Radiochemical Analysis of Important Radionuclides in Nordic Nuclear Industry

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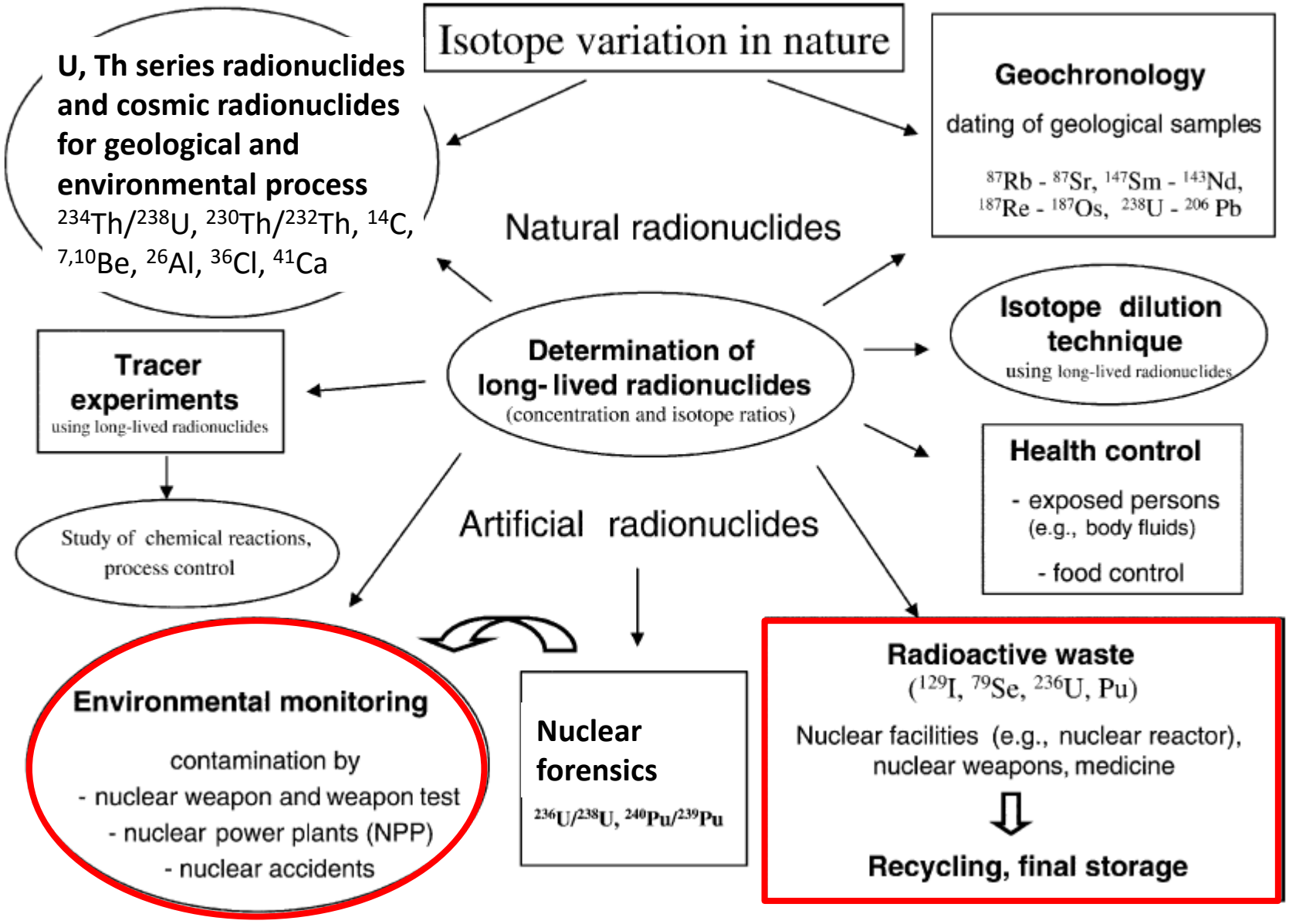
Center for Nuclear Technologies

