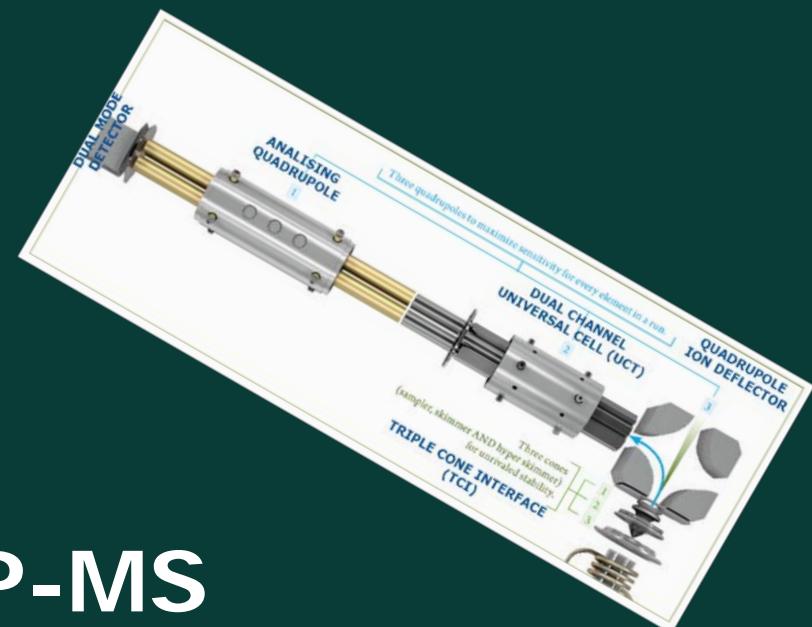
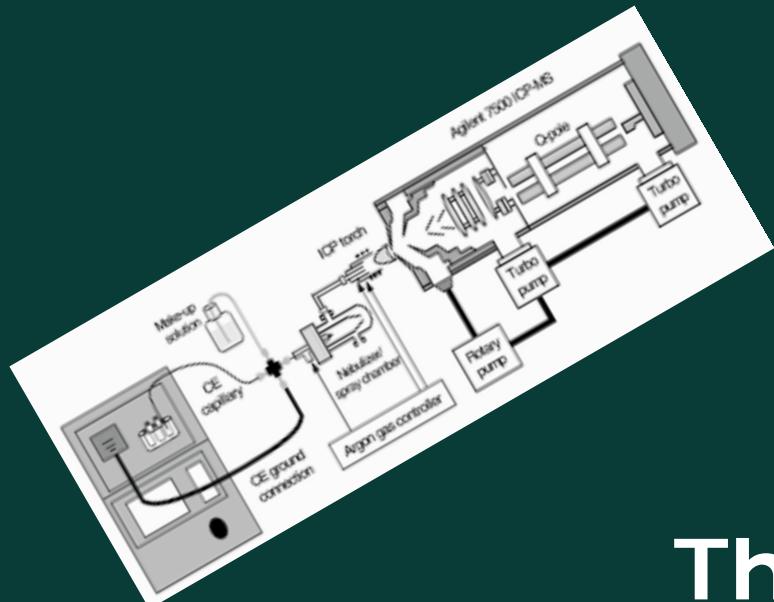




The European Commission's science and knowledge service

Joint Research Centre



The versatility of ICP-MS for the analysis of radionuclides

Laura Aldave de las Heras, Stefaan Van Winckel

JRC Directorate G – for Nuclear Safety and Security

Origin of Radionuclides

Natural Occurring Radionuclides

Primordial Radionuclides : U, Th series

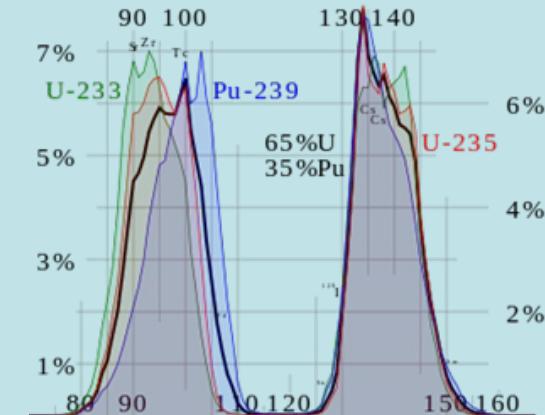
Secondary Radionuclides: Decay products of primordial radionuclides (Ra, Rn, Pb)

Cosmogenic Radionuclides: Cosmic rays (^{14}C)

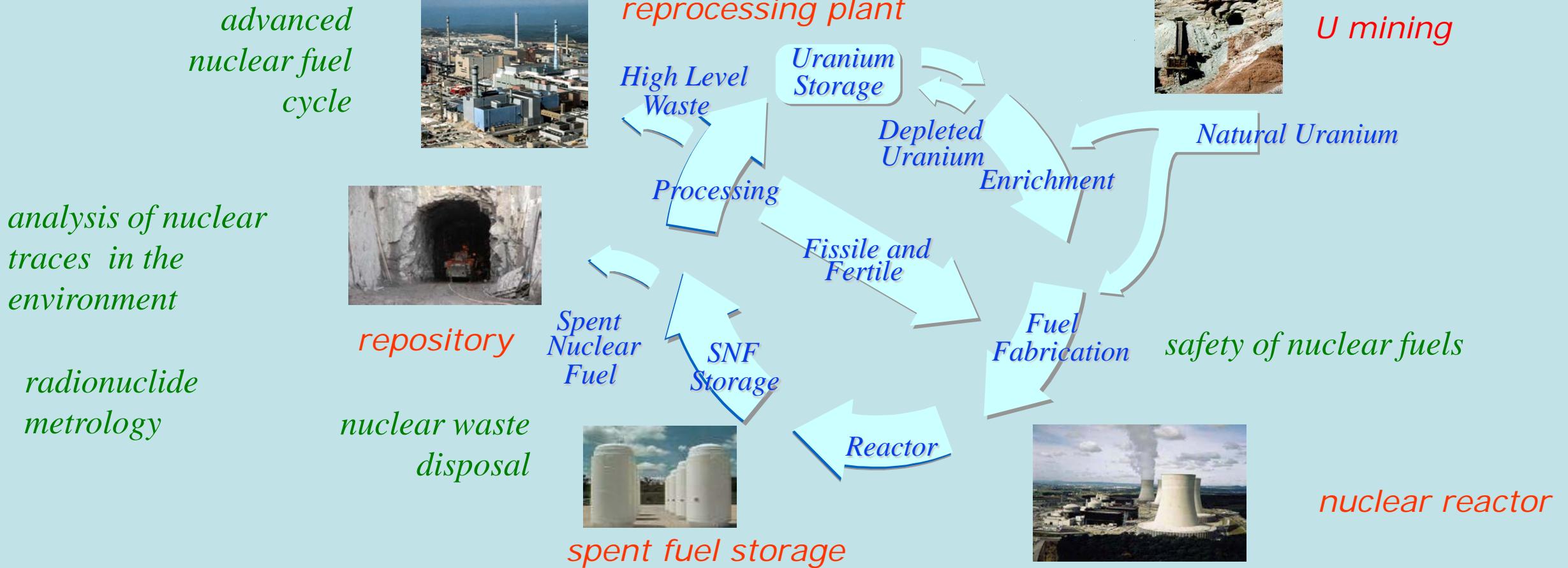
Anthropogenic Radionuclides

(Nuclear reactors, Particle accelerators, Radionuclides generators)

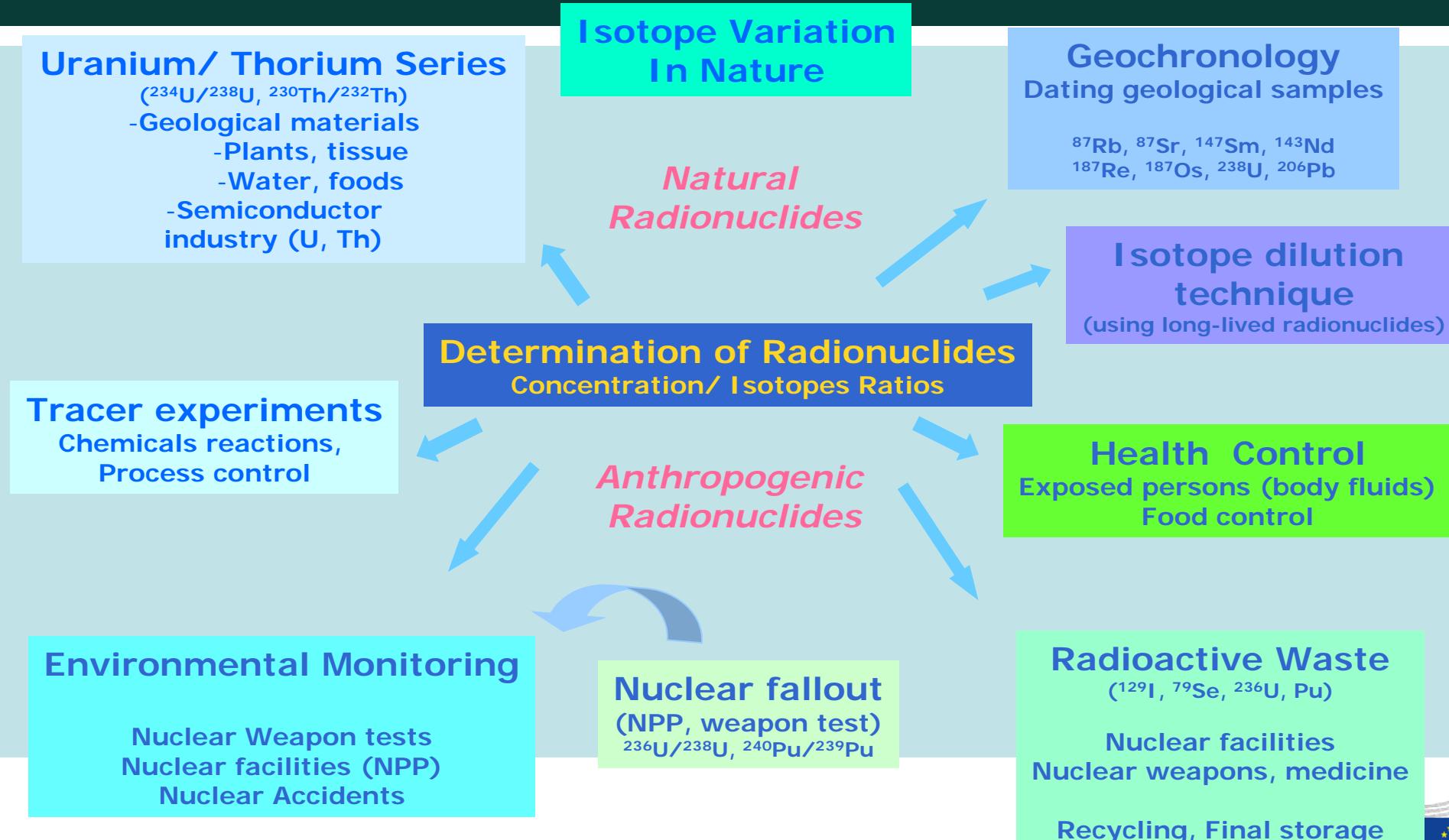
Fission and activation products : Nuclear Fuel Cycle



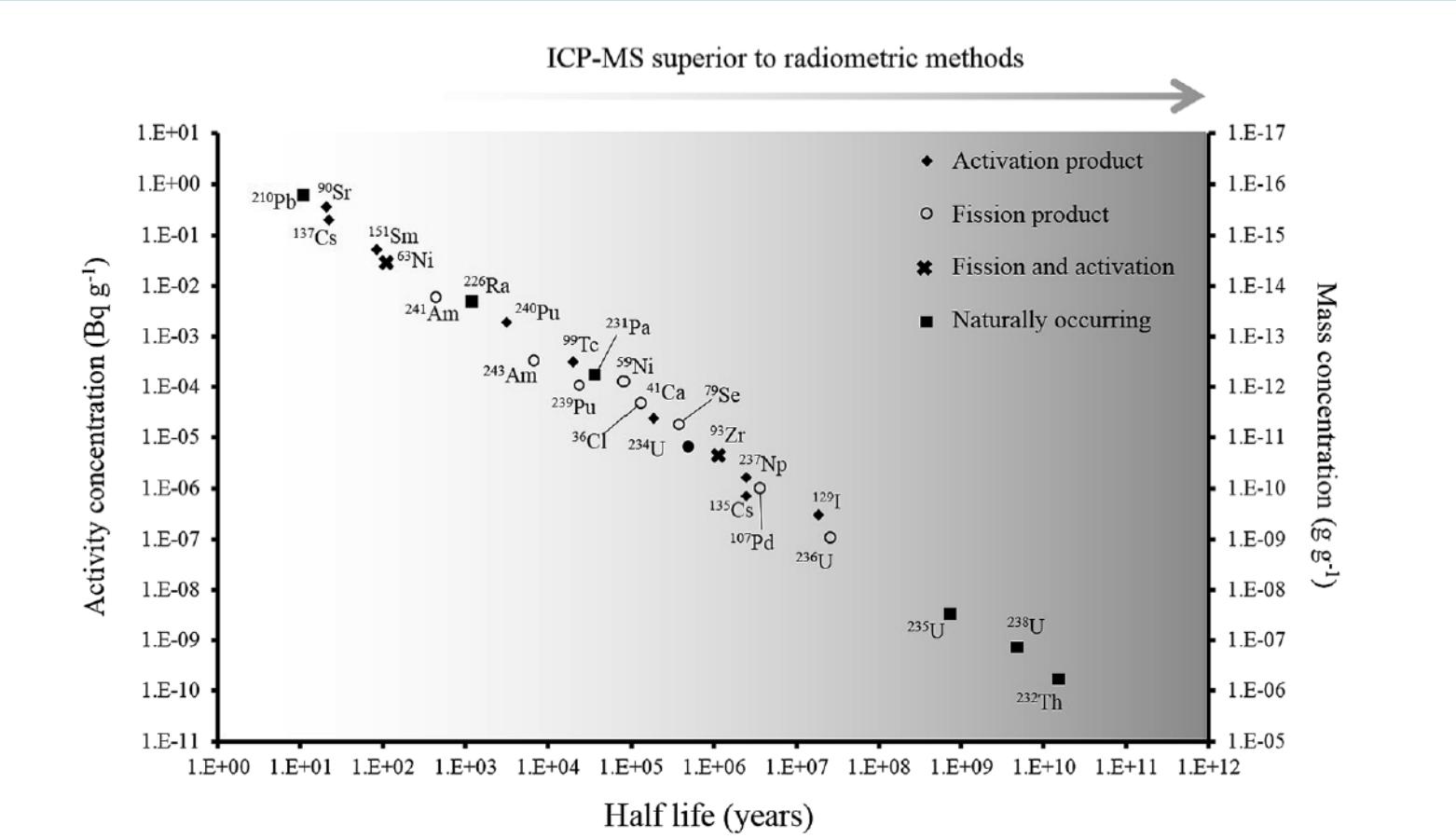
The Nuclear Fuel Cycle



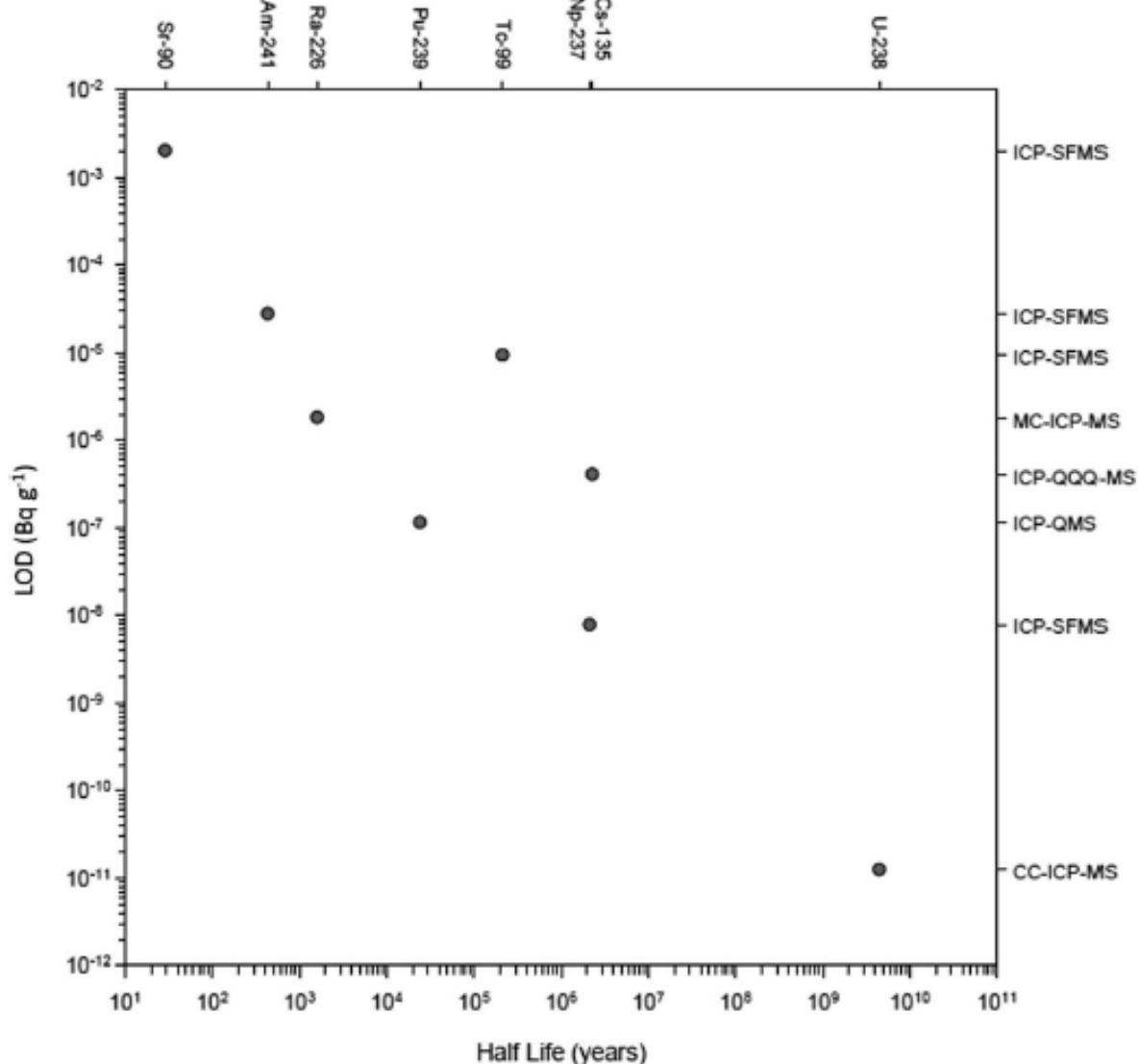
Overview Applications Fields



Radiometric versus Mass Spectrometric Methods



Some detection limits for radionuclides, achieved by MS techniques



Inorganic Mass Spectrometry (trace, ultra-trace, isotope ratio)

ION SOURCE

Evaporation
Atomisation
Ionisation

Thermal ionisation
Plasma ionisation
Electron impact
Ion bombardment
Laser ionisation

ANALYSER

Mass (and energy)
separation of
extracted ion beams

Quadrupole
Magnetic Sector
Electric Sector
Time of flight (TOF)
Orbitrap

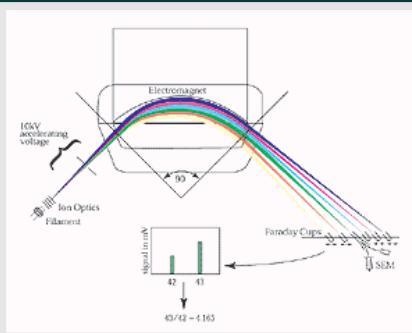
DETECTOR

Ions detection
Single Collector
MC

SEM
Channeltron
Faraday cup
Daly

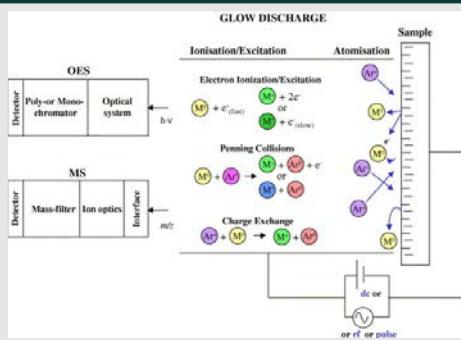
Some established MS techniques

TIMS



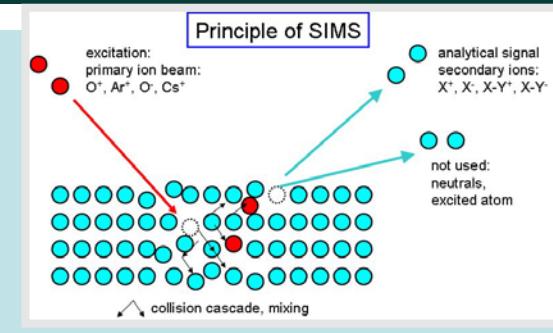
- Isotope ratio. Precision 0.001%
- Mass discrimination
- Mass fractionation effects

