuclides by ICP-MS/MS

Radionuclides: ^{99}Tc, ^{135}Cs, $^{234, 235, 236, 238}U$, $^{239,240,241}Pu$, ^{237}Np, ^{241}Am

Measurement time: 5-10 min.

Detection limit: 10^{-15} - 10^{-12} g/g



Xu et al. Talanta, 2022, 24, 123152.

Agilent 8800/8900 ICP-Q^3-MS/MS

CRC: 4 inlets of collision or reaction gas (He, NH_3, O_2, CO_2, N_2O, H_2, etc.)

Q2: Select target ion for measure

Q1: Control ions entering cell

J. Anal. At. Spectrom., 2017, 32, 1660

NKS Nordic-ICP and ICP-Biodec projects

NKS-403
ISBN 978-87-7893-491-8

Table 1 Instrumentation conditions used in each laboratory for the inter-comparison exercise

	Lab A	Lab B		Lab C		Lab D		Lab E	Lab F
Instrument model	Agilent 8800 ICP-QQQ	Element XR ICP-SFMS		Element XR ICP-SFMS		Nu Plasma MC-ICP-MS	AttoM double-focusing ICP-SFMS	Element 2 ICP-SFMS	Agilent 8800 ICP-QQQ
Radionuclides measured	^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U	^{238}U, ^{239}Pu, ^{240}Pu, ^{42}Pu	^{234}U, ^{235}U, ^{238}U	^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U	^{239}Pu, ^{240}Pu, ^{242}Pu, ^{238}U	^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu
Auto-sampler	AS X-520 (CETAC))	No	No			ASX110	ASX260	SC2 DX	AS X-520 (CETAC))
Nebulizer	MicroMist (Borosilicate glass)	Conikal nebulizer	Conikal nebulizer	MicroMist nebulizer	PFA nebulizer	Meinhard and Desolvating nebulizer (DSN)	Meinhard nebulizer	PFA-ST	MicroMist quartz
Spray chamber	Quartz, , Scott-type double-pass	Twister spray chamber	Twister spray chamber	Cyclonic spray chamber	Cyclonic spray chamber	Cyclonic spray chamber	Cyclonic double pass spray chamber	Quartz baffled micro cyclonic with dual gas inlet	Quartz, Scott-type double-pass
Typical sensitivity, cps/ppq ^{238}U	0.7	2	1.8	1.2	6	2	2	0.8	1.5 with s-lens (s-lens for Pu and x-lens for U)
^{238}UH$^+$/U$^+$	1/14892	1/104000	1/104000		1/100000		3/100000		None

An inter-comparison exercise on the application of ICP-MS techniques for measurement of long-lived radionuclides

Journal of Radioanalytical and Nuclear Chemistry (2018) 315:565–580
https://doi.org/10.1007/s10967-018-5697-4

On the application of ICP-MS techniques for measuring uranium and plutonium: a Nordic inter-laboratory comparison exercise

Jixin Qiao[1] · Petra Lagerkvist[2] · Ilia Rodushkin[3] · Susanna Salminen-Paatero[4] · Per Roos[1] · Syverin Lierhagen[5] · Karl Andreas Jensen[6] · Emma Engstrom[3] · Yann Lahaye[7] · Lindis Skipperud[6]

Determination of Pu and Am in biological and nuclear decommissioning samples

Jixin Qiao, Susanna Salminen-Paatero, Simon Jerome, Karl Andreas Jensen, Estela Reinoso-Maset, Petra Lagerkvist, Emmi Myllykyla, Petri Hovi, Lindis Skipperud, Mathias Salomon Hvid

Jixin Qiao [1]
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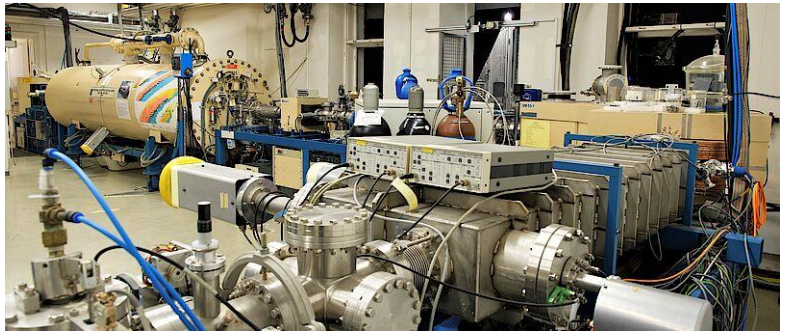
Ilia Rodushkin [3]
Susanna Salminen-Paatero [4]
Per Roos [1]
Syverin Lierhagen [5]
Karl Andreas Jensen [6]
Emma Engstrom [3]
Lindis Skipperud [6]

Conclusions

It is concluded that inter-laboratory comparison for the determination of radionuclides using ICP-MS techniques are much needed within the Nordic society. Experience can be shared between the laboratories by performing inter-comparison exercises and by having user meetings with the intention to discuss radionuclides measurements using ICP-MS. For the coming years, inter-comparison exercises and ICP-MS user meetings, activities similar to those within the NKS projects, are desired within the ICP-MS community.