Application of Radionuclides

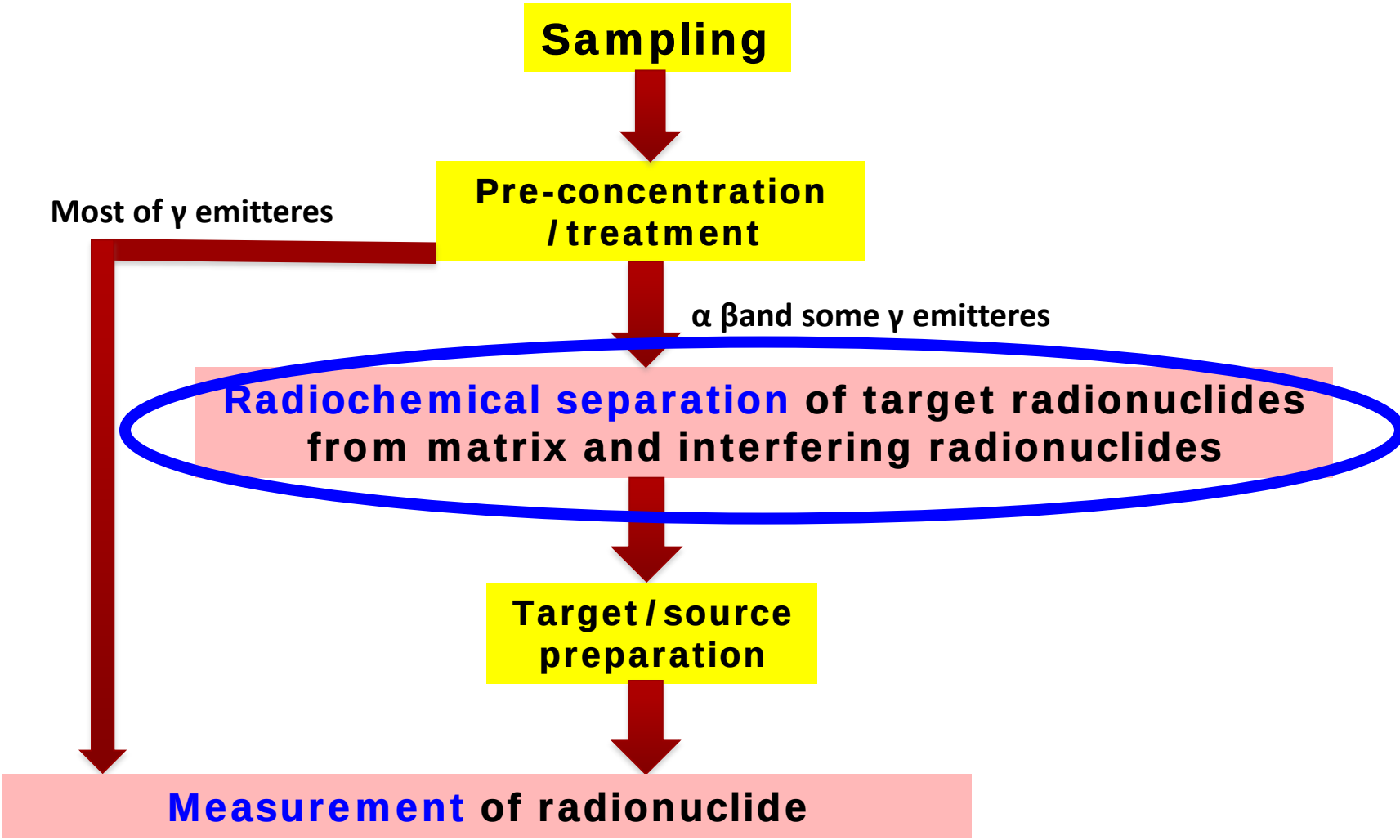


Becker, 2003

Radionuclides of interest in environmental radioactivity and nuclear industry

- Important artificial radionuclides in the environment
  - ✓ ^{3}H, ^{14}C, ^{90}Sr, ^{137}Cs, ^{134}Cs, ^{99}Tc, ^{129}I, $^{238,239,240,241}Pu$, ^{237}Np, ^{241}Am, etc.
- Important radionuclides in nuclear industry and decommissioning
  - ✓ ^{3}H, ^{14}C, ^{90}Sr, ^{137}Cs, ^{134}Cs, ^{99}Tc, ^{129}I, $^{238,239,240,241}Pu$, ^{237}Np, ^{241}Am, ^{242}Cm, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{60}Co, ^{133}Ba, ^{135}Cs ^{152}Eu, ^{79}Se, ^{93}Zr, ^{93}Mo, ^{94}Nb, etc.

Procedure for Radiochemical Analysis of Radionuclides



Nuclear power plants in Nordic countries

Nuclear power plants in Sweden
(view)
Active plants
Closed plants
Unfinished plants

Nuclear power plants in Finland
(view)
Active plants
Planned plants

EU Recommendations of for reporting discharges from NPP, 2004/2/Euratom

Key nuclear	Required Ld, Bq/m^3		List of radionuclides	
	Air releases	Liquid discharge	Air	Liquid
Kr-85	0.0001		^{41}Ar, ^{87}Kr,^{88}Kr	
Xe-133	0.0001		^{135}Xe, ^{137}Xe	
S-35	0.1	30,000		^{55}Fe, ^{63}Ni
Sr-90	0.02	1000	^{89}Sr	
Pu-239+Pu-240	0.005	6000	^{238}Pu	
241Am	0.005	50	^{242}Cm,^{243}Cm, ^{244}Cm	
Total alpha	0.01	1000		
H-3	1000	100,000		
C-14	10			

Decommissioning activities of Nordic nuclear facilities

Methods developed for decommissioning in DTU Nutech

Sample type	Nuclides	Measurement method	Sample amount (g)	MDA(Bq/g)
soil, sediment, vegetation, animal tissues (organics)	^{3}H	LSC	2 g	0.1 Bq/g
	^{14}C	LSC		0.05 Bq/g
	^{55}Fe	LSC	20 grams	0.05 Bq/g
	^{63}Ni	LSC		0.01 Bq/g
	^{36}Cl	LSC		0.01 Bq/g
	^{129}I	LSC		0.01 Bq/g
	^{41}Ca	LSC		0.15 Bq/g
	^{90}Sr	Beta counting		0.01 Bq/g
	^{99}Tc	Beta counter /ICP-MS		0.01 Bq/g
	^{94}Nb	γ-spectrometry		0.5 Bq/g
	^{238}Pu	α-spectrometry		0.01 Bq/g
	^{239}Pu	α-spectrometry /ICP-MS		0.01 Bq/g
	^{240}Pu	α-spectrometry /ICP-MS		0.01 Bq/g
	^{241}Pu	ICP-MS		0.3 Bq/g
	^{241}Am	α-spectrometry		0.01 Bq/g
	^{244}Cm	α-spectrometry		0.01 Bq/g

Methods developed for decommissioning in DTU Nutech

Sample type	Nuclides	Measurement method	Sample amount (g)	MDA(Bq/g)
Water	^{3}H	LSC	5 ml	0.05 Bq/ml
	^{14}C	LSC	20 ml	0.02 Bq/ml
	^{55}Fe	LSC	100 ml	0.01 Bq/ml
	^{63}Ni	LSC		0.002 Bq/ml
	^{36}Cl	LSC		0.002 Bq/ml
	^{129}I	LSC		0.002 Bq/ml
	^{41}Ca	LSC		0.02 Bq/ml
	^{90}Sr	Beta counting		0.002 Bq/ml
	^{99}Tc	Beta counter /ICP-MS		0.002 Bq/ml
	^{94}Nb	γ-spectrometry		0.1 Bq/ml
	^{238}Pu	α-spectrometry		0.002 Bq/ml
	^{239}Pu	α-spectrometry /ICP-MS		0.002 Bq/ml
	^{240}Pu	α-spectrometry /ICP-MS		0.002 Bq/ml
	^{241}Pu	ICP-MS		0.07 Bq/ml
	^{241}Am	α-spectrometry		0.002 Bq/ml
	^{244}Cm	α-spectrometry		0.002 Bq/ml

NKS-B STANDARDMETHOD project 2014 & 2015

Standardization of radioanalytical methods for determination of important radionuclides for environmental assessment and waste management in Nordic nuclear industry

Participants/Partners:

DTU, Denmark :	Xiaolin Hou
Forsmark AB, Sweden:	Anders Falk/Mattias Olsson
OKG, Sweden:	Sofie Englund,
Ringhals AB, Sweden:	Olof Gottfridsson
Studsvik AB, Sweden:	Charlotta Askeljung
STUK,Finland	Kaisa Vaaramaa
Loviisa NPP, Finland:	Laura Togneri/ Miia Lampen
Olkiluoto NPP,Finland:	Hannele Hirvonen

NKS STANDMETHOS project

The goals of the project:

- A Nordic network on radioanalysis of waste and environmental samples
- Overview of the present status of radioanalysis in Nordic labs
- Summary of the currently applied radioanalytical methods for some important radionuclides including ^{63}Ni, ^{55}Fe, ^{14}C and ^{3}H in all Nordic labs.
- Optimized methods for routine analysis of waste and environmental samples (e.g. ^{63}Ni in discharges and environmental water)
- Identification of the demands from Nordic industries for new radioanalytical methods.

Overview of the present status of radioanalysis in Nordic labs (1)

Country	Organization	Purpose of analysis	Main radionuclides
Denmark	Technical University of Denmark	Environmental radioactivity, radioecology, environmental trace, characterization of decommissioning waste, emergency preparedness	^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63}Ni, ^{89,90}Sr, ^{99}Tc, ^{129}I, ^{210}Po, ^{210}Pb, ^{222}Rn, ^{226,228}Ra, isotopes of U, Th and Pu, ^{237}Np, ^{241}Am, ^{244}Cm, gross alpha, gross beta
Norway	Institute for Energy Technology (IFE)	Environmental radioactivity, waste management.	^{3}H, ^{89,90}Sr, ^{210}Po, ^{210}Pb, ^{222}Rn, ^{226,228}Ra, Isotopes of U, Th and Pu, ^{237}Np, ^{241}Am, gross alpha, gross beta
	Norwegian University of Life Sciences	Environmental radioactivity, radioecology, environmental trace,	^{89,90}Sr, ^{99}Tc ^{210}Po, ^{210}Pb, ^{222}Rn, ^{226,228}Ra, Isotopes of U, Th and Pu, ^{237}Np, ^{241}Am
	Norwegian Radiation Protection Authority (NRPA)	Environmental radioactivity and radioecology, environmental trace, emergency preparedness	^{89,90}Sr, ^{99}Tc, ^{1210}Po, ^{210}Pb, ^{222}Rn, ^{226,228}Ra, Isotopes of U, Th and Pu, ^{237}Np, ^{241}Am, gross alpha, gross beta

