Validation of radiochemical methods for the determination of difficult-to-measure nuclides using LSC

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DTM nuclides

Method validation principles

Examples for method validation:

- ^{90}Sr
- ^{93}Zr

Major issues in validation of ^{63}Ni and ^{59}Ni

Difficult-to-measure (DTM) nuclides

Properties:

long half-life - long-term effect, small specific activity

low amounts/activities

α particles, electrons (β, Auger), X-rays – absorption, self-absorption

Nuclide	Half-life		Decay mode	β_{Max}	Specific activity	Occurance/ field of application		
				keV	Bq/g			
^{90}Sr	29,1	y	β−	546	5,04E+12	DN	WD	EM, MT
^{93}Zr	1,53	10^6 y	β−	90	9,27E+07	DN	WD	
^{59}Ni	76400	y	EC, β+	(X: 6,9)	2,94E+09		WD	
^{63}Ni	100	y	β−	67	2,09E+12	DN	WD	

DN=decommissioning of nuclear facilities

WD=waste depository

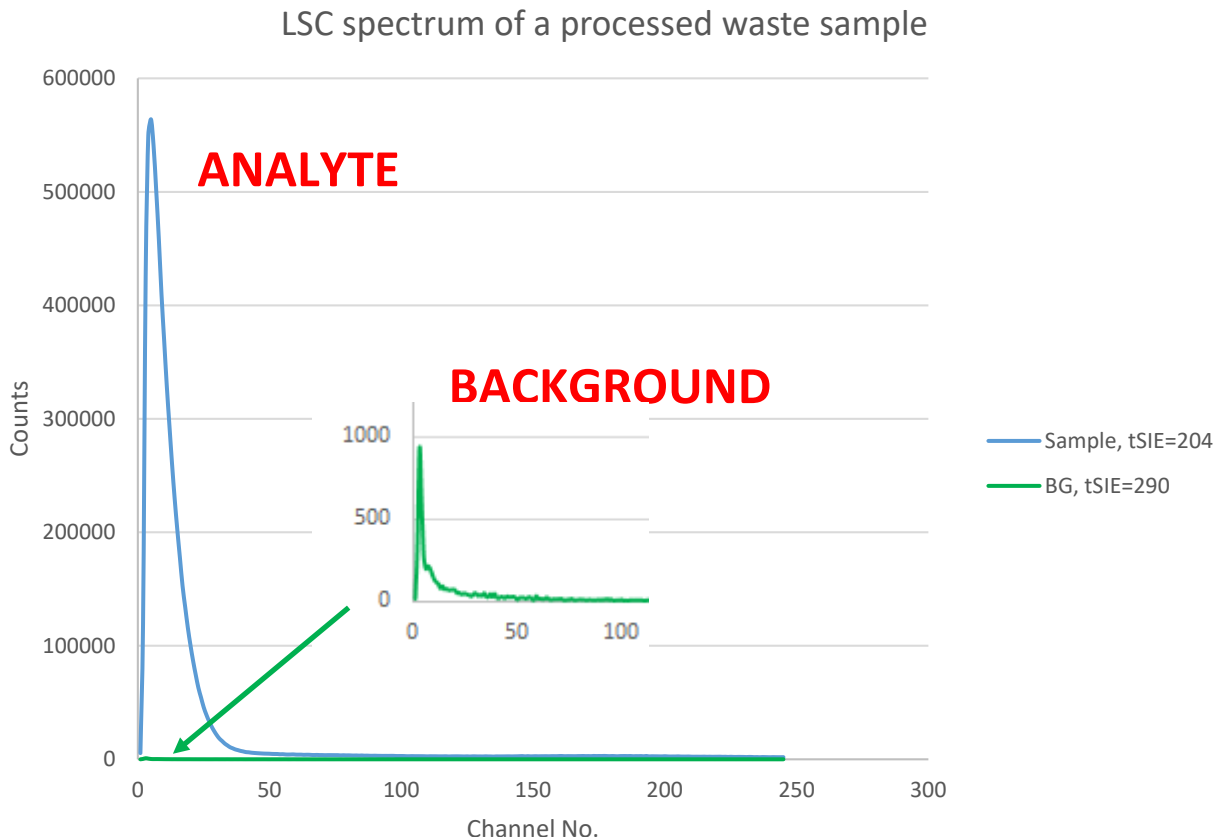
EM=environmental monitoring

MT=medical tracer

β spectrometry by LSC

High detection efficiency (close to 100 %)
No absorption/self-absorption

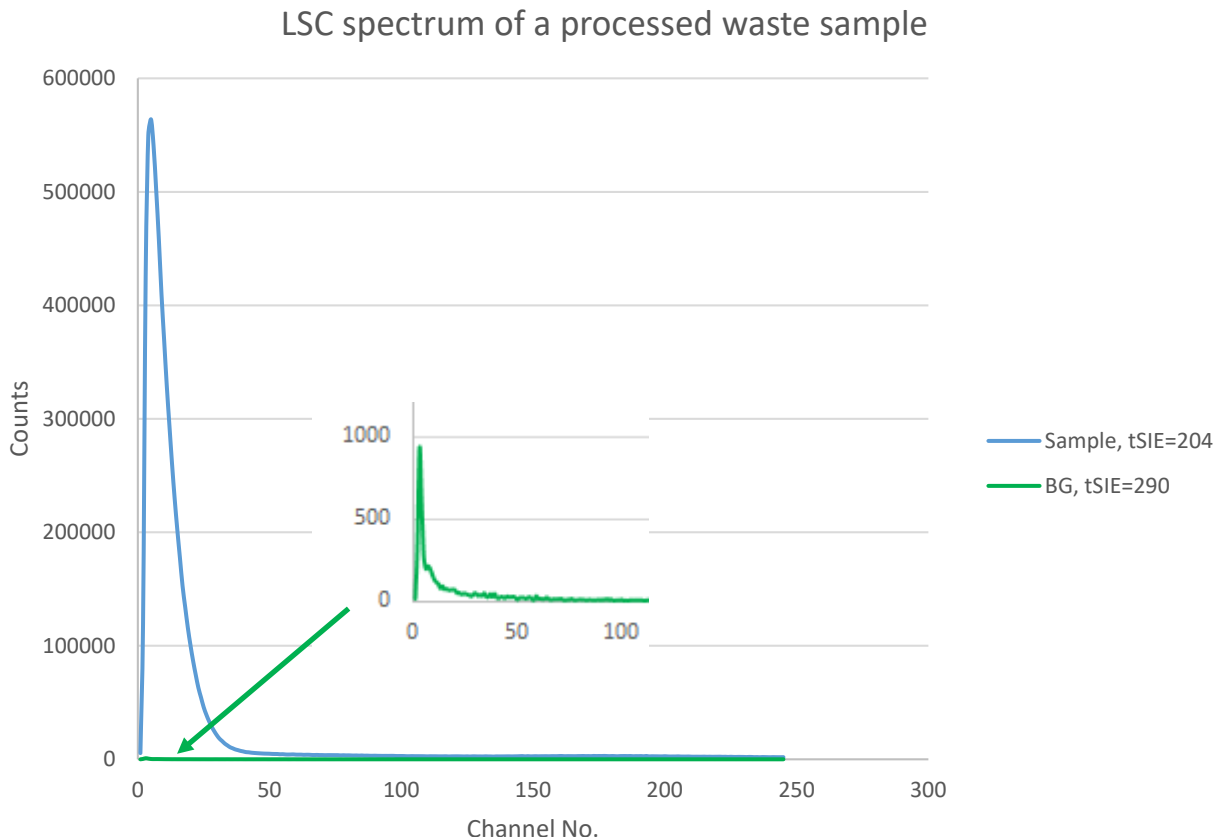
Quench effect – quench correction possibilities
Poor energy resolution (around 10 %)