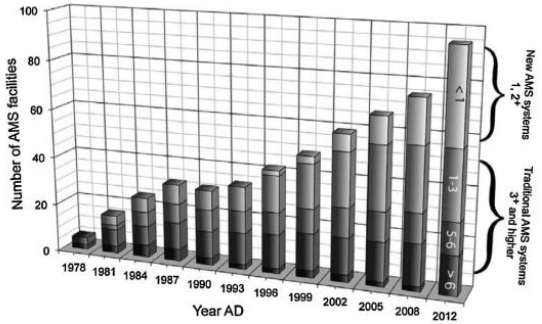
Measurement of radionuclides by AMS and TIMS



AMS at "VERA" (Vienna Environmental Research Accelerator)

Table 1. Overview of research areas where AMS measurements are used (updated from Ref. [10]).

Domain	Research area	Radionuclide[a]
Technosphere	Half-life measurements	^{32}Si, ^{41}Ca, ^{41}Ca, ^{44}Ti, ^{60}Fe, ^{79}Se, ^{126}Sn, ^{146}Sm, ^{182}Hf
	Depth profiling in fusion walls	^{3}H
	Possible fusion plasma thermometer, ^{27}Al(n,2n)^{26}Al	^{26}Al
	Nuclear reaction studies for nucleosynthesis in stars	^{14}C, ^{10}Be, ^{26}Al, ^{36}Cl, ^{41}Ca, ^{44}Ti, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{68}Ge, ^{146}Sm, ^{202}Pb, ^{209m}Bi, ^{230}Th, ^{231}Pa
	Neutron dosimetry of the Hiroshima bomb	^{36}Cl, ^{41}Ca, ^{63}Ni
	Nuclear safeguards	$^{146, 149, 151}$Sm, ^{233}U, ^{236}U, ^{237}Np, $^{239, 240, 241, 242, 244}$Pu



The ingrowth of the number of AMS facilities since 1978.

Walter Kutschera (2016), Advances in Physics: X, 1:4, 570-595.

Determination of Ultratrace Level ^{135}Cs and ^{135}Cs/^{137}Cs Ratio in Small Volume Seawater by Chemical Separation and Thermal Ionization Mass Spectrometry

Liuchao Zhu, Changkun Xu, Xiaolin Hou,* Jixin Qiao, Yonggang Zhao, and Guorong Liu

Cite This: *Anal. Chem.* 2020, 92, 6709–6718 | Read Online

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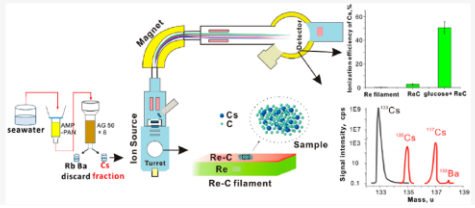


Table 2 Different Applications of TIMS in Nuclear Science and Technology

Stage	Measurement	Remarks
Mining	Isotopic composition of U	Build-up national and international libraries for data on useful signatures from different mines; discovering natural reactor
Enrichment	^{235}U/^{238}U isotope amount ratio	^{235}U enrichment R&D studies and at plant
Fuel fabrication	Isotopic composition data of U and Pu	Chemical quality assurance of fuel materials in nuclear fuel cycle; to determine fertile and fissile content
Reactor (for fuel)	Burn-up determination, build-up and depletion of different isotopes of U, Pu	Post-irradiation studies for developing and verifying theoretical reactor codes; for developing isotope correlations
Reactor (for moderator/coolant)	Isotopic composition and concentration of boron, Gd	B_2O_3 mixed with D_2O added in PHWRs, periodic determination required; Gd in coolant for fuel failure
Reactor for burnable poison	Isotopic composition of Gd, Dy *etc.*	For determining depletion in neutron absorbing isotopes
Reprocessing plant	Concentration and isotopic amount ratio data on U, Pu	Nuclear material accounting, input accountability at reprocessing plant
Nuclear forensics	Isotopic composition, amount, age determination	Isotope amount ratio data for Th, Pa, U, Np, Pu, Am, Sr, Nd, Pb, O *etc.*, amount ratio of daughter to parent
Environmental and biological samples	Isotopic composition and amount (concentration) of actinides	For accidental releases and nuclear tests
R&D studies	Half-lives, fission yields of stable isotopes, cross-sections *etc.*	Fundamental nuclear data required for various applications
Enriched stable and radioactive isotopes	Isotopic composition	For preparing isotopic reference materials gravimetrically and for characterisation of isotopes to be used as spikes in ID-TIMS
Round-robin experiments	Isotopic composition and concentration	For proficiency testing of different international laboratories

Anal. Methods, 2016, 8, 942.