GDMS



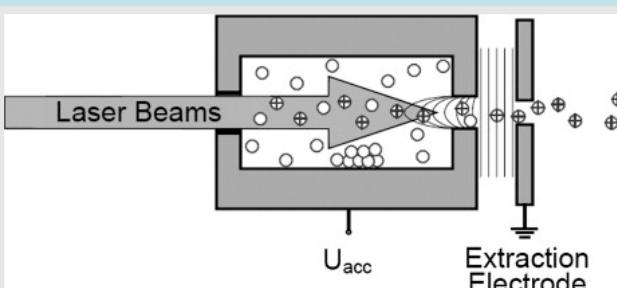
- Direct trace and depth profile solids
- Argon gas glow discharge at 0.1-1 Torr
- DL < ng/g

SIMS



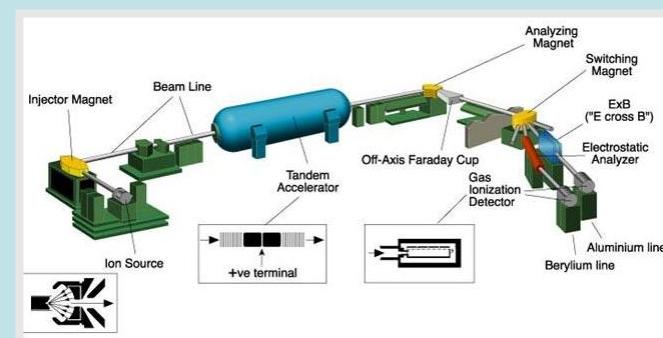
- Surface mapping; Depth profile (nm)
- Isotope Ratio
- Characterization Hot particles

RIMS



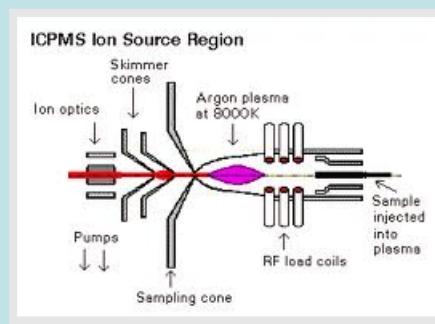
- High selective, ultrasensitive. Isotope Ratio
- ⁴¹Ca, ⁹⁰Sr, ⁹⁹Tc, ¹³⁵Cs, ²¹⁰Pb, ²³⁶U, ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, ²⁴²Pu, ²⁴⁴Pu
- DL 10⁻¹⁵ to 10⁻¹⁸ g

AMS



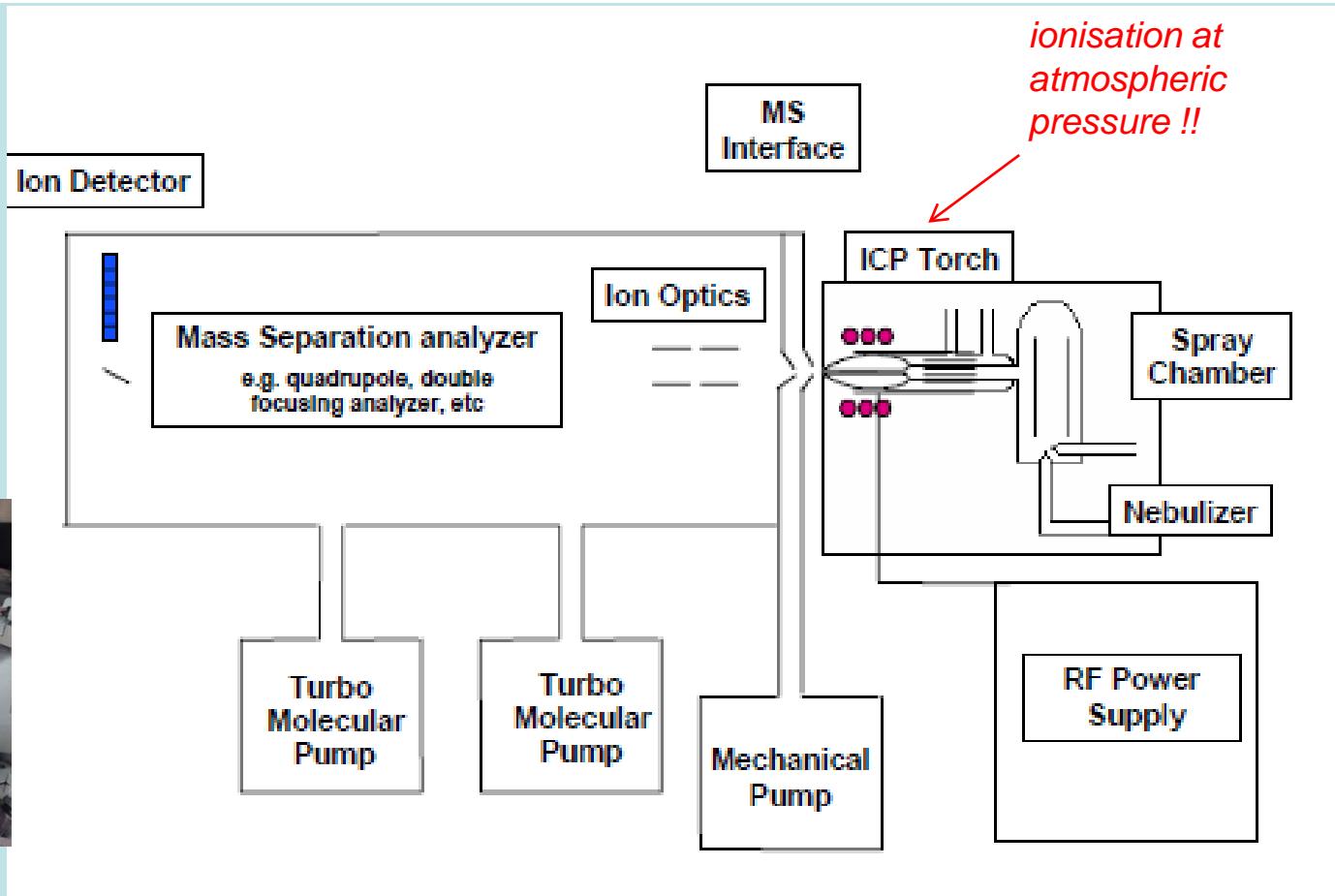
- High selective, ultrasensitive. Isotope Ratio
- Exotic radionuclides: ³He, ¹⁴C, ¹⁰Be, ²⁶Al, ¹²⁹I, ³²Si, ¹⁸²Hf, ²¹⁰Pb, ²³⁶U, ²⁴⁴Pu

ICPMS

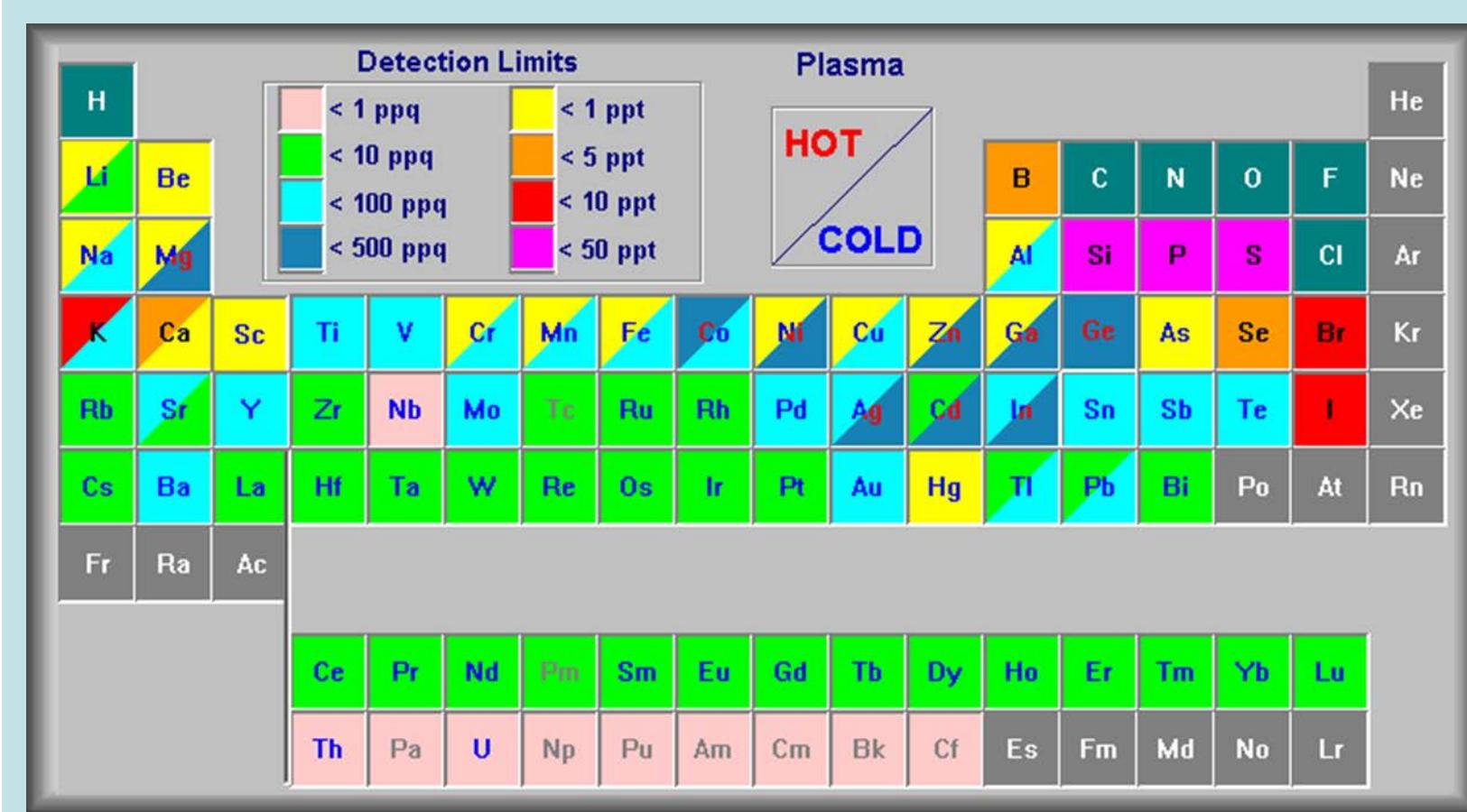
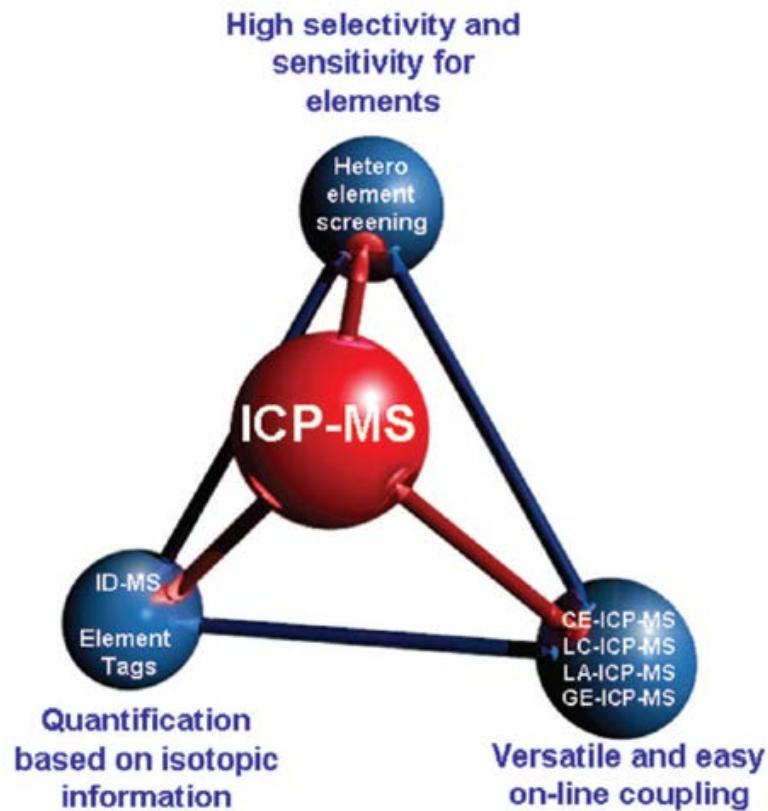


- Most frequently used
- Ultra-trace and Isotope Ratio
- Easy Quantification

Inductively Coupled Plasma - MS



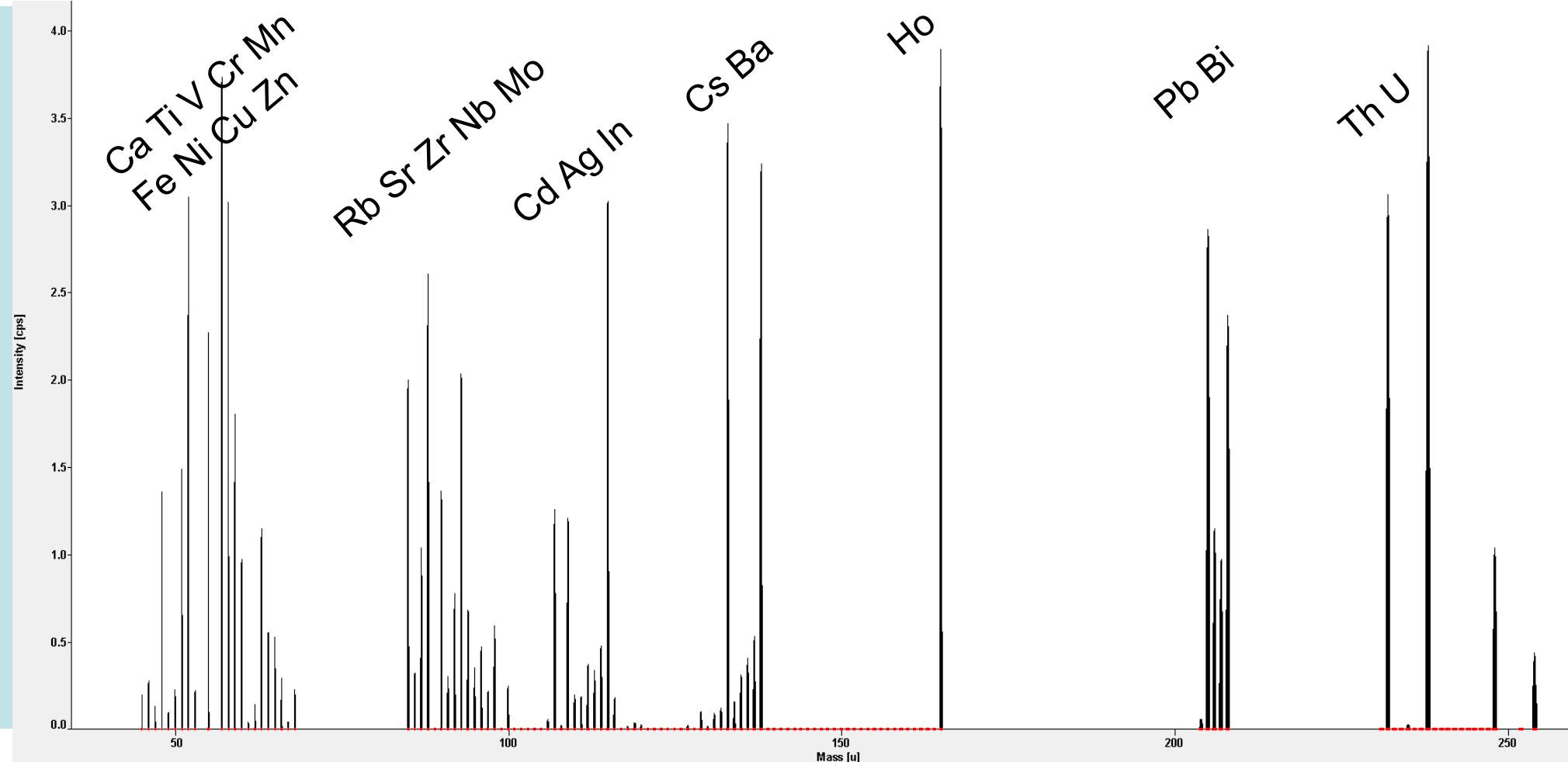
ICP-MS: a powerful analytical technique



Main advantages and drawbacks

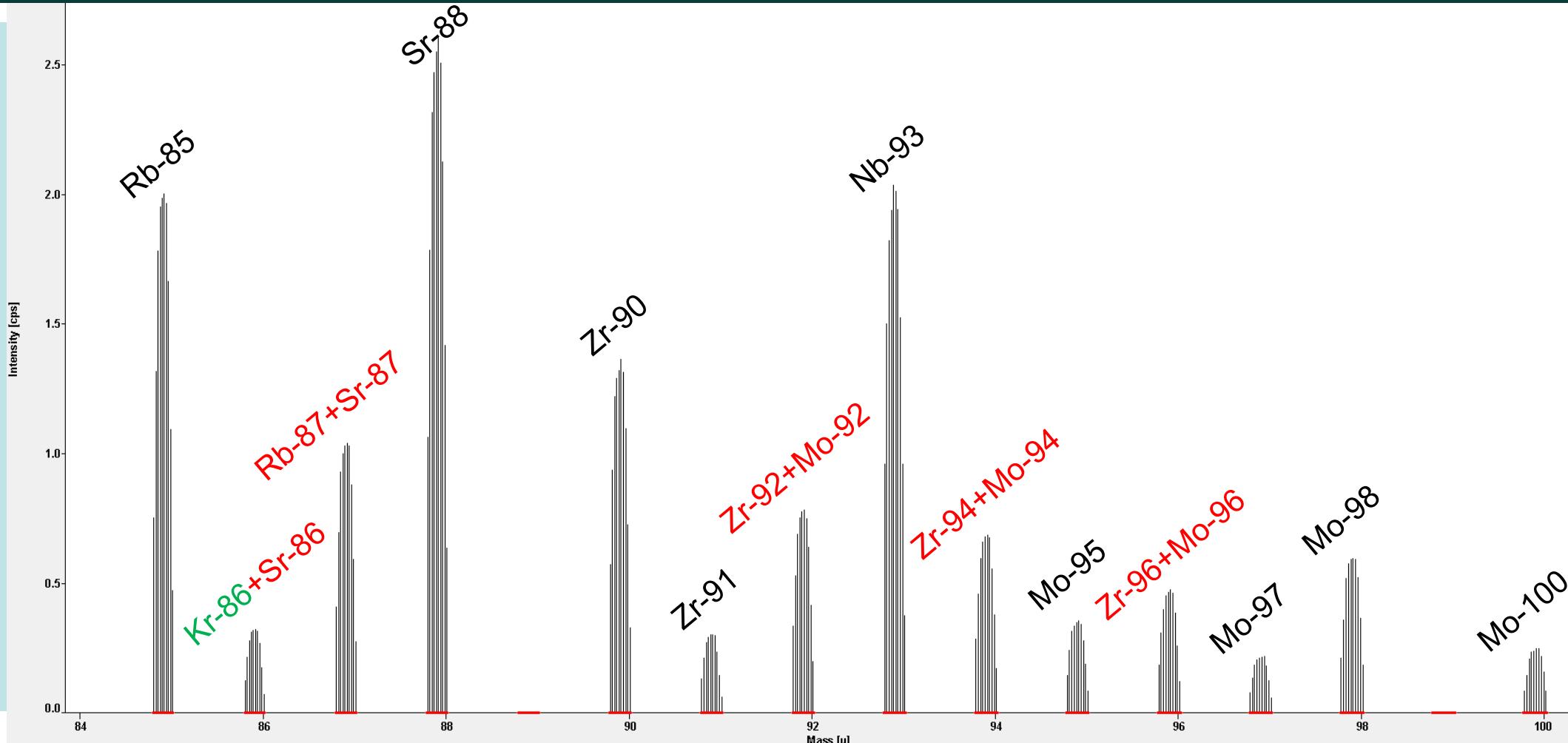
- Detection of nearly all of the elements (isotopes)
- Very low detection limits (ppb – ppt – ppq)
- Good precision (0.2 – 3% relative standard deviation)
- Broad dynamic concentration range (5-11 orders of magnitude)
- Spectral interferences (isobaric ions; polyatomic ions; ...)
- Abundance sensitivity

Keep these drawbacks – pitfalls – difficulties in mind



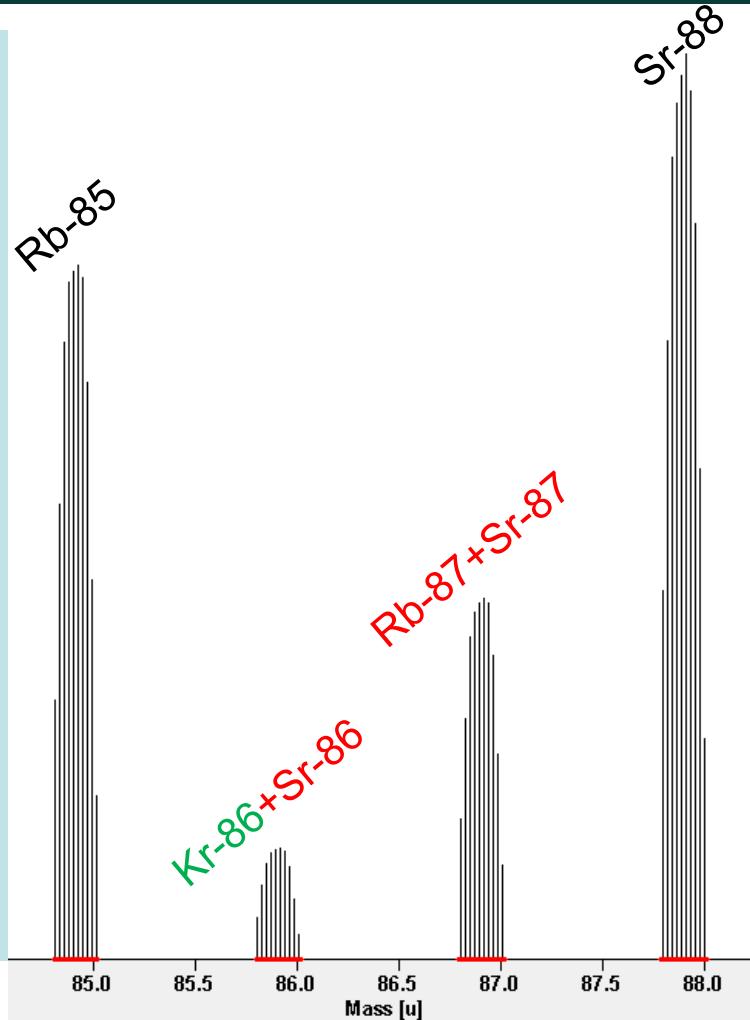
Overview spectrum of a multi-element standard solution

Spectral interferences (1): isobaric interferences



Same spectrum of a multiple-element standard solution, zoomed in on Rb - Mo

Spectral interferences (2): effect on ME calibration...