Continuous nature of β decay/spectra



Which analyte?
^{3}H – 18 keV
^{63}Ni – 67 keV
^{151}Sm – 77 keV
^{93}Zr – 90 keV
^{85}Sr, ^{59}Ni, ^{55}Fe …

LSC measurement

Chemical separation procedure
High selectivity - to remove interfering nuclides



Which analyte?

^{3}H – 18 keV

^{63}Ni – 67 keV

^{151}Sm – 77 keV

^{93}Zr – 90 keV

^{85}Sr, ^{59}Ni, ^{55}Fe …

Method validation

by either or the combination of any the following techniques

1. calibration using reference standards or reference materials,
2. inter-laboratory comparisons, e.g. PT
3. systematic assessment of the factors influencing the result,
4. assessment (of the uncertainty of the results) based on scientific understanding of the theoretical principles of the method and practical experience,
5. comparison of results achieved with other methods

ISO/IEC 17025 (2005): General requirements for the competence of testing and calibration laboratories

^{90}Sr determination

Nuclide	Half-life		Decay mode	β_{Max} keV	Specific activity Bq/g
^{90}Sr	29.1	y	β−	546	5,04E+12
^{90}Y	64	h	β−	2280	2,01E+16

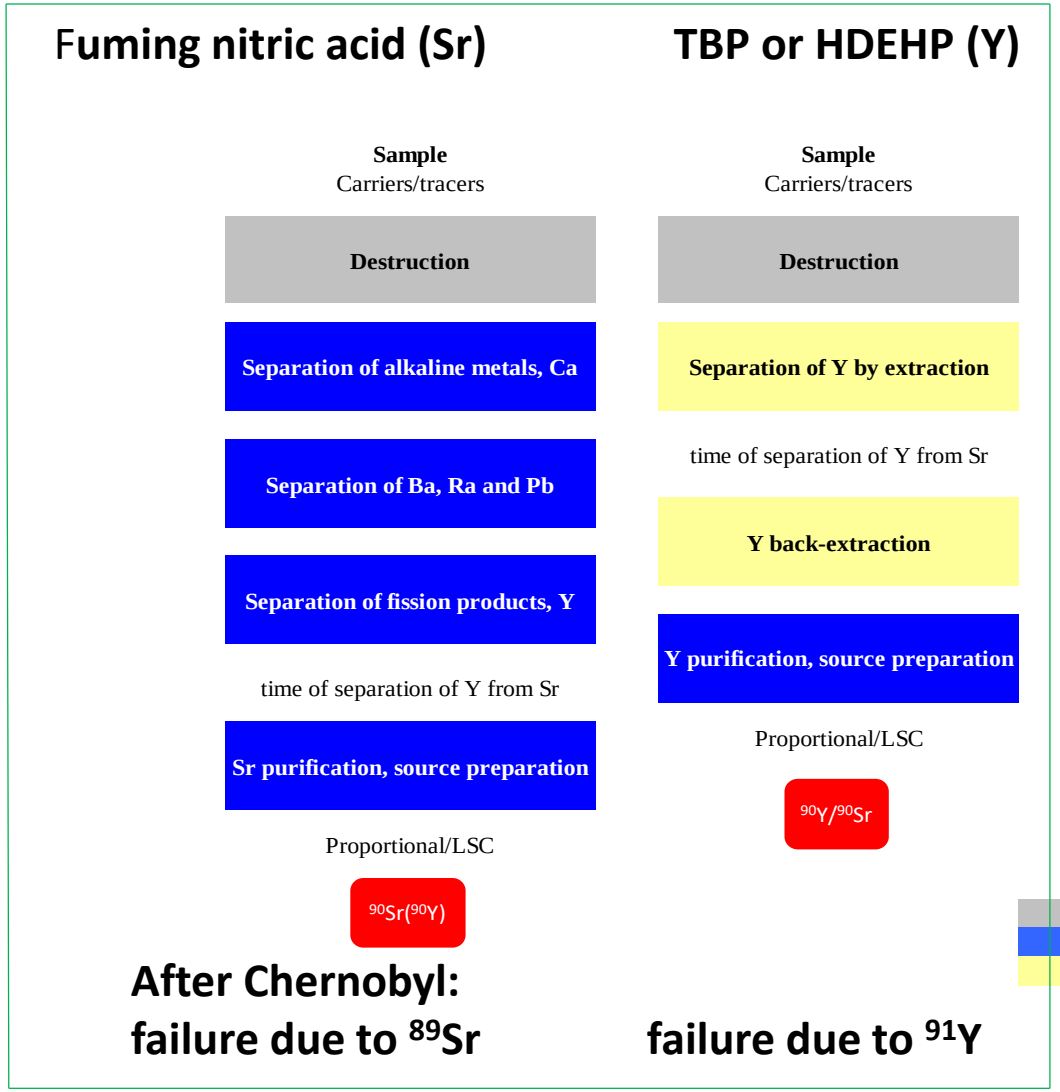
Standard validation techniques:

1. Use of **CRM**,
2. Participation in **PTs**
3. Systematic assessment of the factors influencing the result - fish bone
4. Assessment based on scientific understanding

Validation issue

5. No good independent method for validation

^{90}Sr determination



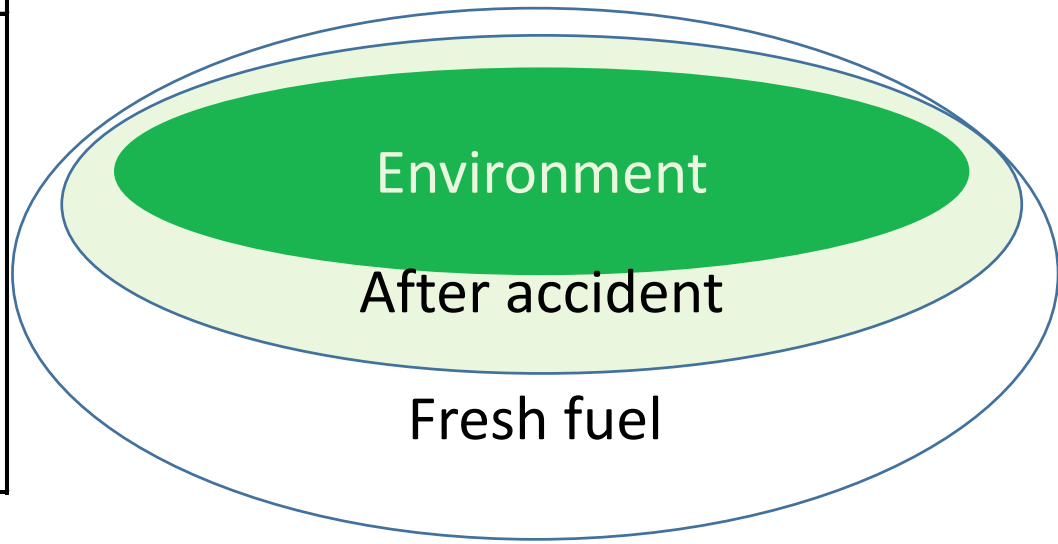
Methods validated under normal conditions can fail during accidents!

^{90}Sr / ^{89}Sr determination

Analytes and possible interferences in radiostrontium analysis:

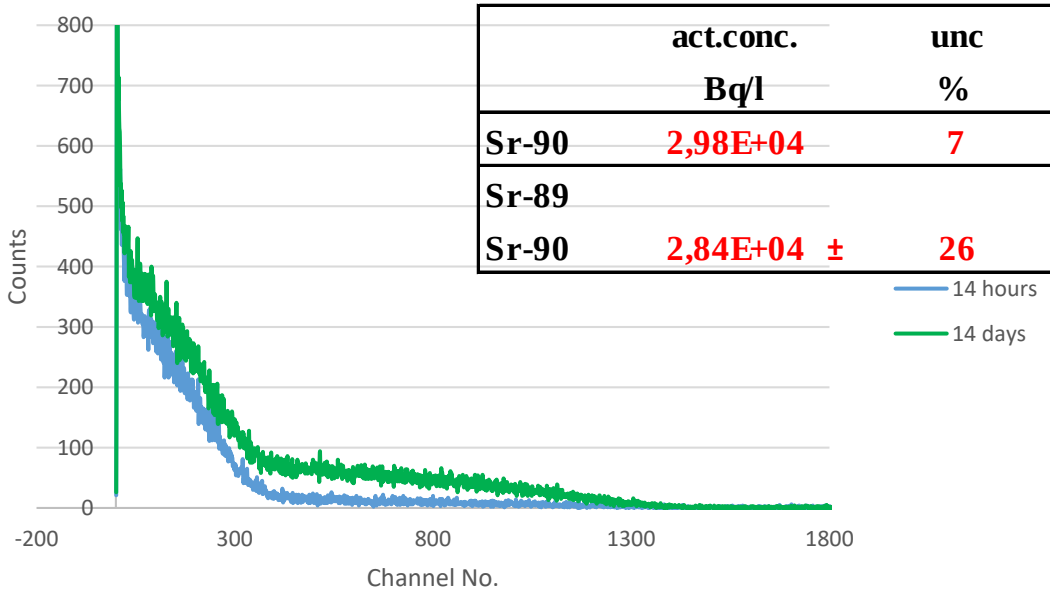
$^{90}Sr \longrightarrow {}^{90}Y \longrightarrow {}^{90}Zr$ (stable)