Overview of the present status of radioanalysis in Nordic labs (2)

Country	Organization	Purpose of analysis	Main radionuclides
Finland	Radiation and Nuclear Safety Authority (STUK)	Environmental radioactivity, bioassay of radioactivity, emergency preparedness	^{3}H, ^{14}C, ^{89,90}Sr, ^{99}Tc, ^{210}Po, ^{210}Pb, ^{222}Rn, ^{226,228}Ra, ^{234}U, ^{235}U, ^{238}U, ^{232,230,228}Th, ^{239,240}Pu, 241Am, gross alpha, gross beta
	University of Helsinki	Environmental radioactivity and radioecology, analysis of nuclear waste	^{3}H, ^{14}C, ^{41}Ca, ^{89,90}Sr, ^{210}Po, ^{210}Pb, ^{222}Rn, ^{226,228}Ra, Isotopes of U, Th and Pu, ^{237}Np, ^{241}Am, gross alpha, gross beta
	Loviisa NPP	**Monitoring of radioactivity in the power plant, discharges and surrounding environment**	**^{3}H, ^{14}C, ^{63}Ni, ^{89,90}Sr, gross alpha, gross beta**
	Olkiluoto NPP	**Monitoring of radioactivity in the power plant, discharges and surrounding environment**	**^{3}H, ^{14}C, ^{89,90}Sr, gross alpha, gross beta**

Overview of the present status of radioanalysis in Nordic labs (3)

Country	Organization	Purpose of analysis	Main radionuclides
Sweden	**Forsmark NPP**	**Monitoring of radioactivity in the power plant, discharges and surrounding environment**	**^{3}H, ^{14}C, ^{63}Ni, ^{90}Sr, gross alpha, gross beta**
	Oskarhamn NPP	**Monitoring of radioactivity in the power plant, discharges and surrounding environment**	**^{3}H, ^{14}C, ^{55}Fe, ^{63}Ni, ^{89,90}Sr, ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{244}Cm, ^{243,244}Cm, gross alpha, gross beta**
	Ringhals NPP	**Monitoring of radioactivity in the power plant, discharges and surrounding environment**	**^{3}H, ^{14}C, ^{63}Ni, ^{89,90}Sr, ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{244}Cm, ^{243,244}Cm, gross alpha, gross beta**
	Studsvik Nuclear AB	Waste management, characterization of decommissioning waste, emergency preparedness	^{3}H, ^{14}C, ^{36}Cl, ^{55}Fe, ^{63}Ni, ^{89,90}Sr, ^{99}Tc, ^{129}I, ^{210}Po, ^{226,228}Ra, Isotopes of U, Th and Pu, ^{237}Np, ^{241}Am, ^{242}Cm, ^{244}Cm
	Lund University	Radioecology, environmental trace, emergency preparedness	^{14}C, ^{55}Fe, ^{63}Ni, ^{89,90}Sr, ^{99}Tc, ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{244}Cm, ^{243,244}Cm, gross alpha, gross beta
	Swedish Defence Research Agency	emergency preparedness, radioecology, nuclear decommissioning	^{3}H, ^{14}C, ^{63}Ni, ^{89,90}Sr, ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{244}Cm, ^{243,244}Cm, gross alpha, gross beta
	Swedish Radiation Safety Authority (SSM)	Environmental radioactivity, emergency prepardness	^{90}Sr, ^{210}Po, ^{238}Pu, ^{239,240}Pu, gross alpha, gross beta etc.

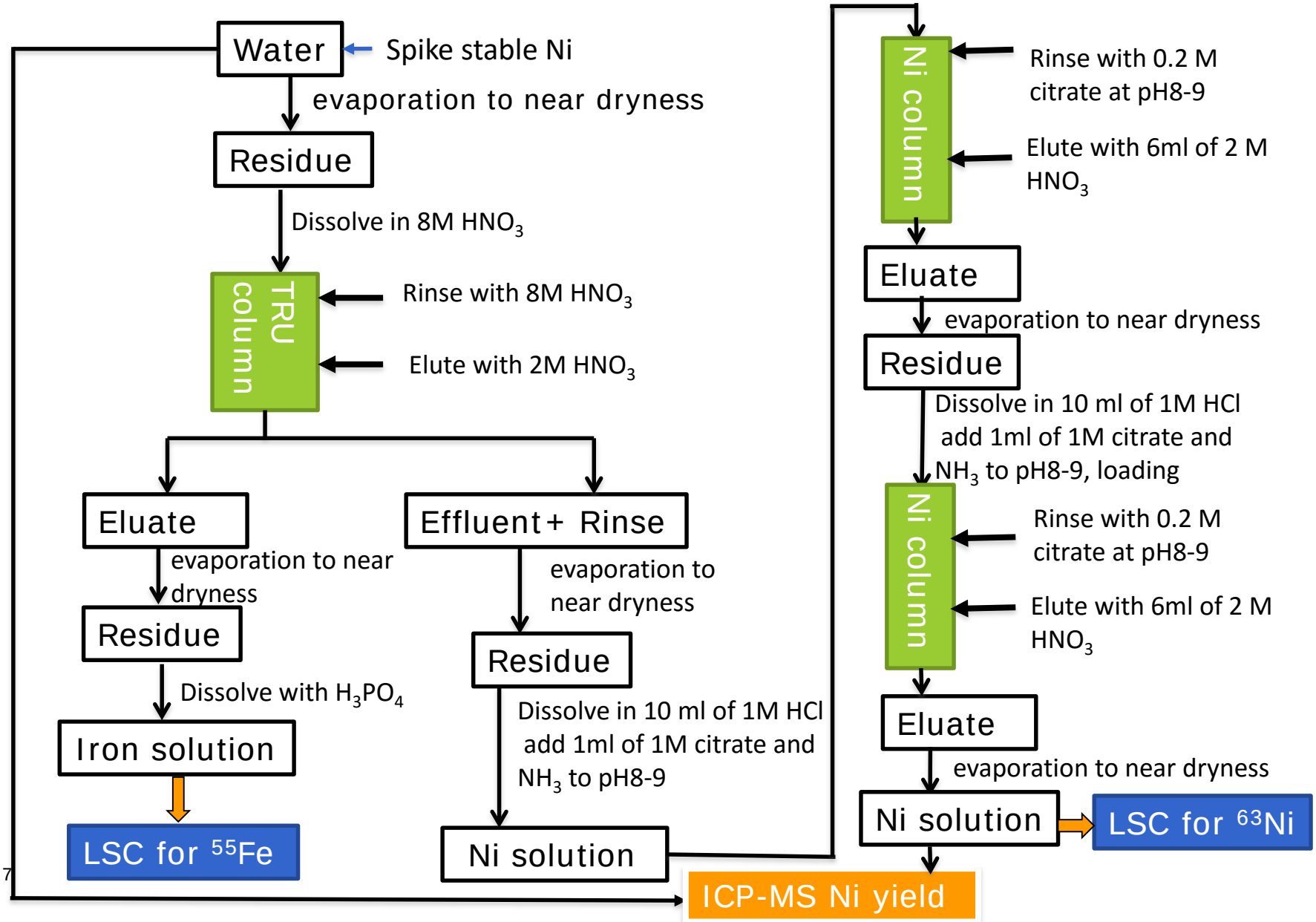
Summary of the currently applied radioanalytical methods for ^{63}Ni, ^{55}Fe, ^{3}H, ^{14}C and ^{90}Sr in Nordic labs (1)