- Calibration curve per nuclide (per *amu*)
→ Sensitivity per nuclide (cps/ppb)

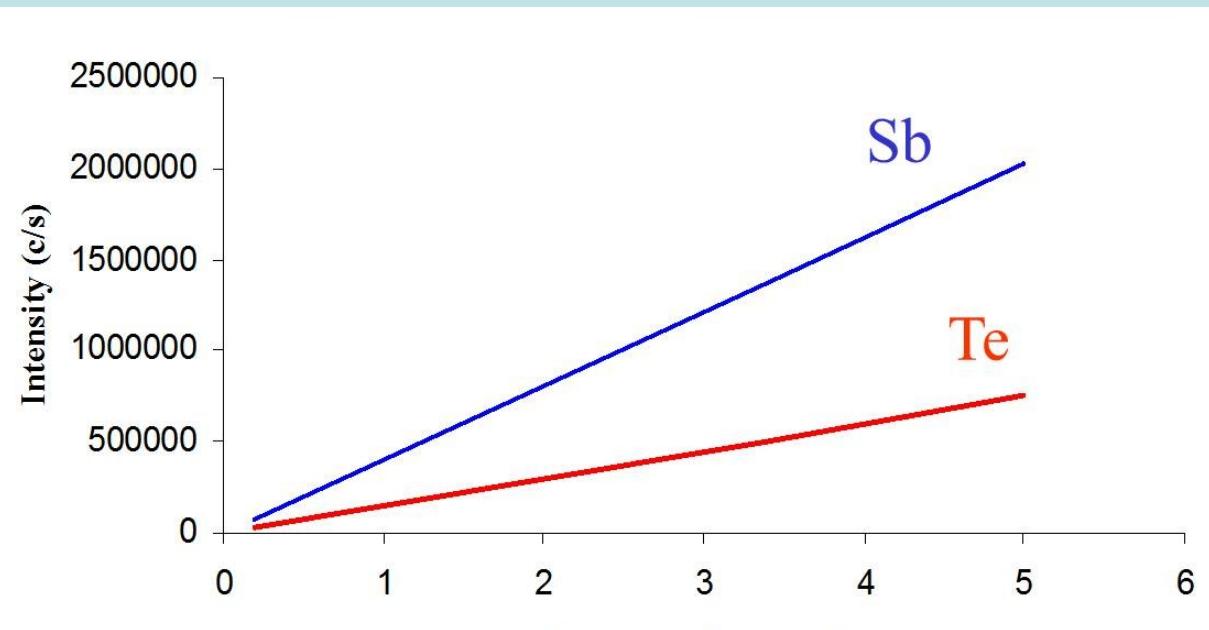
ppb in St sol	0.20	1.00	...
Rb-85	0.161	0.744	...
Sr-86	0.022	0.102	...
Rb-87+Sr-87	0.078	0.359	...
Sr-88	0.184	0.851	...
...

- Calibration with multi-element standard solutions
→ be aware of isobaric interferences!

	cps/ppb
Rb-85	2 445 941
Sr-86	2 694 053
Rb-87+Sr-87	2 531 995
Sr-88	2 714 893
...	...



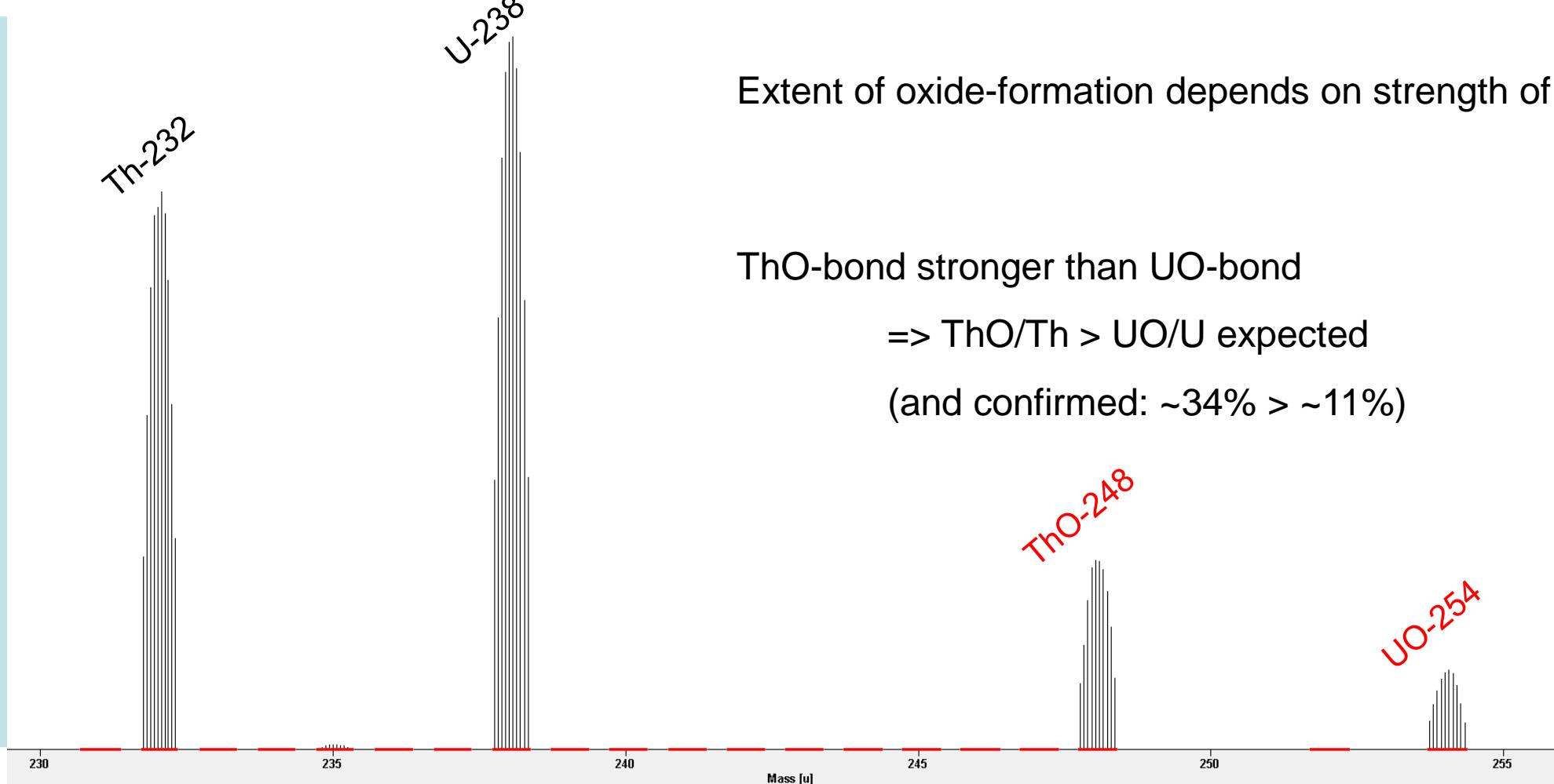
Spectral interferences (3): effect on ME calibration...



- Calibration of nuclear samples with natural standards
→ be aware of possible differences!

e.g. mass 125 = ^{125}Te in standard solution
but can be ^{125}Sb in nuclear sample,
and the sensitivities for Te and Sb are really different...

Spectral interferences (4): polyatomic interferences



Extent of oxide-formation depends on strength of **oxide bond**:

D°_{298}	kJ/mol
Th	854
U	761

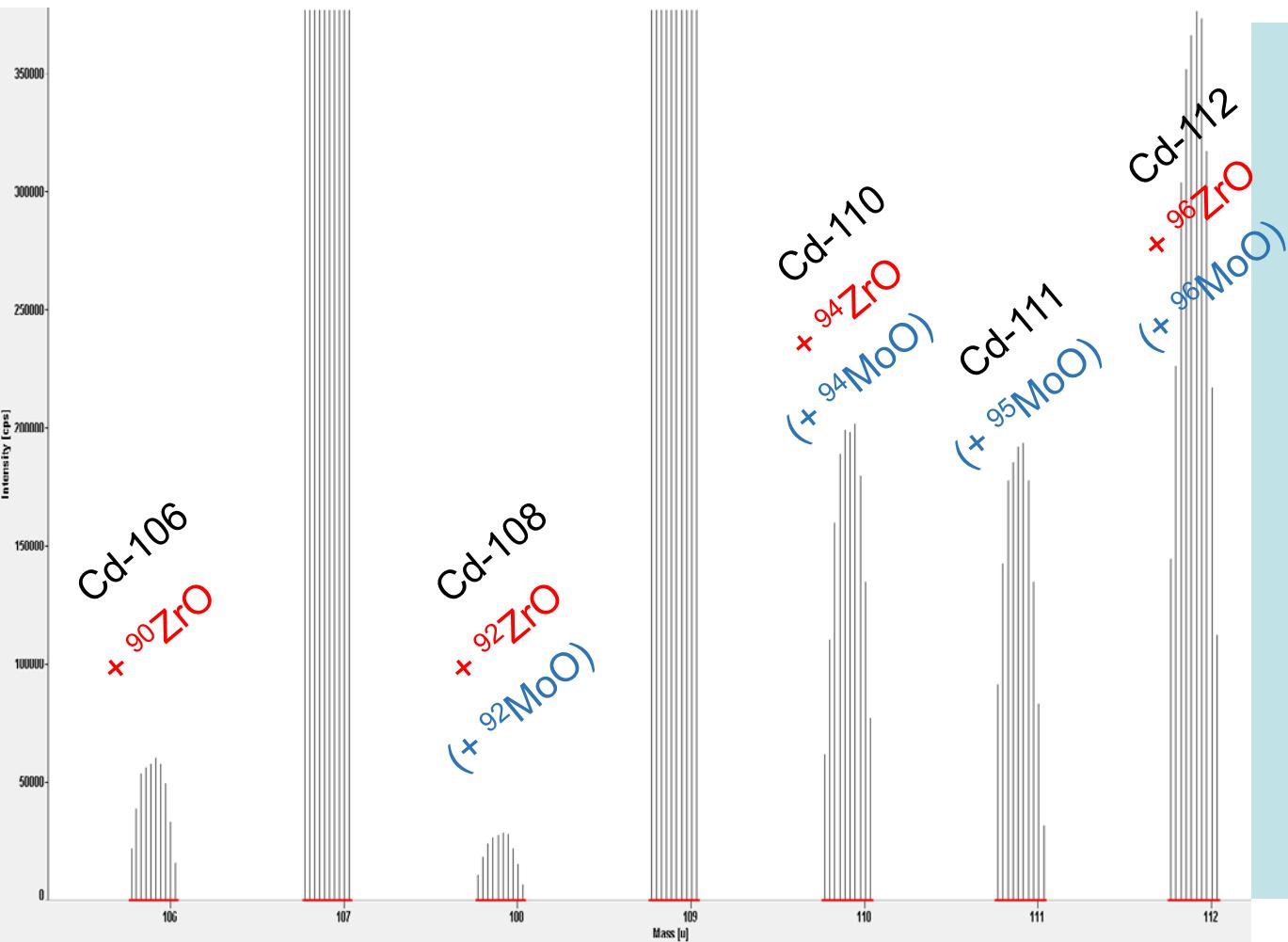
ThO-bond stronger than UO-bond

=> ThO/Th > UO/U expected

(and confirmed: ~34% > ~11%)

Same spectrum of a multiple-element standard solution, zoomed in on Th - U

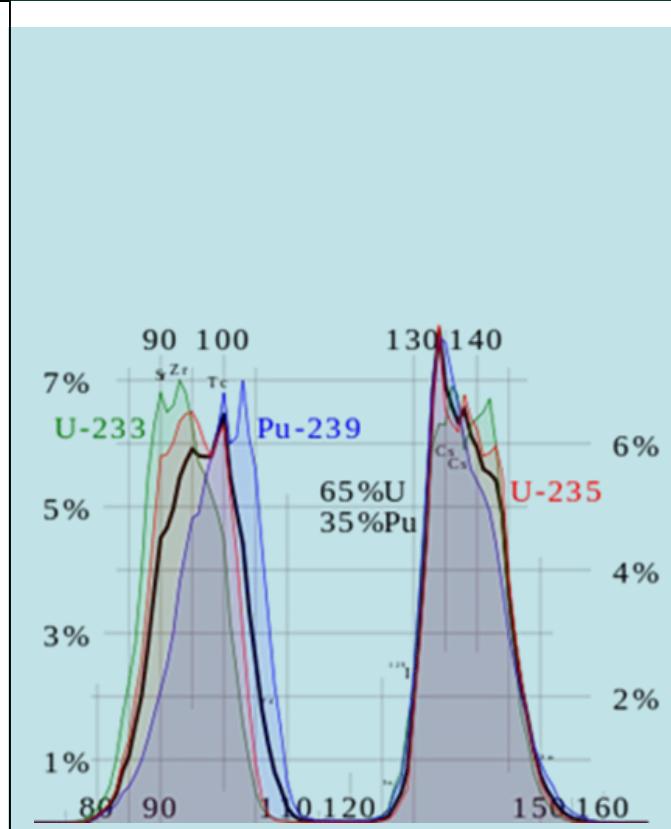
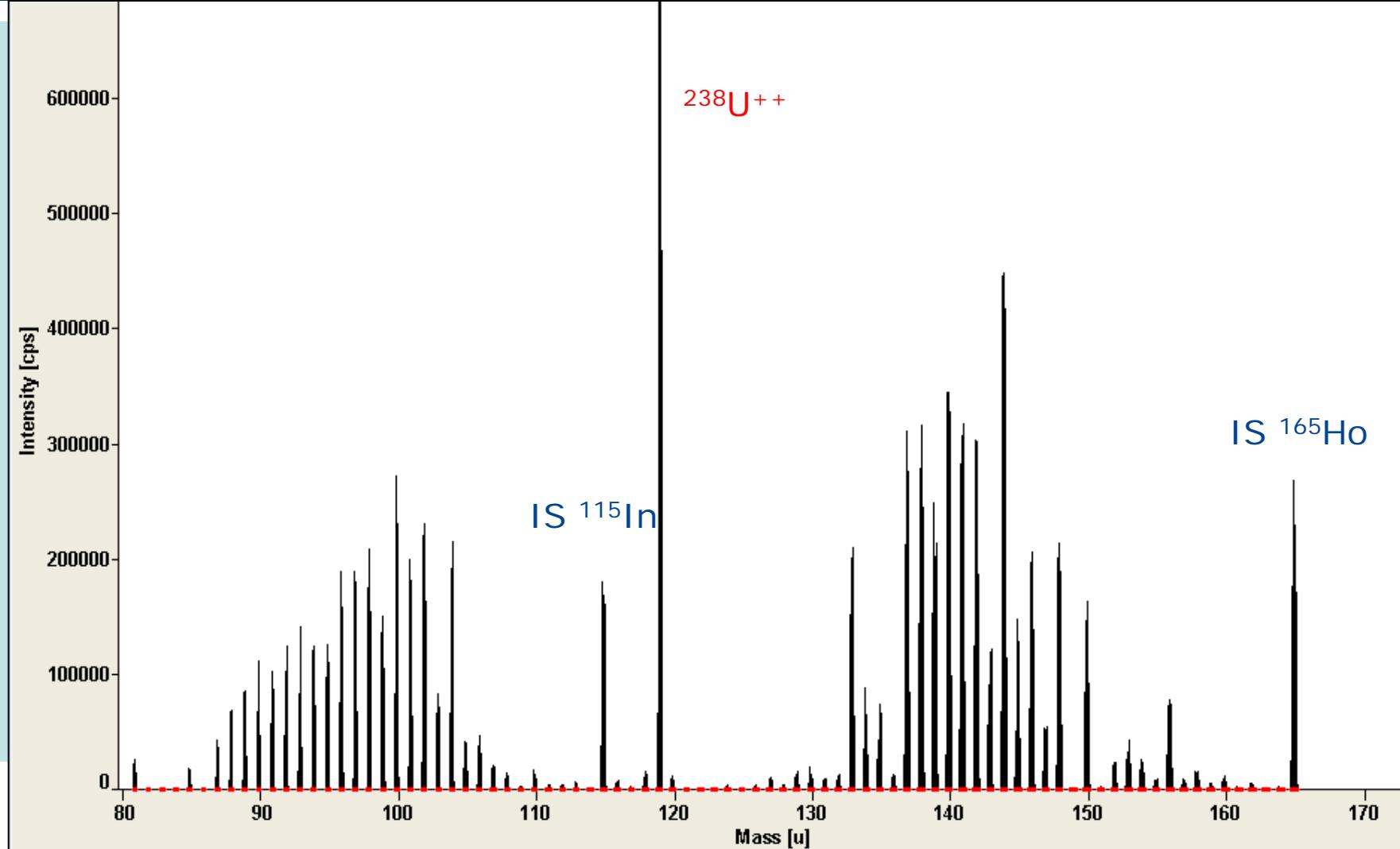
Spectral interferences (5): effect on ME calibration...



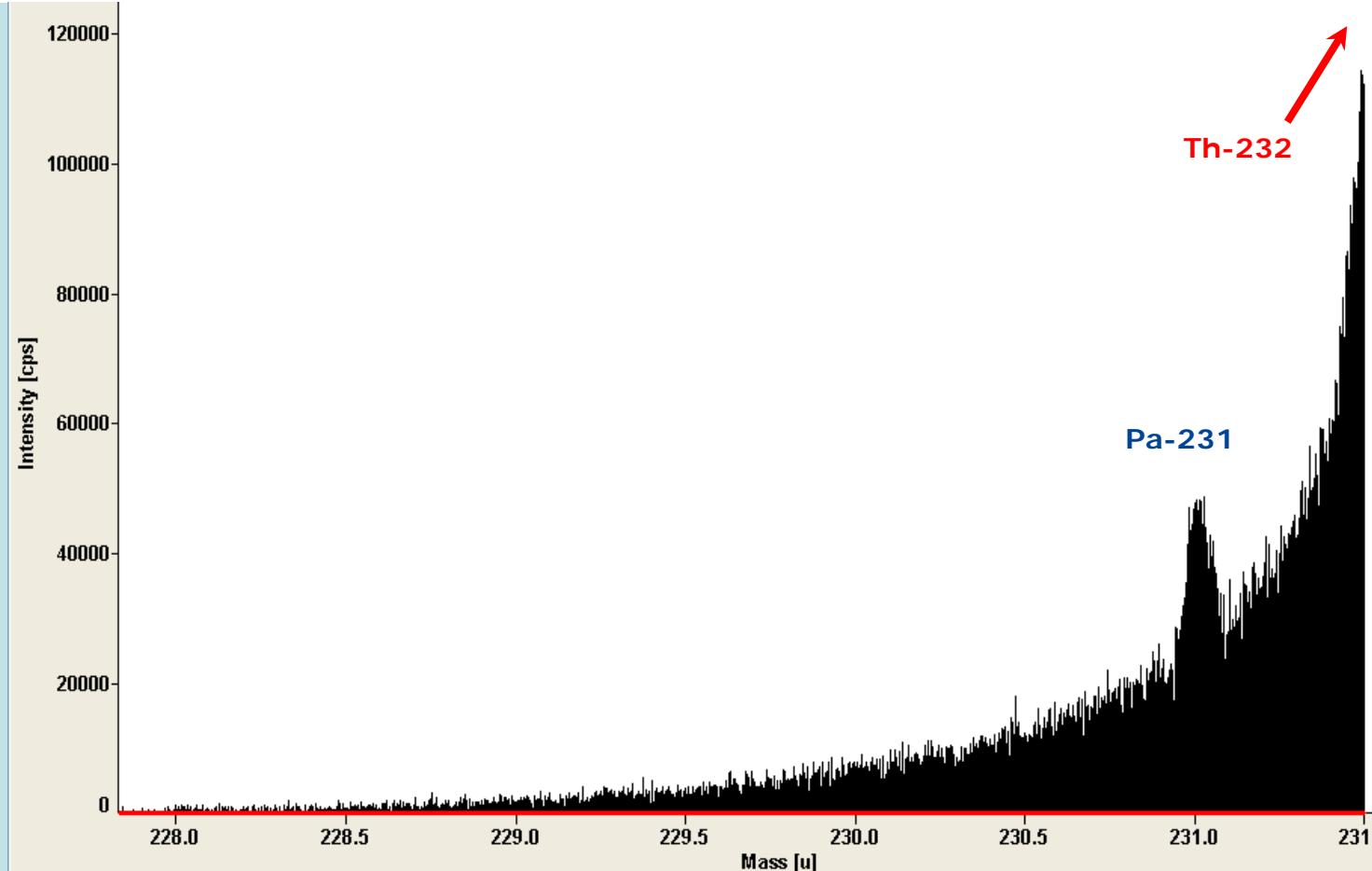
- Calibration with multi-element standard solutions
→ be aware of polyatomic interferences!

	cps/ppb	
Cd-106 (1.25%)	4 351 177	+ ZrO
Ag-107 (51.8%)	1 886 084	+ ZrO
Cd-108 (0.89%)	2 847 215	+ ZrO (+ MoO)
Ag-109 (48.2%)	1 934 181	+ NbO
Cd-110 (12.5%)	1 273 318	+ ZrO (+ MoO)
Cd-111 (12.8%)	1 192 612	(+ MoO)
Cd-112 (24.1%)	1 173 480	+ ZrO (+ MoO)
...

