Radiological characterization of waste

Nordic effort on optimization and standardization of the radioanalytical methods for hard-to-measure radionuclid

Xiaolin Hou

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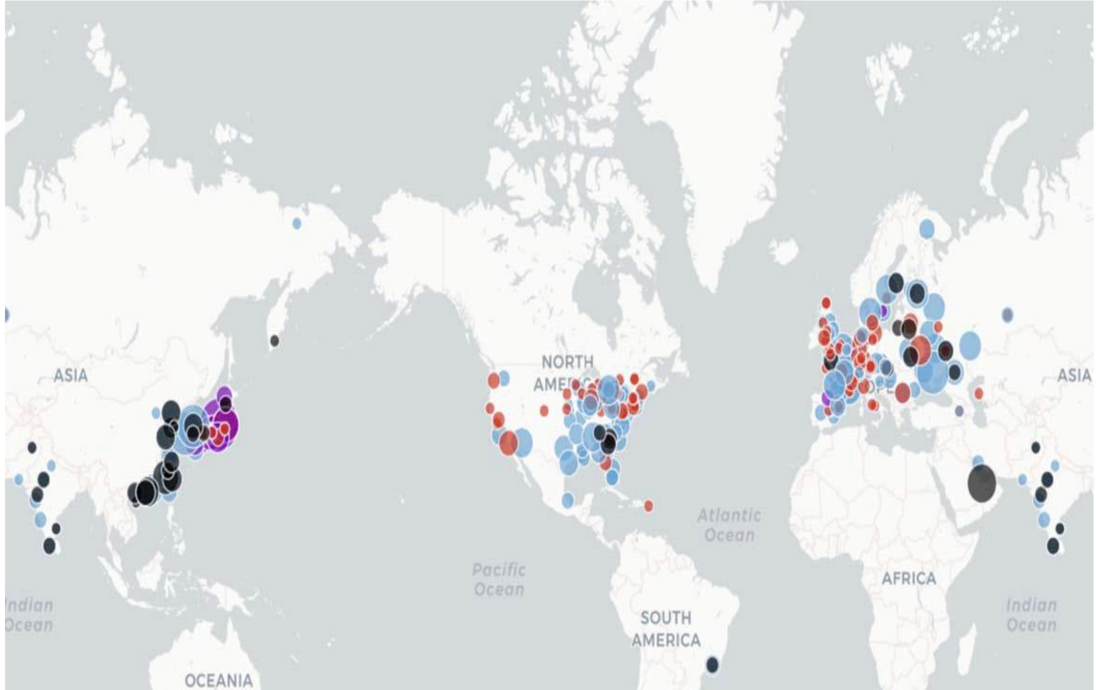
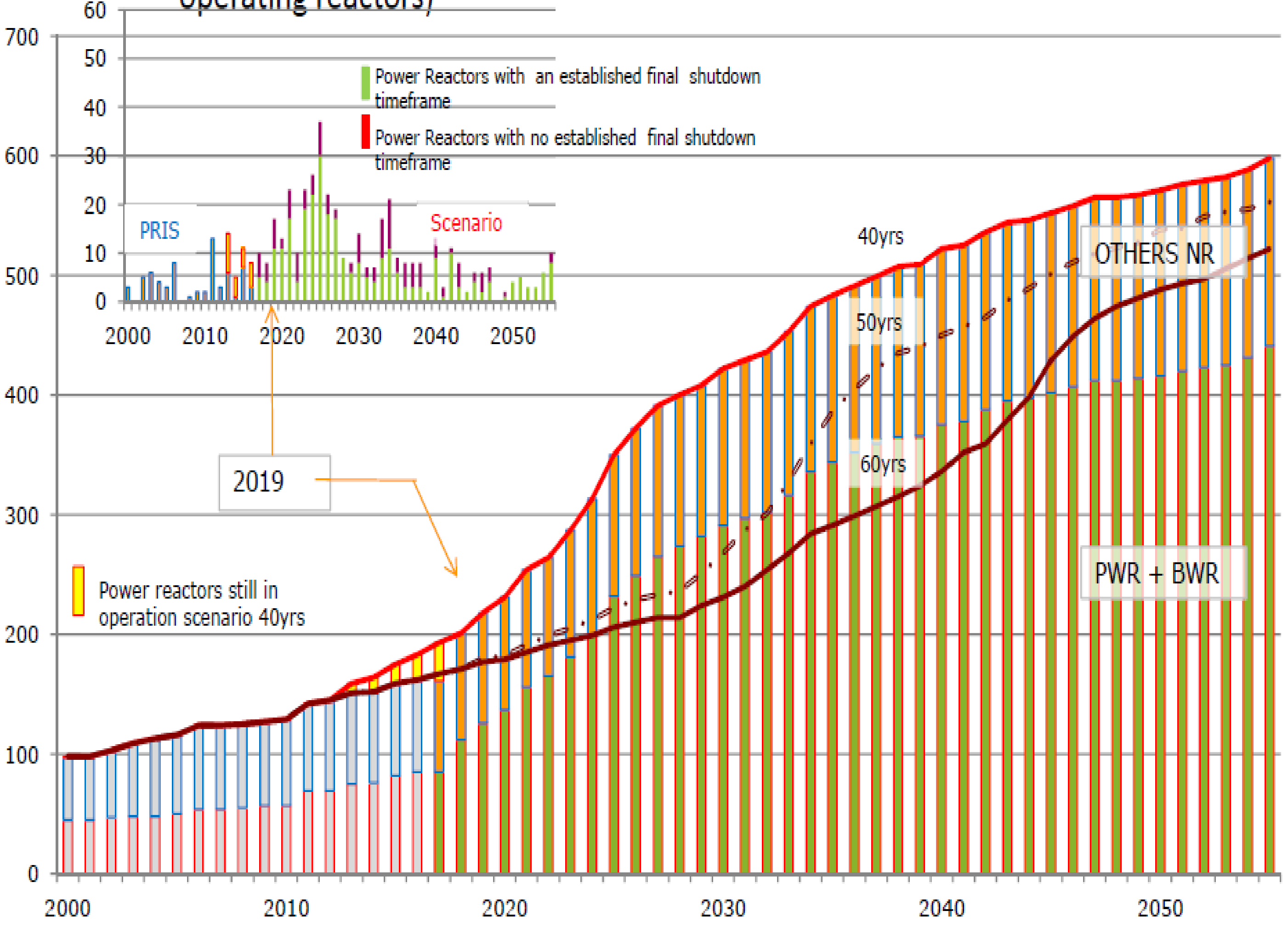
Decommissioning – growing industry

Nuclear Power reactors all over the world (451 units by Dec. 2020)



Most of radionuclides were produced in NPPs and remained in the spent nuclear fuel elements, as well as materials in the reactors

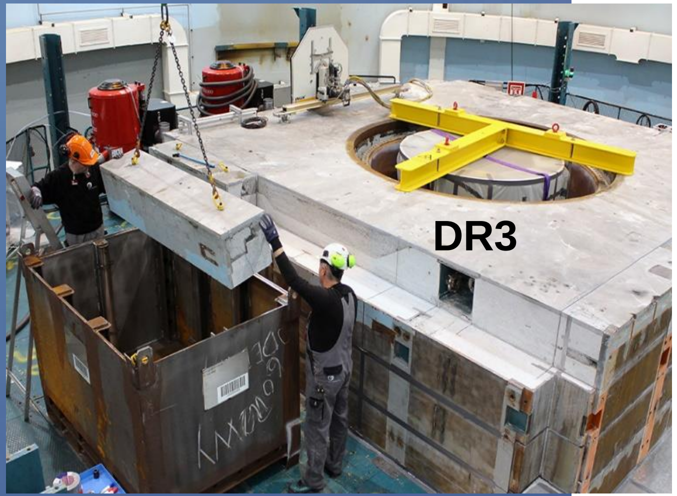
IAEA study 2017: Shutdown scenario (assumption of 40 years life time for operating reactors)



IAEA Power Reactor Information System (PRIS), https://www.iaea.org/pris/

Decommissioing of nuclear facilities

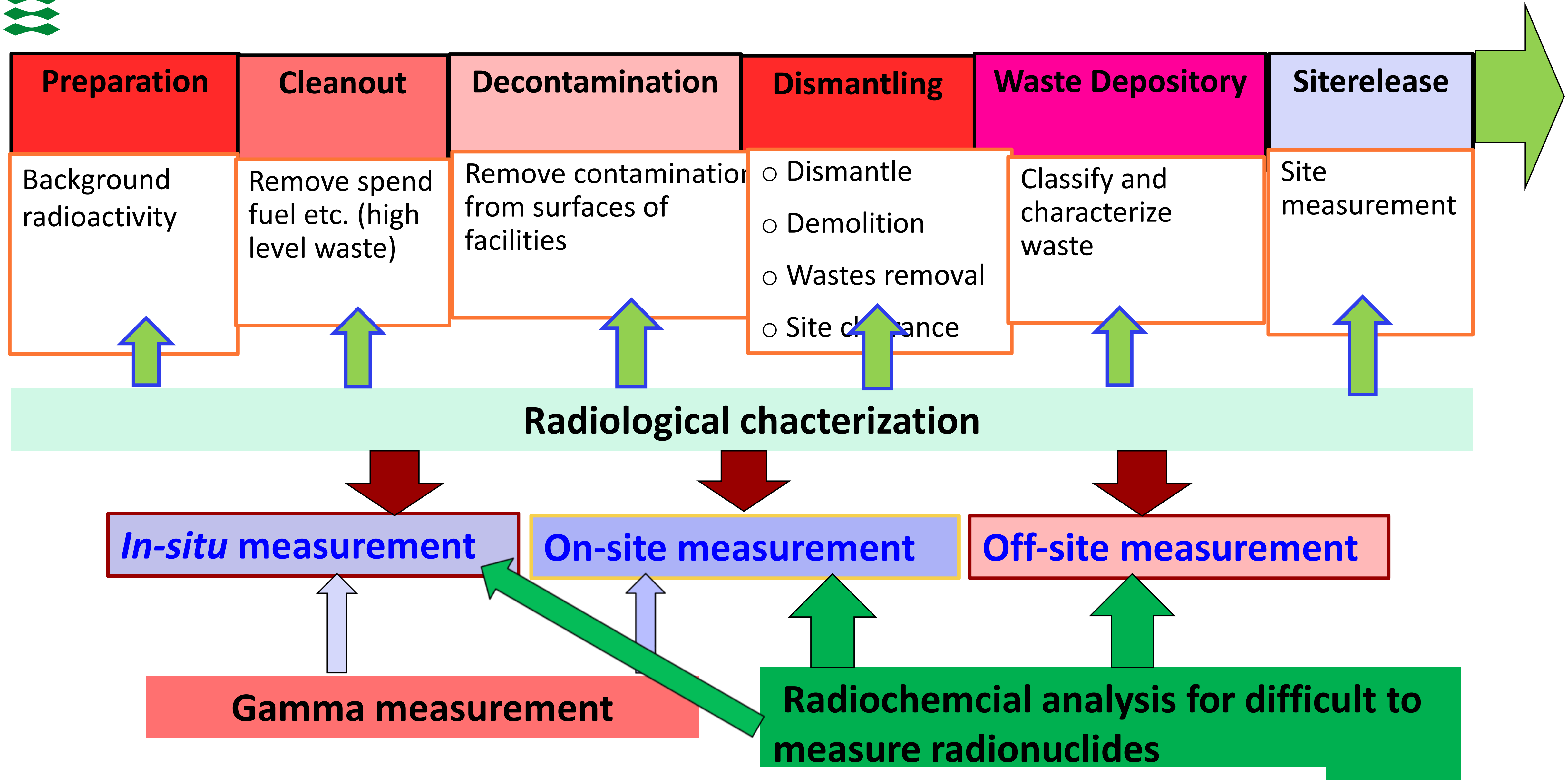
- 2000: Close of of DR3 and start decommissioning of all nuclear facilities at Risø
- 2021, DR1, DR2 and hot cell were decommissioned
- DR3 is on the way to be decommissioning



DTU

Nordic nuclear facilities for decommissioning

Process of decommissioning nuclear facilities



Rapid and accurate determination of DTM radionuclides

Analysis of Radionuclides

Sampling

Pre-concentration

γ- spectrometry
(**^{137}Cs, ^{134}Cs, ^{210}Pb, ^{7}Be,** ^{131}I, ^{241}Am)

Radiochemcial separation of target radionuclides from matrix and interferring radionuclideds

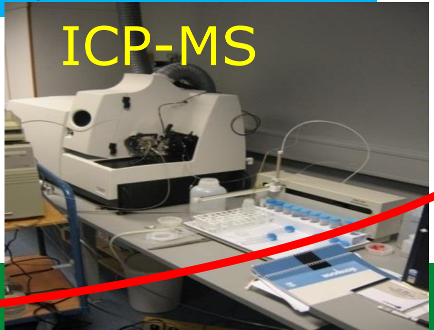
β- couting
(^{3}H, ^{14}C, ^{55}Fe, ^{63}Ni, ^{41}Ca, ^{36}Cl, ^{93}Mo, **^{99}Tc,** ^{90}Sr)

α- spectrometry
($^{238,239,240}Pu$, ^{241}Am, ^{242}Cm, ^{210}Po, ^{226}Ra, ^{222}Rn)

AMS
(^{129}I, ^{236}U, ^{14}C, ^{10}Be, ^{26}Al, ^{36}Cl, ^{59}Ni, ^{41}Ca)

ICP-MS
(^{135}Cs, ^{239}Pu, ^{240}Pu, ^{237}Np, **^{99}Tc**)

Other MS

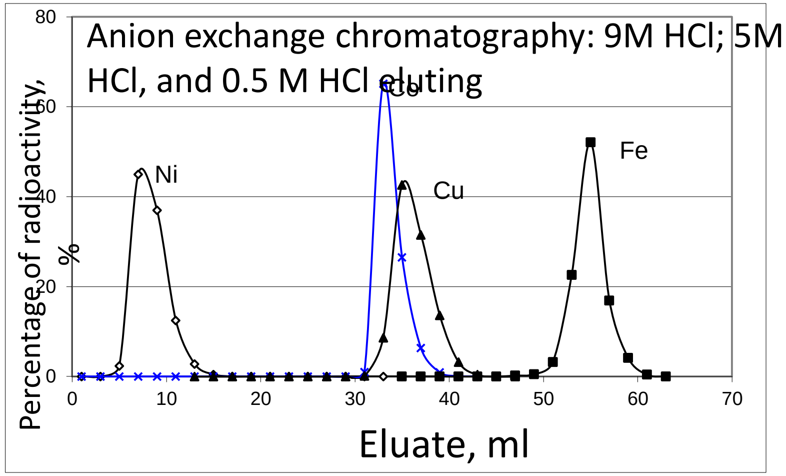


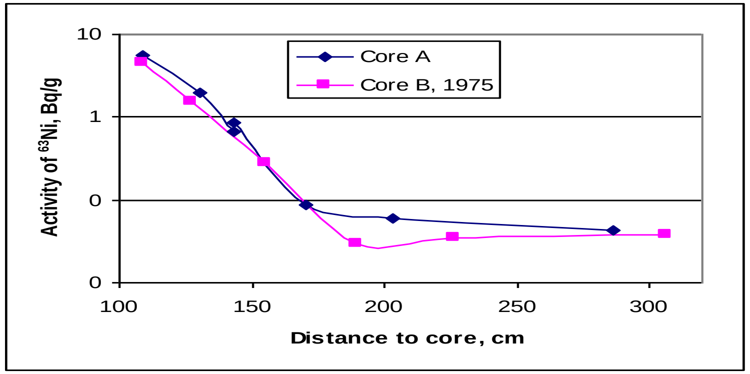
Developed radioanalytical methods in STR group for Environmental studies and decommissioning

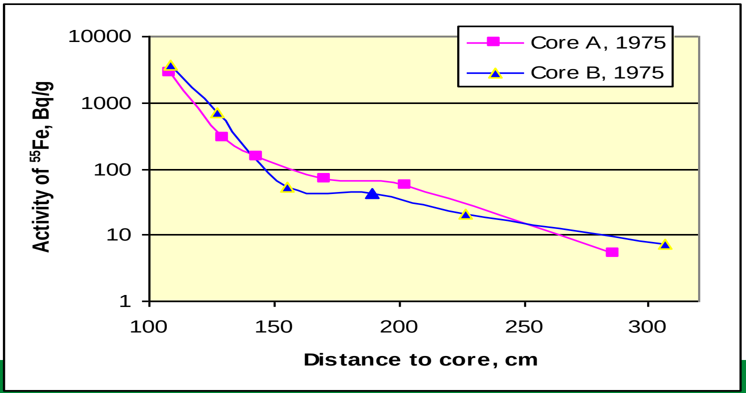
	Environmental studies	Decommissioning
Sample/matrix	• Air (aerosol, gaseous radionuclides), Precipitaton (rain, snow, etc.) • Water (sea, lake/river, groundwater), • Soil, sediment, peat, rock, • Plants (seaweed, vegetable, grains, etc.) • Annimal tissues (meat, fish, etc.)	• Concrete (stone, sand, brick, etc.) • Metals (iron, stainless, carbon steel, steel, copper, alluminum, lead, zirconium alloy, metal oxides, etc.) • Granphite, coolant water, • Resins, concentrated slurry • Paint, plastics, PVC, oil, etc. • Soil, sediment, etc.
Major radionuclides (hard-to measure)	^{3}H, ^{14}C, ^{55}Fe, ^{63}Ni, ^{90}Sr, ^{99}Tc, ^{129}I, ^{135,137}Cs, ^{210}Pb, ^{210}Po, ^{222}Rn, ^{226,228}Ra, ^{233,234,235,236,238}U, ^{237}Np, ^{238,239,240,241}Pu, ^{241}Am, etc.	^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63}Ni, ^{90}Sr, ^{94}Nb, ^{93}Mo, ^{99}Tc, ^{129}I, ^{234,235,236,238}U, ^{237}Np, ^{238,239,240,241}Pu. ^{241}Am, ^{243,244}Cm, etc.
Radionuclides (γ)	^{7}Be, ^{134,137}Cs, ^{131}I, ^{210}Pb, ^{241}Am, etc.	^{54}Mn, ^{59}Fe, ^{58,60}Co, ^{110m}Ag, ^{125}Sb, ^{133}Ba, ^{134,137}Cs, ^{152,154,155}Eu, etc.