Nuclide	Sample type	Method	Laboratory
^{63}Ni	Water	TRU-Ni resin	Forsmark, Oskarhamn and Ringhals NPP , Loviisa NPP
		Preciptiation-ion exchange-Ni resin	DTU Nutech, STUK,
	Concrete, graphite, metals	Preciptiation-ion exchange-Ni resin	DTU Nutech
^{55}Fe	Water	TRU chromatography	Oskarhamn NPP
		Preciptiation-anion exhcange chromatography	DTU Nutech, Loviisa
	Concrete, graphite, metals	Acid digestion/leaching, hydroxide preciptiation, anion exchange chromatography	DTU Nutech
^{3}H	Water	Distillation	All labs
	Soil sample (concrete, graphite, soil)	Combustion using Packard Oxidizer	DTU Nutech, STUK
		Combustion using tube furnance	Studsvik
	Air	3H collector (as tritium water)	Oskarhamn, Ringhals, Forsmark NPP , DTU Nutech

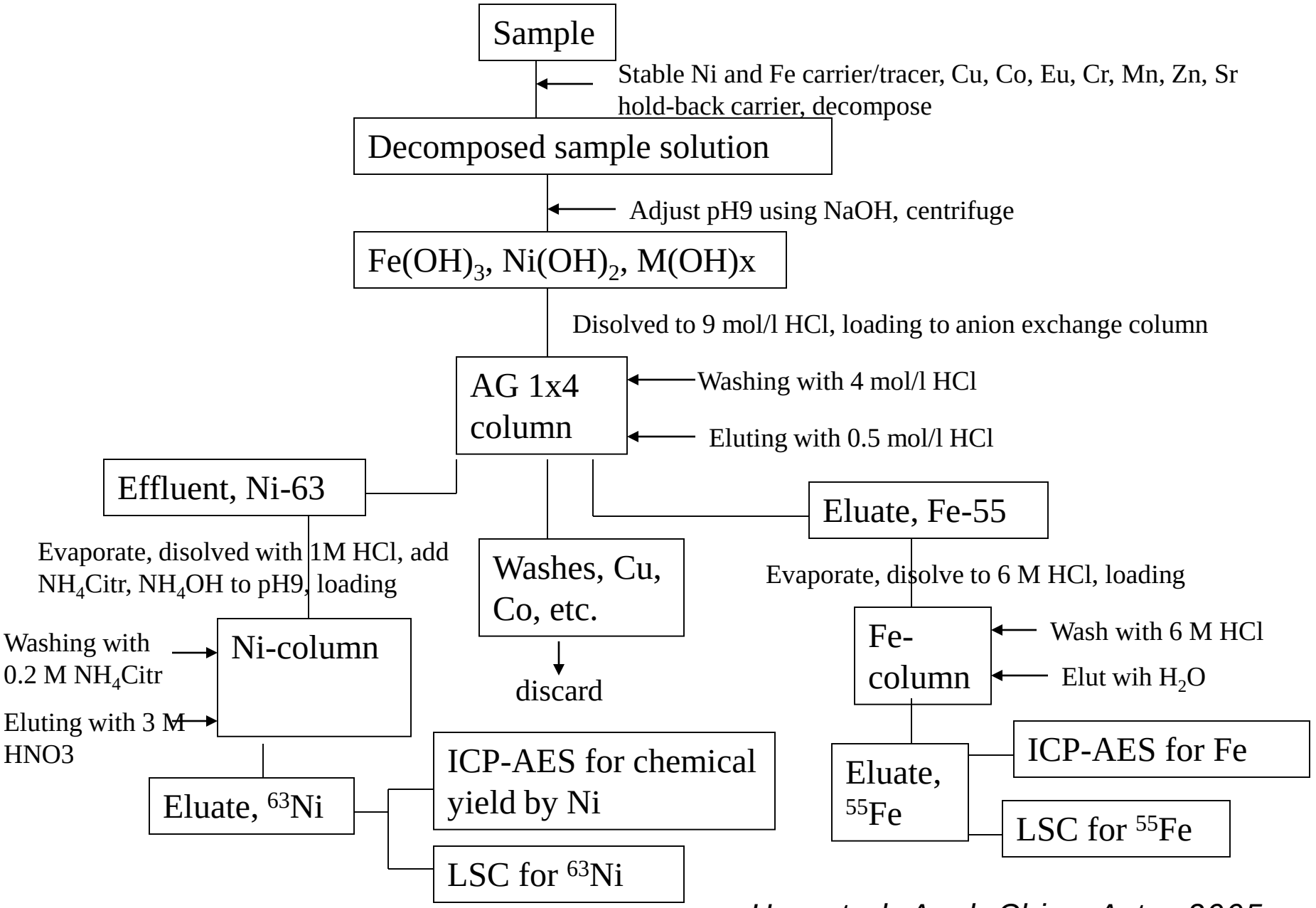
Summary of the currently applied radioanalytical methods for ^{63}Ni, ^{55}Fe, ^{3}H, ^{14}C and ^{90}Sr in Nordic labs (2)

Nuclide	Sample type	Method	Laboratory
^{90}Sr	Water	Carbonate precipitation, Ca(OH)2 precipitation, Sr (Ra, Ba, Pb) precipitation, $Y_2(C_2O_4)_3$ precipitation for ^{90}Y	DTU Nutech
		Oxalate precipitation, chromate preciptiation to remove Pb, carbonate precipitation of Sr, extraction chromatography using Sr resin	STUK
		Cation exchange chromatography or phosphate preciptiation + extraction chromatography using Sr resin	Oskarhamn, Ringhals NPP
		Direct solvent extraction of Y	Forsmark NPP
	Environmental and biological samples, Concrete, graphite, metals	Ashing, acid digestion (HCl, or HNO_3+HCl), separation using the same precedure as for water sample	DTU Nutech, STUK,
^{14}C	Water	Evaportation follow by combustion	DTU Nutech
	Soil sample (concrete, graphite, soil metals)	Combustion using Packard Oxidizer	DTU Nutech, STUK
		Combustion using tube furnance	Studsvik
	Air	14C collector (Carbosorb?)	Oskarhamn, Ringhals, Forsmark NPP

Analytical Procedure for ^{55}Fe and ^{63}Ni using by Labs in the Swedish NPPs



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



Hou et al. Anal. Chim. Acta, 2005

Three Inter-comparison Samples

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.