Spectral interferences (6): doubly charged ions



Trace analysis: be aware of 'abundance sensitivity'



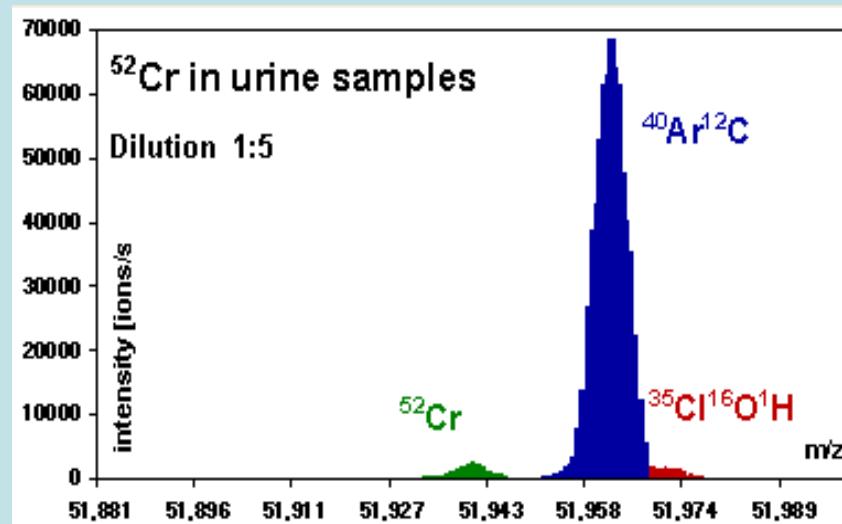
$$\text{Abundance sensitivity} = \frac{X \pm 1}{X}$$

Spectrum shows interference
of matrix element Th-232
on trace element Pa-231
due to peak tailing
(abundance sensitivity not good enough)

Resolution: $R = m/\Delta m$

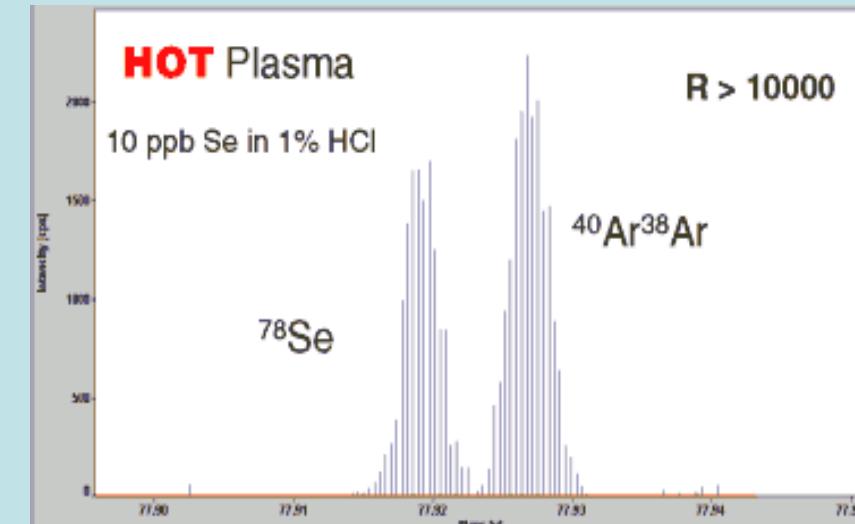
Resolution needed:

$^{44}\text{Ca} <> ^{12}\text{C}^{16}\text{O}_2$	2700
$^{52}\text{Cr} <> ^{12}\text{C}^{40}\text{Ar}$	2400
$^{75}\text{As} <> ^{40}\text{Ar}^{35}\text{Cl}$	7800
$^{78}\text{Se} <> ^{40}\text{Ar}^{38}\text{Ar}$	9980



Not possible:

$^{40}\text{Ca} <> ^{40}\text{Ar}$	192 500
$^{238}\text{Pu} <> ^{238}\text{U}$	200 800
$^{241}\text{Am} <> ^{241}\text{Pu}$	11 000 000



Trace analysis: the issue of 'BLANKS'

mass	BLANK1	BLANK2	BLANK3
85	509	9935	9370
86	1263	4660	8776
87	670	3672	7036
88	5522	26189	63583
89	928	443	813
90	9169	23544	22513
91	2267	5299	5222
92	5504	9421	9077
93	324	209	167
94	4630	8968	8392
95	2547	1036	852
96	4152	2760	2540
97	2117	1106	1009
98	4616	2923	2420
99	112	404	362
100	3229	2158	1837

«representative blank solutions» are very important, though often not so straightforward to get...

- Each step in preparing samples (dissolution, dilution, ...) is a possible source of contamination
- Multiple Blanks are often a pure necessity !
- Example showing different Blank intensity levels for different Blanks...

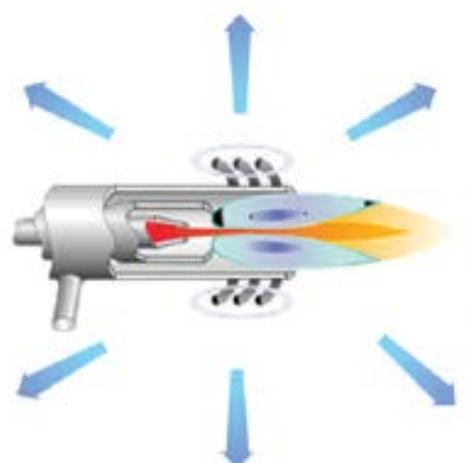
Types of ICP-MS (interference separation/reduction)

Multi-Collector
MC-ICP-MS
Precise isotope ratios

Quadrupole
ICP-Q-MS
Fast scan speed

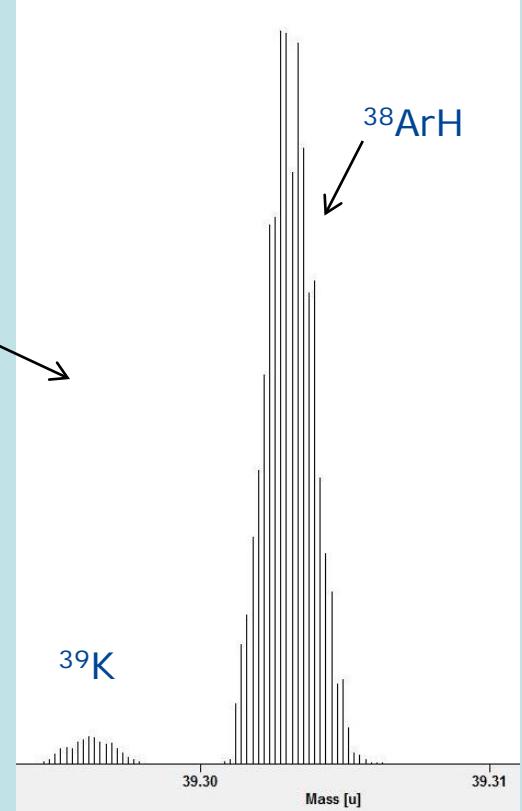
Dynamic Reaction Cell
ICP-DRC-MS
Collision and Reaction Cell
CRC-ICP-MS
Interference reduction, fast scan speed

Time of Flight (TOF)
ICP-TOF-MS
Mattauch-Herzog
MH-ICP-MS
Simultaneous data acquisition of the entire m/z range



High Resolution
HR-ICP-SF-MS
High sensitivity and physical interference separation

Triple-Quadrupole
ICP-QQQ-MS
Improved interference reduction



peaks separated in HR
(at expense of sensitivity...)

Summary: two majors problems

- Isobaric and polyatomic interferences with same nominal mass as the analyte to determine
- Low abundance sensitivity (tailing)

Some (polyatomic) interferences resolved using double focusing sector field ICPMS at resolution required (strong reduction sensitivity)

Collision/reaction cell quadrupole ICPMS with appropriate gas can suppress interfering isobaric ions

→ Coupling separation techniques to ICPMS

Some Radionuclides of Interest-Examples

Radionuclide	Interferences		Detection limit (mBq mL^{-1})
	Isobaric	Polyatomic ions	
⁷⁹ Se,	⁷⁹ Br,	⁷⁸ Se ¹ H, ⁴⁰ Ar ³⁹ K, ¹⁶ O ⁶³ Cu, ¹⁴ N ⁶⁵ Cu, ¹² C ⁶⁵ Zn	5
⁹⁰ Sr,	⁹⁰ Zr	⁸⁹ Y ¹ H, ¹⁶ O ⁷⁴ Ge, ¹² C ⁷⁸ Se, ¹⁴ N ⁷⁶ Se, ⁴⁰ Ar ⁵⁰ Ti	400
⁹³ Mo	⁹³ Nb, ⁹³ Zr	⁹² Mo ¹ H, ⁹² Zr ¹ H, ¹⁴ N ⁷⁹ Br, ¹² C ⁸¹ Br, ⁴⁰ Ar ⁵³ Cr	300
⁹³ Zr	⁹³ Nb, ⁹³ Mo	⁹² Mo ¹ H, ⁹² Zr ¹ H, ¹⁴ N ⁷⁹ Br, ¹² C ⁸¹ Br, ⁴⁰ Ar ⁵³ Cr	1
⁹⁹ Tc	⁹⁹ Ru	⁹⁸ Ru ¹ H, ⁹⁸ Mo ¹ H, ¹⁸ O ⁸¹ Br, ¹⁶ O ⁸³ Kr, ⁴⁰ Ar ⁵⁹ Co, ³⁶ Ar ⁶³ Cu, ⁶⁴ Zn ³⁵ Cl, ⁶² Zn ³⁷ Cl,	0.1
¹²⁶ Sn	¹²⁶ Xe, ¹²⁶ Te	¹²⁵ Te ¹ H, ¹² C ¹¹⁴ Cd, ¹⁴ N ¹¹² Cd, ⁴⁰ Ar ⁸⁶ Kr, ¹⁶ O ¹¹⁰ Pd, ¹⁶ O ¹¹⁰ Cd, ⁴⁰ Ar ⁸⁶ Sr	0.5
¹²⁹ I	¹²⁹ Xe	¹²⁸ Xe ¹ H, ¹²⁷ I ¹ H ₂ , ¹²⁸ Te ¹ H, ⁴⁰ Ar ⁸⁹ Y, ¹⁴ N ¹¹⁵ In, ¹⁶ O ¹¹³ Cd	0.037
¹³⁵ Cs	¹³⁵ Ba	¹³⁴ Ba ¹ H, ¹³³ Cs ¹ H ₂ , ¹³⁴ Xe ¹ H, ¹⁴ N ¹²¹ Sb, ¹² C ¹²³ Sb, ⁴⁰ Ar ⁹⁵ Mo, ¹⁶ O ¹¹⁹ Sn	0.01
²¹⁰ Pb	²¹⁰ Po	²⁰⁹ Bi ¹ H, ¹⁶ O ¹⁹⁴ Pt, ¹⁴ N ¹⁹⁶ Pt, ⁴⁰ Ar ¹⁷⁰ Er, ¹² C ¹⁹⁸ Hg, ¹² C ¹⁹⁸ Pt, ⁴⁰ Ar ¹⁷⁰ Yb, ¹ H ²⁰⁹ Bi	27
²²⁶ Ra		⁴⁰ Ar ¹⁸⁶ W, ¹⁷ O ¹ H ²⁰⁹ Bi, ⁴⁰ Ar ¹⁸⁶ Os, ¹⁸ O ²⁰⁸ Pb	0.3
²³¹ Pa		⁴⁰ Ar ¹⁹¹ Ir, ³⁶ Ar ¹⁹⁵ Pt	1
²³⁰ Th		²²⁹ Th ¹ H, ⁴⁰ Ar ¹⁹⁰ Os, ³⁶ Ar ¹⁹⁴ Pt	1
²³² Th		²³¹ Pa ¹ H, ⁴⁰ Ar ¹⁹² Os, ⁴⁰ Ar ¹⁹² Pt	0.00002
²³⁴ U		²³² Th ¹ H ₂ , ⁴⁰ Ar ¹⁹⁴ Pt	0.11
²³⁵ U		²³⁴ U ¹ H, ⁴⁰ Ar ¹⁹⁵ Pt	0.00004
²³⁸ U		²³⁷ Np ¹ H, ¹² C ²²⁶ Ra, ⁴⁰ Ar ¹⁹⁸ Hg, ⁴⁰ Ar ¹⁹⁸ Pt, ³⁶ Ar ²⁰² Hg	0.000006
²³⁷ Np		²³⁵ U ¹ H ₂ , ⁴⁰ Ar ¹⁹⁷ Au	0.0001
²³⁹ Pu		²³⁸ U ¹ H, ⁴⁰ Ar ¹⁹⁹ Hg, ³⁷ Cl ²⁰² Hg, ³⁵ Cl ²⁰⁴ Hg	0.010
²⁴⁰ Pu		²³⁹ Pu ¹ H, ²³⁸ U ¹ H ₂ , ⁴⁰ Ar ²⁰⁰ Hg, ³⁶ Ar ²⁰⁴ Hg, ³⁶ Ar ²⁰⁴ Pb	0.040
²⁴¹ Pu	²⁴¹ Am	²⁴⁰ Pu ¹ H, ⁴⁰ Ar ²⁰¹ Hg, ³⁵ Cl ²⁰⁶ Pb, ¹⁵ N ²²⁶ Ra	20
²⁴¹ Am	²⁴¹ Pu	²⁴⁰ Pu ¹ H, ⁴⁰ Ar ²⁰¹ Hg, ³⁵ Cl ²⁰⁶ Pb, ¹⁵ N ²²⁶ Ra	0.6



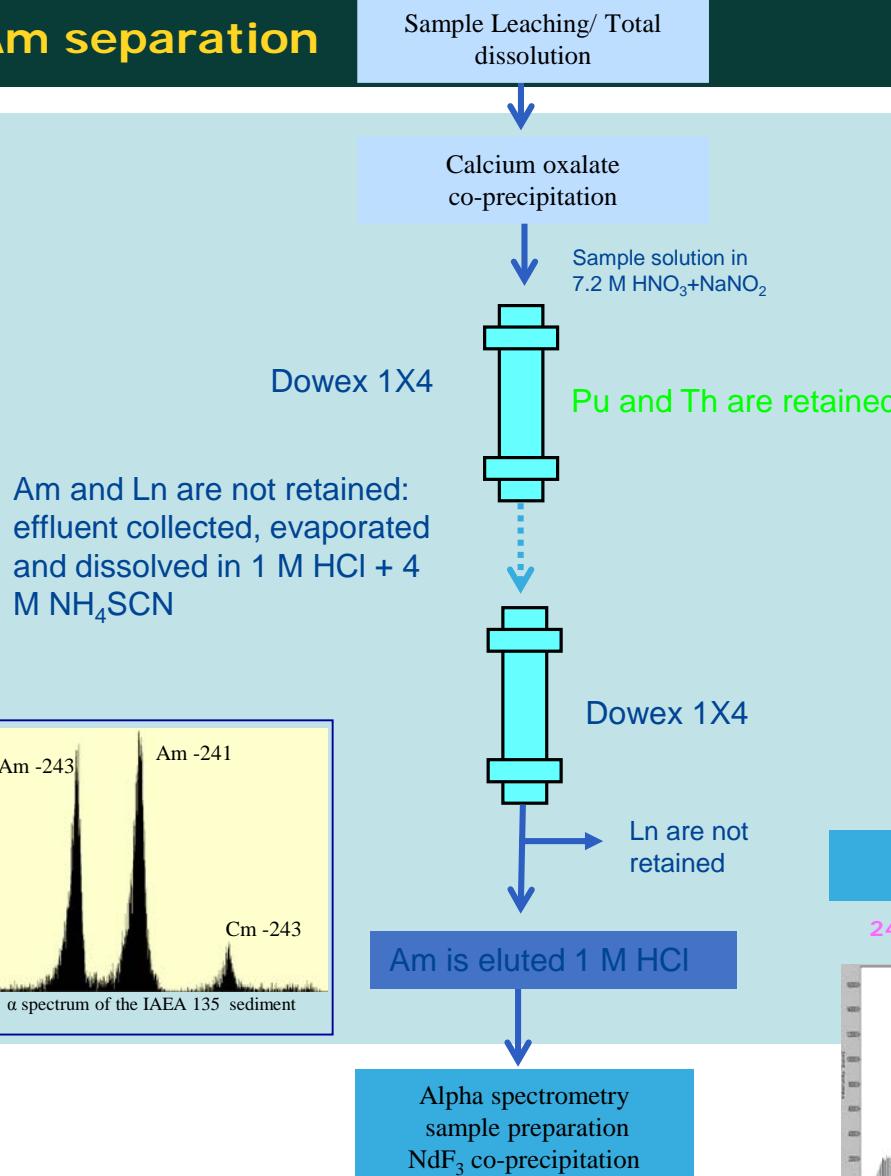
Pu isotopes and Am concentrations (fg/g) in different Environmental Samples

*Sample Type	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Am
Soil	0,1	26-1836	4,7-332	0,16
Grain Vegetables	3×10^{-6} - 2×10^{-4}	0,1-2,3	0,02-0,5	$1,6 \times 10^{-6}$
Lichen	-	1049-2620	140-474	5,5-16
Sea Water	-	2×10^{-4} - 2×10^{-2}	4×10^{-5} - 3×10^{-3}	6×10^{-5}

* Global Fallout weapons test ratio $^{240}\text{Pu}/^{239}\text{Pu} = 0,18$

Classical Methods

Am separation



Sample Leaching/ Total dissolution

Sample solution in 7.2 M HNO₃+NaNO₂

Dowex 1X4

- a) 7.2 M HNO₃
- b) 10M HCl
- c) 0.35 M HCl+0.018 M HF

Pu separation

Pu sample preparation
NdF₃ co-precipitation

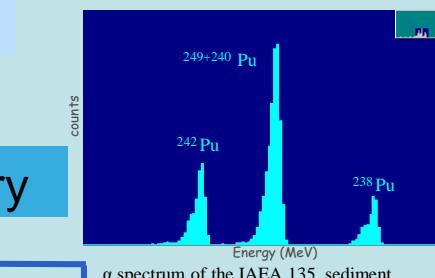
Cellulose nitrate Filters

Alpha Spectrometry

238Pu/239+240Pu

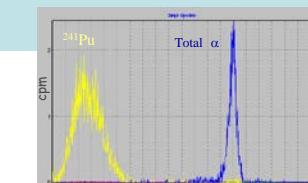
ICPMS

240Pu/239Pu



LSC

241Pu

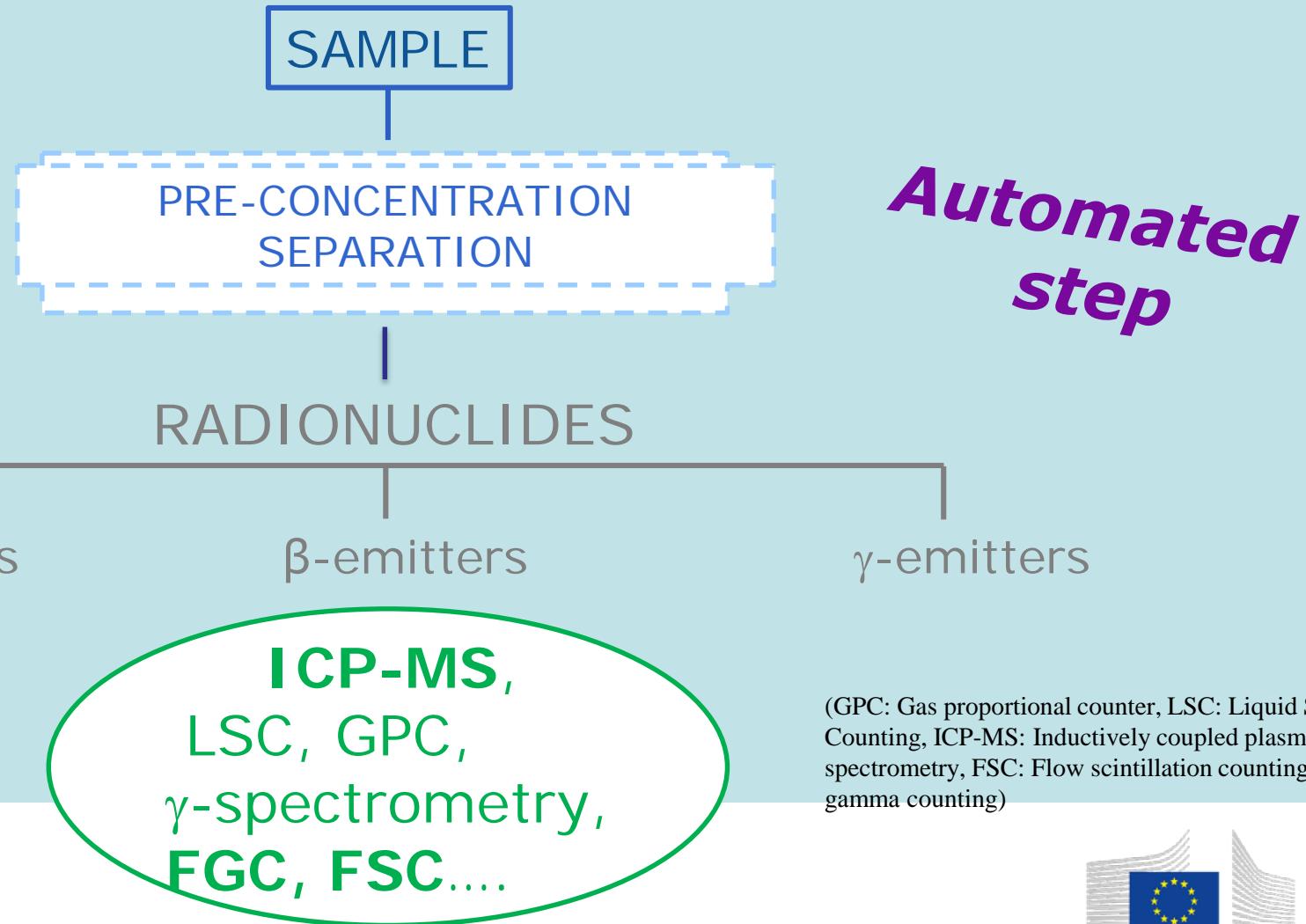


Different approaches for the analysis of radionuclides using separation techniques