Conclusions

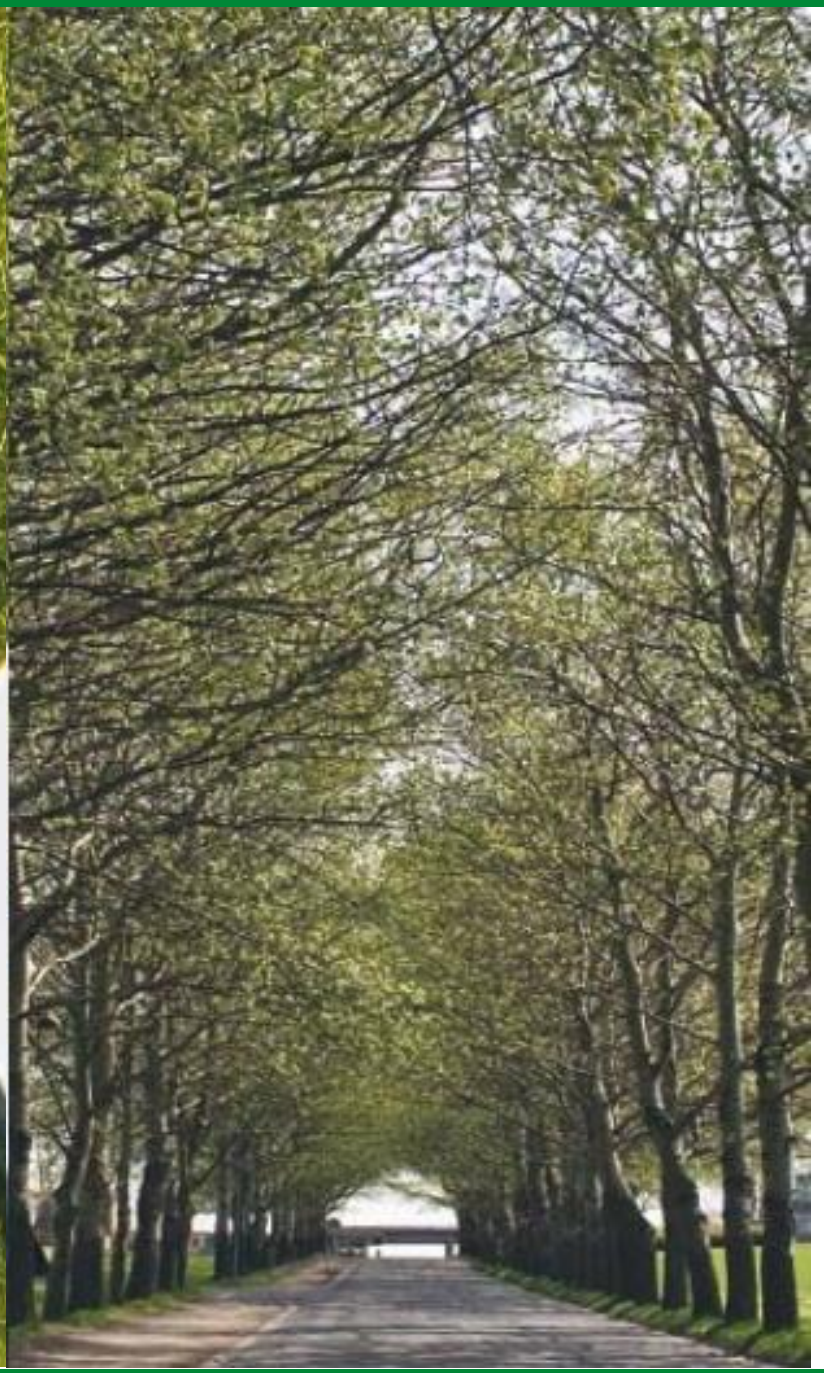
- **Up-to-date methods development for effective radiochemical analyses is necessary.**
- **Automation techniques and modern mass spectrometric instruments could be helpful to improve the efficiency.**
- **This work highlights the need of a continuous cooperation among radiochemists within the Nordic and international communities.**

Method Development

Laboratory Automation

Modern Instruments

Continuous Cooperation



Thank you!

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