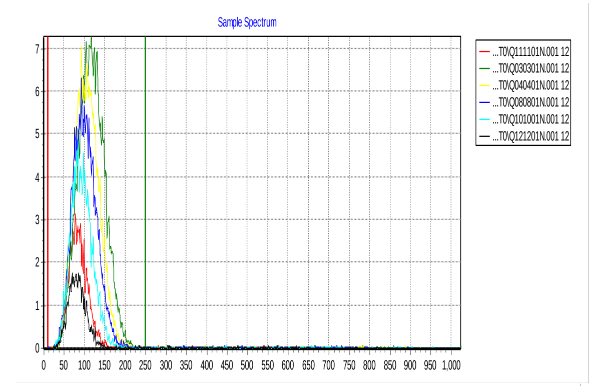
Analysis of ^{55}Fe and ^{63}Ni in decommissioning waste

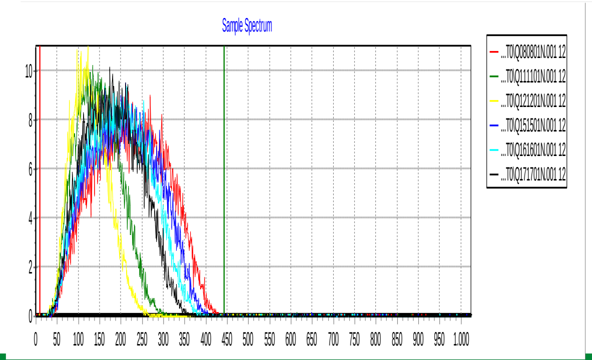
Element	Recovery or decontamination factor
Ni^{2+}	> 98.5%
Fe^{3+}	$>10^6$
Co^{2+}	$>10^6$
Ba^{2+}	$>10^6$
Eu^{3+}	$>10^6$
Cs^{+}	$>10^6$
Sr^{2+}	$>10^6$

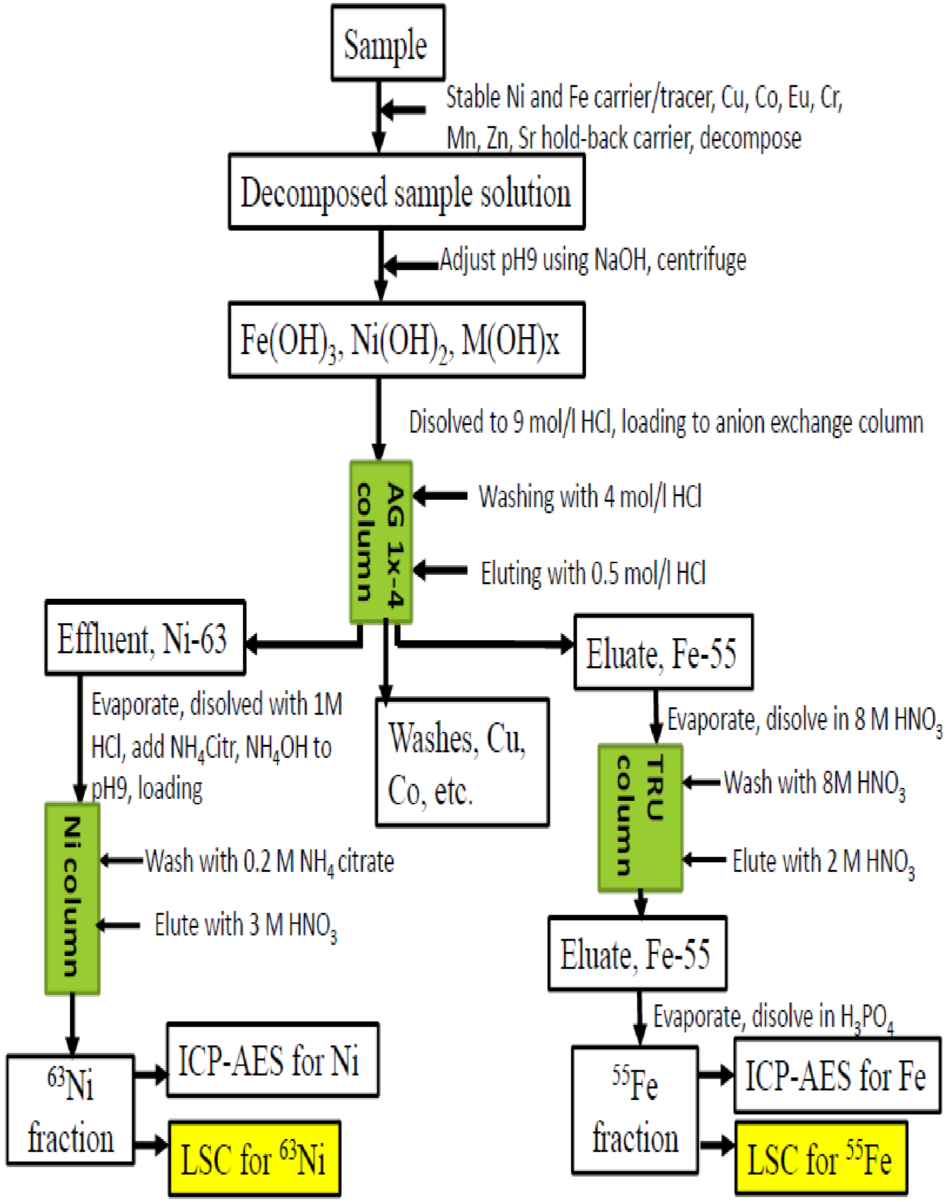




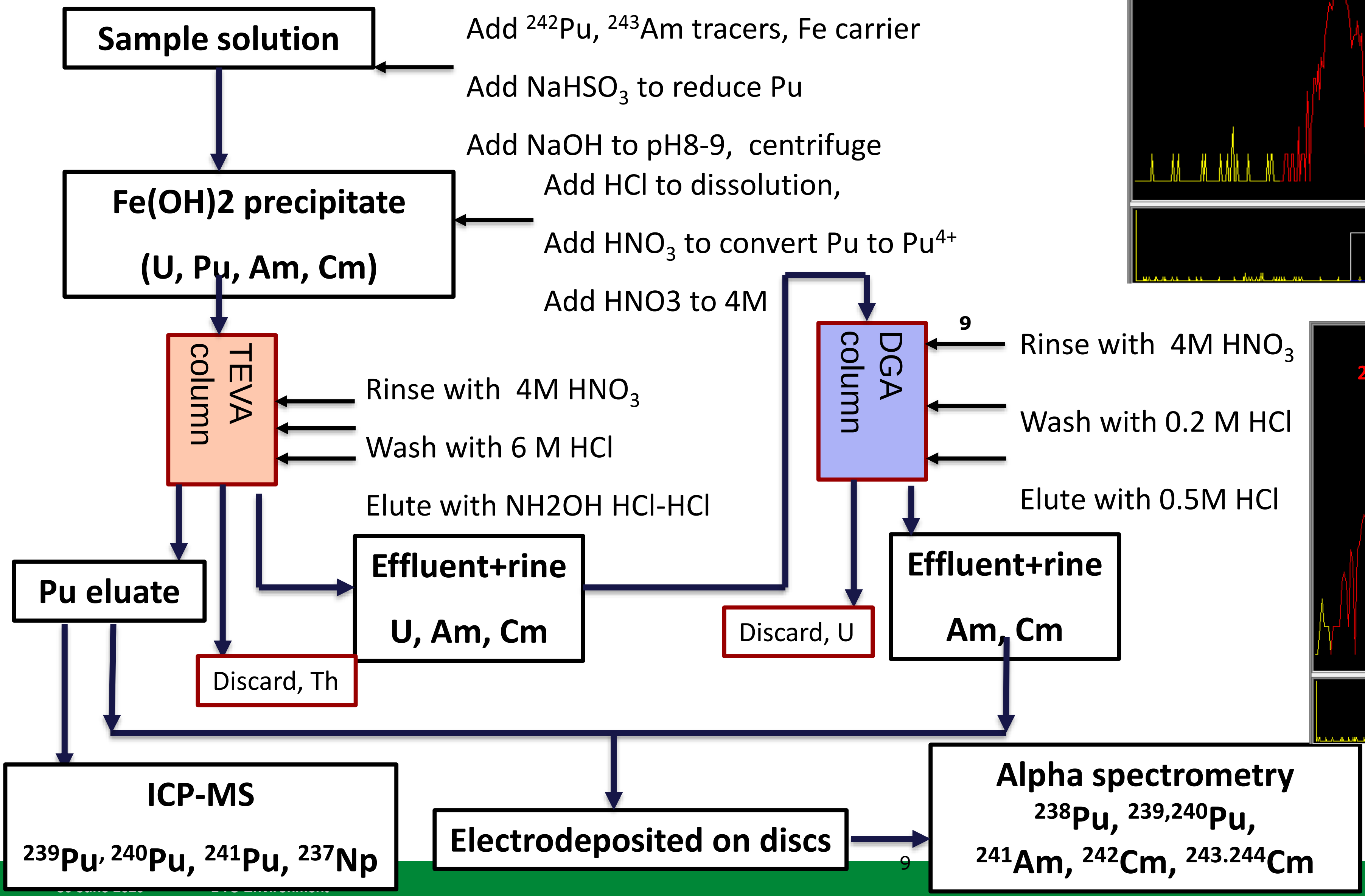


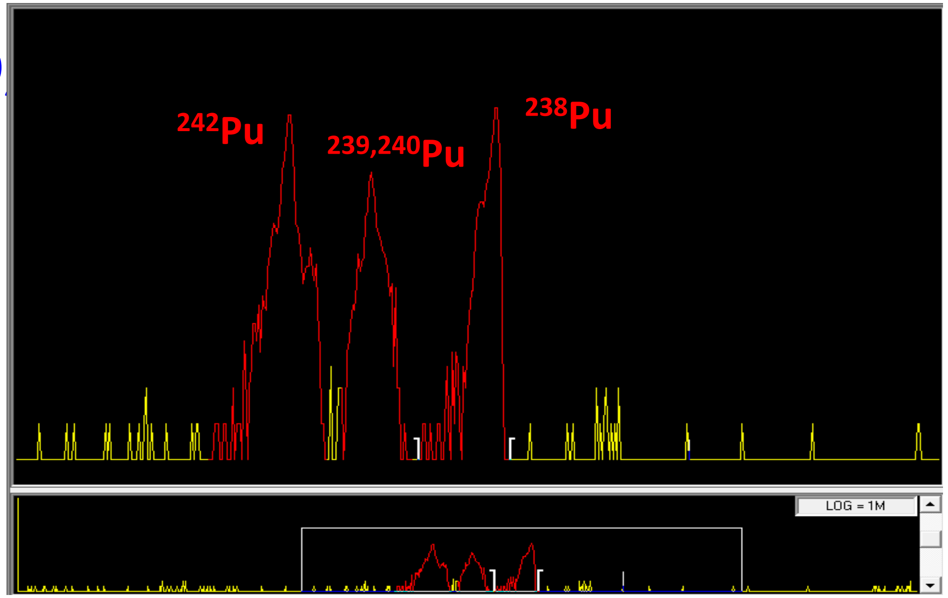


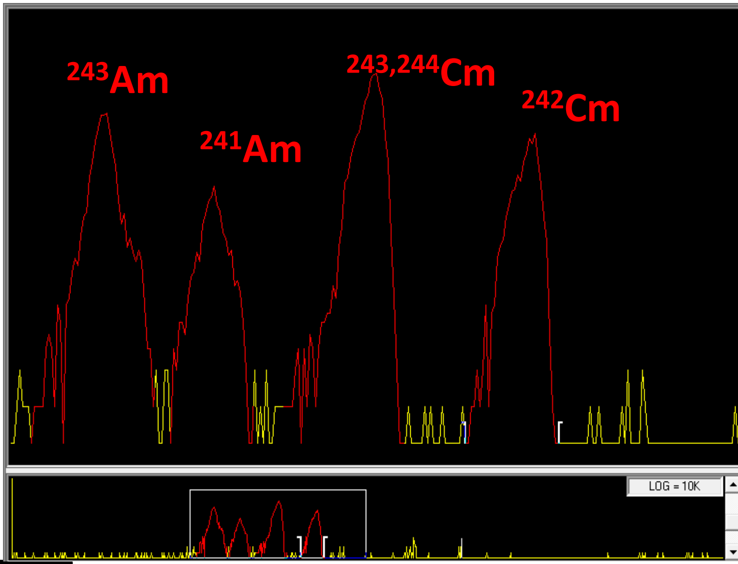




Analytical method for determination of Pu, Np, Am and Cm isotopes (TEVA-DGA)







Projects of radiological characterisation for decommissioning and operation of nucear reactors at DTU, Risø

- **Danish decommissioning**: DR1, DR2, DR3, hot cell, radiological survey of surrounding facilities (2001-now)
- **Barseback NPP RKL and HINT projects** (2017-2021)
- **Oskarshamn NPP RKL and SERIN projects** (2021-2013)
- **Ågesta NPP project** (2009-2012)
- **Finish Loviisa NPP projects** (characrterisation of operation waste of resin and slurry) (2017-2023)
- **Australian ANSTO project** (2 research reactors) (2012-2015)
- **Ignalina (Lithania) NPP** project (2010-2015)

Nordic efforts on optimization and standardization of the radioanalytical methods for hard-to-measure radionuclides

Project	Co-ordinator	Activities	Outputs
STANMETHOD 2014, 2015	DTU (7 Nordic labs)	• Summary of methods used Nordic labs for radionuclides determination • 2 intercomparison excercise insimulated water and reactor water, • 2 Nordic standard methods for 63Ni and 55Fe in reactor water and environmental samples	Reports: NKS-327, NKS-357, Scientific papers: JRNC article
Optimethod 2018, 2019	DTU (12 Nordic labs)	• 2 intercomparison excercise for isotopes of Pu, Am and Cm in simulated water, reactor water and filter • Optimized methods for determination of actinides in reactor water and filter	Reports: NKS-415, NKS-436, Scientifical papers: JRNC article
DTM Decom 2020, 2021	VTT	Inter-comparison	NKS-429, NKS-441, JRNC papers
RESINA 2022	VTT	Intercomparison	

Publications by NKS projects.

nks
Nordic nuclear safety research

NKS-327
ISBN 978-87-7893-408-6

rogress on Standardization of Radioanalytical
ethods for determination of important radionu-
des for environmental assessment and waste
management in Nordic nuclear industry

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January 2015

nks
Nordic nuclear safety research

NKS-356
ISBN 978-87-7893-440-6

dization of Radioanalytical Methods
ermination of ^{63}Ni and ^{55}Fe in Waste
and Environmental Samples

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January 2016

nks
Nordic nuclear safety research

NKS-415
ISBN 978-87-7893-504-5

mination of Isotopes of Pu,
Reactor Water Samples –
f OptiMethod 2018 project

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January 2019

nks
Nordic nuclear safety research

NKS-436 ISBN 978-87-7893-526-7

nt alpha emitters in nuclear samples –
OptiMethod 2019 project report

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May 2020

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CrossMark

Present status and perspective of radiochemical analysis of radionuclides in Nordic countries

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Journal of Radioanalytical and Nuclear Chemistry (2021) 329:1447–1458
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Check for updates

Analyzing alpha emitting isotopes of Pu, Am and Cm from NPP water samples: an intercomparison of Nordic radiochemical laboratories

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Abstract
Radioanalytical methods for the determination of isotopes of Pu, Am and Cm in water samples from nuclear power plants were compared and further developed in a Nordic project (Optimethod) through two intercomparison exercises among Nordic laboratories. With this intercomparison, the analytical performance of some laboratories was improved by modification of the analytical method and adopting new techniques. The obtained results from the two intercomparisons for alpha emitting transuranium isotopes are presented, and the lessons learnt from these intercomparison exercises are discussed.

Keywords Actinides · Radioanalytical methods · Extraction chromatography · Nuclear power plant samples · Water samples · Alpha spectrometry

Introduction

Nordic co-operation has been continuing among institutes in the fields of radiochemistry and nuclear safety via Nordic nuclear safety research (NKS) programs for over 40 years.