Nuclide	Half-life		Decay mode	β_{Max} keV	Specific activity Bq/g
^{89}Sr	50.6	d	β−	1501	
^{90}Sr	**29.1**	**y**	**β−**	**546**	**5,04E+12**
^{90}Y	**64**	**h**	**β−**	**2280**	
^{91}Y	59	d	β−	1544	
^{91}Sr	9,7	h	β−, γ	2700	
^{92}Sr	2,6	h	β−, γ	568	



Old waste

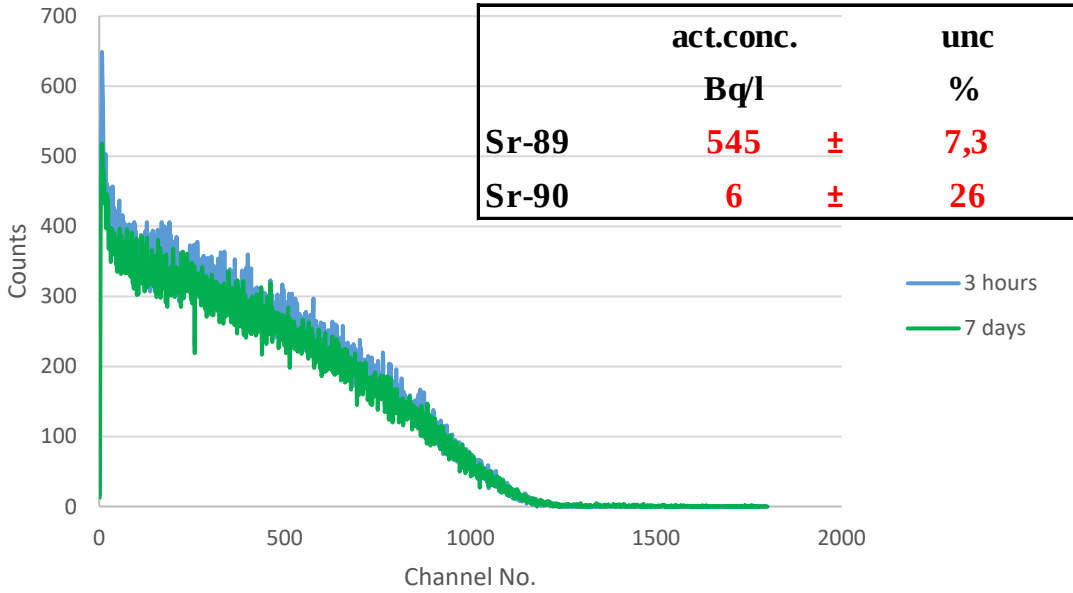
^{90}Sr LSC spectrum of H16-3 waste sample



	act.conc. Bq/l		unc %	LD Bq/l	Remark
Sr-90	2,98E+04		7		supposing no Sr-89
Sr-89				1,08E+03	supposing Sr-89
Sr-90	2,84E+04	±	26	1,87E+02	

Fresh coolant

^{89}Sr, ^{90}Sr LSC spectrum of 10TV20 primary coolant sample



	act.conc. Bq/l		unc %	LD Bq/l
Sr-89	545	±	7,3	0,4
Sr-90	6	±	26	3

Radiostrontium determination using Sr crown ether in nuclear samples

- separation after 2-5 days of **cooling**
- **repeated counting** after 2 weeks
- checking the shape of LS spectra
- calculations described in IAEA-AQ-27_web

Validation of the method for Radiostrontium determination

Conclusions

^{90}Sr results can be validated by measurement of reference materials, by participation in inter-laboratory comparisons.

It is important to assess all influencing factors, such as the presence of other Sr and Y isotopes, or other possible contamination (radionuclides of K, Ba, Pb) by performing ingrowth/decay measurements as part of method validation.