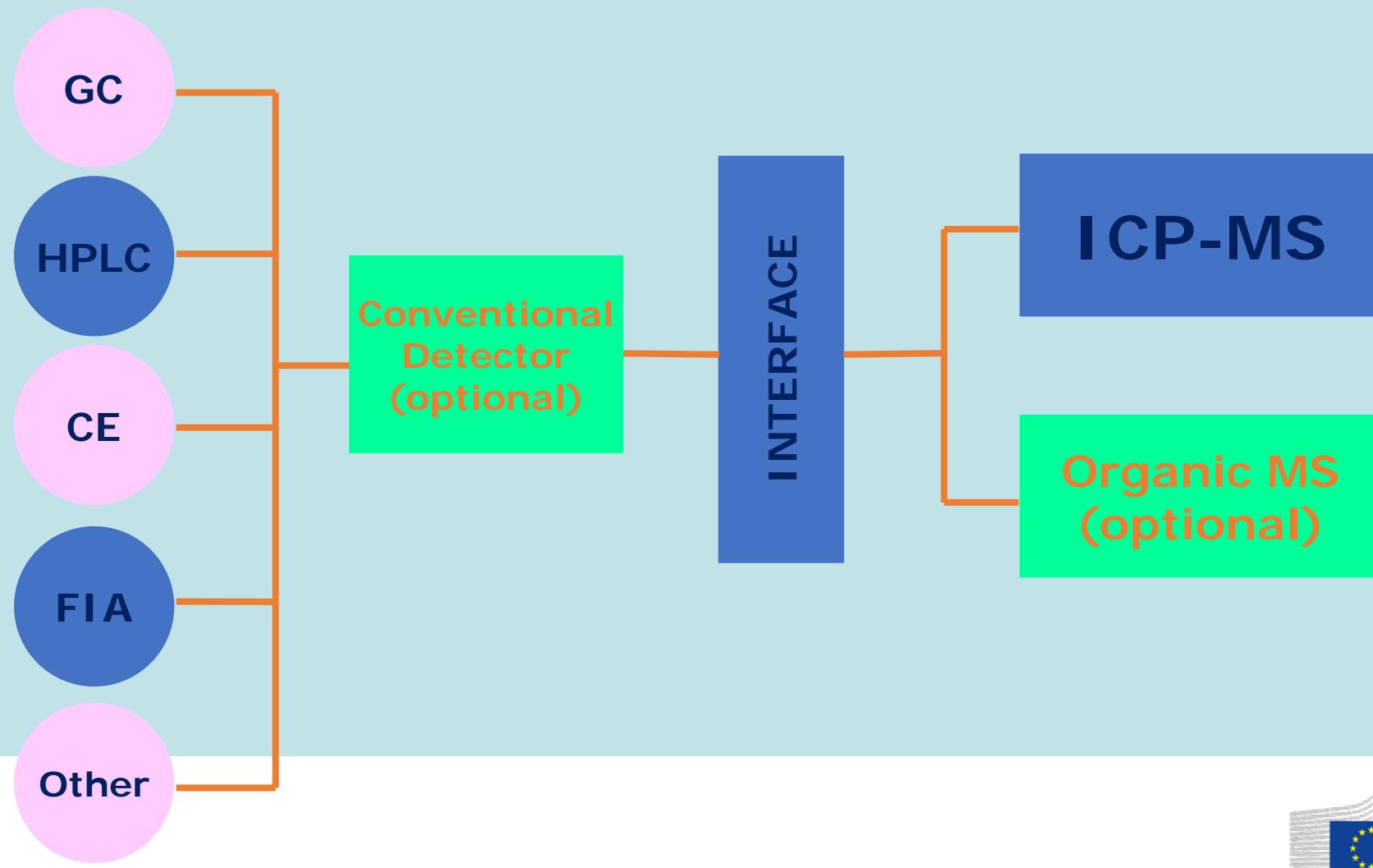
Level of automation is limited:

- **Sample Type & Activity**
- **Detector**

**Full/Partial
Automated**

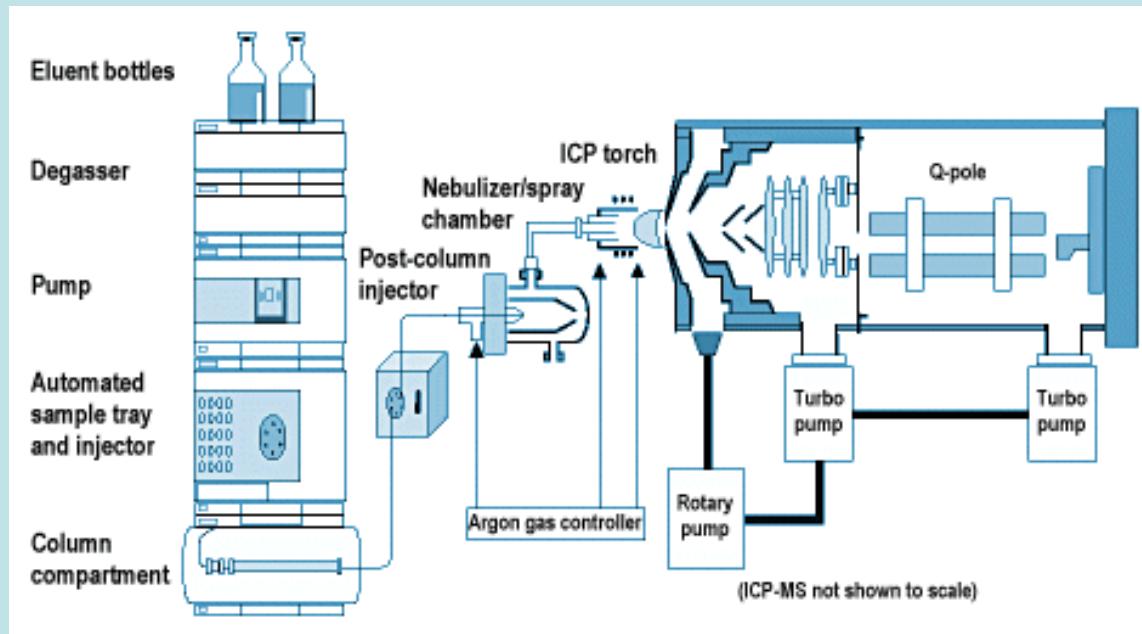


Schematic of a generic hyphenated system



Separation Techniques Coupled to ICPMS

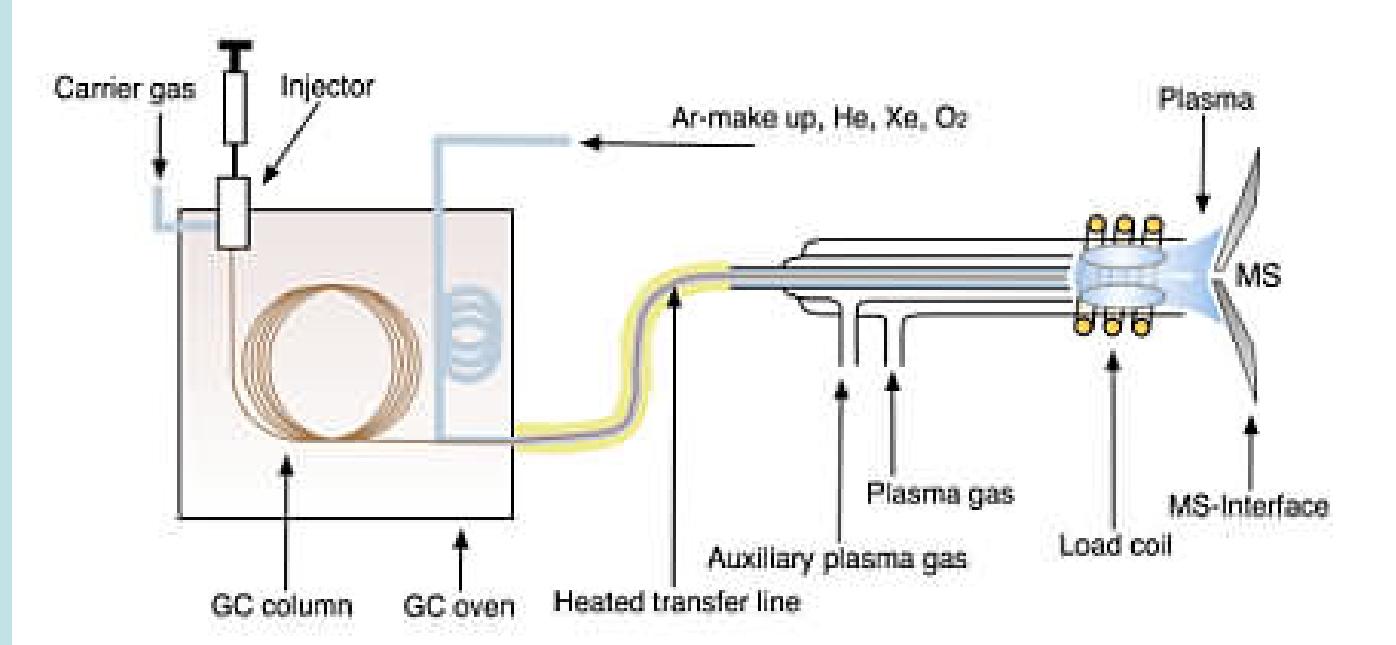
High Performance Liquid Chromatography (HPLC)



composition and flow rate of the eluent
plasma temperature, electron density, aerosol generation or analyte transport
overall ionisation process inside plasma

Separation Techniques Coupled to ICPMS

Gas Chromatography

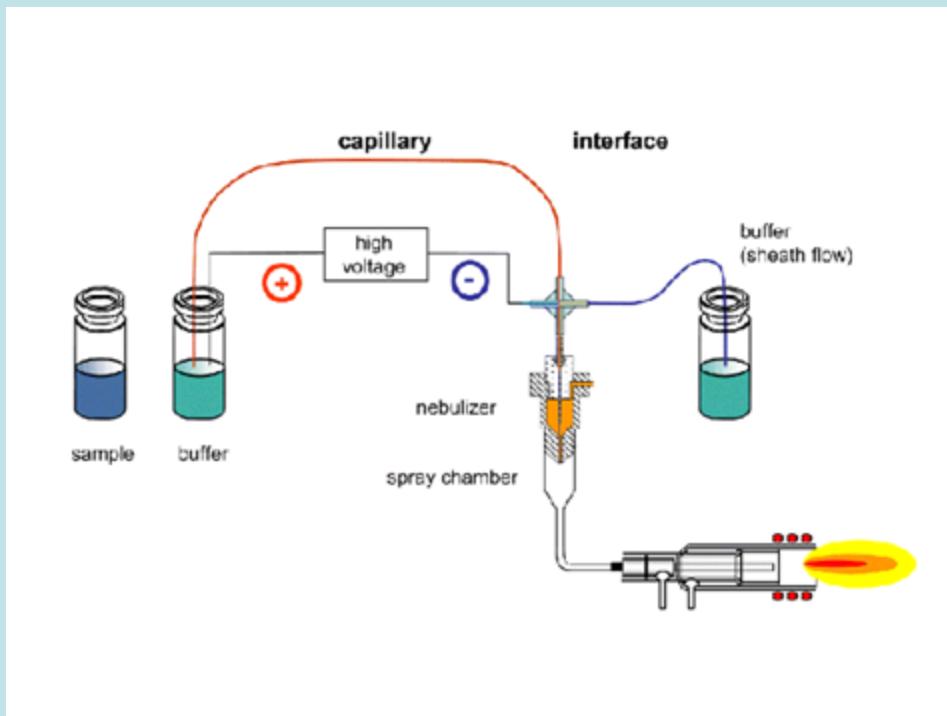


avoidance of thermal degradation of the analyte species in the injector and column

condensation at the interface during transport from the end of the column to the ICP torch

Separation Techniques Coupled to ICPMS

Capillary Electrophoresis



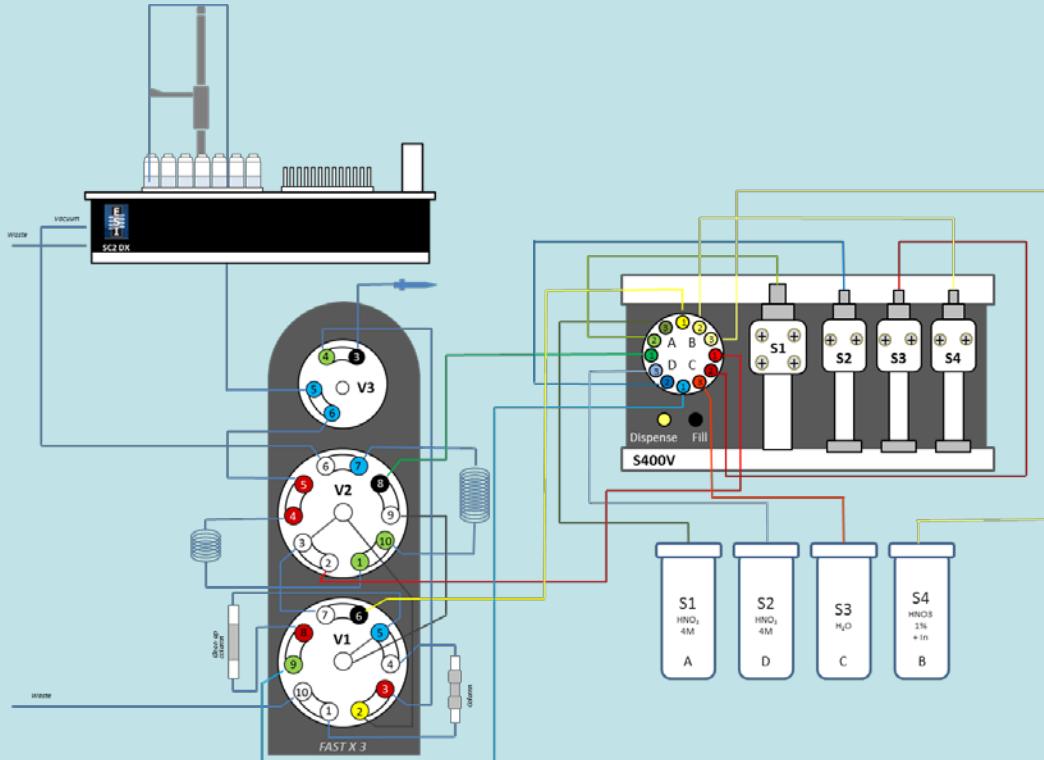
less straightforward
than HPLC or GC.

low flow rate of CE that limit the
choice of a nebulizer

necessity to apply a high voltage
across the capillary and keeping
the electrode grounded.

Separation Techniques Coupled to ICPMS

Flow injection/Sequential injection Analysis



Easy and efficient determination of low pg/g levels of key radionuclides

Automated and versatile sample uptake and introduction capabilities

Reduction of sample preparation achieving good detection limits

Separation Techniques Advantages

Rapid separation

Direct connection to ICPMS (no CE)

Automated operation possible

Reduction of chemical reagents and waste

Less cross-contamination

Examples Separations

Radionuclide	Interferences (m/z)	Method feature	FIA method: Column / Eluents
⁷⁹ Se	³⁸ Ar ⁴⁰ ArH ⁺ , ⁷⁹ Br ⁺ , ³⁹ K ⁴⁰ Ar ⁺ , ¹⁵⁸ Gd ²⁺ , ⁶³ Cu ¹⁶ O ⁺	Pre-concentration/ Separation	<i>Nobias</i> ^a Acetate 0.5 mol l ⁻¹ pH 4 ^b HNO ₃ 8%
⁷⁹ Se		Speciation	<i>Anion Exchange</i> Phosphate 0.2 mol l ⁻¹ , pH 8
¹²⁶ Sn	¹²⁶ Te ⁺ , ¹²⁶ Xe ⁺ , ¹¹⁰ Pd ¹⁶ O ⁺ , ¹¹⁰ Cd ¹⁶ O ⁺	Pre-concentration/ Separation	<i>Nobias</i> ^a Acetate 0.5 mol l ⁻¹ pH 6 ^b HNO ₃ 8%
¹³⁵ Cs	¹³⁵ Ba ⁺	Separation	^b NH ₄ NO ₃ 5 mol l ⁻¹ CG5A ^a HNO ₃ 2 mol l ⁻¹ CG12A ^a HNO ₃ 50 mmol l ⁻¹
⁹⁰ Sr	¹⁸⁰ W ²⁺ , ¹⁸⁰ Hf ²⁺ , ⁵⁸ Ni ¹⁶ O ₂ ⁺ , ⁷⁴ Ge ¹⁶ O ⁺ , ⁵² Cr ³⁸ Ar ⁺ , ⁵⁰ V ⁴⁰ Ar ⁺ , ⁵⁴ Fe ³⁶ Ar ⁺ , ⁵⁰ Ti ⁴⁰ Ar ⁺ , ⁹⁰ Zr ⁺	Pre-concentration/ Separation	<i>Sr-resin</i> ^a HNO ₃ 4 mol l ⁻¹ ^b MQW

- Nobias Chelate-PA1 a hydrophilic methacrylate with immobilised EDTA and IDA functional groups
- CG5A mixed be with cationic and anionic exchangers
- CG12A carboxylate/phosphonate cation exchanger
- Sr resin :1.0M 4,4'(5')-di-t-butylcyclohexano 18-crown-6 in 1-octanol

Resins for Radiochemical Applications

Resin Name	Radionuclides
CL resin	^{36}Cl , ^{129}I
Cs Resin	^{135}Cs , ^{137}Cs
DGA resin	Am, Y, Ra (Actinides & Lanthanides)
RE resin	Th, U, Np, Pu, Am, Cm, rare earth elements
Sr resin/ Pb resin	Sr / Pb
TEVA® Resin	Tc, Th, Np, Pu, Am/Lanthanides
UTEVA® Resin	Th, U, Np, Pu
TRU Resin	Fe, Th, Pa, U, Np, Pu, Am, Cm
NOBIAS-chelate PA-1®	REE's, transition metals, metalloids