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In many of the past NKS-funded projects, intercomparison exercises have been performed for evaluating the performance of different separation and detection methods used in Nordic radiochemistry laboratories, as well as for developing new advanced methodologies [1–5]. In a recent two-year NKS project called Optimethod, two intercomparison campaigns were organized with the aim to analyze alpha emitting isotopes of transuranium elements in different NPP (nuclear power plant) water samples [6, 7]. In both intercomparisons, transuranium isotopes ^{238}Pu, $^{239+240}$Pu, ^{241}Am, ^{242}Cm and $^{243+244}$Cm were radiochemically separated and measured by alpha spectrometry. In some participating laboratories, ICP-MS was also utilized for measurement of ^{239}Pu and ^{240}Pu individually. In total 12 partners, including all Swedish and Finnish nuclear power plants, some Nordic academic research institutes and radiation safety authorities participated in this project focusing on the intercomparison

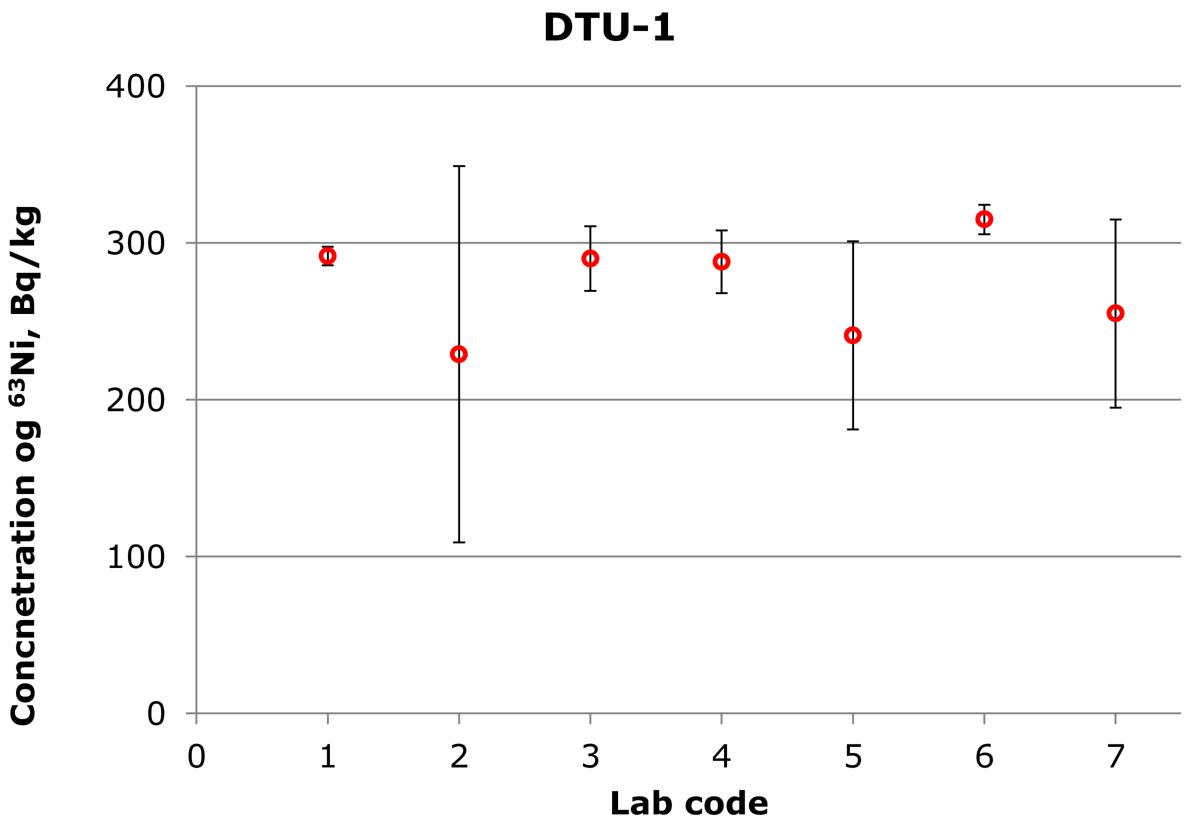
NKS-Standard Methods projects: STANMETHOD 2014 and 2015

Three Inter-comparison Samples (2014)

Code	Sample	Matrix	Radionuclides
DTU-1	Spiked water	1.0 L in HNO_3	^{63}Ni, ^{55}Fe, ^{60}Co, and ^{137}Cs
Forsmark-1	Reactor coolant water collected from Forsmark NPP	1.0 L water in HNO_3	^{63}Ni, ^{55}Fe, ^{3}H, ^{51}Cr, ^{58}Co, ^{60}Co, ^{110m}Ag, ^{99}Mo, ^{122}Sb, ^{144}Ce;
Forsmark-2	Acid digested filter	5 mL inHNO_3 and H_2SO_4	^{63}Ni, ^{55}Fe, ^{54}Mn, ^{58}Co, ^{60}Co, ^{65}Zn.

Institue	63Ni			55Fe
	DTU-1	F-1	F-2	
DTU Nutech	x	x	x	x
Studsvik AB	x	x	x	
Forsmark	x	x	x	
OKG	x	x	x	
Ringhals AB	x	x	x	
STUK	x	x	x	
Loviisa	x	x		x
IFE				

Analytical results of ^{63}Ni in DTU-1 (Spiked water)



TRU+Ni column	Anion exchange + Ni column
2,3,4,5	1, 7

All reported data are acceptable, and not significant different with the spiked value !

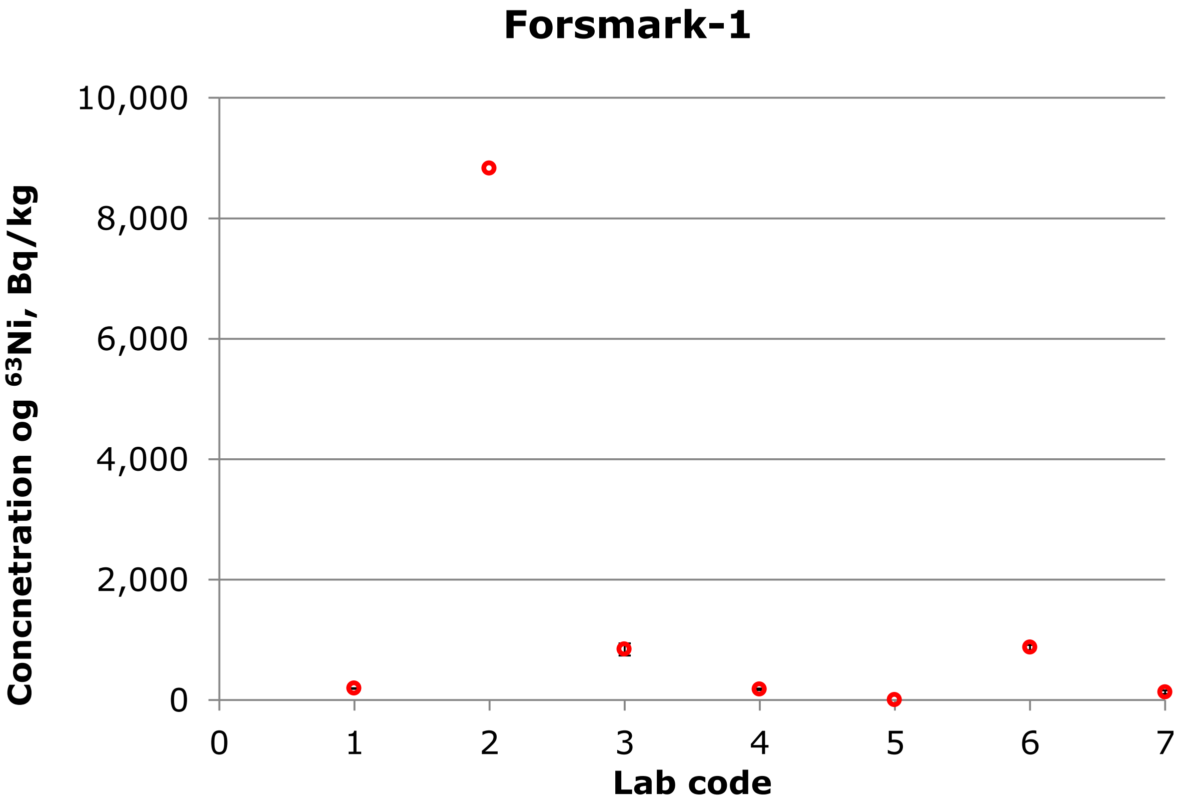
Measured Value:

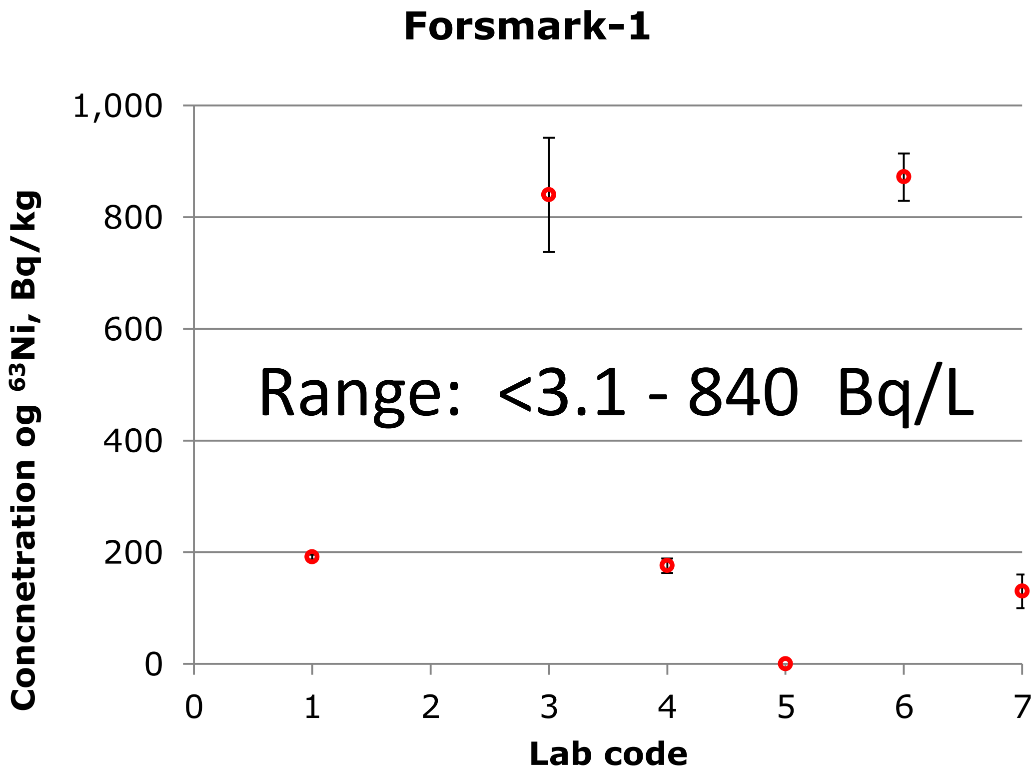
Range: 229-315 Bq/L

Average: 273.3±31.4 Bq/L

Spiked value : 290.2±3.2 Bq/L

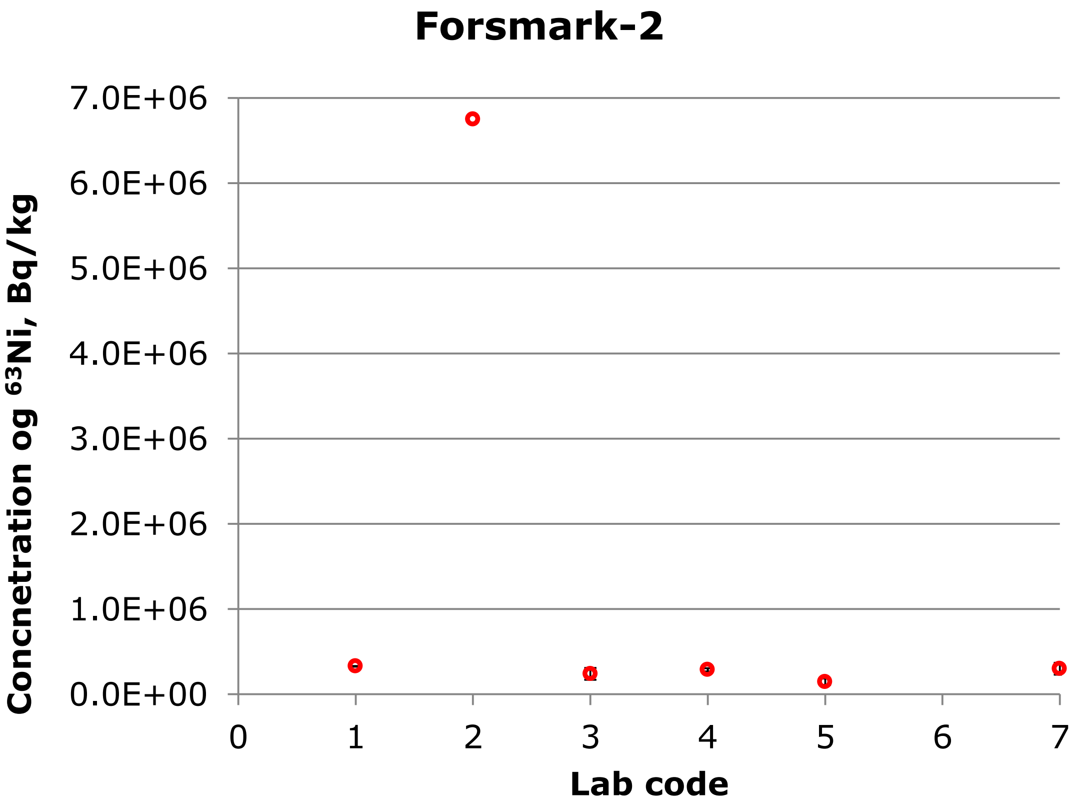
Analytical results of ^{63}Ni in Forsmark-1 (reactor coolant water with high ^{58}Co activity)

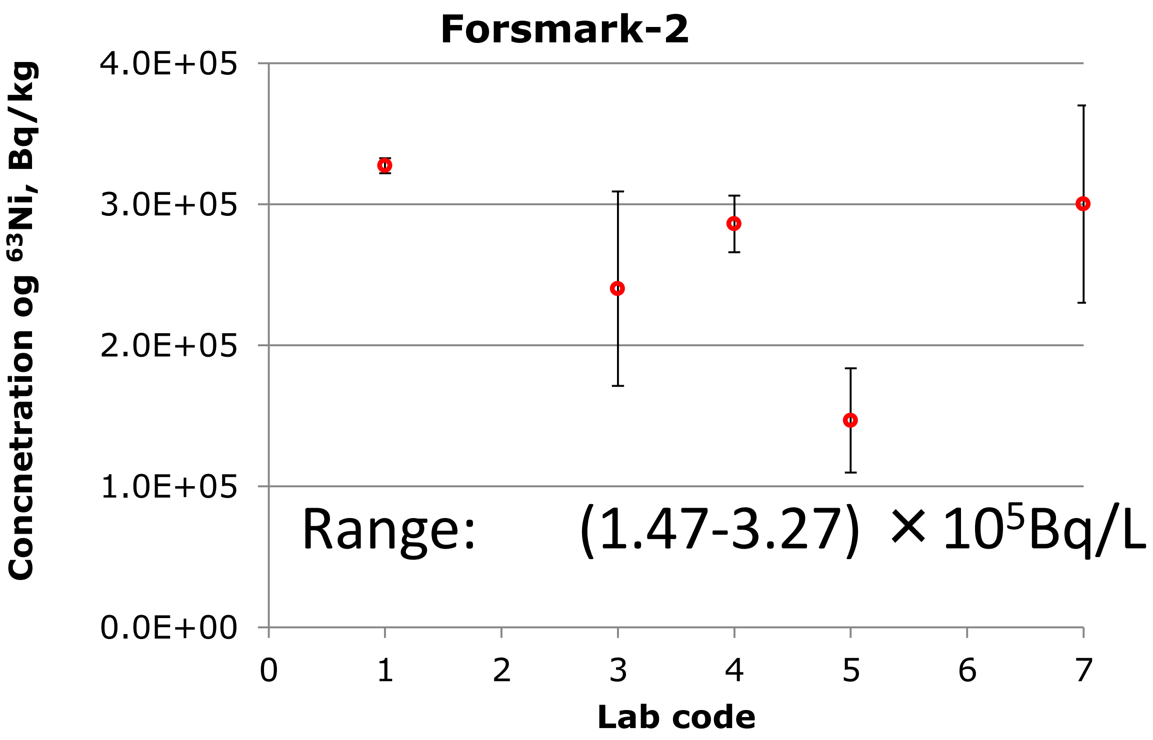




The abnormal highest data from one lab was excluded

Analytical results of ^{63}Ni in Forsmark-2 (digested filter)