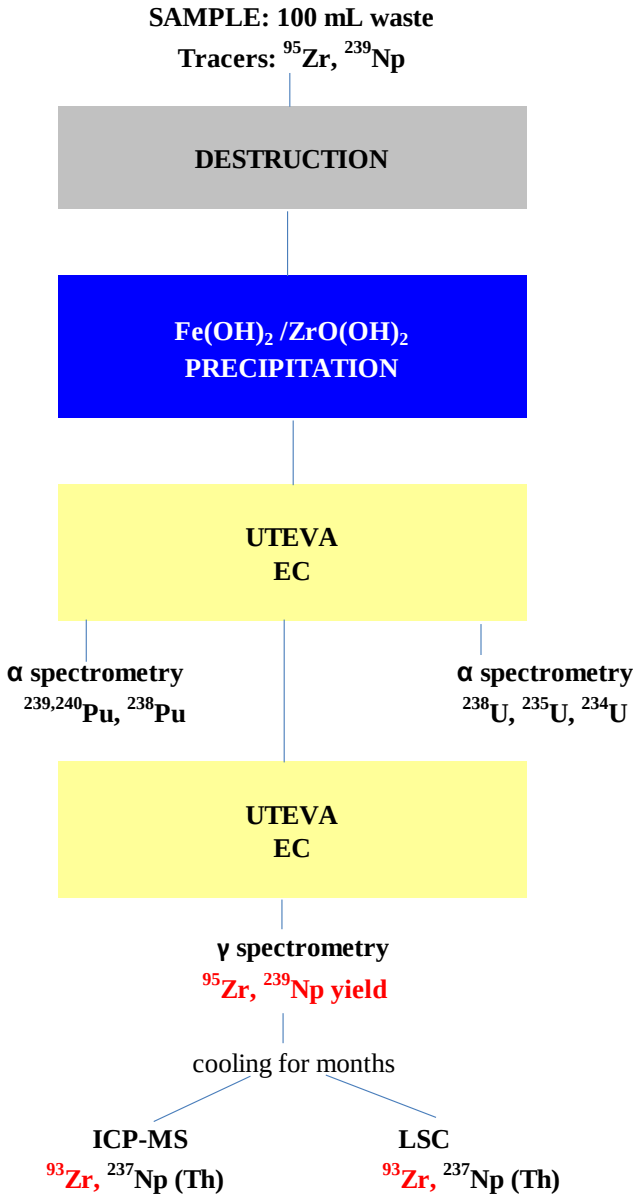
^{93}Zr determination

Nuclide	Half-life	Decay mode	β_{Max} keV	Specific activity Bq/g	Occurance/ field of application		
^{93}Zr	1,53 10^6 y	β−	90	9,27E+07	DN	WD	

Validation issues: No ^{93}Zr standard
No reference material
No intercomparison exercise

Validation option:
comparison of independent methods: **LSC**
ICP-MS

^{93}Zr determination



Carrier free tracers by NAA of U
Purification on UTEVA
γ spectrometry

Repeated separation on UTEVA
to purify Zr

Yield: Zr: 60-90%
Fluctuating significantly due to Zr adsorption to surfaces.

^{93}Zr determination

ICP-MS (Agilent Triplequad 8800)

Possible interferences in ICP-MS	**Countermeasures**
isobaric interference: **stable Nb** (^{93}Nb), ^{93m}Nb, ^{93}Mo	Nb decontamination DF>10^3
abundance sensitivity: **stable Zr** (^{92}Zr, ^{94}Zr)	mathematical correction
polyatomic interferences, e.g. $^{92}Zr^{1}H$	mathematical correction

LSC (Perkin Elmer Tricarb 2800)

Possible interferences in LSC	
^{95}Zr-^{95}Nb tracer	cooling, correction
α emitting nuclides (^{237}Np, ^{232}Th, ^{230}Th…)	spectrometric separation
any contamination (^{110m}Ag… ^{93m}Nb)	chemical purification

Measurement of ^{93}Zr by ICP-MS

- Background correction
- Correction for measurement instability using internal standard (Rh)

$$I_{net} = (I_{measured} - I_{blank}) \cdot \frac{I_{Rh,ref}}{I_{Rh}}$$

- Correction for abundance sensitivity due to stable Zr (^{92}Zr, ^{94}Zr)

$$I_{net,cor.} = I_{net} - I_{net,Zr92+94} \cdot f_1$$

$f_{(93/92+94)}$: 4.4 10-5 cps/cps

- Calibration with stable Zr standard solution(^{92}Zr)

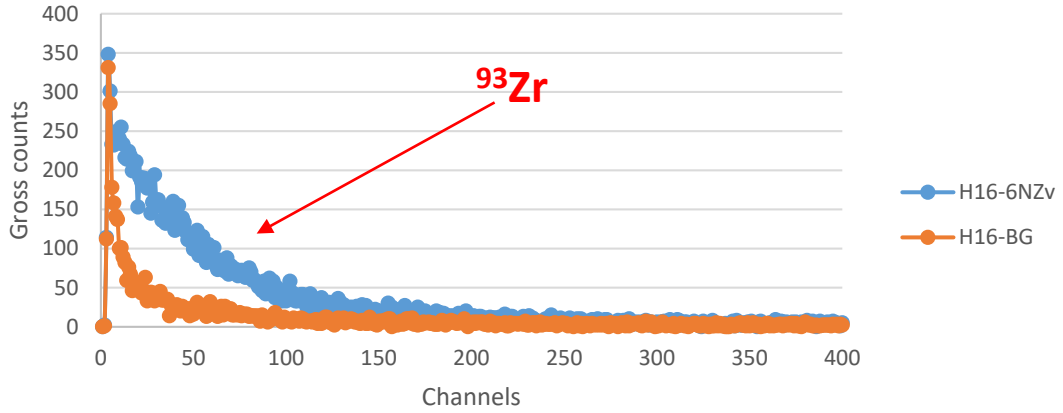
$$C_{Zr-93} = \frac{I_{net,cor}}{I_{net,cor,Zr-92std}} C_{Zr-92std}$$