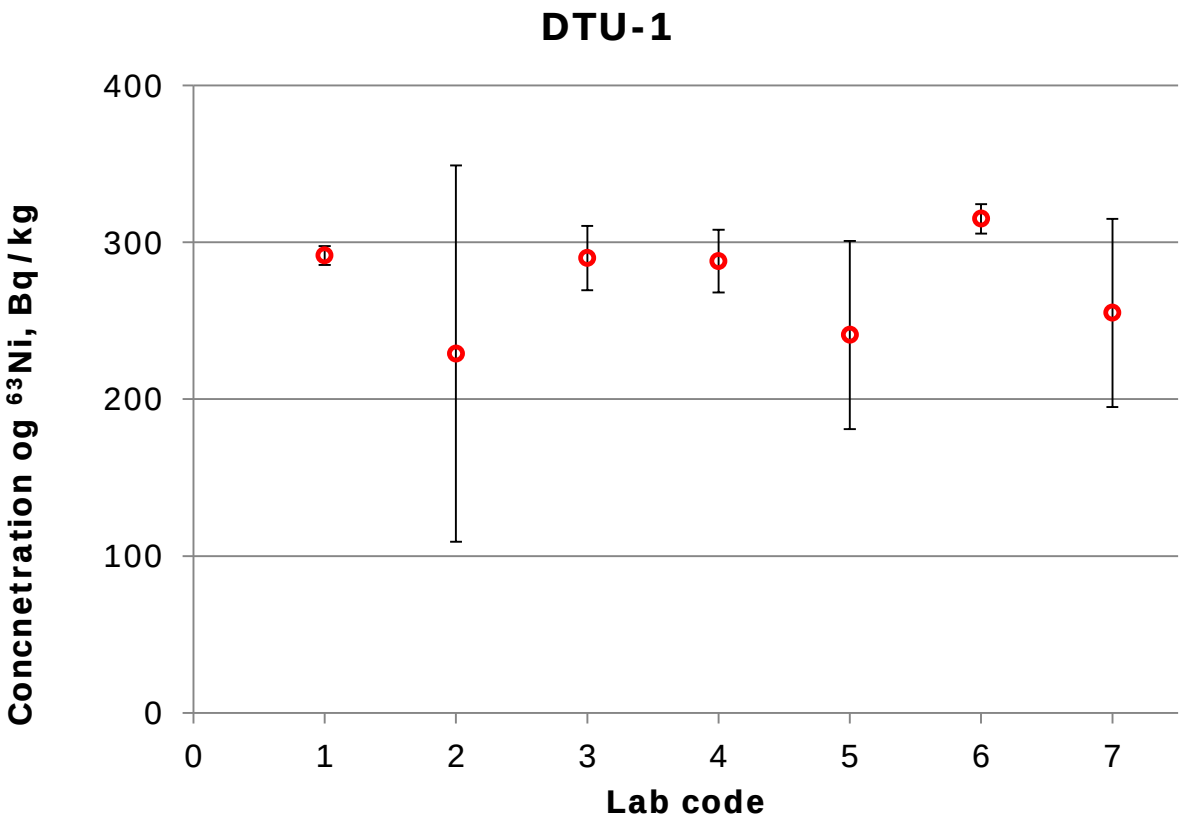
Laboratories participate in comparison and reported results

Institue	63Ni			55Fe
	DTU-1	Forsmark-1	Forsmark-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

Methods used for determination of ^{63}Ni and ^{55}Fe

Institue	63Ni			55Fe
	TRU+1 Ni column	TRU+2 Ni Column	$Fe(OH)_3$ precipitation +anion excheng+ Ni resin	$Fe(OH)_3$ precipitation+ anion excheng
DTU Nutech			x	x
Studsvik AB				
Forsmark		x		
OKG		x		
Ringhals AB	x			
STUK			x	
Loviisa		x		

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 !

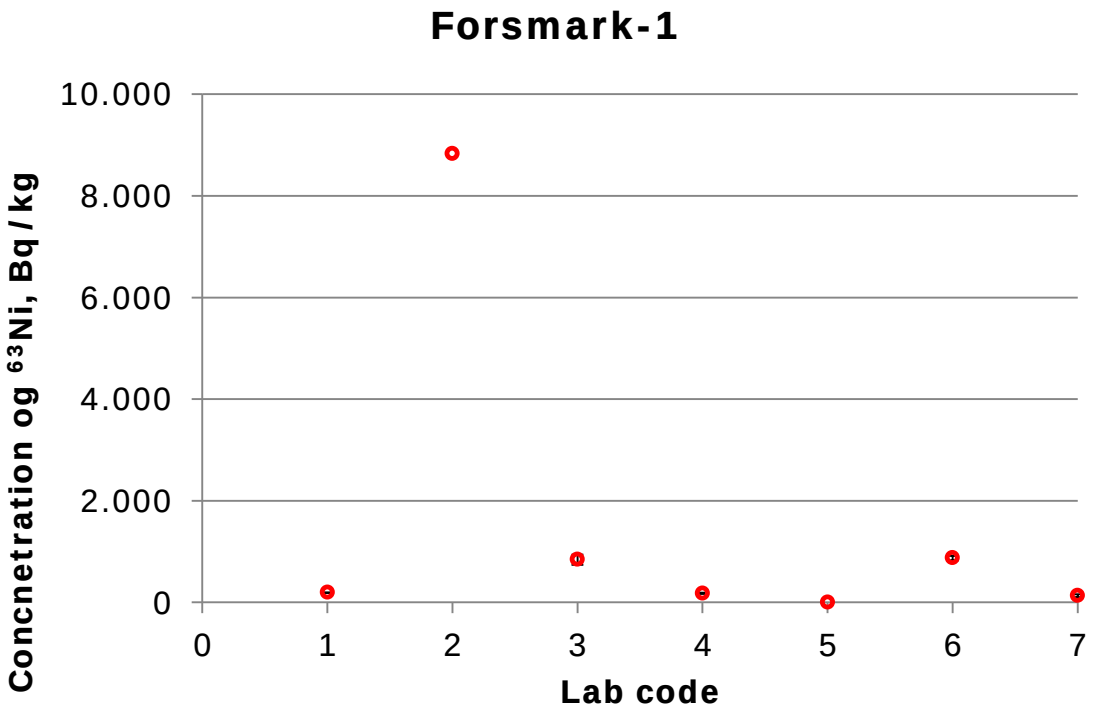
Measured Value:

Range: 229-315 Bq/L

Average: 273.3±31.4 Bq/L

Spiked value ： 290.2±3.2 Bq/L

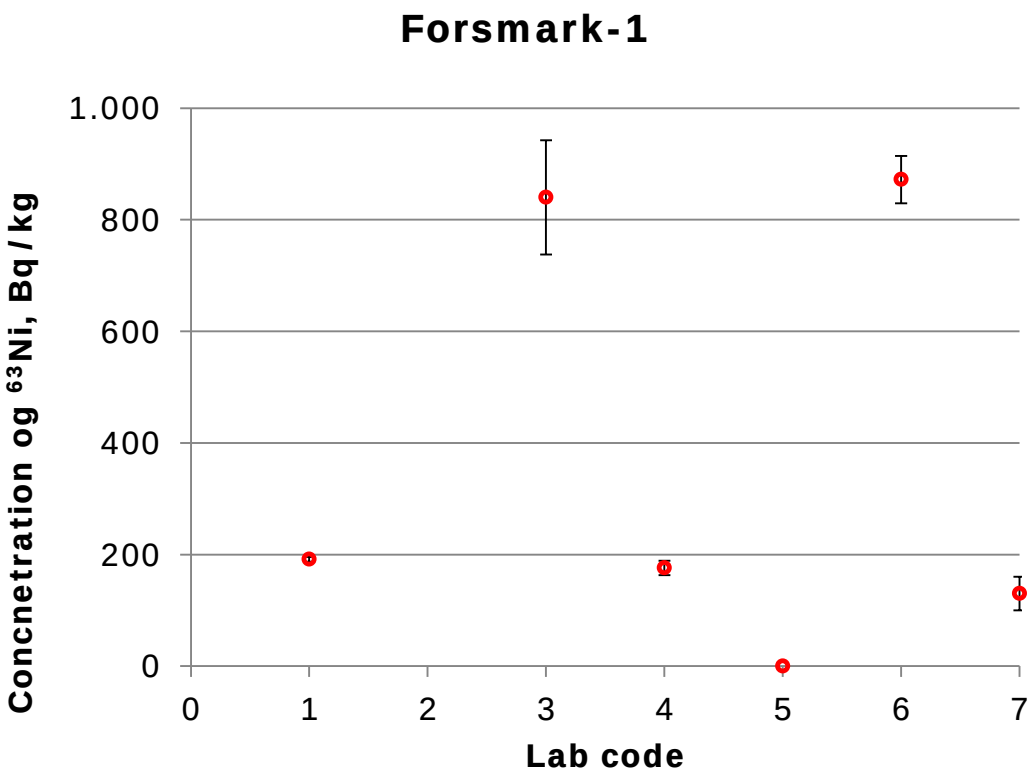
Analytical results of ^{63}Ni in Forsmark-1 (reactor coolant water with high ^{58}Co activity)



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

The method used by Lab 2 is lack of the ability to separate the interfering nuclides from the Ni. It is declared that the results for Forsmark-1 and Forsmark-2 samples is reliable.