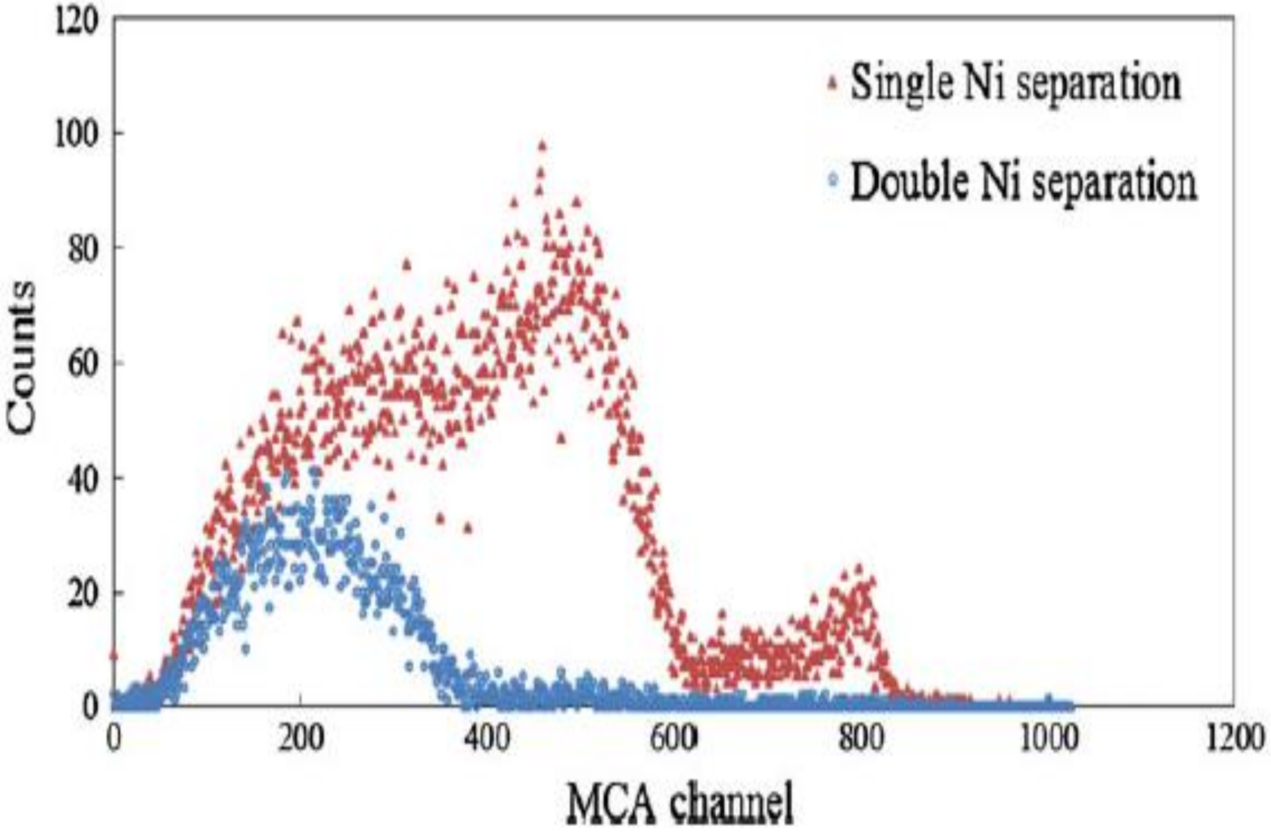


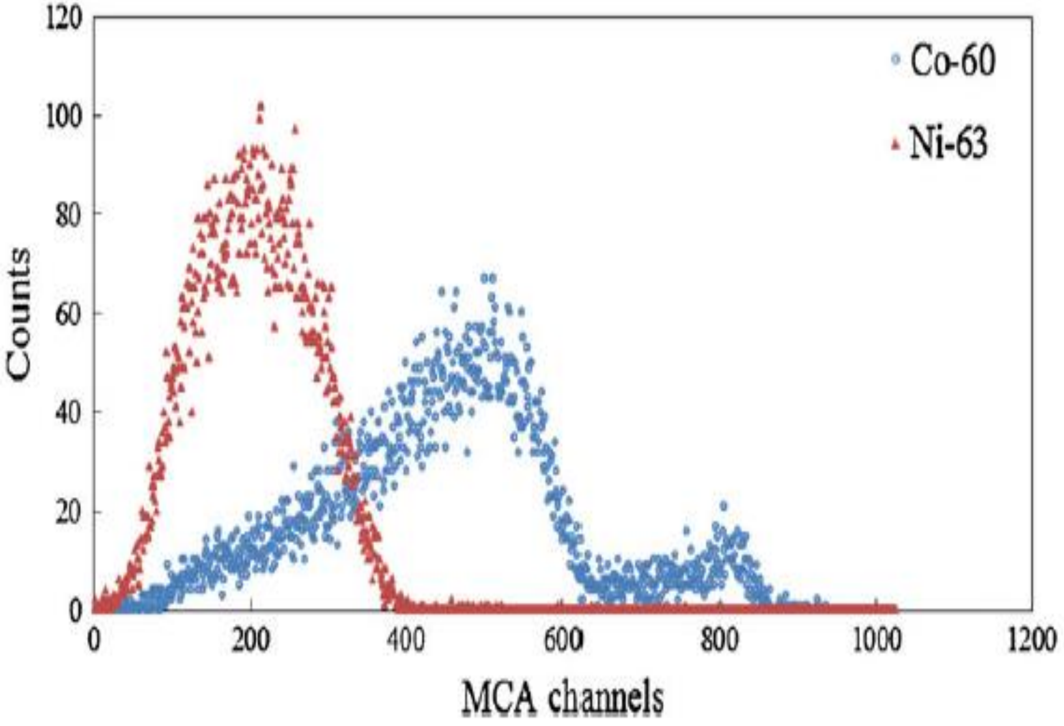


The abnormal data from one lab was excluded

It might be attributed to high radio-cobalt in the samples and unsuitable correction for ^{58}Co content in this sample. This demonstrated the need for reliable method for real sample analysis.

LSC spectra of ^{63}Ni separated from reactor water in the labs of the Swedish NPPs





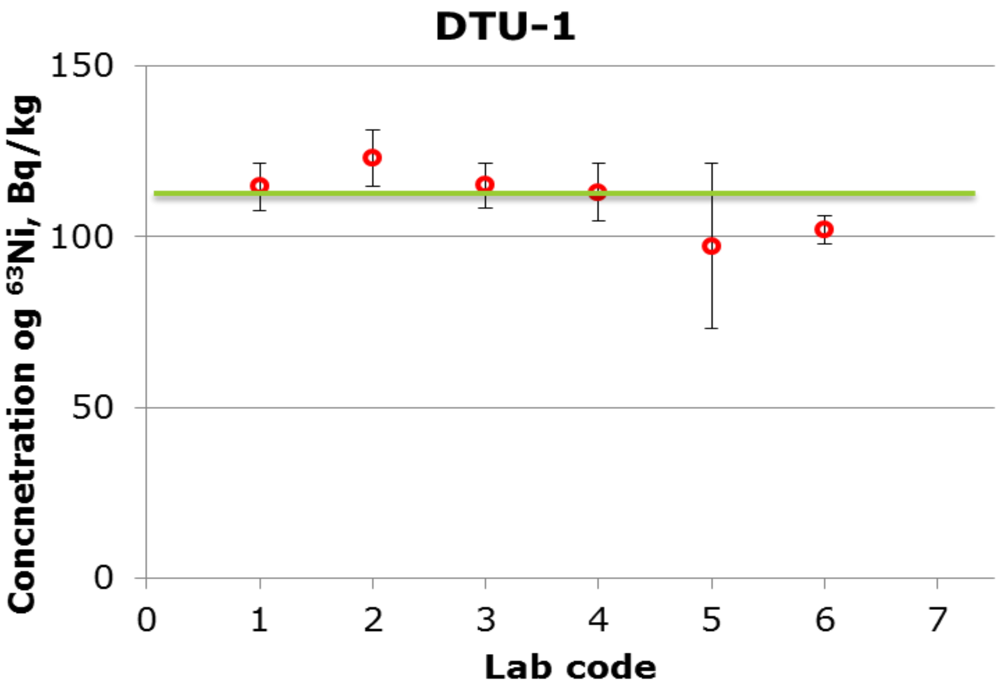
Problems: interference from high level ^{58}Co and ^{60}Co in reactor water, insufficient removal of radiocobalt in 63Ni samples.

Eriksson et al. JRNC, 2013

Inter-comparison Samples (2015)

Code	Sample	Matrix	Radionuclides
DTU-1	Spiked water	1.0 L in HNO_3	^{63}Ni, ^{55}Fe, ^{60}Co, ^{137}Cs and ^{152}Eu
Forsmark-1	Reactor coolant water collected from Forsmark NPP	2.0 L water in HNO_3	^{63}Ni, ^{55}Fe, ^{3}H, ^{51}Cr, ^{58}Co, ^{60}Co, ^{110m}Ag, ^{122}Sb, ^{144}Ce;

Analytical results of ^{63}Ni in DTU-1 (Spiked water)



Code	63Ni concentration, Bq/kg (decay corrected to 1st May, 2015)	
	DTU-1 (Spiked solution)	
	Value	Uncertainty (k=1)
1	114.7	6.9
2	123.0	8.1
3	115.0	6.6
4	113.0	8.5
6	102.0	4.0
5	97.3	24.3
Spiked value	**114.34**	**3.15**

Measured Value:

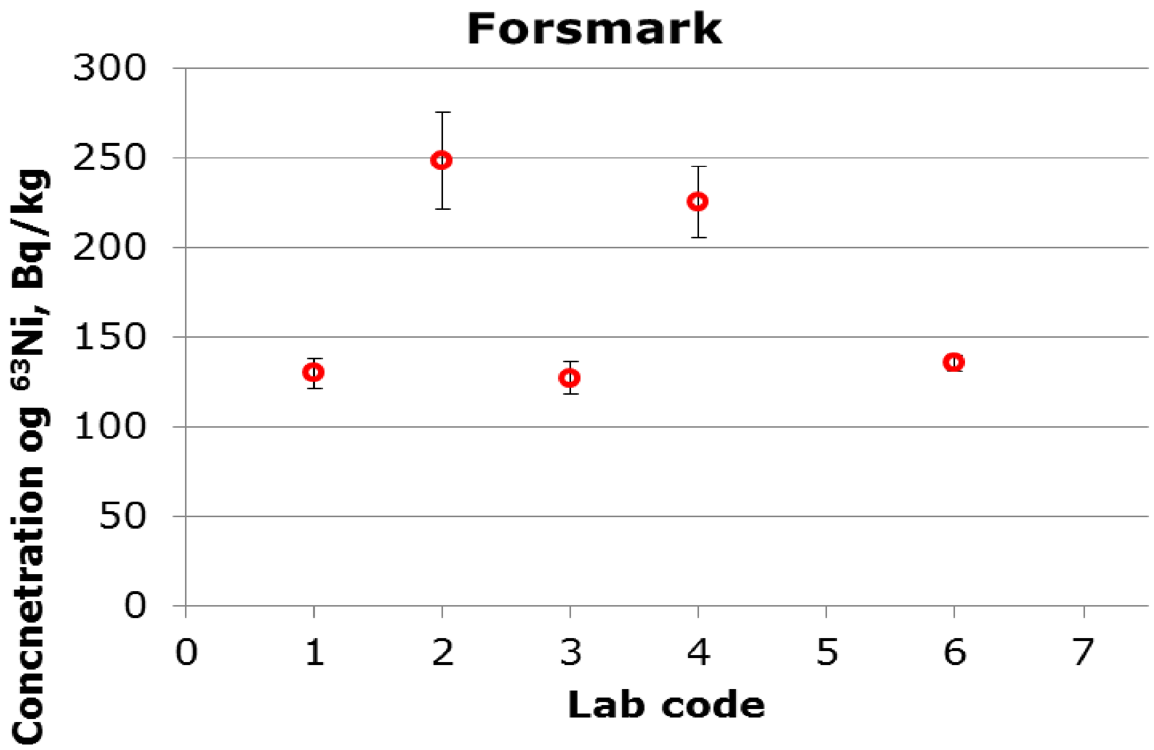
Range: 97-123 Bq/L

Average: 110.8±9.4 Bq/L

Spiked value : 114.3.2±3.2 Bq/L

All reported data are acceptable, and not significant different with the spiked value !

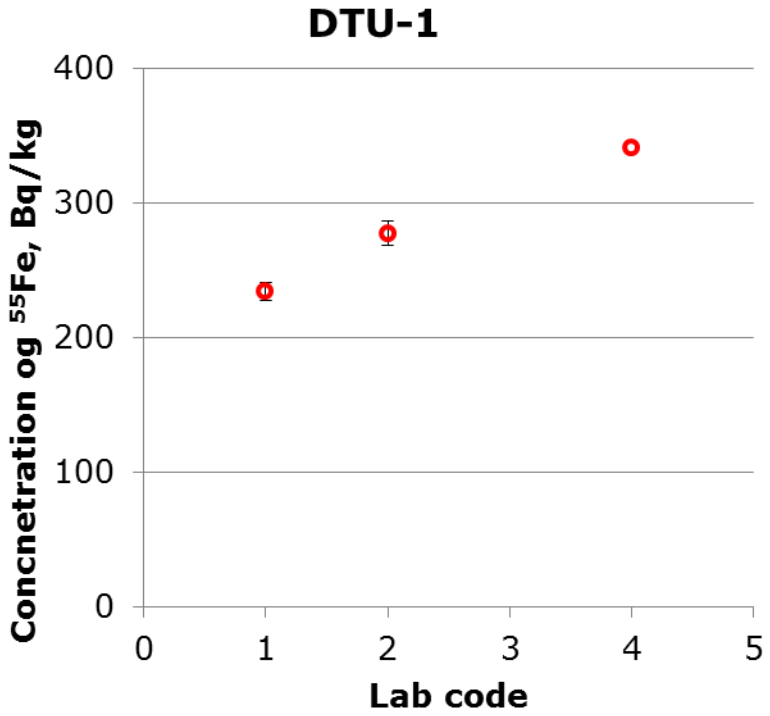
Analytical results of ^{63}Ni in Forsmark-1 (reactor coolant water with high ^{58}Co activity)



Code	^{63}Ni concentration, Bq/kg (decay corrected to 1st May, 2015)	
	Forsmark (coolant)	
	Value	Uncertainty (k=1)
1	129.6	8.30
2	248.0	26.80
3	127.0	9.40
4	225.0	20.00
6	135.0	4.00
5	<219	

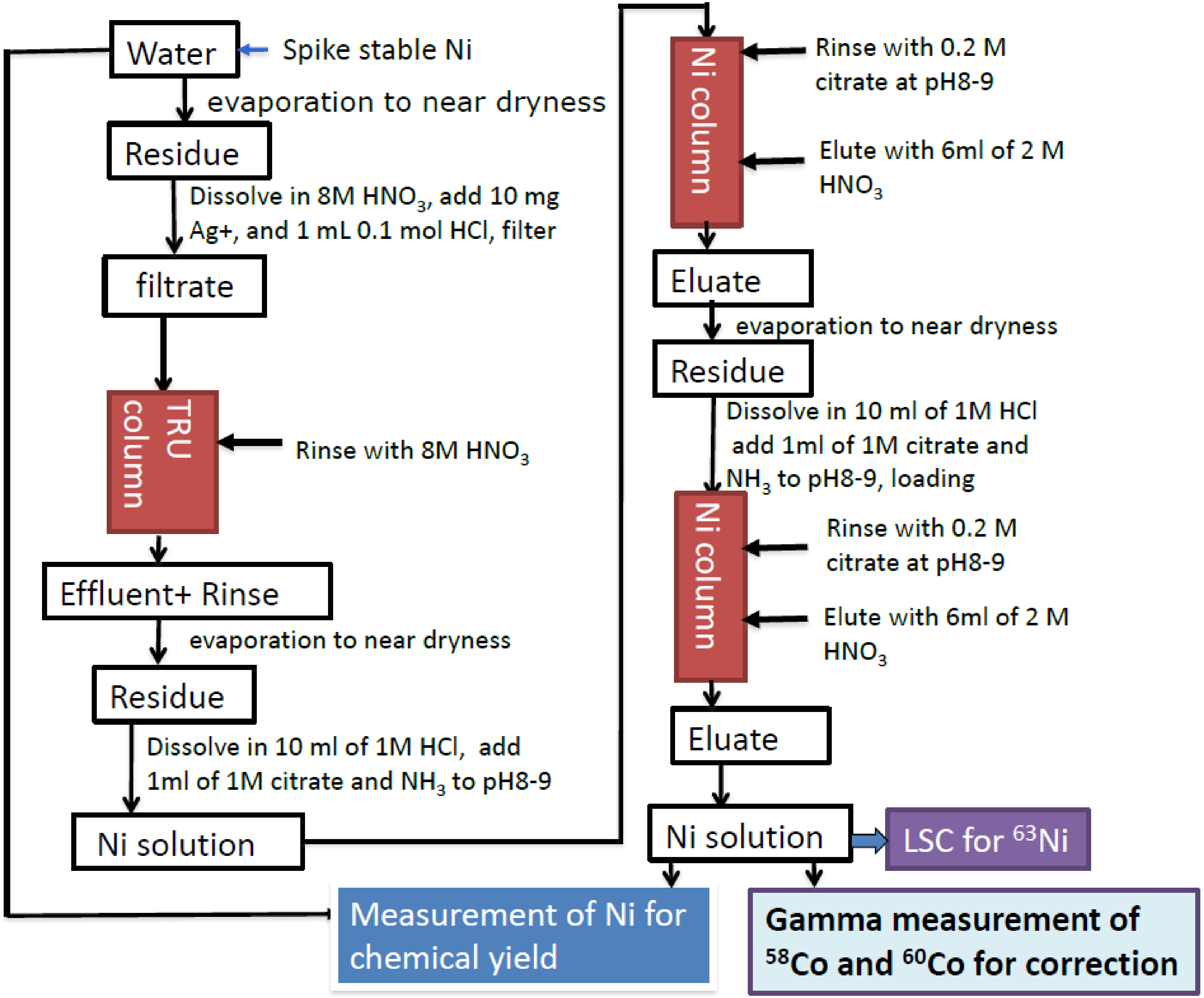
Analytical results of ^{55}Fe in DTU-1 (Spiked water)