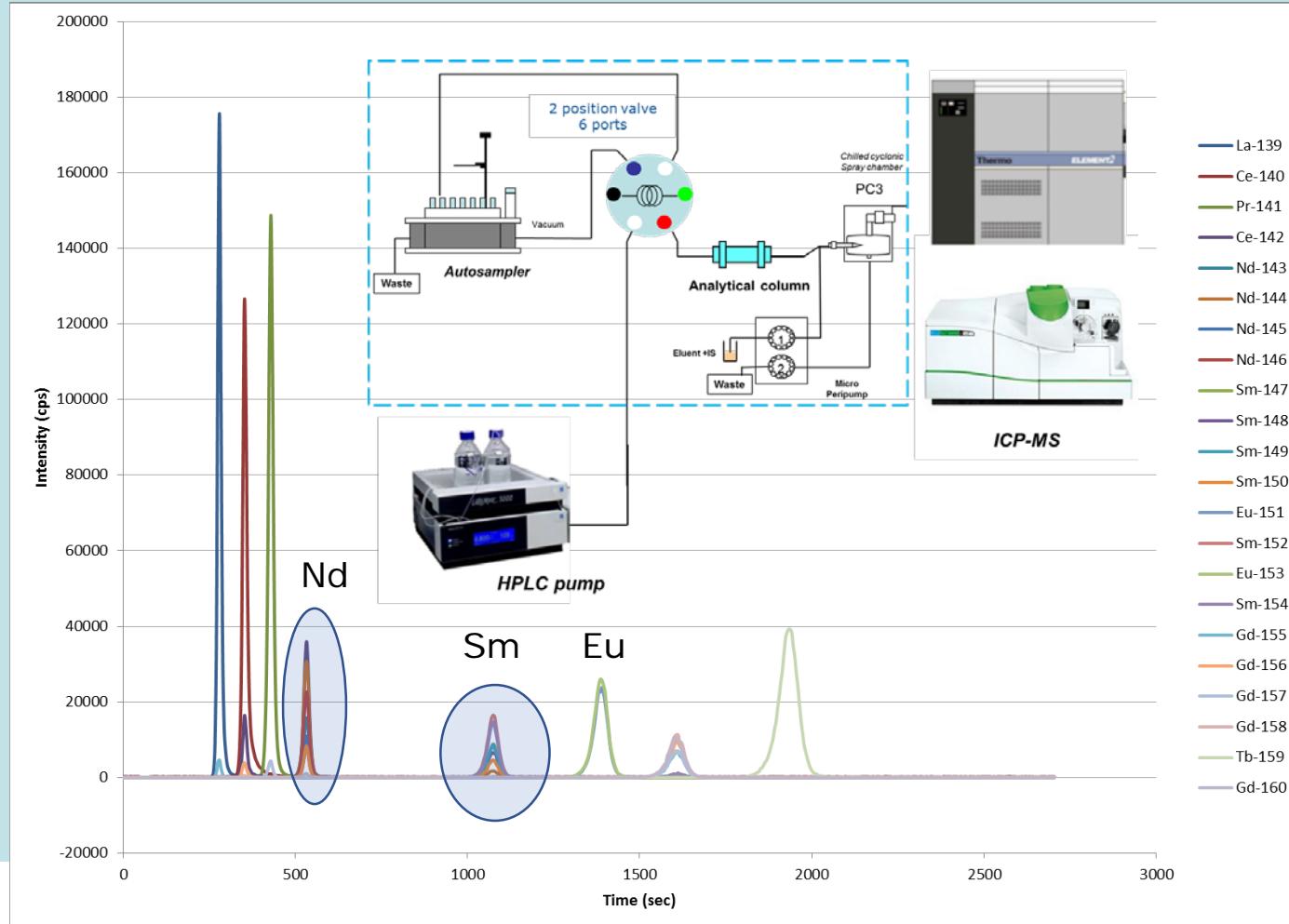


Analytical Challenge: Sm-151

- Sm-151 is a lanthanide element fission product (0.53 %)
- Pure beta emitting ($E_{\max} = 76\text{keV}$)
- Half-life of 94.7 years
- Specific activity $9.25 \times 10^{-11} \text{Bg g}^{-1}$
- Quantification
 - Nuclear fuel burn up
 - Nuclear waste characterisation
- Typical method: LSC following separation from other RE elements and Am-241

HPLC Sm Isotopes

Isobaric interferences arise from stable ^{151}Eu (47.81%) and polyatomic species ^{119}Sn $^{16}\text{O}_2$, ^{133}Cs ^{18}O , ^{134}Ba ^{17}O , ^{135}Ba ^{16}O and ^{150}Nd ^1H



Decommissioning NPP (Sm-151)

Nuclear waste final repository (Burn-up credit)

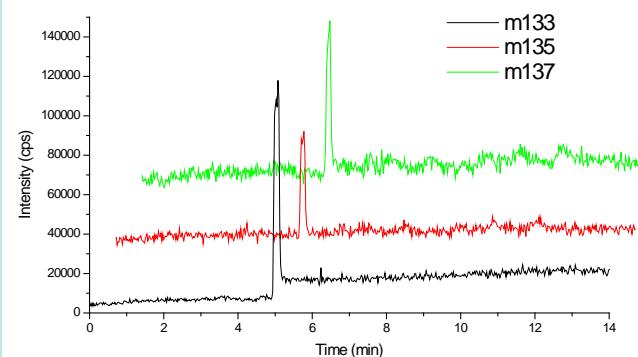
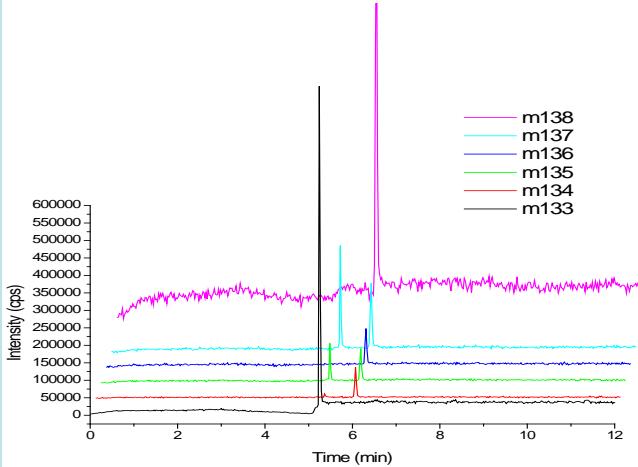
Analytical Challenge: Cs-135 and Cs-137

- Fission products (Cs-135: 6.58 %; Cs-137: 6.22 %)
- Present in the environment: releases from NPP, reprocessing facilities, nuclear accidents, fallout from atmospheric weapons tests
- Cs-137 ($t_{1/2}$ 30.07 years). Important radionuclide in radiation protection, environmental & monitoring and waste disposal
- Cs-135($t_{1/2}$ 2.3×10^6 years) low radiation risk; significant contributor to the long term radiological risk associated with deep geological disposal
- $^{135}\text{Cs}/^{137}\text{Cs}$ ratio varies with reactor, weapon and fuel type (forensic tool to identify the source of radioactive contamination)

Analytical Challenge: Cs-135 and Cs-137

- Cs-137 decays by beta emission to ^{137m}Ba , accompanied by gamma ray emission of 661.7 keV(85.1% yield): γ -spectrometry
- Cs-135 decays with a maximum beta particle energy of 269 keV, however measurement by beta counting is restricted (Cs-137: 5 orders of magnitude higher)
- **Key challenge for mass spectrometric measurement**
 - removal of isobaric interferences from naturally occurring ^{135}Ba and ^{137}Ba (isotopic abundances 6.6% and 11.2%, respectively),
 - peak tailing from stable ^{133}Cs (isotopic abundance 100%),
 - and polyatomic interferences including $^{95}\text{Mo}^{40}\text{Ar}$, $^{97}\text{Mo}^{40}\text{Ar}$, $^{119}\text{Sn}^{16}\text{O}$ and $^{121}\text{Sb}^{16}\text{O}$.

CE Cs Isotopes



Isotopic Ratio	CE-HR-ICP-MS ($\mu\text{g/mL}$)
$^{134}\text{Cs}/^{137}\text{Cs}$	$0,041 \pm 0,009$
$^{135}\text{Cs}/^{137}\text{Cs}$	$0,385 \pm 0,057$

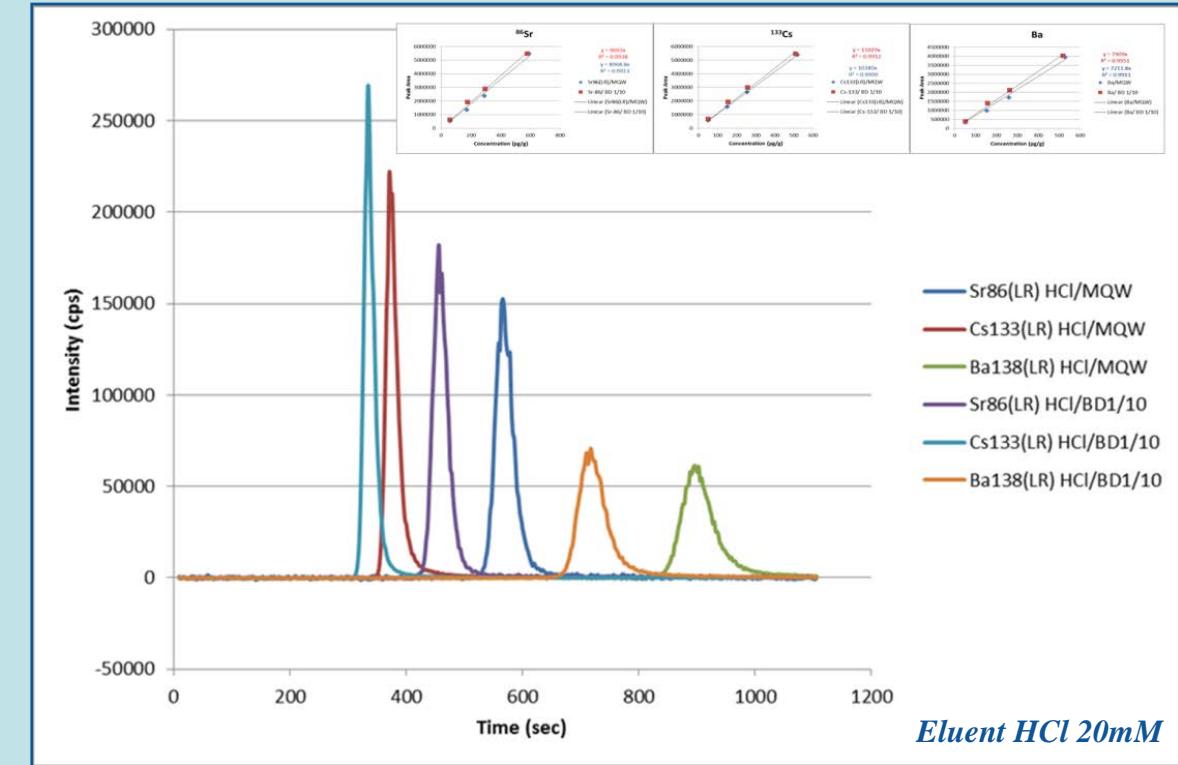
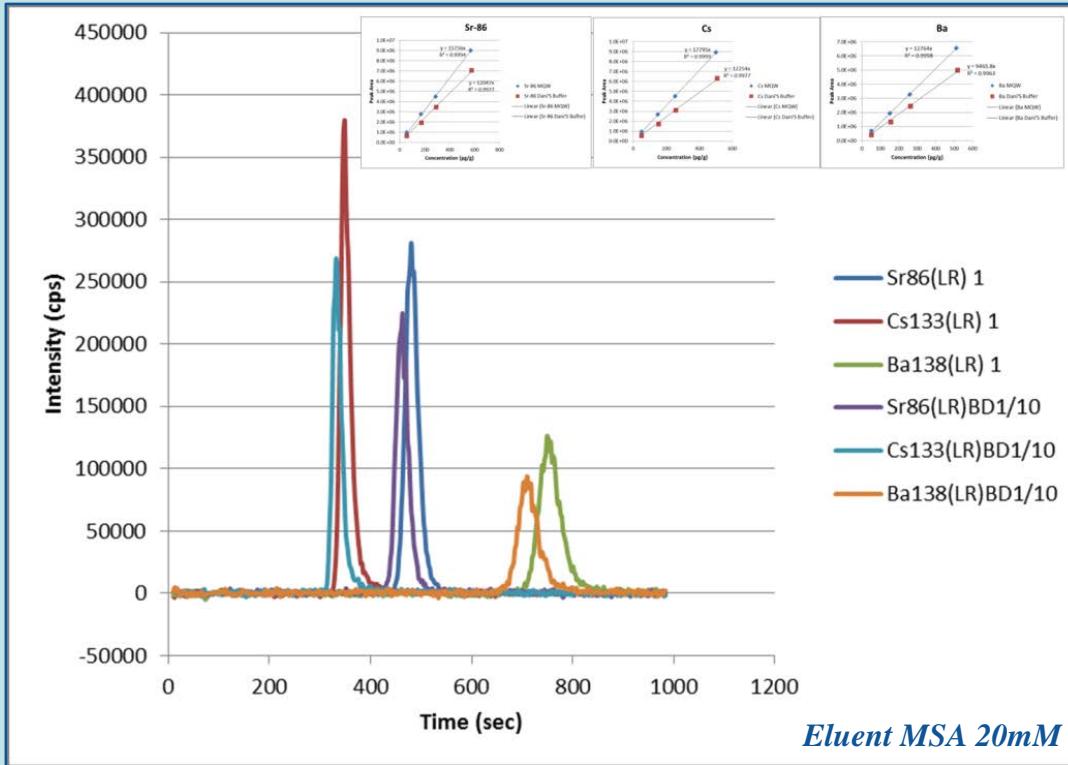
Isotope	CE-HR-ICP-MS (ng/mL)	Spectrométrie γ (ng/mL)	HR-ICP-MS (ng/mL)
^{133}Cs	$5,93 \pm 0,24$		
^{135}Cs	$2,72 \pm 0,16$		
^{137}Cs	$3,56 \pm 0,19$	$3,56 \pm 0,07$	$3,68 \pm 0,14$ fission (Cs + Ba)
Rapport isotopique	CE-HR-ICP-MS	Code de calcul ORIGEN	HR-ICP-MS
$^{135}\text{Cs}/^{137}\text{Cs}$	$0,77 \pm 0,06$	0,72	$0,86 \pm 0,05$

Interferences solved

Isotopic composition available

Good agreement between techniques and calculation codes

FIA Cs-Sr-Ba



CG12A cation exchange column for mono- and divalent cations.

Column resin functionalised with a mixture of carboxylic and phosphonic acid groups.

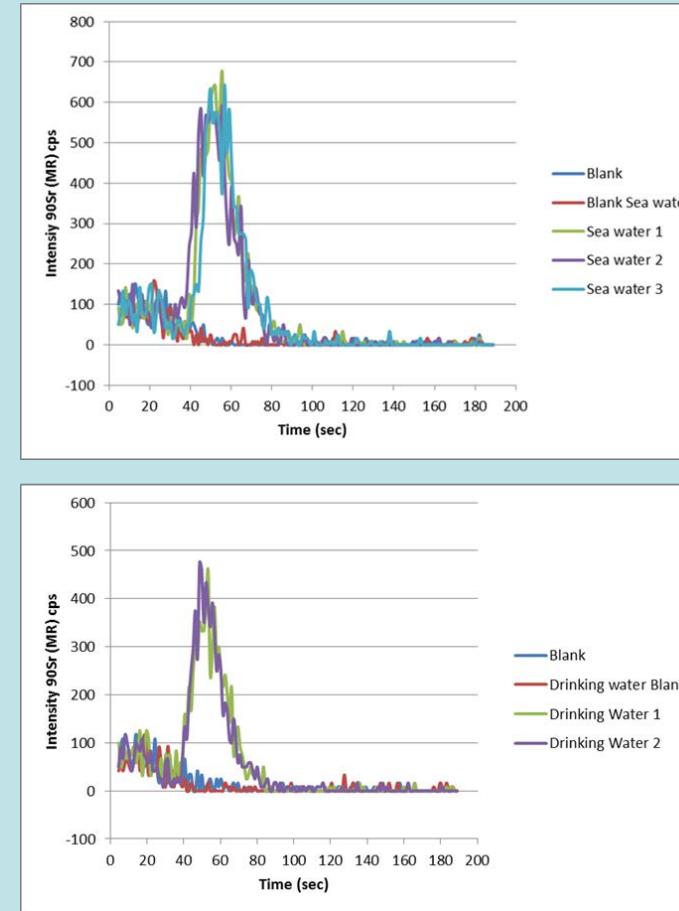
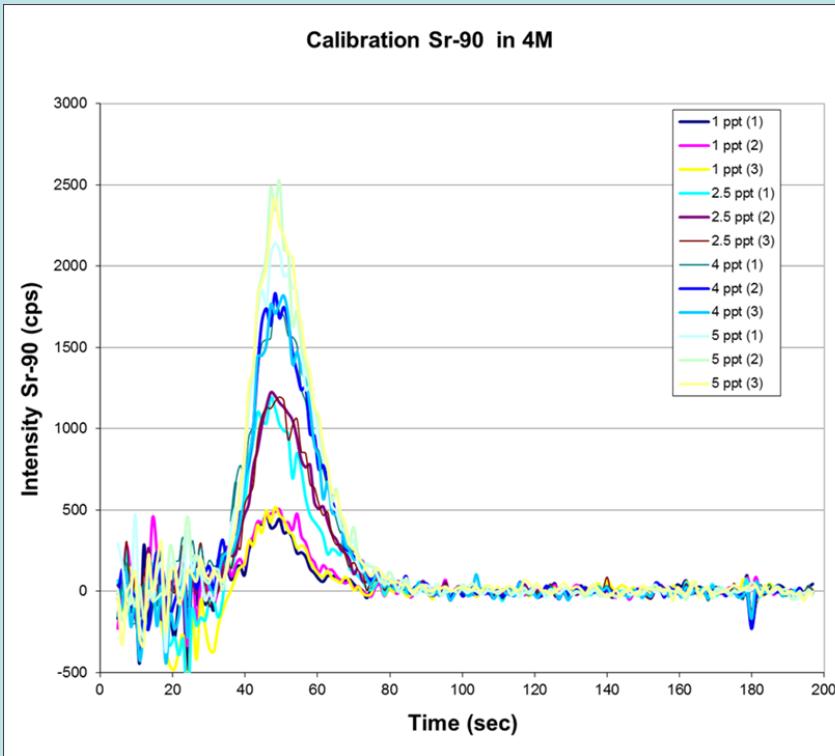
LOD sub pg/g

Analytical Challenge: Sr-90

- ^{90}Sr is a beta-emitting radionuclide (decay energy 0.546 MeV) with a half-life of 28.8 years that decays to ^{90}Y (half-life 2.67 days) and then on to stable ^{90}Zr .
- ***critical importance in nuclear waste management, environmental monitoring and radiation protection,***
- ^{90}Sr is a mobile element that can accumulate in soils and plants via precipitation and ion exchange mechanisms as well as in bones and teeth if inhaled or ingested, because of its similar chemical properties to calcium,
- Beta-counting techniques are applicable to highly sensitive detection of ^{90}Sr , either through direct measurement of ^{90}Sr , or via ^{90}Y (ingrowth of ^{90}Y until secular equilibrium (2-3 weeks).

FIA ^{90}Sr determination

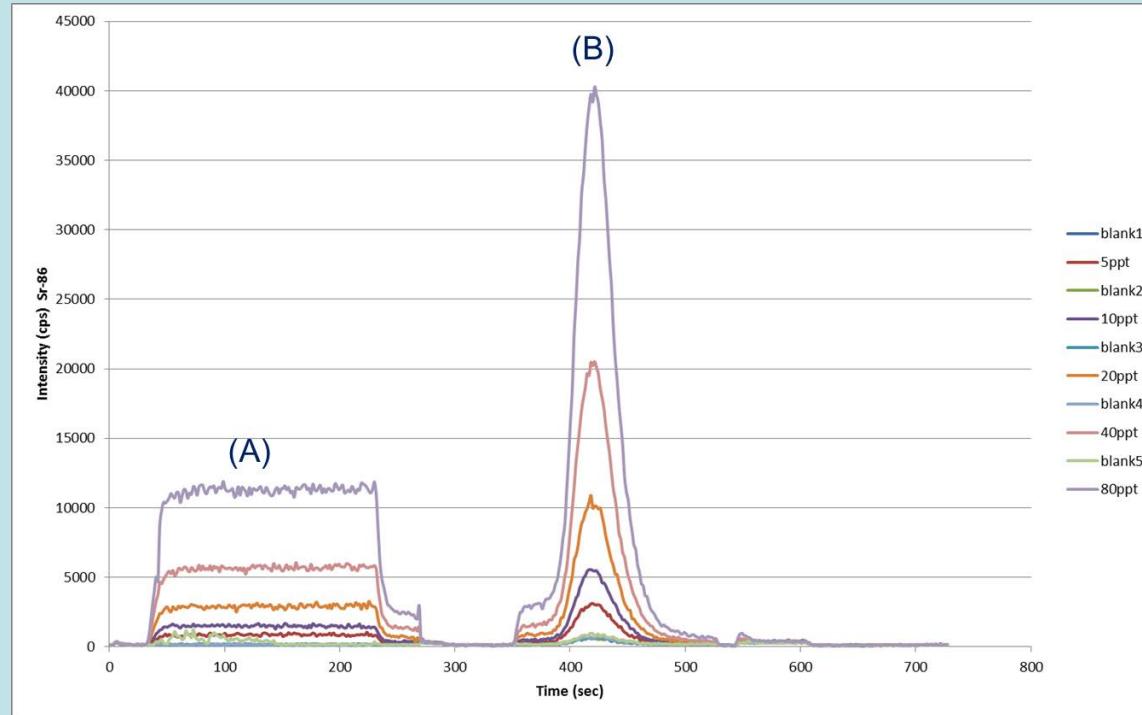
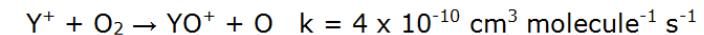
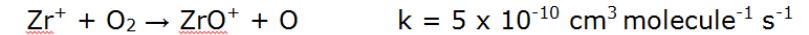
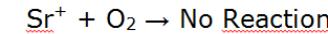
isobaric interference from stable ^{90}Zr (51.45%)
peak tailing from stable ^{88}Sr (82.6%), which is present at high concentrations in environmental samples
Many polyatomic interferences from matrix



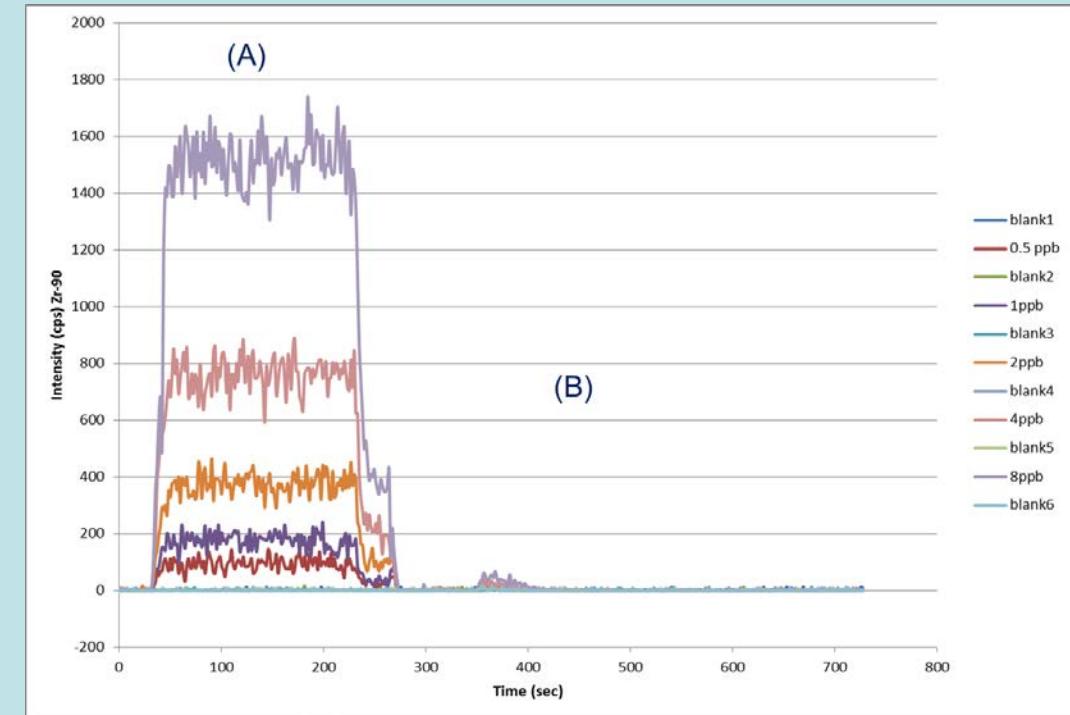
Low Resolution
 $36 \text{ fg g}^{-1} (0.2 \text{ Bq g}^{-1})$

Medium Resolution
 $200 \text{ fg g}^{-1} (1 \text{ Bq g}^{-1})$

Sr Profiles CRC ICP-MS



Sr-86 elution profile in direct (A) and pre-concentration mode (B); concentration interval is 5 to 80 pg g⁻¹.