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



TRU+Ni column	Anion exchange+ Ni column
2,3,4,5,6	1, 7

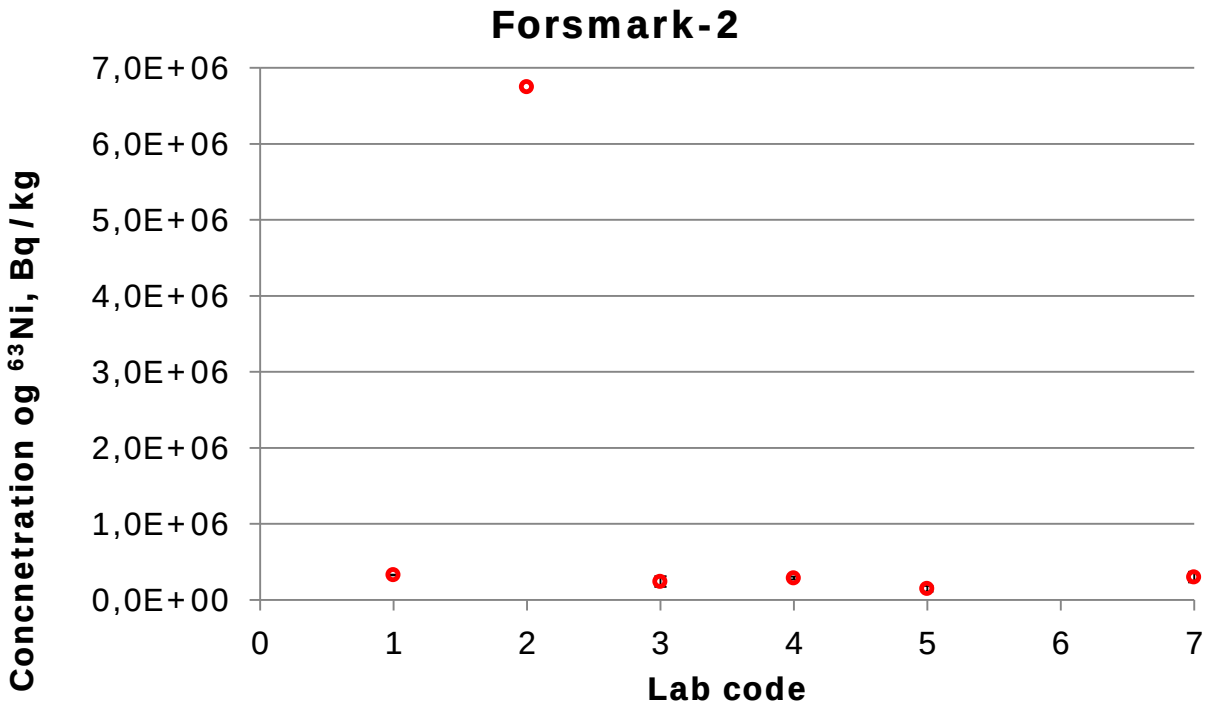
Range:

<3.1 - 840 Bq/L

The abnormal highest data from one lab was excluded

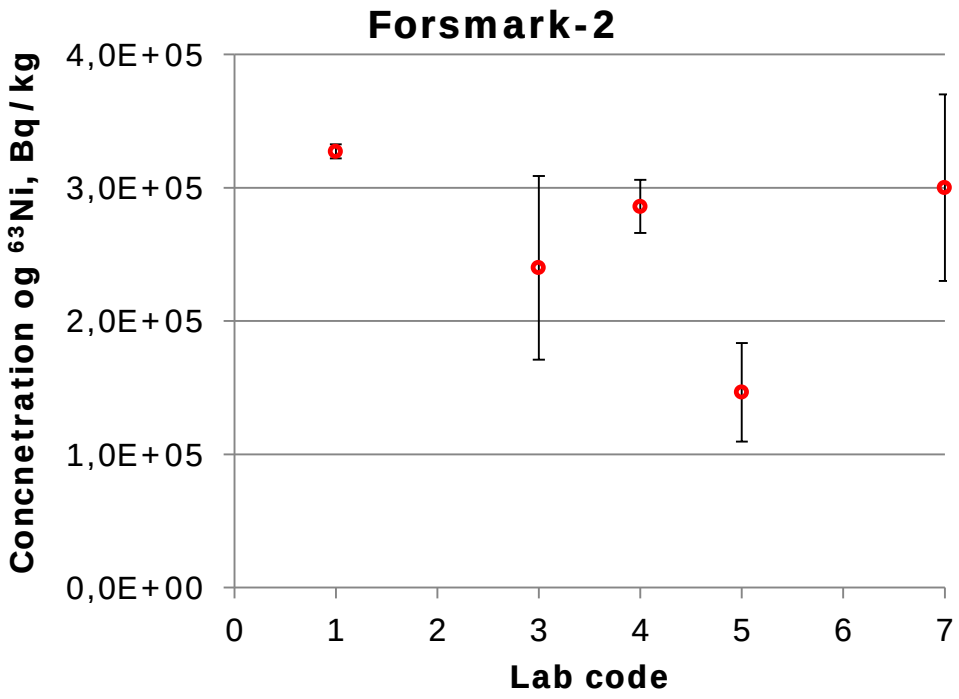
The analytical results of ^{63}Ni in reactor coolant water showed a big variation.
It might be attributed to high ^{58}Co content in this sample. Also
This demonstrated the need for reliable method for real sample analysis.

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



The method used by Lab 2 is lack of the ability to separate the interfering nuclides from the Ni. It is declared that the results for Forsmark-1 and Forsmark-2 samples is reliable.