Code	^{55}Fe concentration, Bq/kg (decay corrected to 1 May 2015)			
	DTU-1 (Spiked solution)		Forsmark-1 (coolant)	
	Value	Unc. (k=1)	Value	Unc. (k=1)
1	238.90	6.90	14.60	7.33
2	277.00	8.90	15.00	0.70
4	341.00	25.6	21.10	1.6
Spiked value	238.0	5.64		

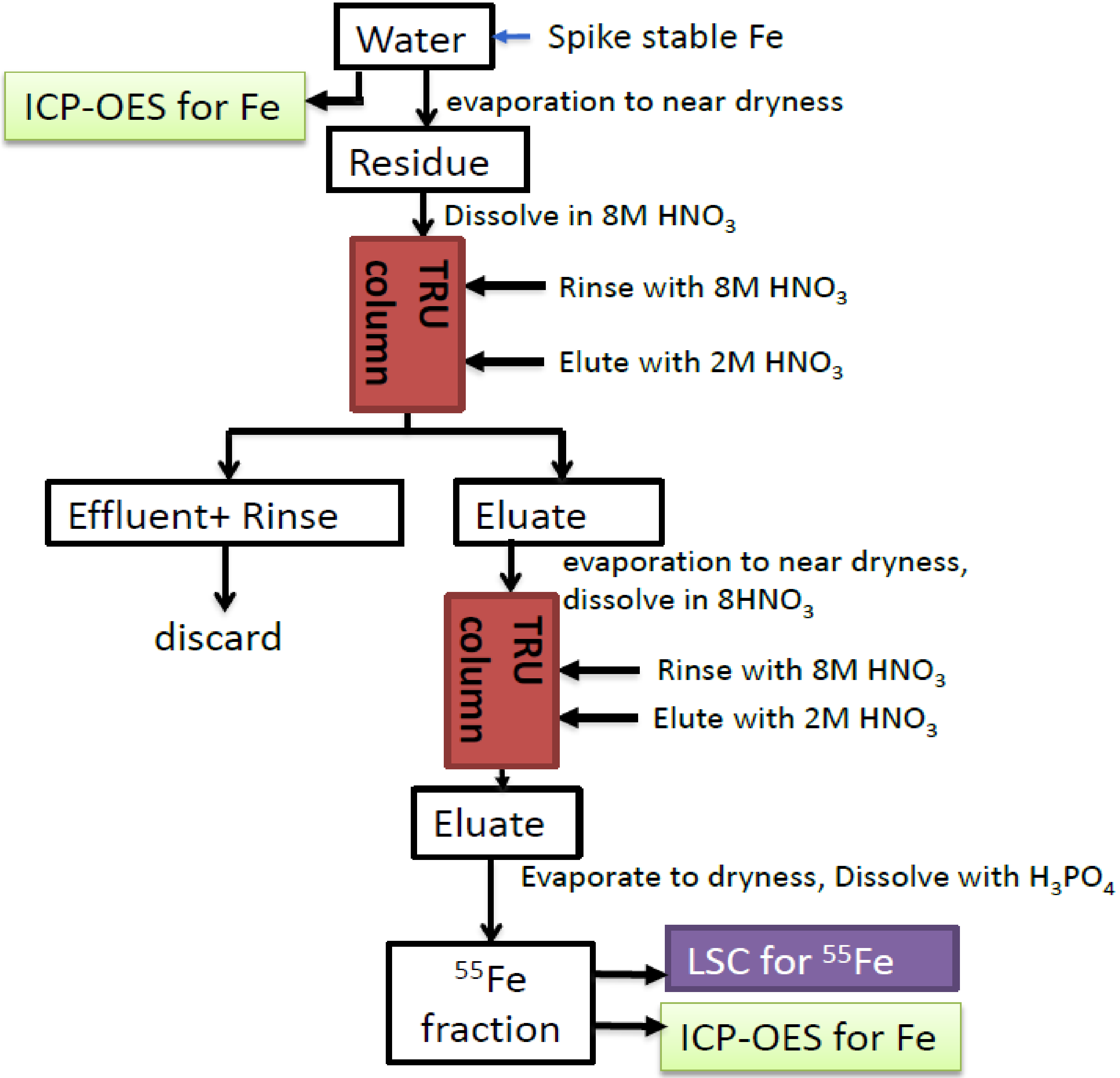


The three measured values for the spiked water are relative ok

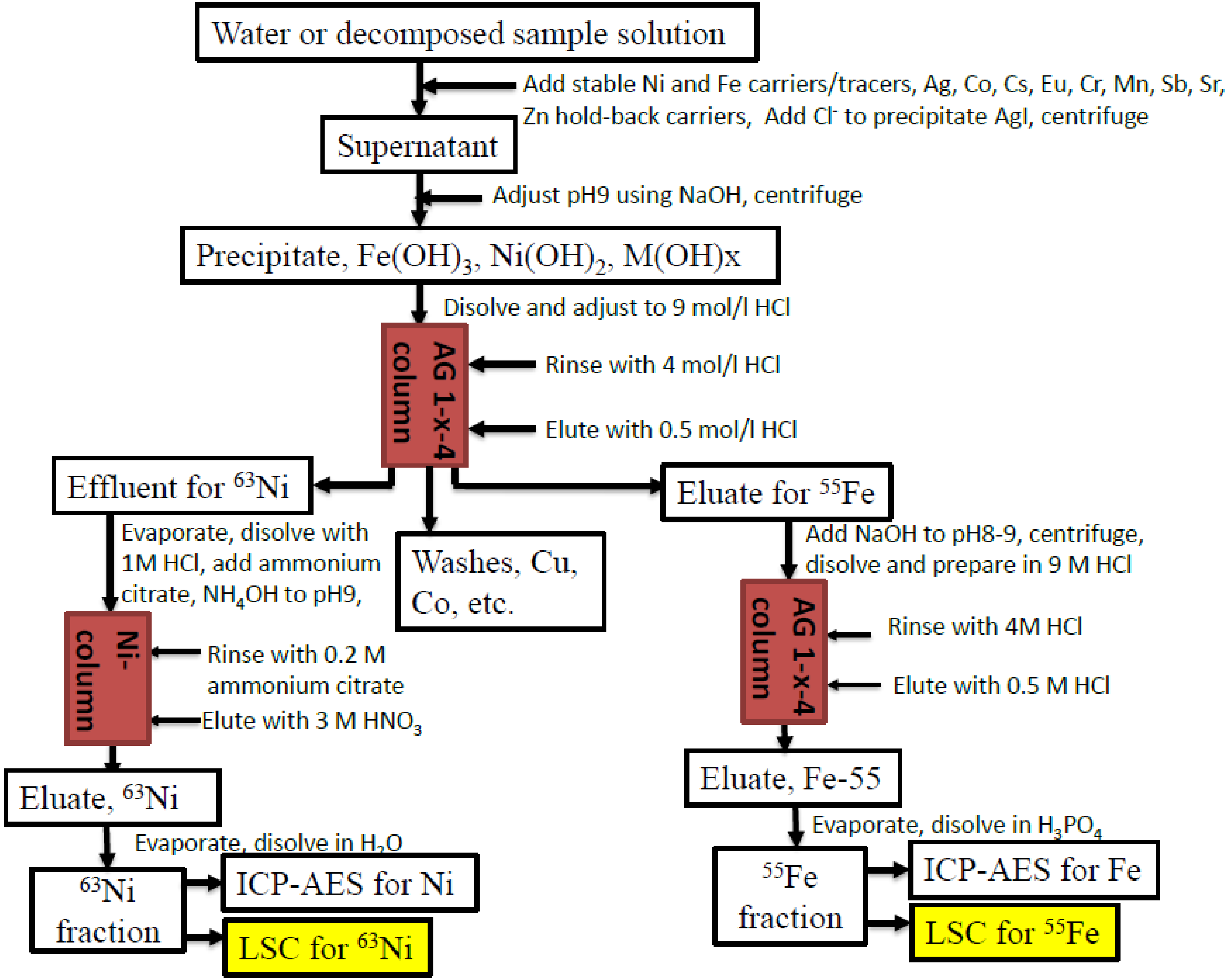
Standardized method for ^{63}Ni in reactor water



Standardized method for ^{55}Fe in reactor water



Standardized method for ^{55}Fe and ^{63}Ni in waste and environemntal samples



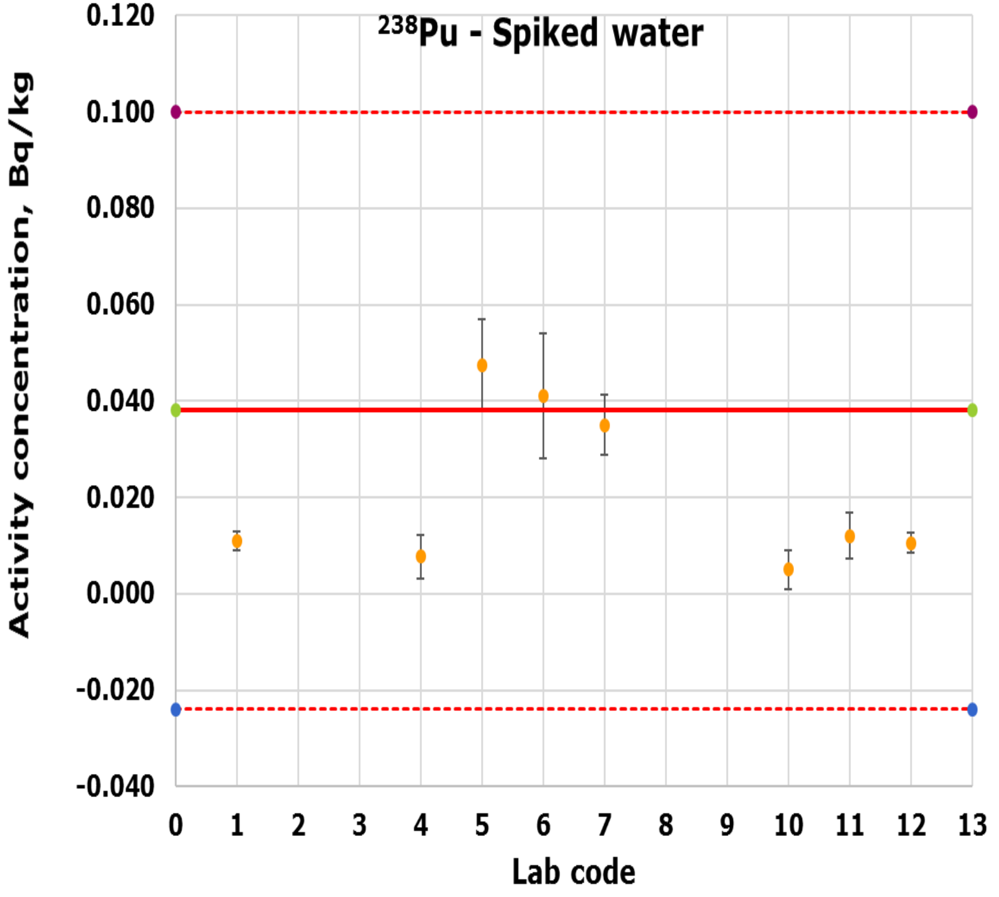
NKS-Opti-Method 2018, 2019

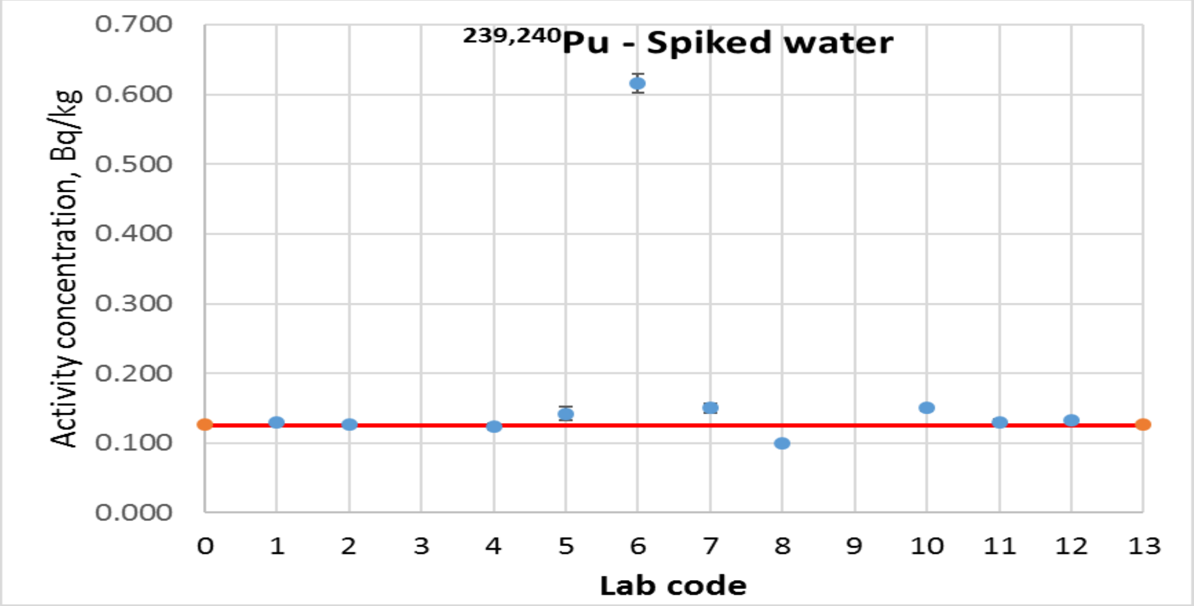
Inter-comparison Samples (2018)

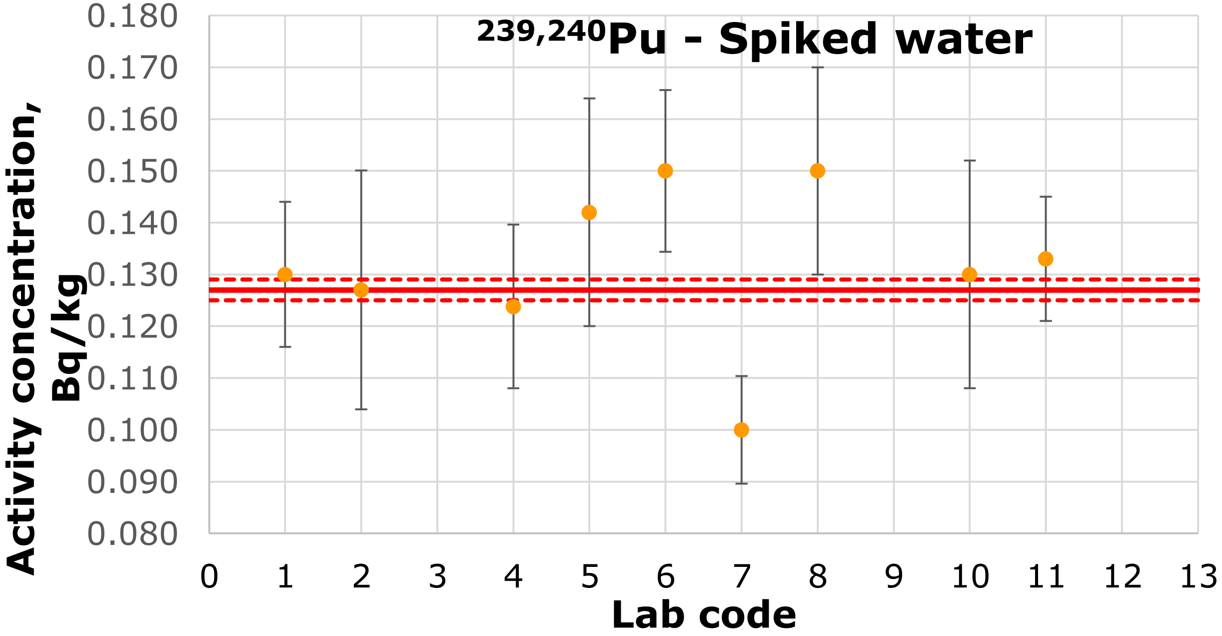
- **Radionuclides**: Pu (^{238}Pu, ^{239}Pu, ^{240}Pu), Am (^{241}Am), Cm (^{242}Cm, ^{243}Cm, ^{244}Cm)
- **Samples**
  - **Real reactor water from Olkiluoto NPP OL-1 unit**, 200 ml. Since there is a fuel leakage in this reactor, the level of alpha emitters in this sample might be higher than other reactors, 0.1-2 Bq/L level is expected. The water has already been collected and acidified;
  - **Artificial water sample**: spiked radionuclides:: ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am and ^{244}Cm. The concentration of alpha emitter will be 0.01-0.2 Bq/L,