(2) Zr-90 elution profile in direct (A) and pre-concentration mode (B); concentration interval is 0.5 to 8 µg L⁻¹.

Quantification

- *External calibration/standard addition*
 - **Synthesized standards to generated calibration curves**
 - **Easy way but depends on matrix complexity**
 - **Sample matrix considerations (standard addition)**
- *Internal standardisation*
 - **Add a spike to the sample and separate together with the sample under same chromatographic conditions**
Difficult to find a IS spike showing suitable chromatographic properties (no interferences, no co-elution)

Quantification

- *Isotopic dilution analysis:*
 - measurement of isotope ratios in samples where the isotopic composition has been altered by the addition of a known amount of an isotopically enriched element
 - Absolute quantitative method (traceable to the primary isotopic standard)
 - excellent precision and accuracy
 - spectral interferences, mass bias, detector linearity...

on-line IDA (OIDA): a mixture of enriched isotopes is added to the samples on-line using a T-connector prior to the ICP-MS nebulizer

Key Radionuclides of Interest

Nuclide	Atom mass	Half-live	Decay mode	Specific activity (Bq/g)	Measurement Method	Application fields
³ H	3.0161	12.3 y	β^-	3.57 x10 ¹⁴	LSC	EM, DN, MT
¹⁴ C	14.0032	5730 y	β^-	1.65 x10 ¹¹	LSC, AMS, GID	DN, EM, D
³⁶ Cl	35.6983	0.301 My	β^-	1.22 x10 ⁹	LSC, AMS	DN, WD, TE
⁴¹ Ca	40.9623	0.103 My	EC	3.14 x10 ⁹	LSC, AMS	DN, WD, MT
⁵⁵ Fe	57.9383	2.73 y	EC	8.36 x10 ¹³	LSC	DN, MT
⁶⁰ Co	59.9338	5.27 y	β^-	5.88 x10 ¹³	γ -Spectrometry	EM, DN, WD
⁵⁹ Ni	58.9343	76400 y	EC + β^+	2.94 x10 ⁹	X-Ray, AMS	DN, WD
⁶³ Ni	62.9297	100.1 y	β^-	2.10 x10 ¹²	LSC, GID	DN, MT, WD, ET
⁷⁹ Se	78.9185	1.13 My	β^-	2.08 x10 ⁸	LSC, AMS, ICP-MS	WD, DN
⁸⁹ Sr	88.9075	50 d	β^-	1.09 x10 ¹⁵	LSC, GID	EM
⁹⁰ Sr	89.9077	29.1 y	β^-	5.06 x10 ¹²	LSC, GID	EM, DN, WD
⁹⁹ Tc	98.9063	0.211 My	β^-	6.34 x10 ⁸	LSC, ICP-MS	EM, ET, WD
¹²⁶ Sn	125.9076	233000 y	β^-	4.57 x10 ⁸	γ -Spectrometry, AMS	DN, WD
¹²⁹ I	129.9050	15.7 My	β^-	6.49 x10 ⁶	AMS, ICP-MS, NAA	ET, MT, WD
¹³⁵ Cs	134.9060	2.3 My	β^-	4.26 x10 ⁷	ICP-MS, TIMS	ET, WD
¹³⁷ Cs	136.9071	30.2 y	β^-	3.20 x10 ¹²	γ -Spectrometry	ET, WD, DN
²¹⁰ Pb	209.9842	22.3 y	β^-	2.83 x10 ¹²	LSC	D, EM
²²⁶ Ra	226.0254	1600 y	α	3.66 x10 ¹⁰	α -Spectrometry, LSC	EM, ET
²²⁸ Ra	228.0311	5.75 y	β^-	1.01 x10 ¹³	LSC or GID (via ²²⁸ Ac)	EM, ET

²²⁹ Th	229.0318	7340 y	α	7.87 x10 ⁹	α -Spectrometry, ICP-MS	ET
²³⁰ Th	230.0331	75380 y	α	7.63 x10 ⁸		EM
²³² Th	232.0381	14050 My	α	4.06 x10 ³		EM
²³⁴ Th	234.0436	24.1 d	β^-	8.56 x10 ¹⁴		LSC
²³³ U	233.0396	0.1492 My	α	3.80 x10 ⁸	α -Spectrometry, ICP-MS	ET, EM
²³⁴ U	234.0410	0.2455 My	α	2.30 x10 ⁸		EM
²³⁵ U	235.0439	703.8 My	α	8.00 x10 ⁴		EM, WD
²³⁶ U	236.0456	23.4 My	α	2.40 x10 ⁶		EM
²³⁸ U	238.0508	4468 My	α	1.24 x10 ⁴	ICP-MS	EM, WD
²³⁷ Np	237.0482	2.144 My	α	2.60 x10 ⁷		EM, ET
²³⁸ Pu	238.0496	87.7 y	α	6.34 x10 ¹¹		ET, EM
²³⁹ Pu	239.0524	24110 y	α	2.30 x10 ⁹		EM, ET, DN, WD
²⁴⁰ Pu	240.0538	6563 y	α	8.40 x10 ⁹	α -Spectrometry, ICP-MS	EM, ET, DN, WD
²⁴¹ Pu	241.0568	14.35 y	β^-	3.82 x10 ¹²		LSC
²⁴² Pu	242.0587	0.3733 My	α	1.46 x10 ⁸		EM
²⁴⁴ Pu	244.0640	80.8 My	α	6.71 x10 ⁵	AMS	EM
²⁴¹ Am	241.0568	432.2 y	α	1.27 x10 ¹¹	γ , α -Spec, ICP-MS	EM, ET, DN, WD

EM: Environmental monitoring;

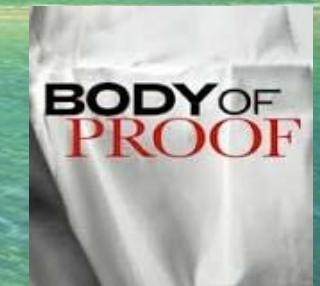
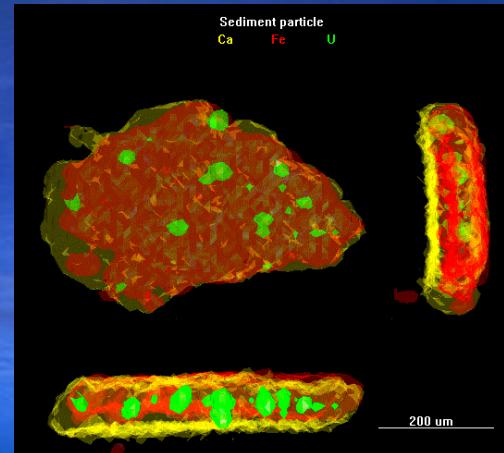
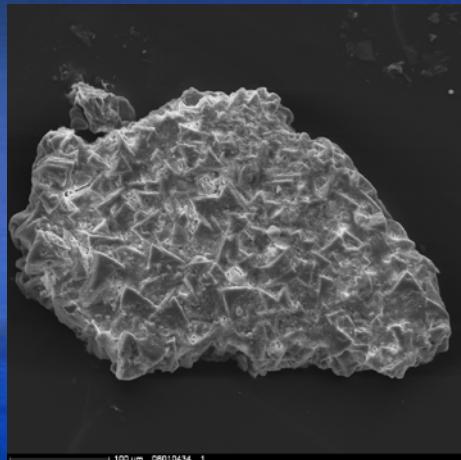
DN: Decommissioning Nuclear Facilities

MT: Medical tracer; ET: Environmental tracer;

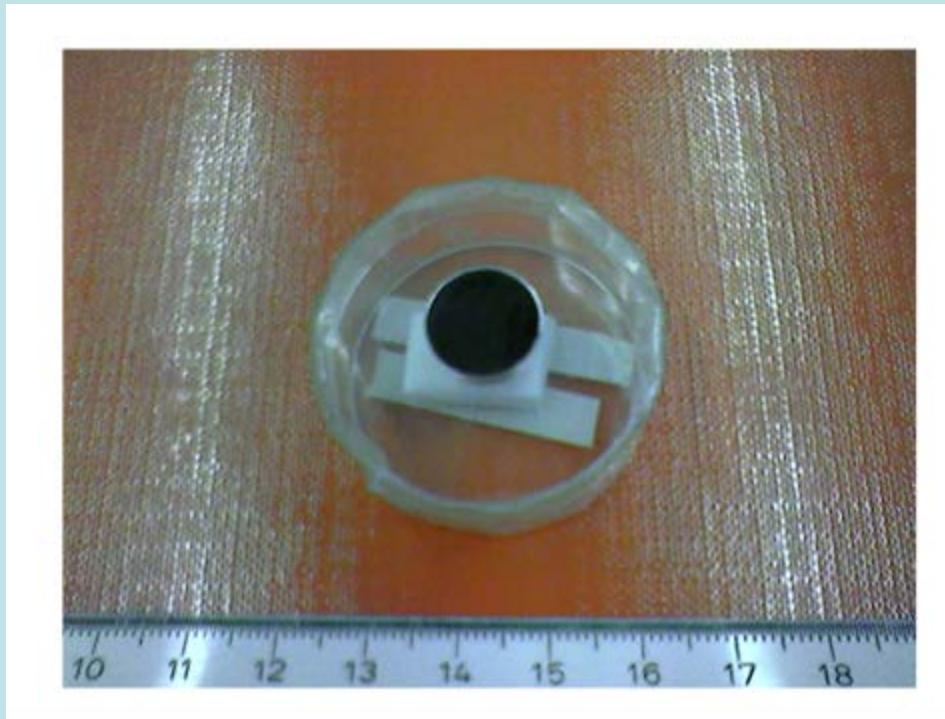
WD: Nuclear waste repository

Case Study

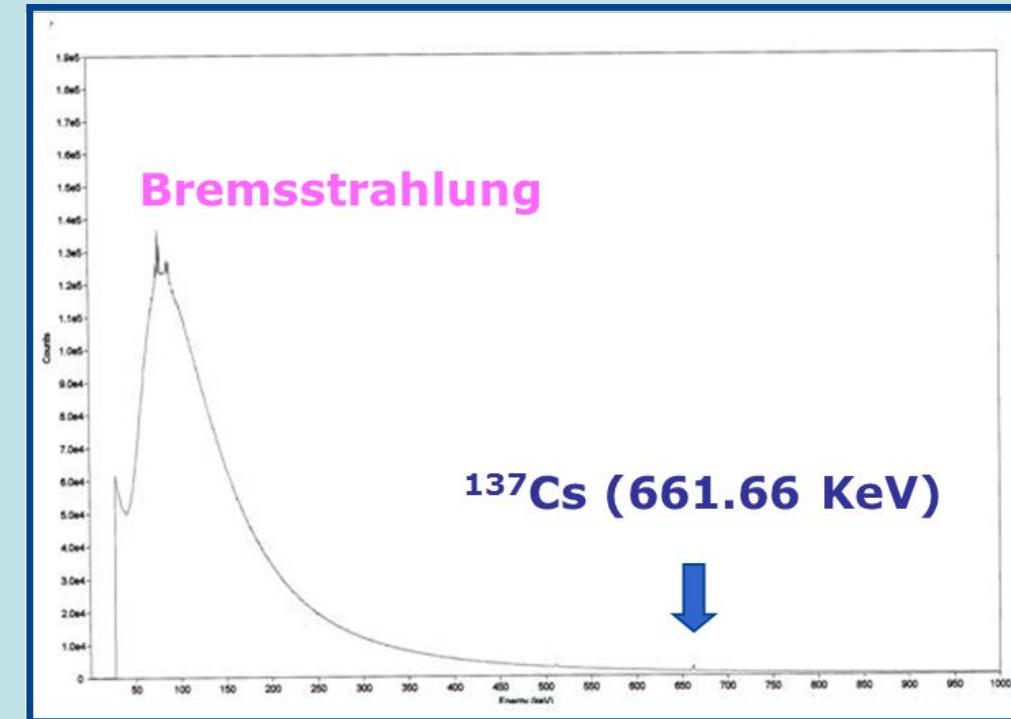
Radioactive Particle Coming from a Beach in North West Europe



γ Spectrometry

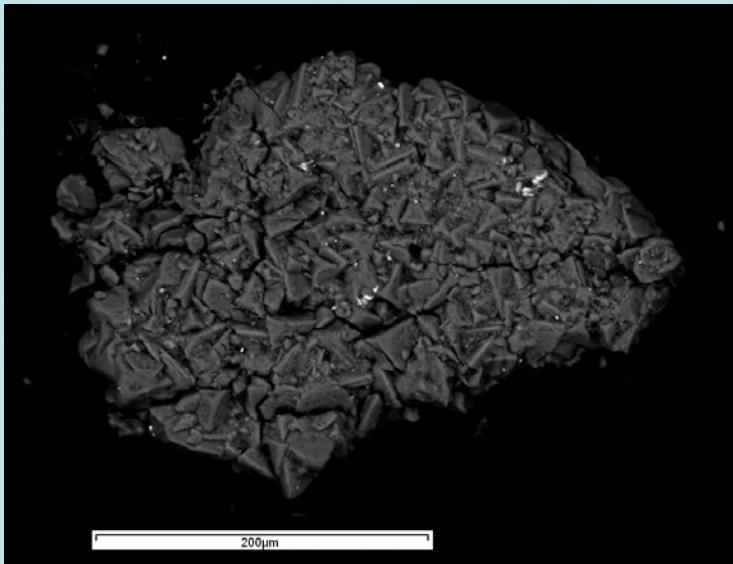


Activity 10^5 Bq

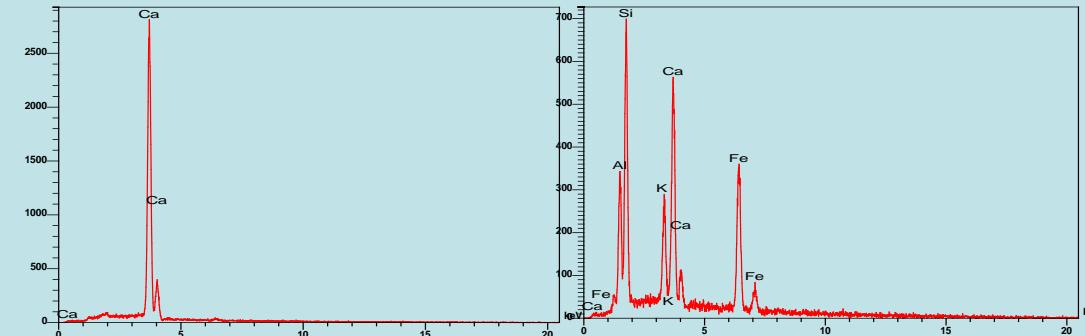


^{137}Cs activity 0.5 Bq
Bremsstrahlung: β decay

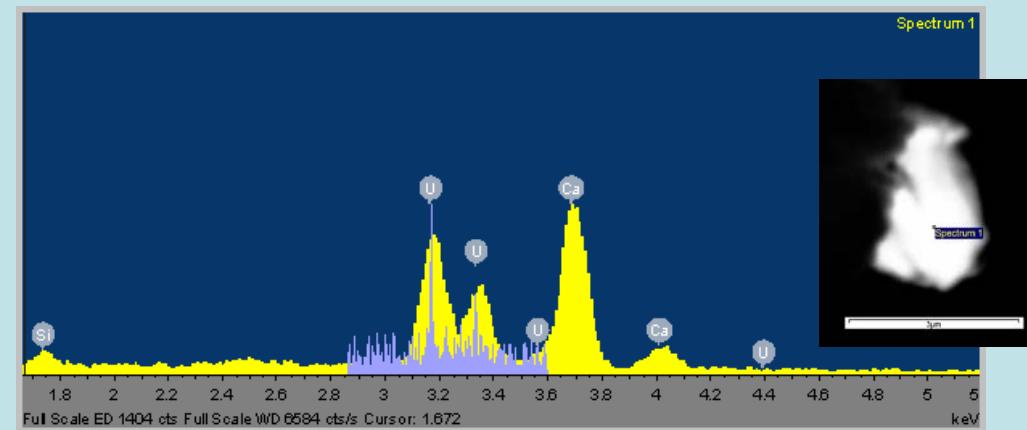
Scanning Electron Microscopy (SEM)



SEM image of the particle in a backscattered mode.

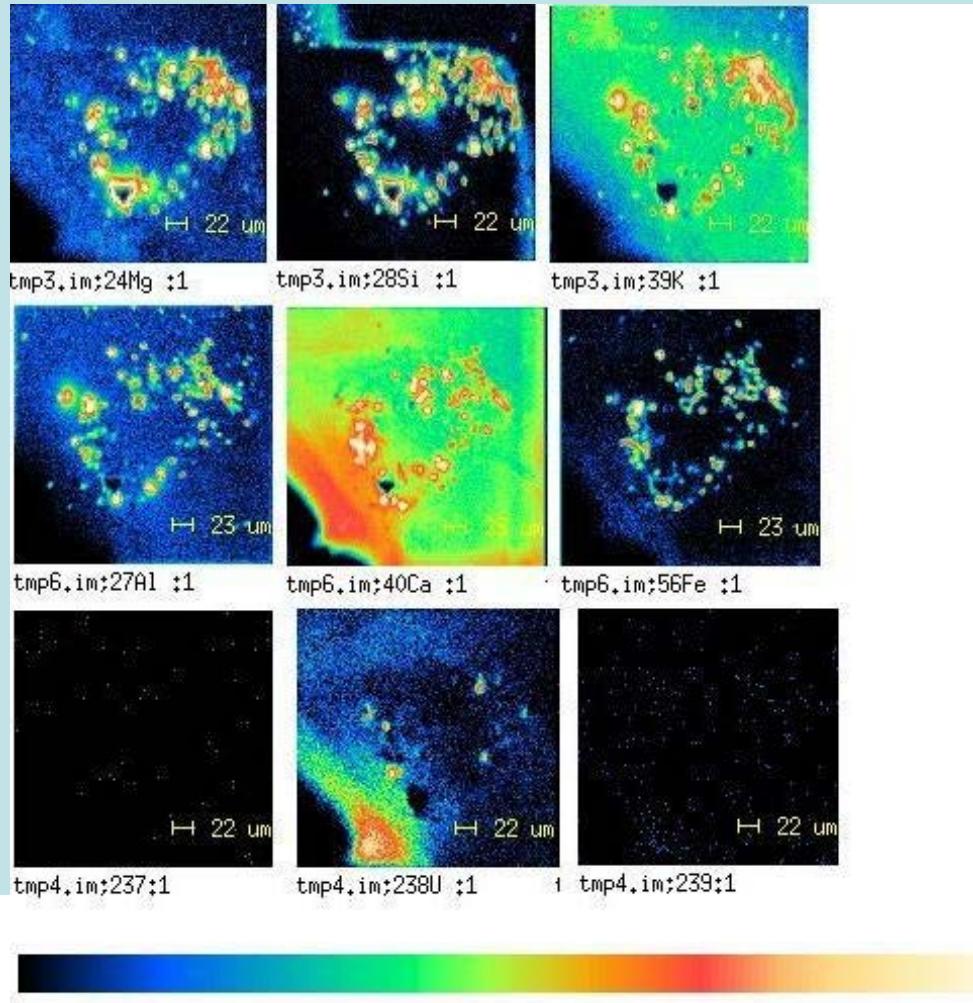


EDX spectra collected in different points



EDX and WDX spectra collected in (U inclusion)