sensitivity: 5.6 10^4 cps/ppb nuclide

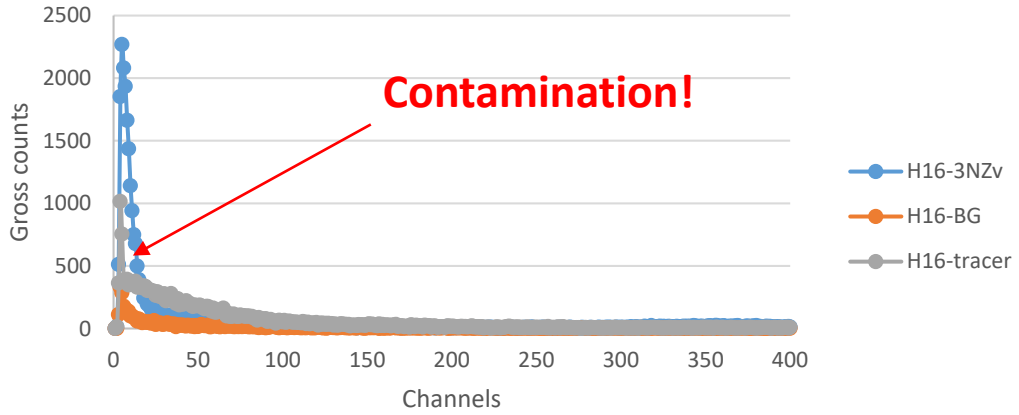
- No correction for isobaric Nb interference

Measurement of ^{93}Zr by LSC

LSC spectra of H16-6 waste sample and the background



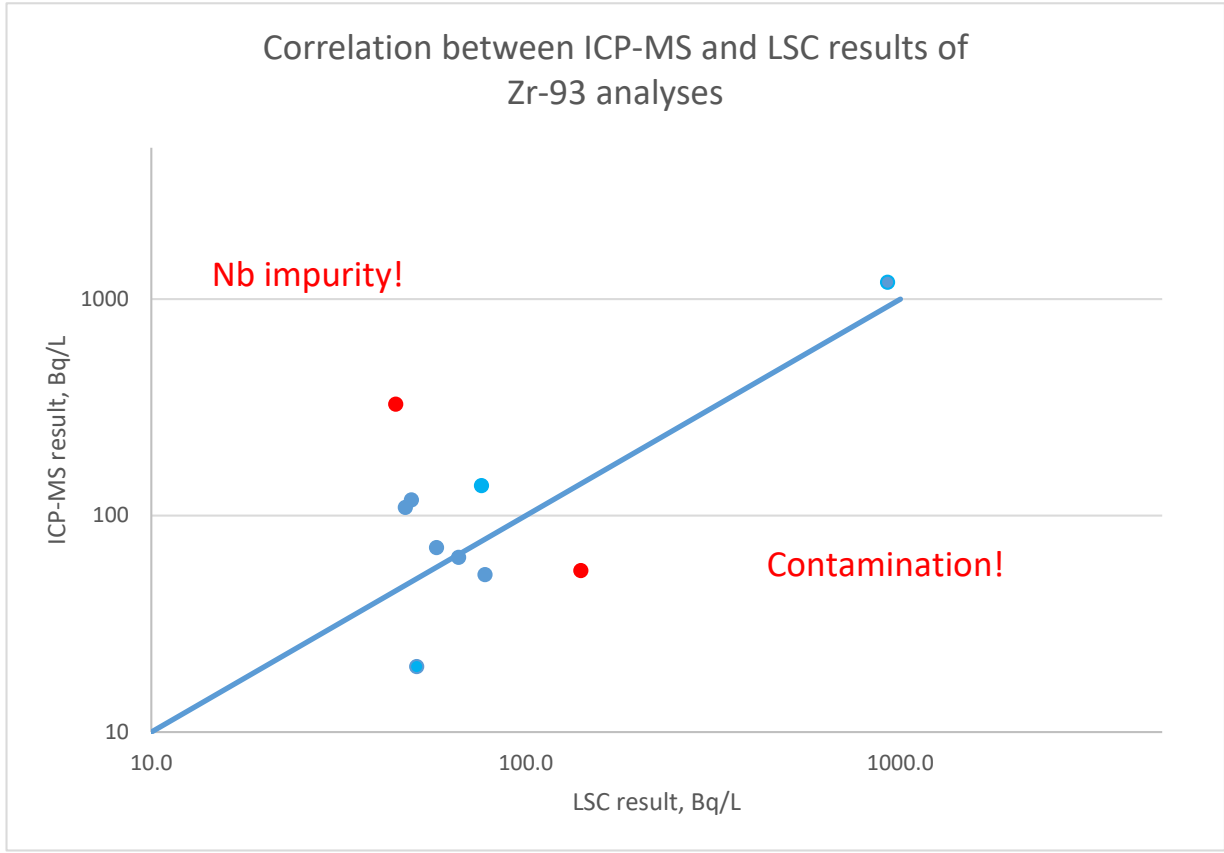
LSC spectra of H16-6 waste sample, the ^{95}Zr tracer and the background



LS spectra can reveal radioactive contamination of Zr fraction!

Measurement of ^{93}Zr by ICP-MS and LSC

Sample	Zr-93		Remark
code	LSC	ICPMS	
	Bq/L	Bq/L	
H16-10	51,1	20,0	
H16-1	77,9	53,3	
H16-9	57,8	71,0	
H16-8	47,8	108,8	
H16-5	49,6	118,0	
H16-2	76,1	137,4	
H16-4	44,9	327,0	Nb impurity
H16-6	924,8	1196,3	
H16-3	140,3	55,7	contamination



Measurement of ^{93}Zr by ICP-MS and LSC

Conclusions

ICP-MS is a sensitive technique to determine ^{93}Zr but small amounts of stable Nb can cause overestimation of the result.

LSC is exposed to the hazards of radioactive contamination. The presence of radioactive Zr tracer reduces the sensitivity.