Nuclide	Activity (Bq/L)	1 SD
Pu-238	**0.038**	0.031
Pu-239	**0.077**	0.001
Pu-240	**0.05**	0.001
Cm-244	**0.195**	0.006
Am-241	**0.07**	0.011
Total alpha activity (Bq/L): 0.43		
Pu: 38 %		
Am: 16 %		
Cm: 45 %		

Analytical results for spiked water sample



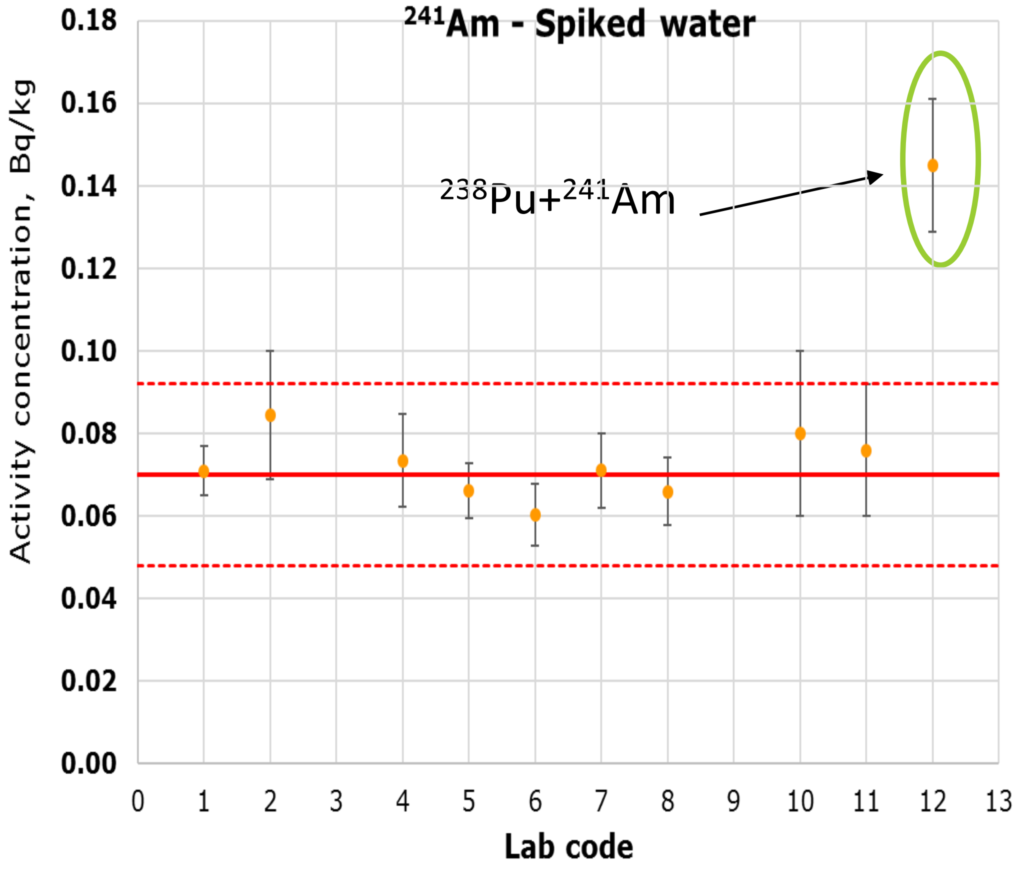


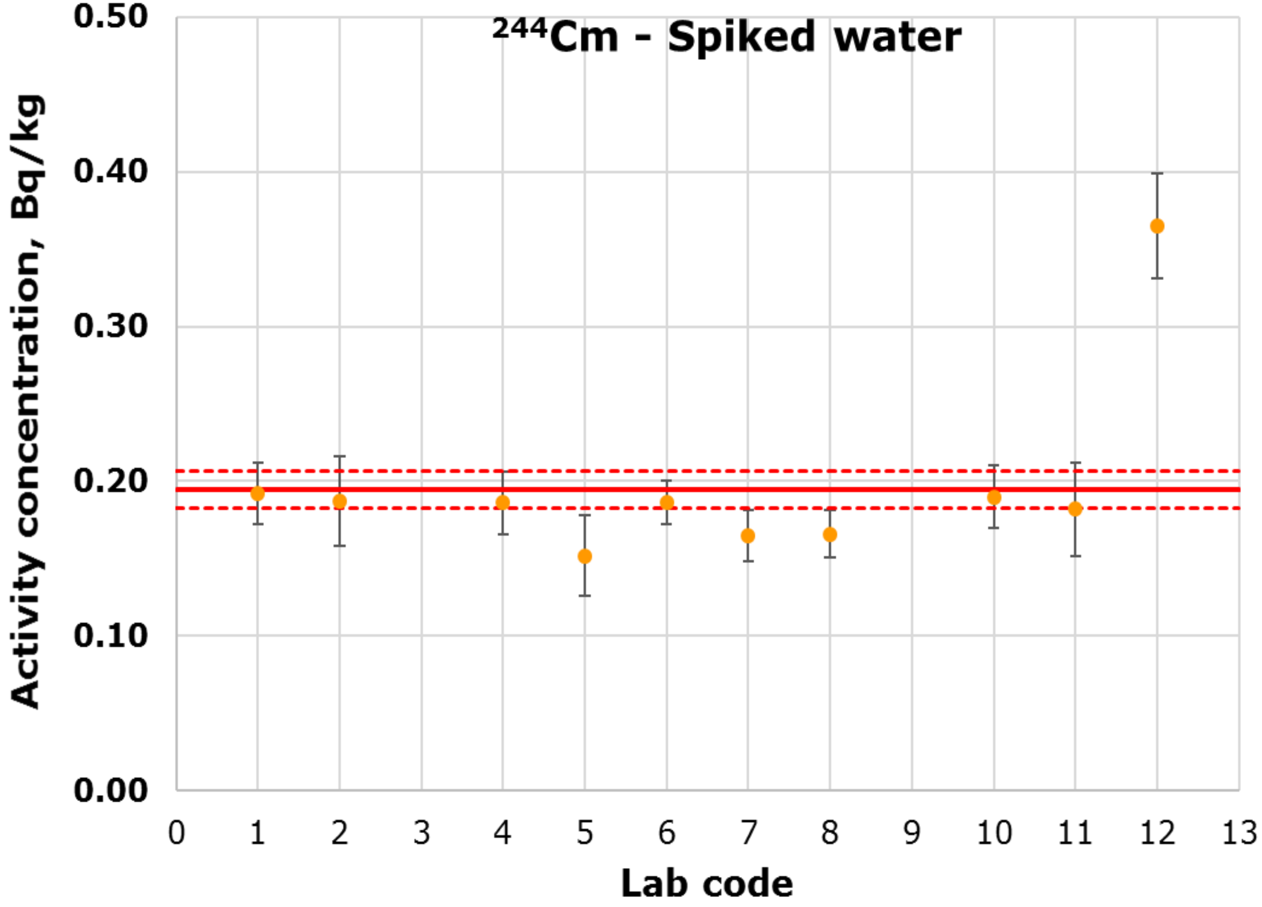


Red Line are the spiked value and uncertainty 2σ

The abnormal highest data were excluded

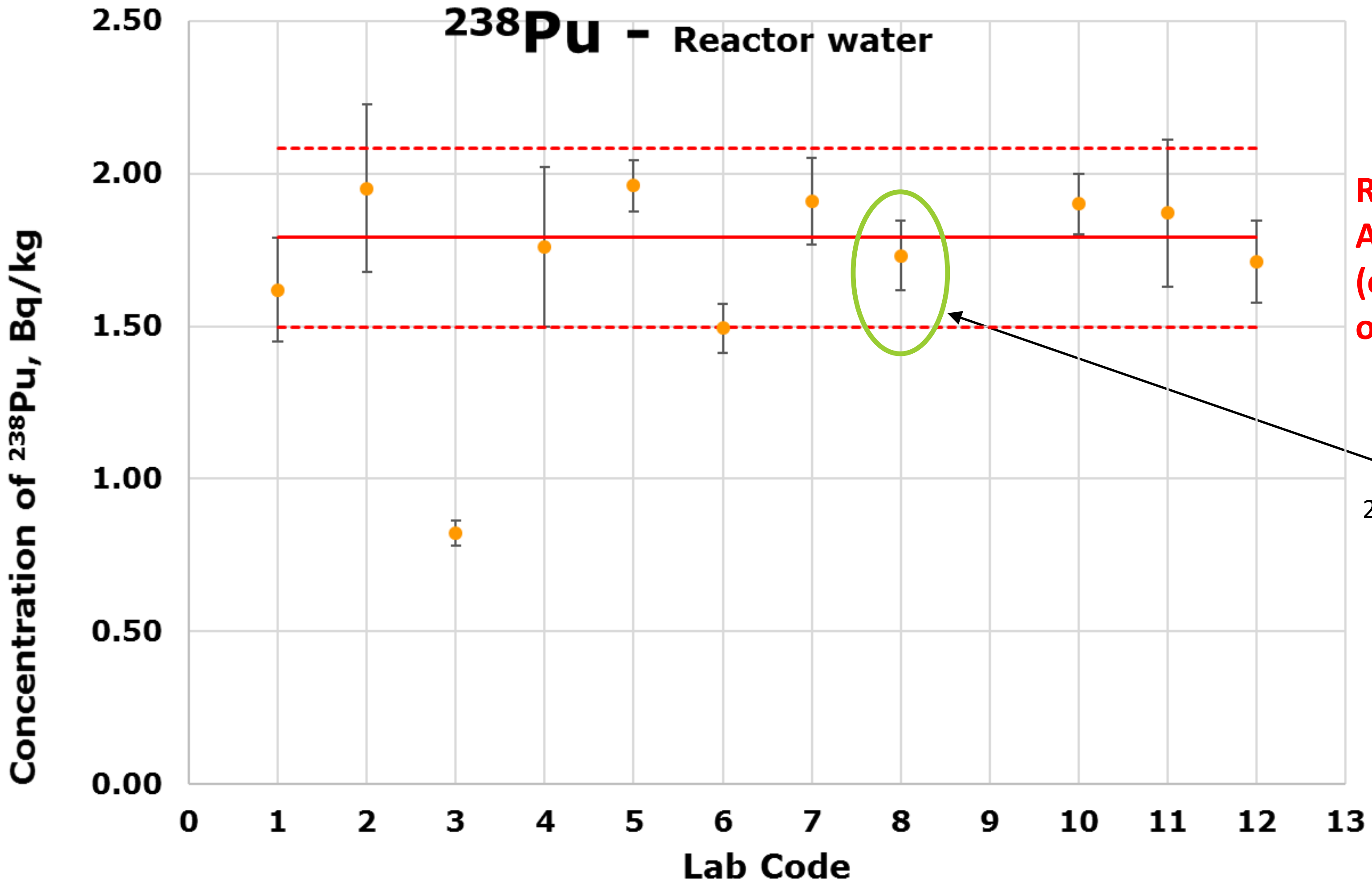
Analytical results for spiked water sample (Chalmers)





Red Line is the spiked value and uncertainty 2σ

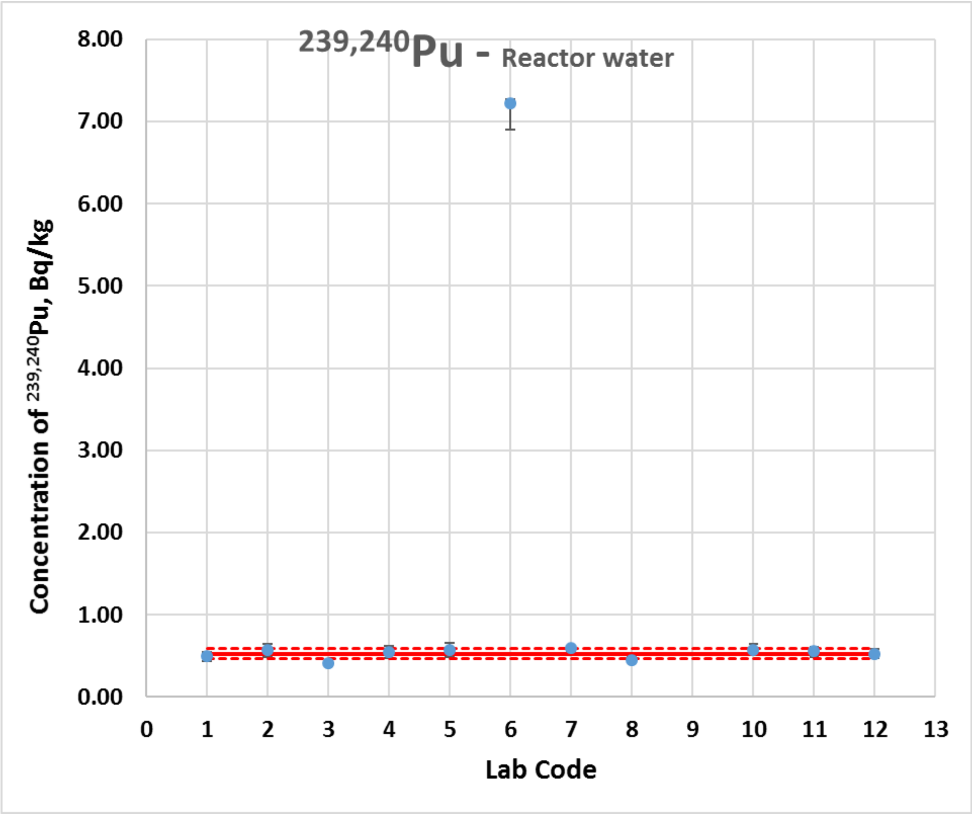
Analytical results for reactor coolant water sample (OL-1 reactor)

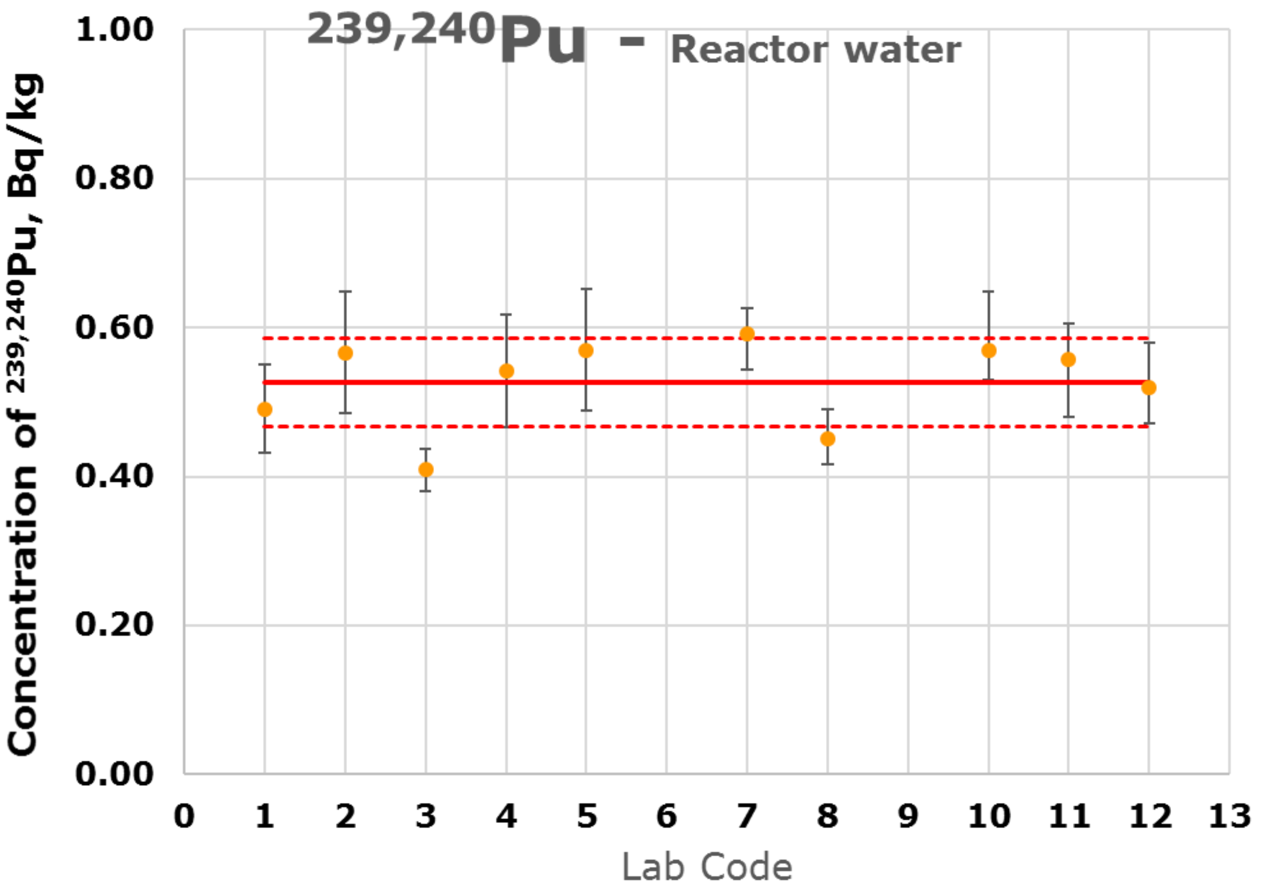


Red Line is the Average and 2SD (excluding most out points)