SIMS Isotope Mapping/Isotopic Composition

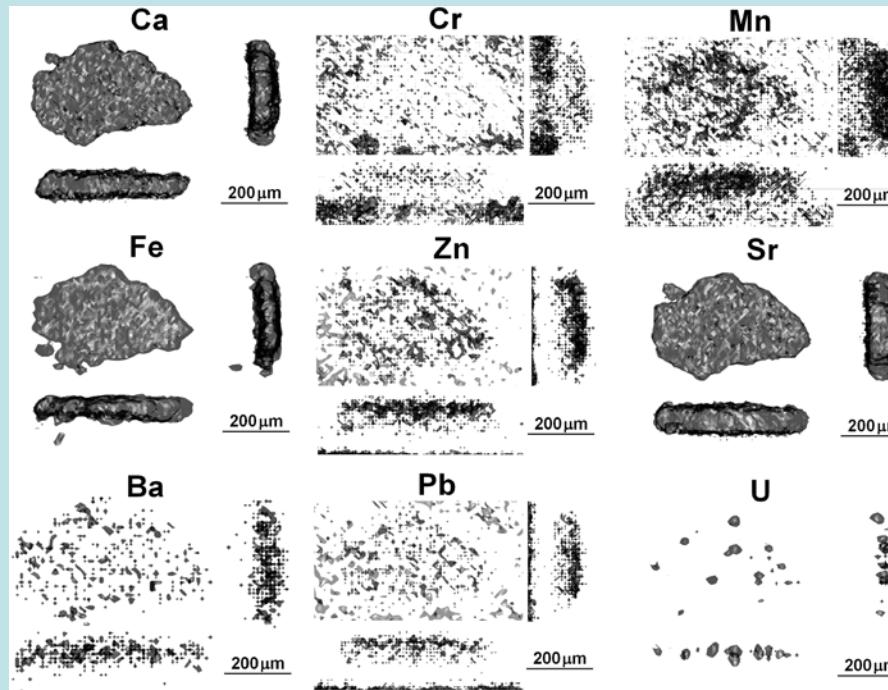
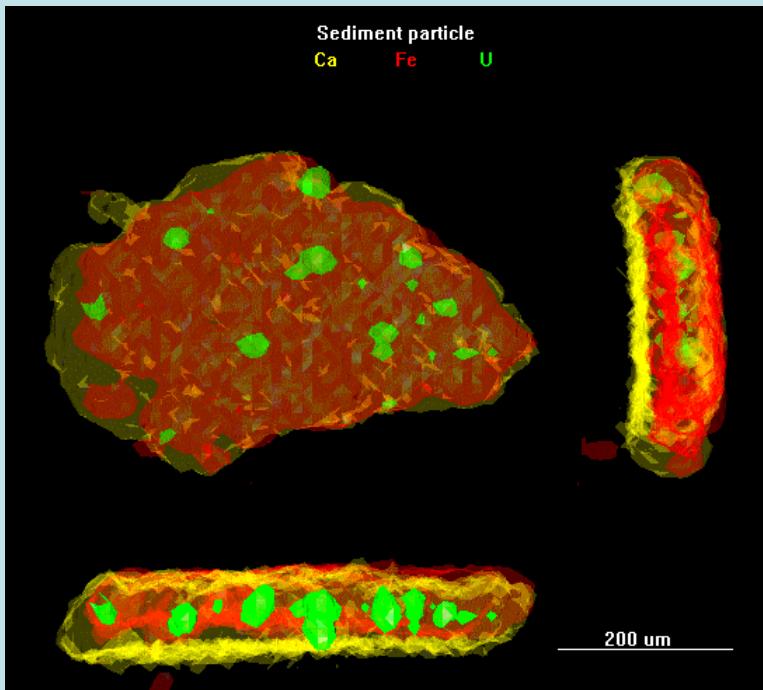


Isotope	Wt %
^{234}U	$0,0046 \pm 0,0005$
^{235}U	$0,3117 \pm 0,0022$
^{236}U	$0,0571 \pm 0,0005$
^{238}U	$99,6266 \pm 0,0023$

Deplete Uranium (^{235}U is 0,3%)
Signature ^{236}U indicating spent fuel reprocessing
(enrichment of reprocessed U)

X-Ray Fluorescence in Confocal Geometry

Spatial distribution of elements in the particle (3D scanning)



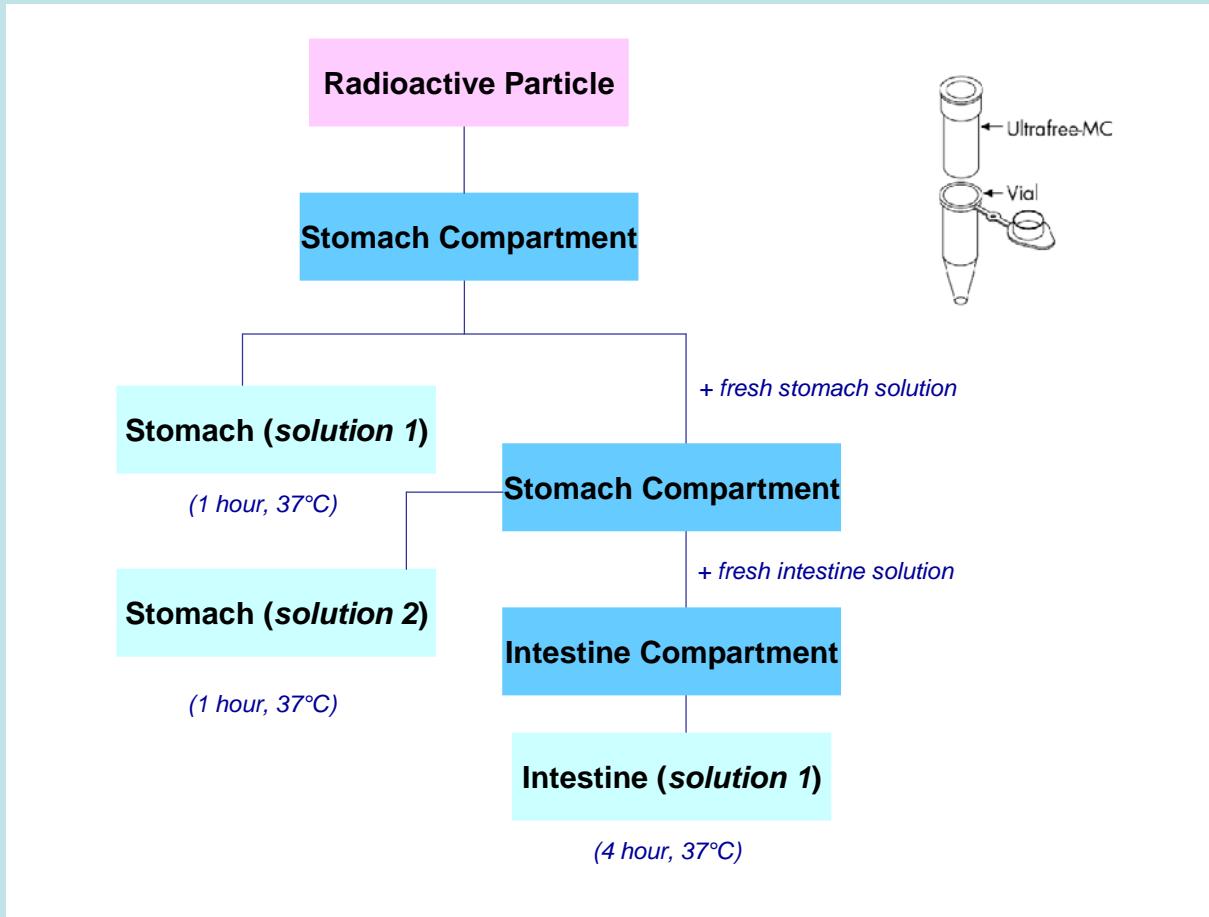
Ca is most abundant,
distributed uniformly (matrix
of the particle)

Fe is not homogenous
(surface)

U (inclusions)

The rest elements distributed
uniformly inside the particle

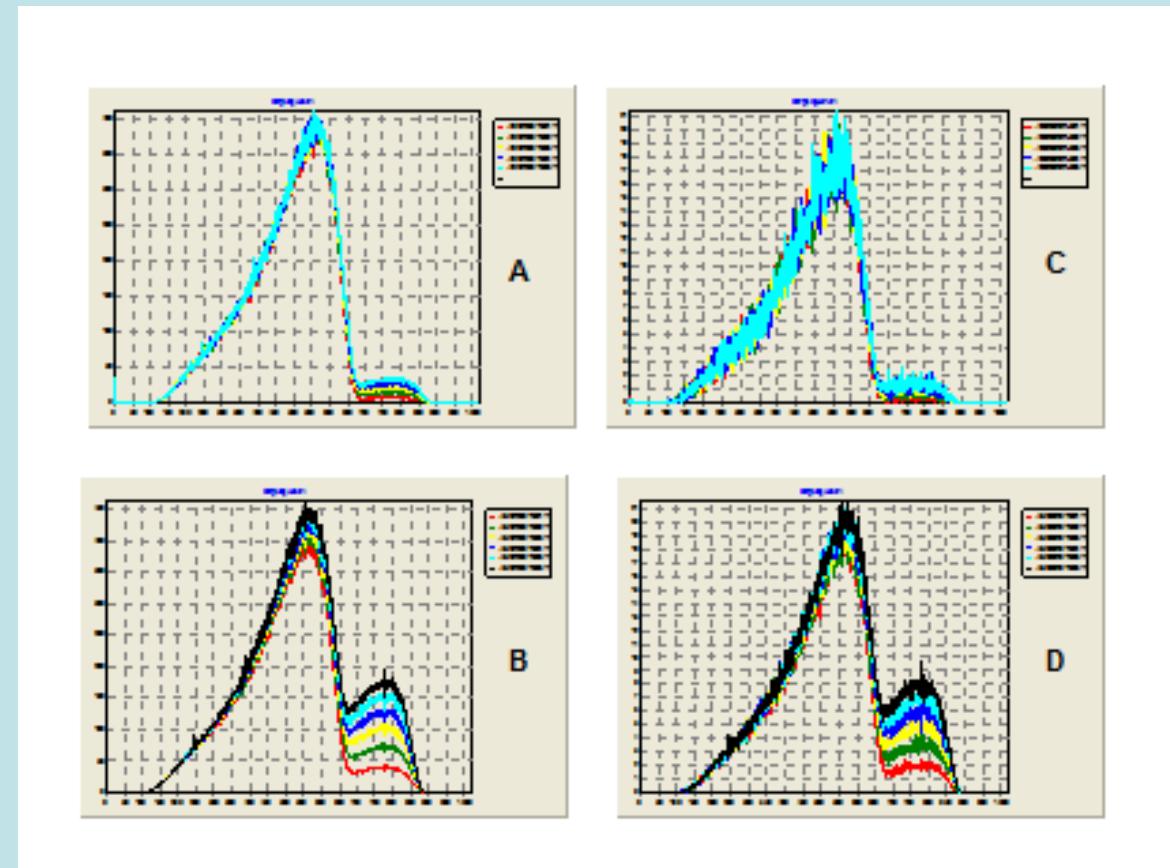
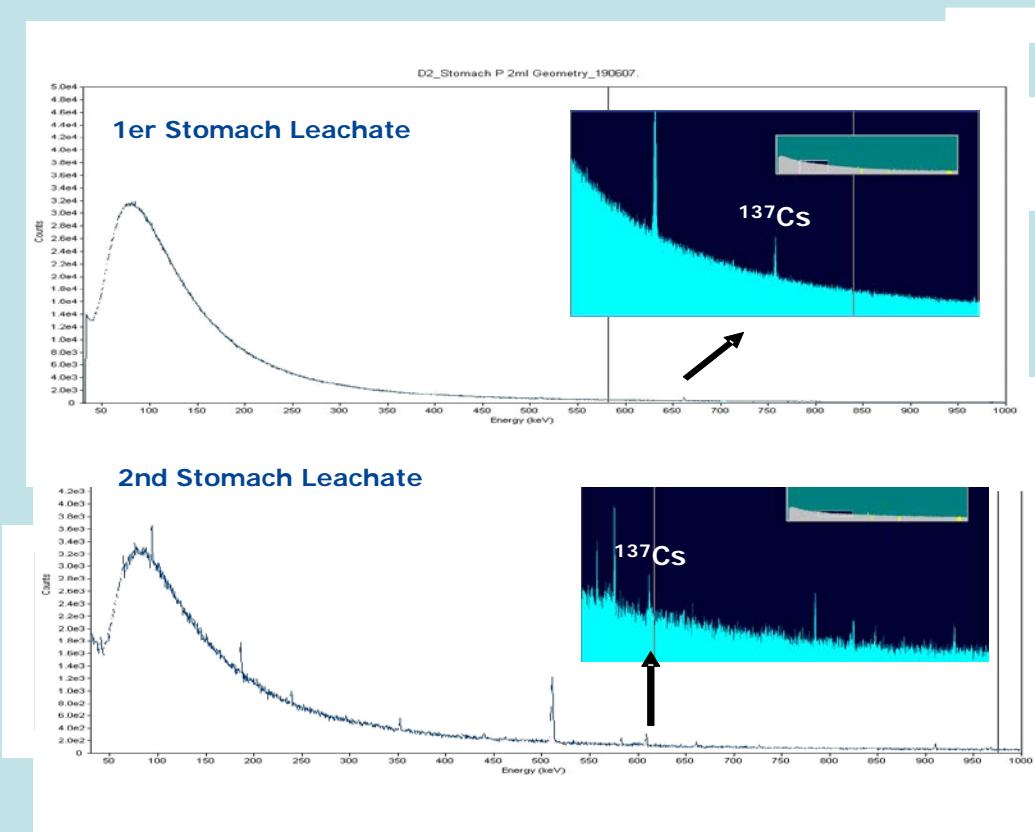
Physiological Model for the Study of the Dissolution Characteristics of Environmental Particles



Leaching in 0.1 mm filter units

Ultracentrifugation

γ Spectrometry & Liquid Scintillation Counting (LSC) of Leachates



Leachates Results

¹³⁷ Cs	Activity (mBq)	± (%)
Particle	516	9
Stomach 1	364	21
Stomach 2	18,5	23
Intestine	< 3,5	

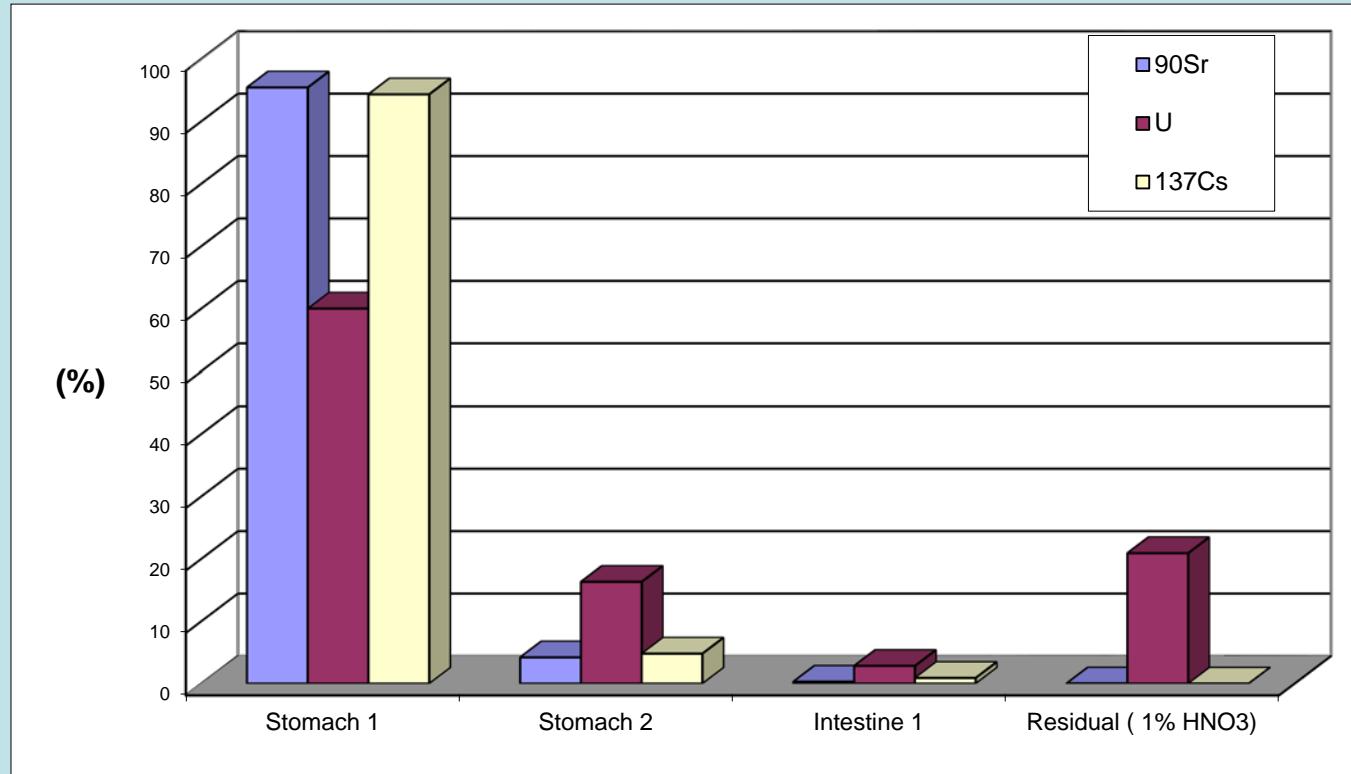
⁹⁰ Sr	Activity (Bq)	± (%)
Stomach 1	23311	0,05
Stomach 2	1036	0,05
Intestine	72	0,07
HNO ₃ 1%	5,6	0,07

Determination of U concentration and isotopic composition by ICP-MS

Isotope	ng	± (%)	% weight	± (%)	mBq	± (%)
^{234}U	1.32E-03	5.23	0.0051	4.88	0.303	5.23
^{235}U	0.106	1.86	0.3977	0.53	0.008	1.87
^{236}U	1.13E-02	4.45	0.0529	1.27	0.026	4.45
^{238}U	26.138	1.89	99.544	0.32	0.325	1.89

Depleted Uranium
Signature ^{236}U indicating
spent fuel reprocessing
(enrichment of
reprocessed U)

Potential Radio toxicological impact



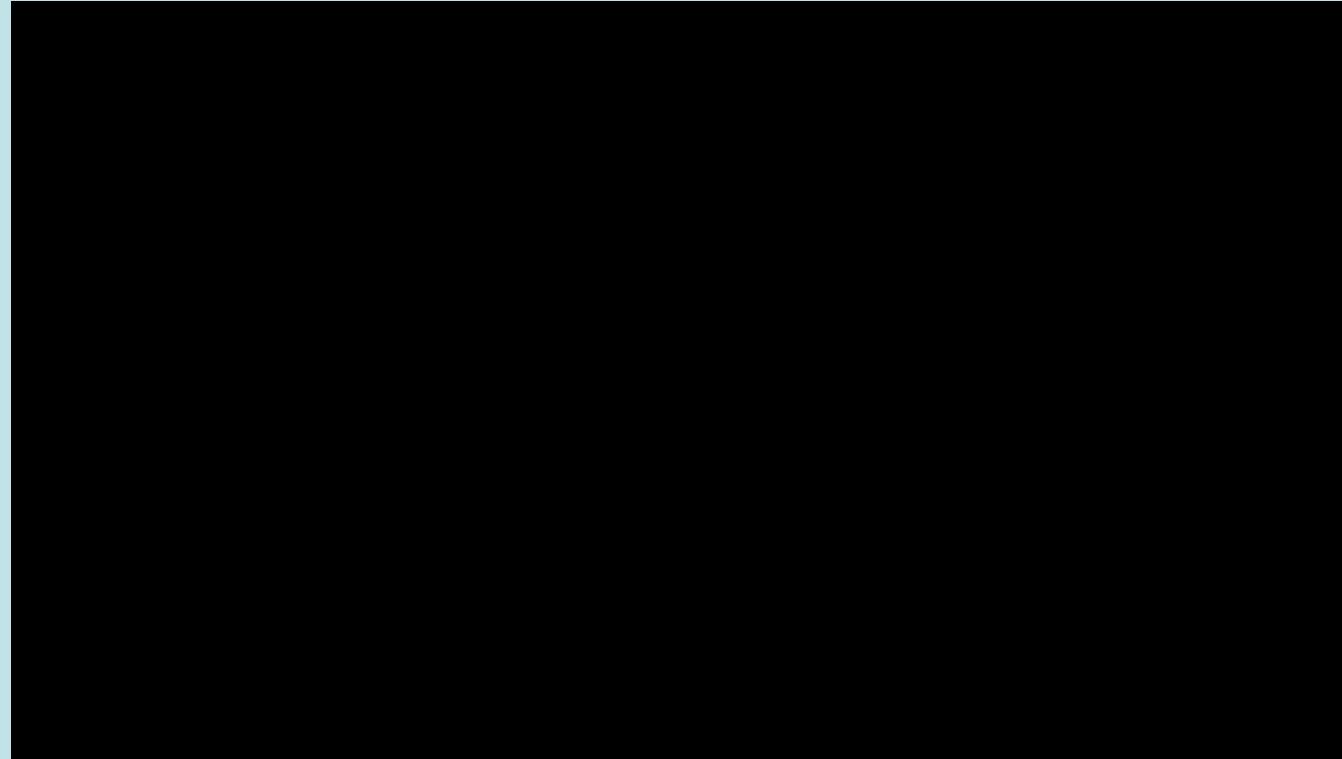
Most of the activity is in the stomach compartment

Radio toxicological impact:

90Sr has same behaviour than Ca in the body
Accumulates in bones and teeth
(20 - 30 % ingested)

Mass Spec/tacular

- <http://www.youtube.com/watch?v=EkAF-OOg858>





Any questions?

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