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



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

The abnormal data from one lab was excluded

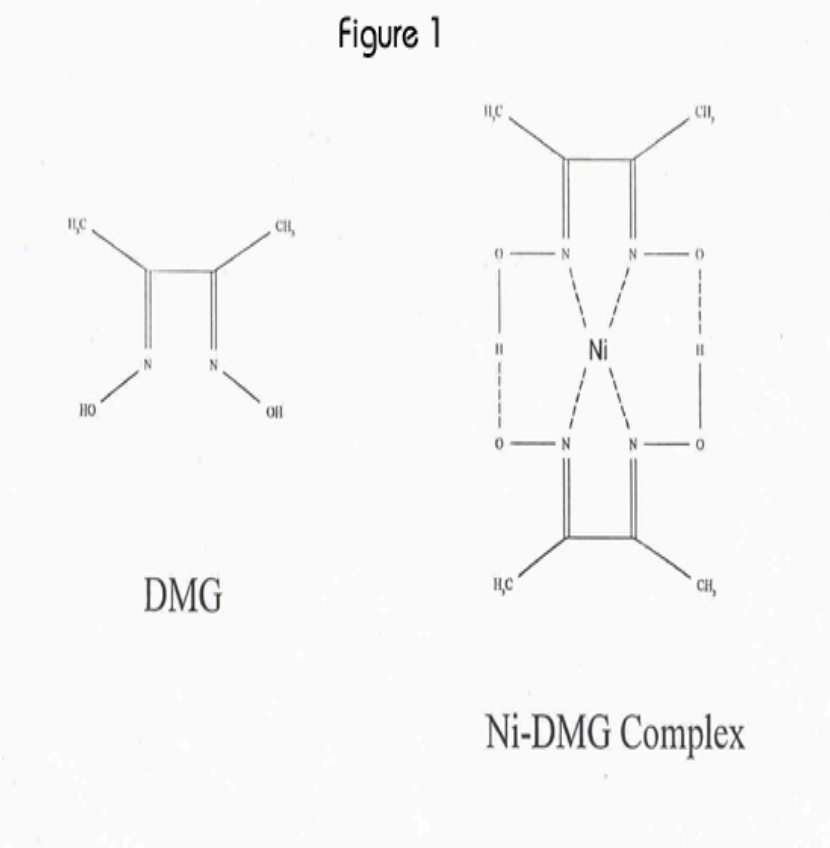
Range: (1.47-3.27) $\times 10^5$Bq/L

Average: (2.60$\pm$0.69) $\times 10^5$Bq/L

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

Code	55Fe concentration, Bq/kg					
	DTU-1 (Spiked solution)		Forsmark-1 (coolant)		Forsmark-2 (digested filter)	
	Value	Uncertainty (k=1)	Value	Uncertainty (k=1)	Value	Uncertainty (k=1)
1	3.11E+02	1.05E+01	7.33E+00	1.40E+00	1.26E+05	3.81E+03
6	3.27E+02	4.57E+01				
3						
4						
5						
7						
Spiked vaue	3.13E+02	6.26E+00				

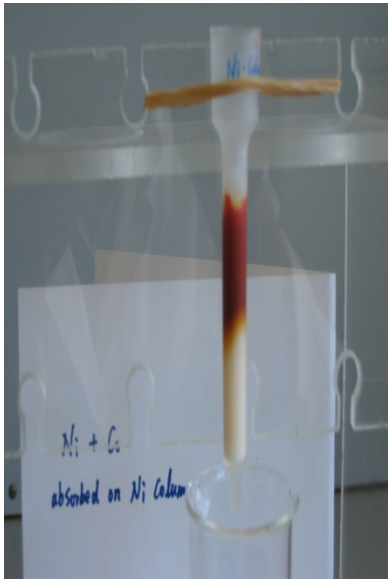
Application of Ni-DMG for separation of Ni



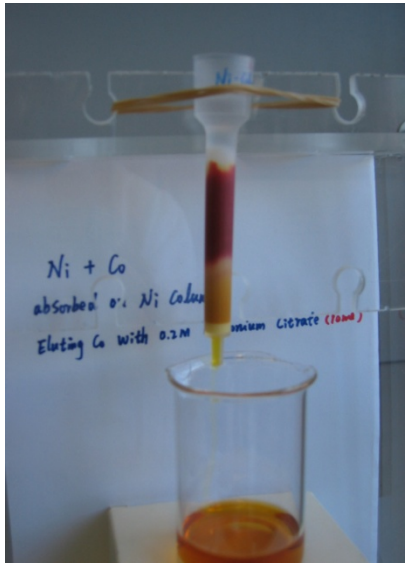
- Ni can form a stable specific complex with dimethylglyoxime. By Ni-DMG precipitation or organic solvent extraction of Ni-DMG complex at low concentration, Ni can be separated from many other elements.
- While, some other metals, such as Co, Cu can also form a complex with DMG and interferring the separation of Ni.

Application of extraction chromatography for Ni separation and ^{63}Ni measurement

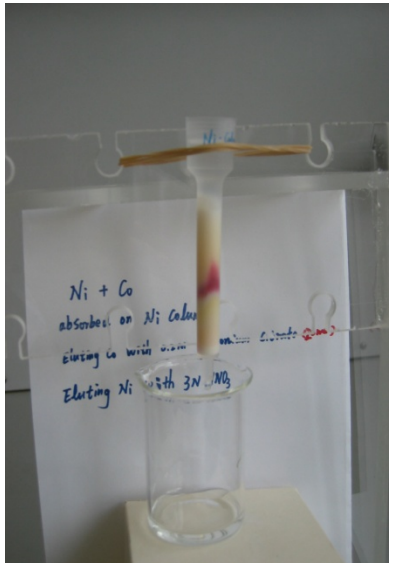
The Nickel Resin contains the DMG inside the pores of a polymethacrylate resin. The nickel-DMG precipitate occurs on the resin , where it is held and readily separated from other elements in the supernatant.