^{238}Pu+^{241}Am

Analytical results for reactor coolant water sample (OL-1 reactor)

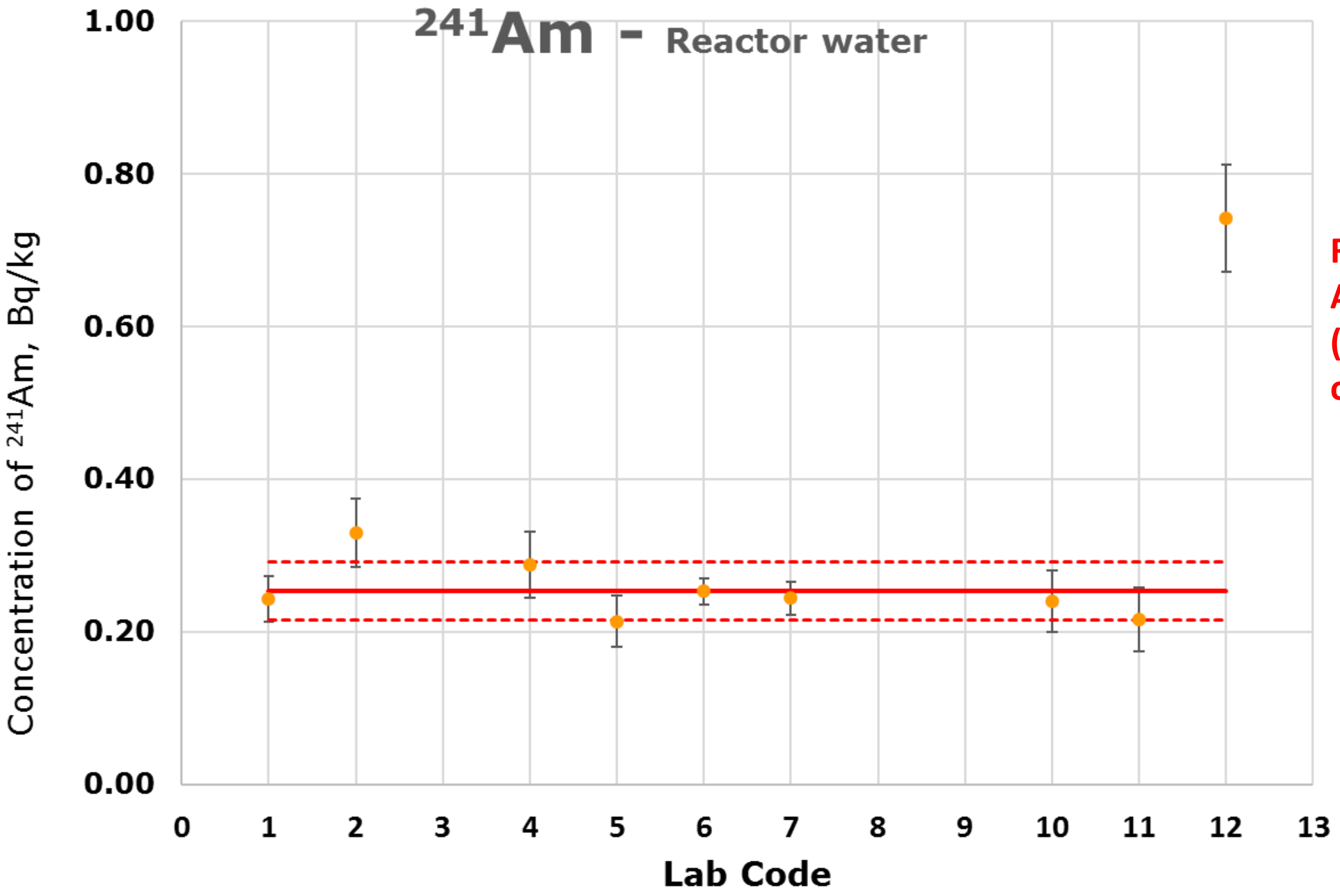




Red Line is the Average and 2SD
(excluding most out points)

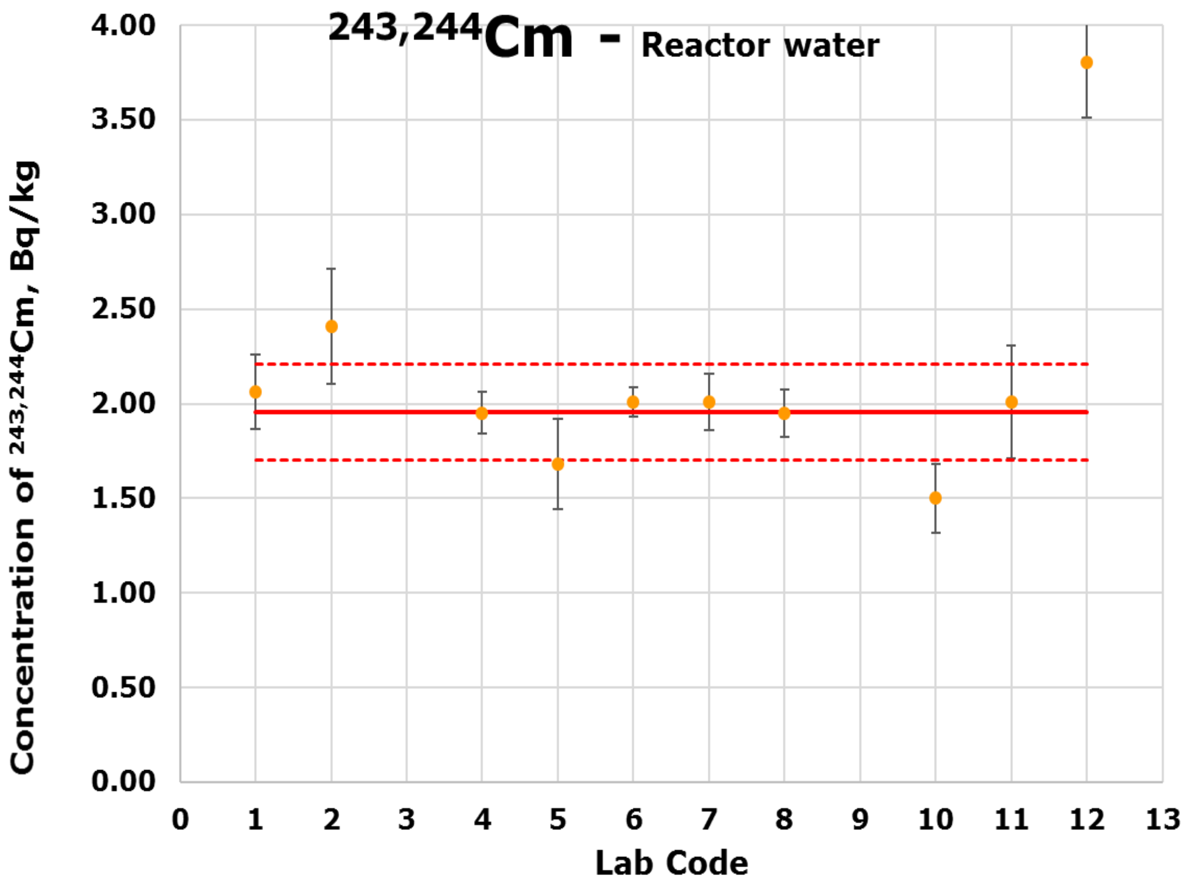
The abnormal highest data from one lab was excluded

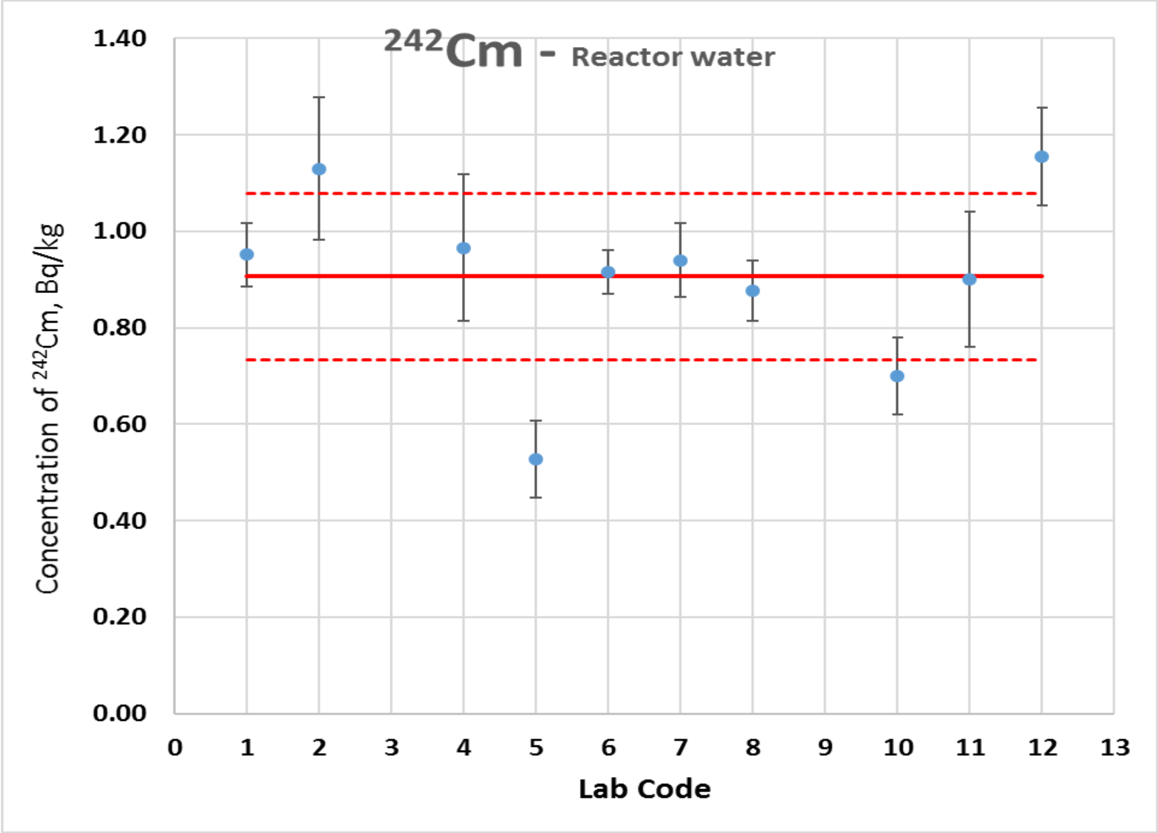
Analytical results for reactor coolant water sample (OL-1 reactor)



Red Line is the Average and 2SD (excluding most out points)

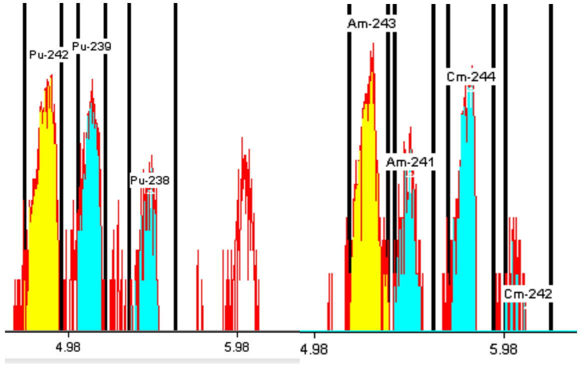
Analytical results for reactor coolant water sample (OL-1 reactor)





Red Line is the Average and 2SD
(excluding most out points)

Artifical sample



Black planchets

Problems

–Black residue in Am-fraction of both samples when evaporated to near dryness before electrodeposition procedure.

–Low total analysis efficiency for Am-fraction of both samples.

–Bad resolution in Pu-fraction of TVO sample.

– Low chemical yield for Pu

OptiMethod 2019 intercomparison samples

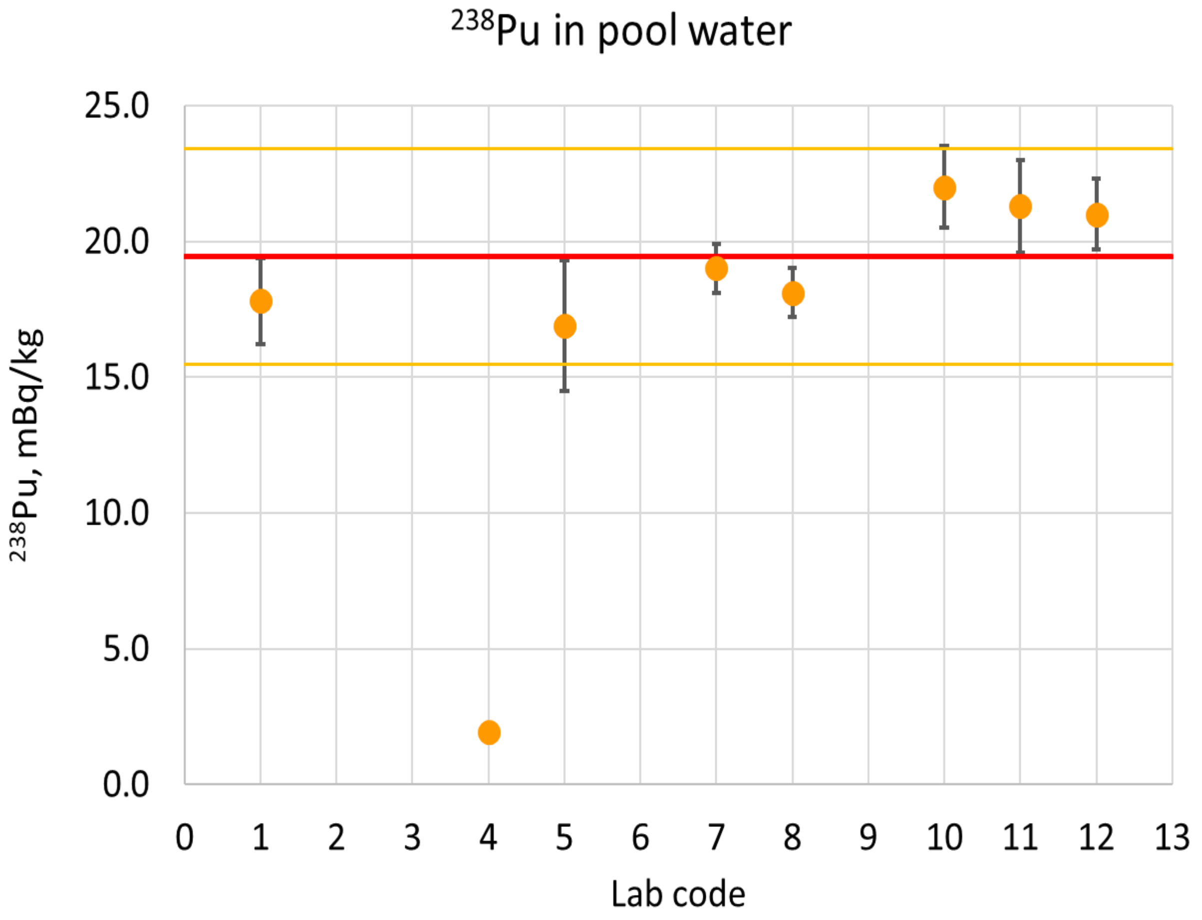
- **Reactor pool water:**

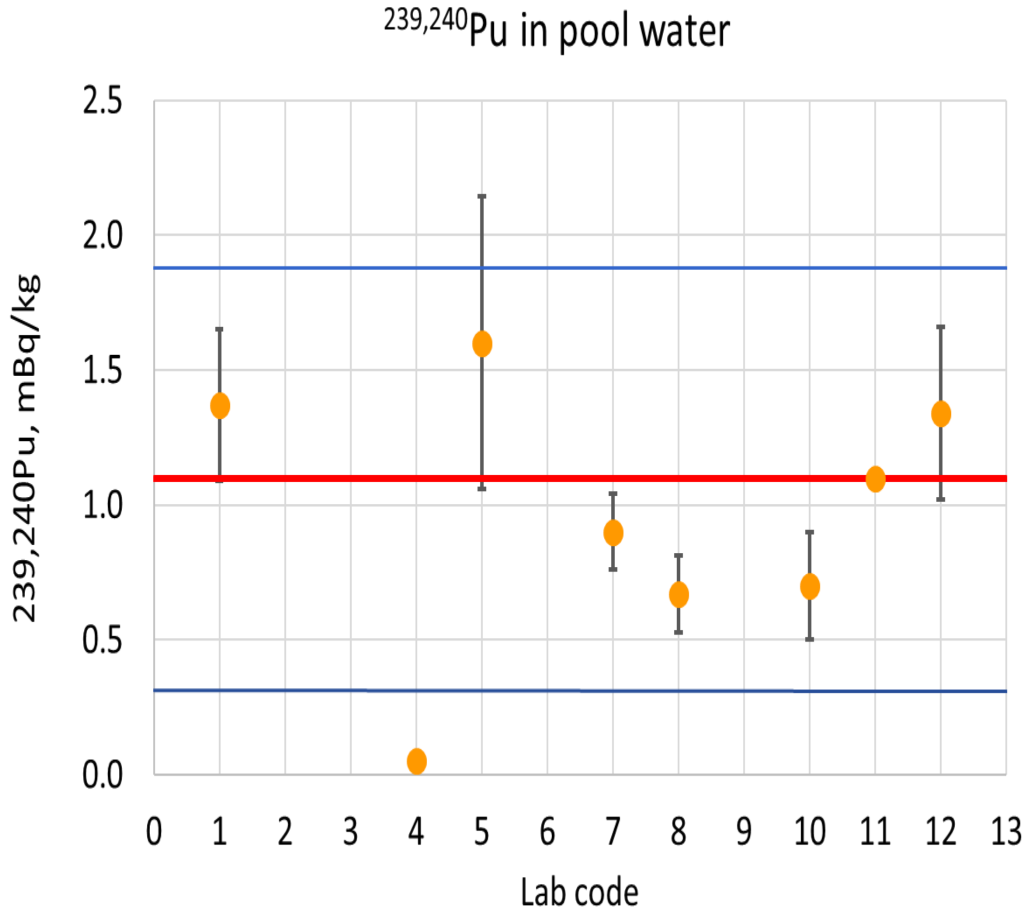
(2 L in HNO_3, pH2, sent to each partners in Dec. 2018; 1-10 mBq/L for ^{239}Pu, ^{241}Am, ^{244}Cm; 5-50 mBq/L for ^{238}Pu; about 100 Bq total activity (^{60}Co)