LSC helps discover deviation from true value.

The method can be validated by the use of two methods.

^{63}Ni and ^{59}Ni determination

Nuclide	Half-life		Decay mode	β_{Max} keV	Specific activity Bq/g	Occurance/ field of application		
^{59}Ni	76400	y	EC, β+	(X: 6,9)	2,94E+09		WD	
^{63}Ni	100	y	β−	67	2,09E+12	DN	WD	

Validation issues: No ^{59}Ni standard

No reference material for ^{59}Ni determination

No intercomparison exercise for ^{59}Ni determination

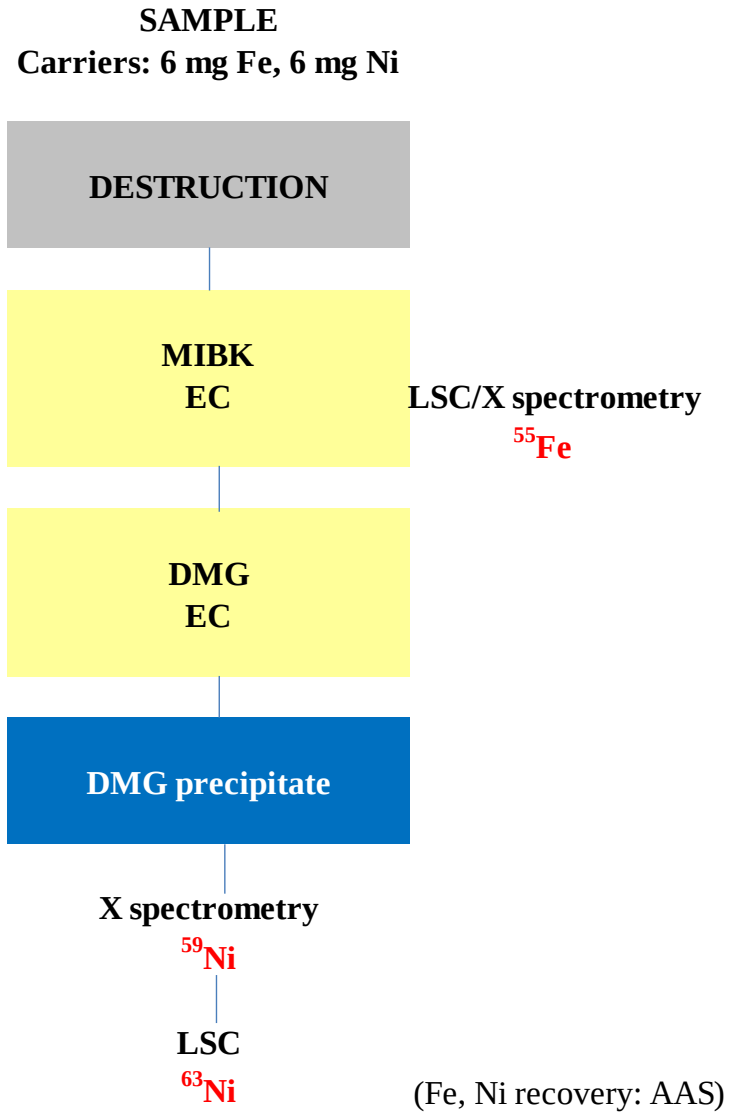
Validation options:

- ^{63}Ni determination in CRM and in PT
- Comparison of independent methods: **LSC for ^{63}Ni,**

X spectrometry for ^{59}Ni

ICP-MS for ^{63}Ni ???, ^{59}Ni???

^{63}Ni and ^{59}Ni determination



Removal of Fe by extraction chromatography

Selective separation of Ni by extraction chromatography (from Co, Cu)

Ni purification by precipitation

Decomposition of DMG

^{63}Ni and ^{59}Ni determination

LSC for ^{63}Ni (Perkin Elmer Tricarb 2800)

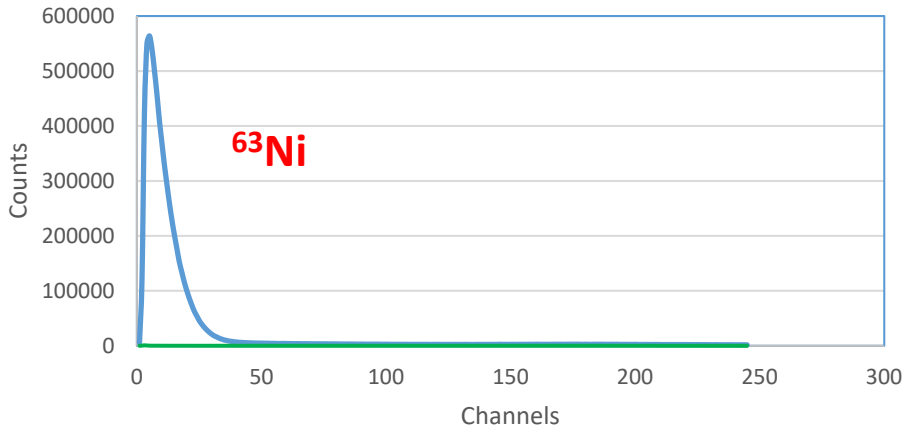
Possible interferences

^{59}Ni	correction if necessary
any contamination (^{110m}Ag… ^{60}Co)	chemical purification