- **Digested filter:**

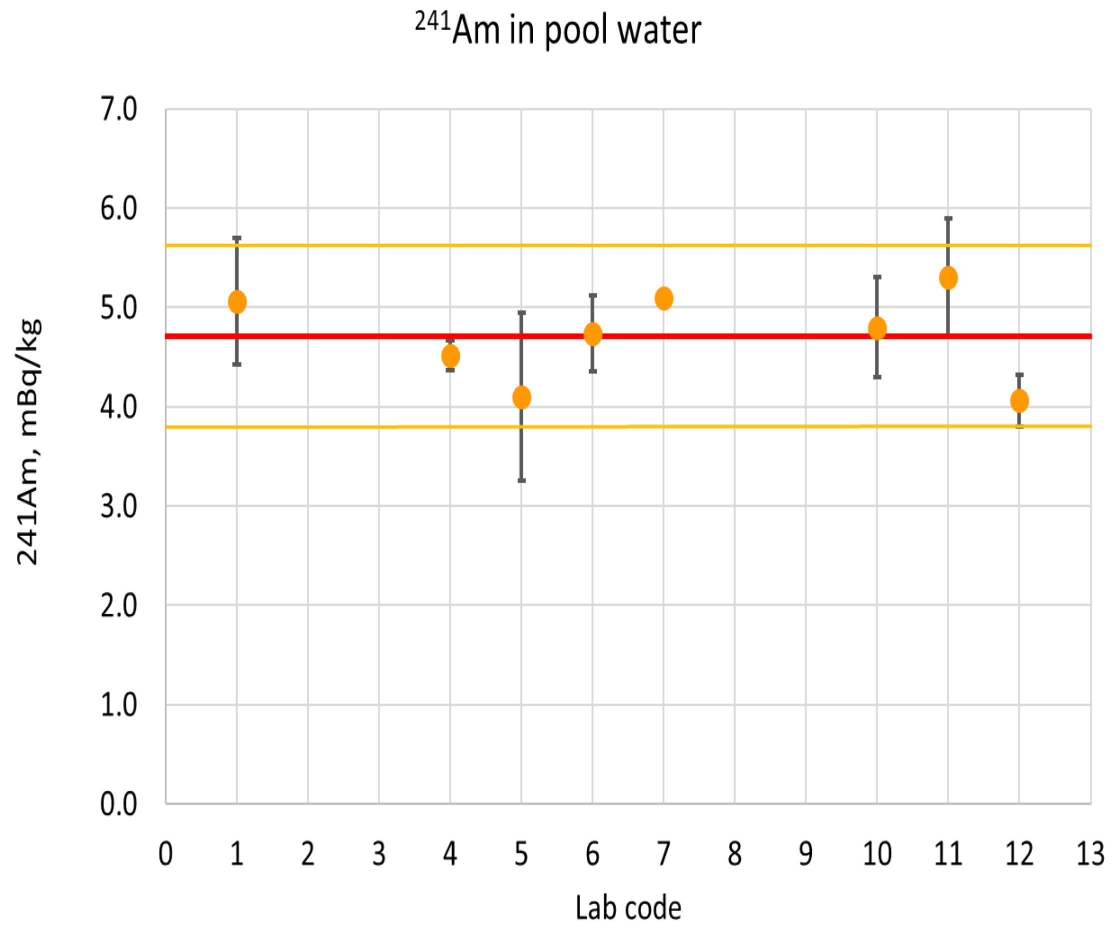
air filter was collected from different parts of the ventilation systems (aerosol sampling) in Forsmark NPP, each filter was digested with 100 ml 5% H_2SO_4, 50 ml of solution was delivered to each lab for inter-comparison analysis. The sample contains low level actinides and relative high Po-210.

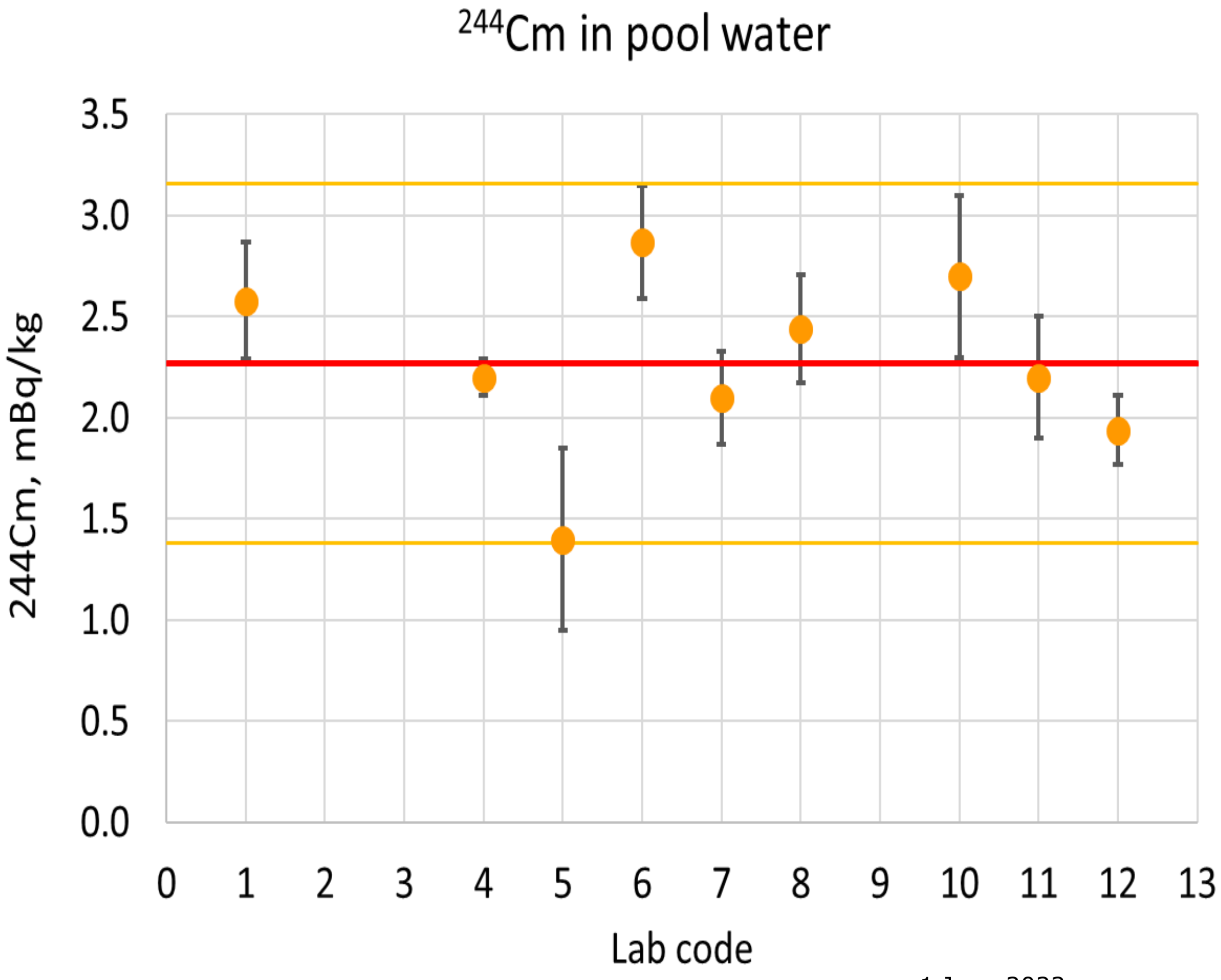
Comparison of the results of ^{238}Pu and ^{239,240}Pu in reactor pool water



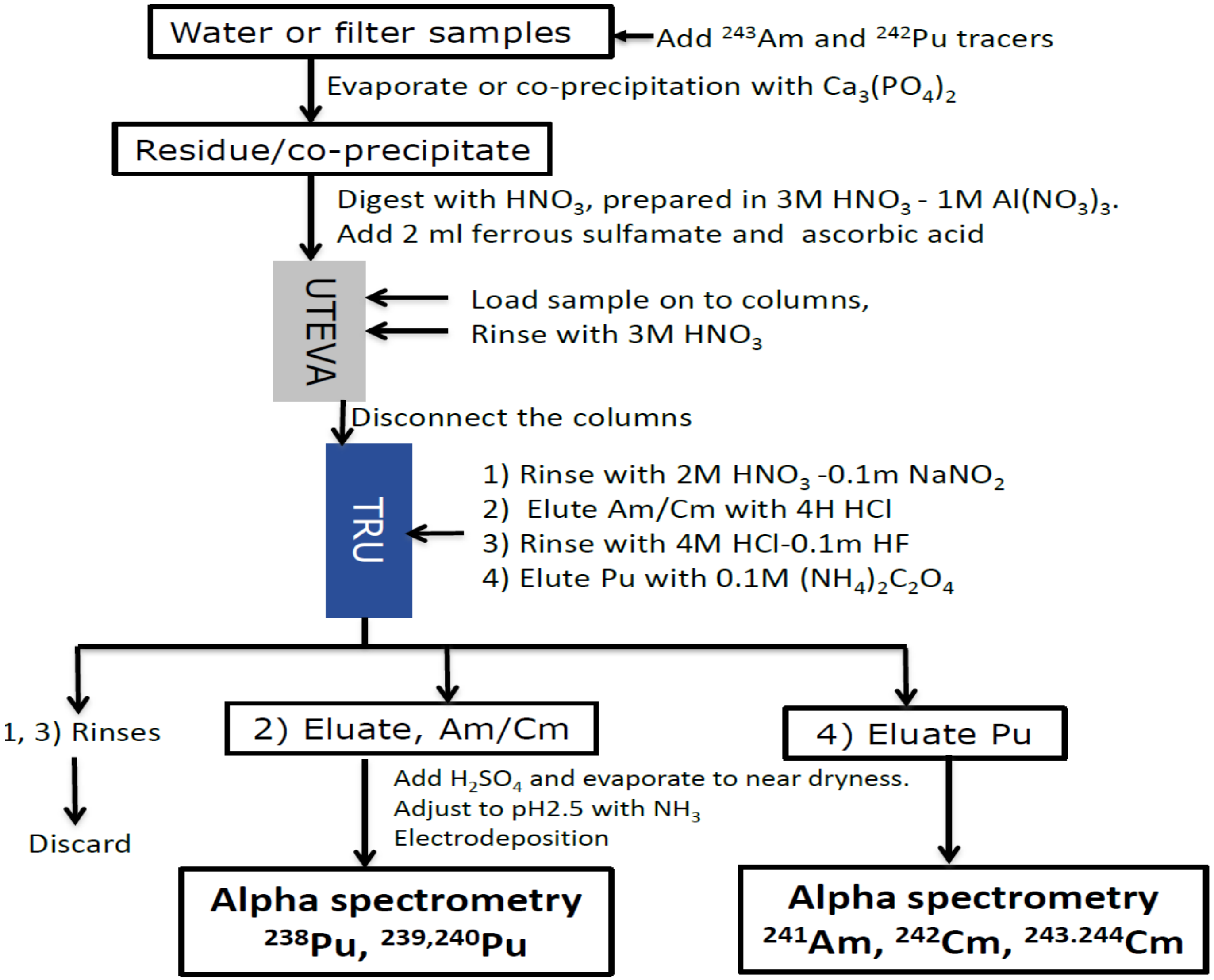


Comparison of the results of ^{241}Am and ^{244}Cm in reactor pool water

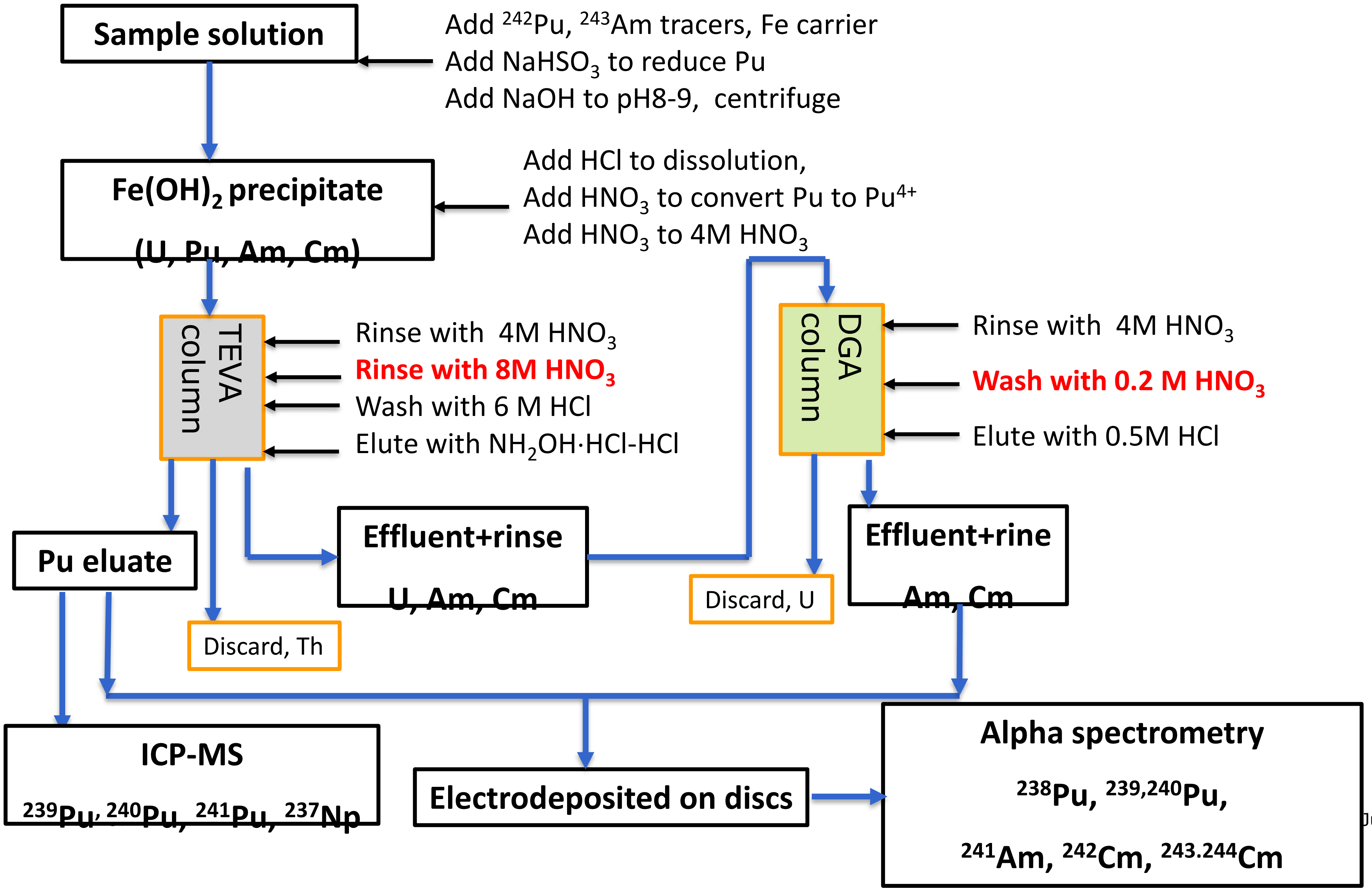




Optimized method-1 for actinide determination



Optimized Method-2 for determination of Pu, Np, Am and Cm isotopes (TEVA-DGA)



Summary and Conclusion

- A number of Nordic labs are performing radiochemical analysis of hard to measure radionuclides for radiological characterization of waste from operation and decommissioning.
- With the support of NKS project, efforts have been given to improve the analytical quality and competence of Nordic labs in radiochemical analysis, and a good improvement have been achieved.
- Some standard and optimized methods have established through NKS project in cooperation of radiochemical analysis groups in University and institute with labs in the Nordic nuclear industries

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  - Cyclife Sweden AB, Sweden
  - Forsmarks Kraftgrupp AB, Sweden
  - Ringhals AB, Sweden
  - Oskarshamn NPP, OKG Aktiebolag, Sweden
  - Swedish Nuclear Fuel and Waste Management Co, Clab (SKB), Sweden
  - Swedish Defence Research Agency (FOI), Sweden
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