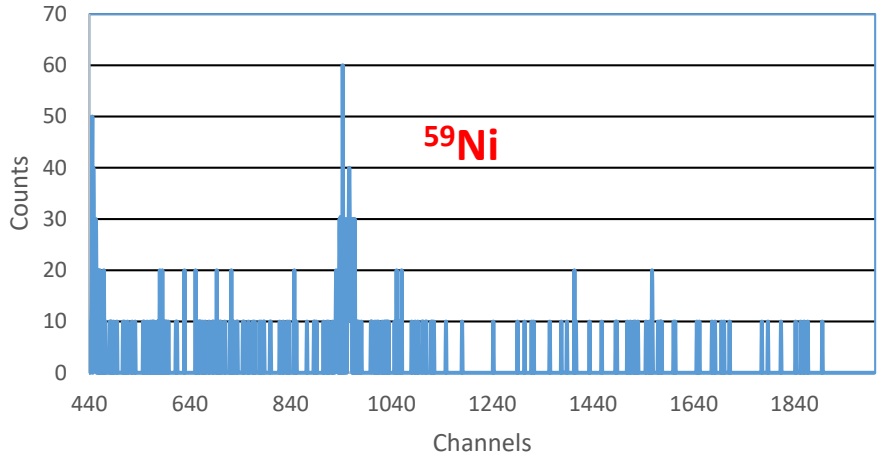
X-ray spectrometry for ^{59}Ni (Si(Li) and MCA)

Possible interferences: none

LSC spectrum of a Ni source from H16-3 waste



X-ray spectrum of a Ni source from H17-4 waste



^{63}Ni and ^{59}Ni determination

ICP-MS (Agilent Triplequad 8800)

Possible interferences in ICP-MS

	Countermeasures
isobaric interference of ^{63}Ni: **stable Cu** (^{63}Cu-^{65}Cu)	mathematical correction
isobaric interferenceof ^{59}Ni: **stable Co** (^{59}Co)	chemical purification
abundance sensitivity: stable Ni (^{58}Ni, ^{60}Ni, ^{62}Ni)	mathematical correction
polyatomic interferences, e.g. ^{58}Ni^{1}H, ^{62}Ni^{1}H	collision cell

Calculation: similar to the case of ^{93}Zr

Validation of ^{63}Ni results

Use of reference materials, participation in PTs

Not waste matrix

	Measured		Reference value		Precision
	^{63}Ni activity concentration Bq/kg	unc Bq/kg	^{63}Ni activity concentration Bq/kg	unc Bq/kg	index %
MAPEP-06-MaS15	**357**	50	**329**	56	22

Measurement by ICP-MS

The presence of a few ppb Cu causes significant overestimation!

	ICP-MS						LSC	ppb	
Sample code	Net intensity at mass 63 (Ni-63+Cu-65) cps	Net intensity at mass 65 (Cu-65) cps	Ni-63 intensity corrected for Cu-63 cps	Ni-63 concentration ppb	Ni-63 activity concentration Bq/mL	Ni-63 activity concentration Bq/L waste	Ni-63 activity concentration Bq/L waste	Cu concentration in waste* ppb	Ni concentration in waste ppm
H16-3/1	3,14E+07	1,48E+07	LD	LD		**LD**	**1,38E+05**	1054	11
H16-3/2	5,15E+07	2,43E+07	LD	LD		**LD**	**1,26E+05**	1328	9
H17-4	7,69E+05	3,64E+05	LD	LD		**LD**	**2,99E+05**	107	28
H17-6	1,92E+06	8,28E+05	8,55E+04	1,53E+00	3,19E+03	**2,87E+06**	**6,42E+05**	76	37

Cu-63/Cu-65 ratio: 2,22

Ni sensitivity: 5,61E+04 cps/ppb nuclide

Ni-63 specific activity: 2,09E+03 Bq/ng

* in ICP-MS sam

Work in high purity environment

Validation of ^{59}Ni results

No reference material, no PT

Measurement by ICP-MS

Sample code	MP-AES measurement Co concentration by AES ppb	Net intensity at mass 59 cps	ICP-MS measurements Ni-59 intensity corrected for Co cps	Ni-59 concentration ppb=ng/mL	Ni-59 activity concentration Bq/mL	Ni-59 activity concentration Bq/L waste	XRF measurements Ni-59 activity concentration Bq/L waste
H16-3/1	1,25E+02	5,10E+06	LD	LD	LD	**LD**	**LD**
H16-3/2	3,10E-01	9,16E+04	7,47E+04	1,33E+00	3,92E+00	**2488**	**LD**
H17-4	LD	7,77E+04	7,77E+04	1,39E+00	4,08E+00	**4587**	**403**
H17-6	LD	1,21E+05	1,21E+05	2,15E+00	6,33E+00	**5694**	**1080**

Co sensitivity: 5,44E+04 cps/ppb

Ni sensitivity (isotopic): 5,61E+04 cps/ppb nuclide

Ni-59 specific activity: 2,94 Bq/ng

The presence of a 1-2 ppb Co causes significant overestimation!

^{63}Ni and ^{59}Ni determination

Conclusions

^{63}Ni results obtained by LSC can be validated by the measurement of reference materials, participation in intercomparison exercises.

Techniques for validation of ^{59}Ni results obtained by X–ray spectrometry are not available.

MESSAGES

Conventional techniques of method validation are not always sufficient or available.

The accuracy of ^{90}Sr results can be confirmed by performing repeated measurements.

^{93}Zr results can be validated by comparing LSC and ICP-MS measurements.

Validation of ^{63}Ni and ^{59}Ni results by comparing LSC/X-ray spectrometry and ICP-MS measurements has failed due to the presence of a few ppb Cu or Co.