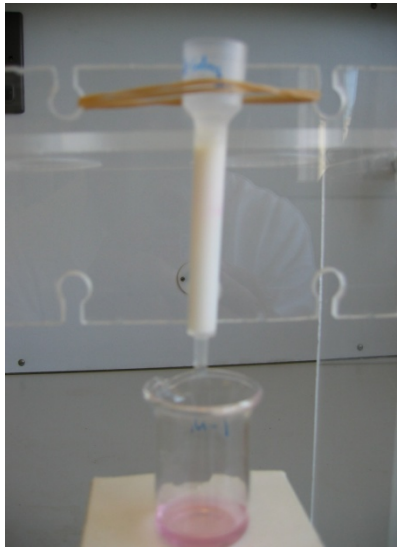
1. Loading of solution



2. Washing with 0.2 M ammonium citrate to remove other elements

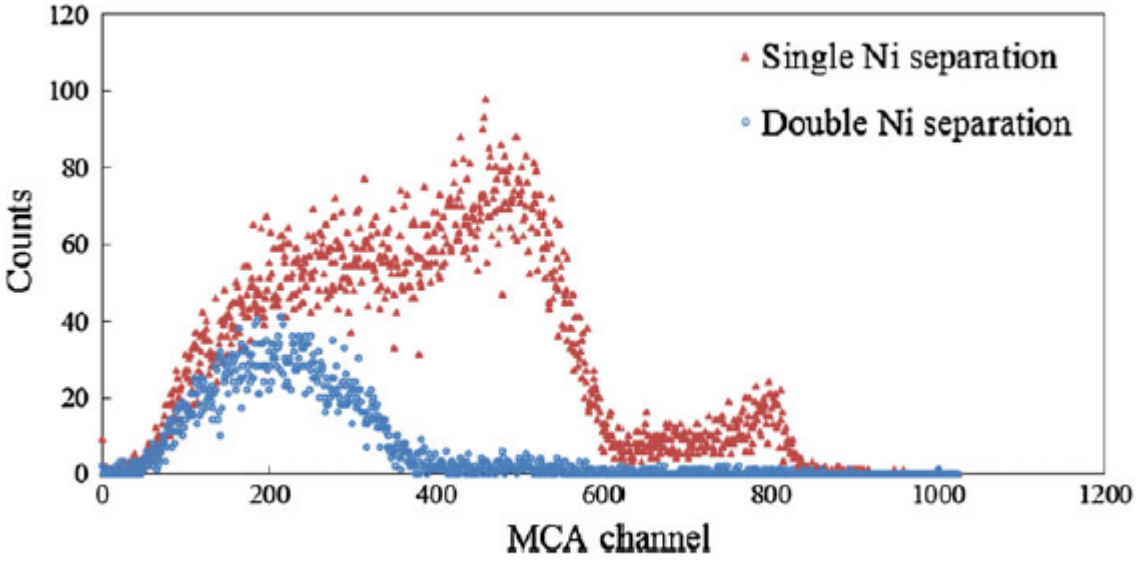


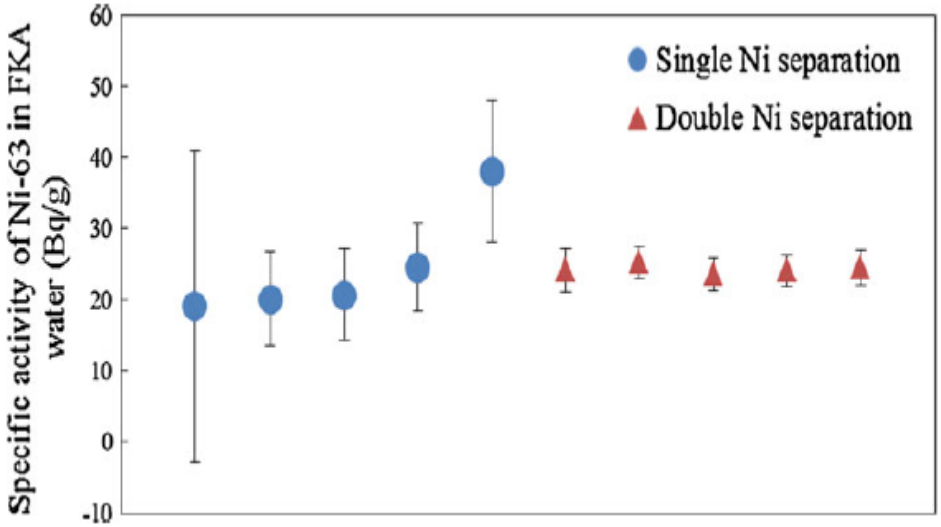
3. Eluting Ni using HNO3

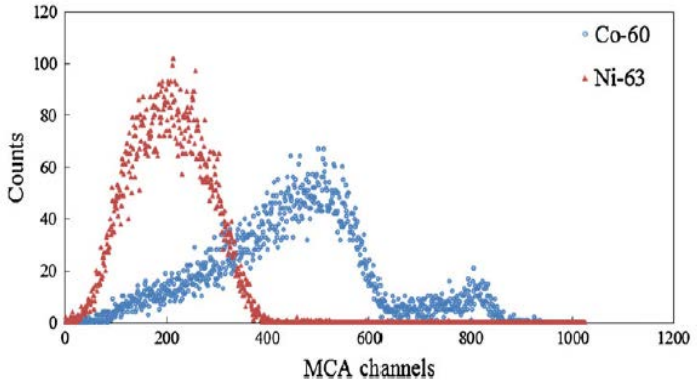


4. Evaporte eluted Ni-DMG solution to 0.1-0.2 ml for LSC

Analytical Procedure for ^{55}Fe and ^{63}Ni using by Labs in the Swedish NPPs

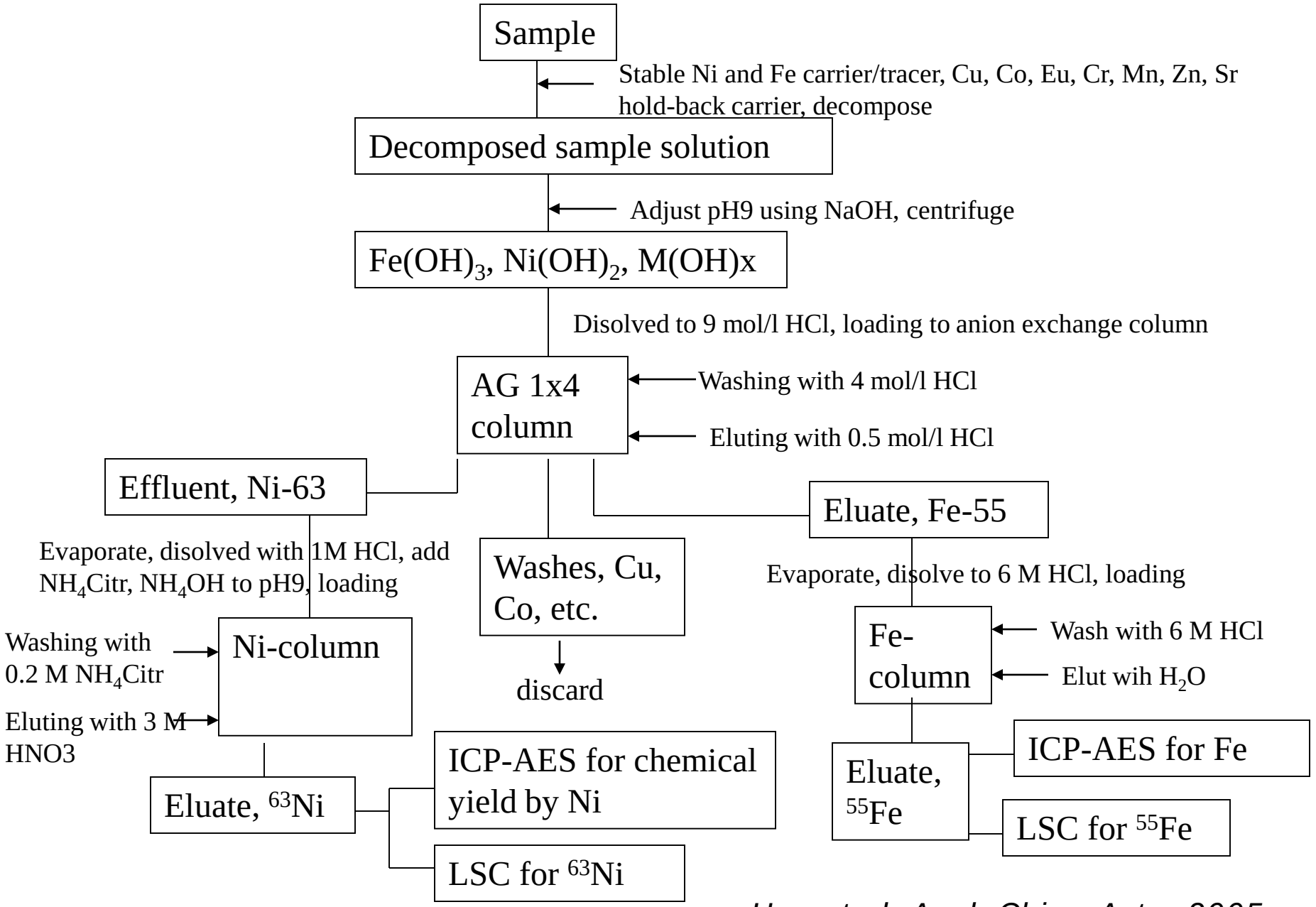






Eriksson et al. JRNC, 2013

DTU analytical procedure for ^{63}Ni and ^{55}Fe



Hou et al. Anal. Chim. Acta, 2005

Separation of Ni from Co, Eu, Ba using ion exchange chromatography

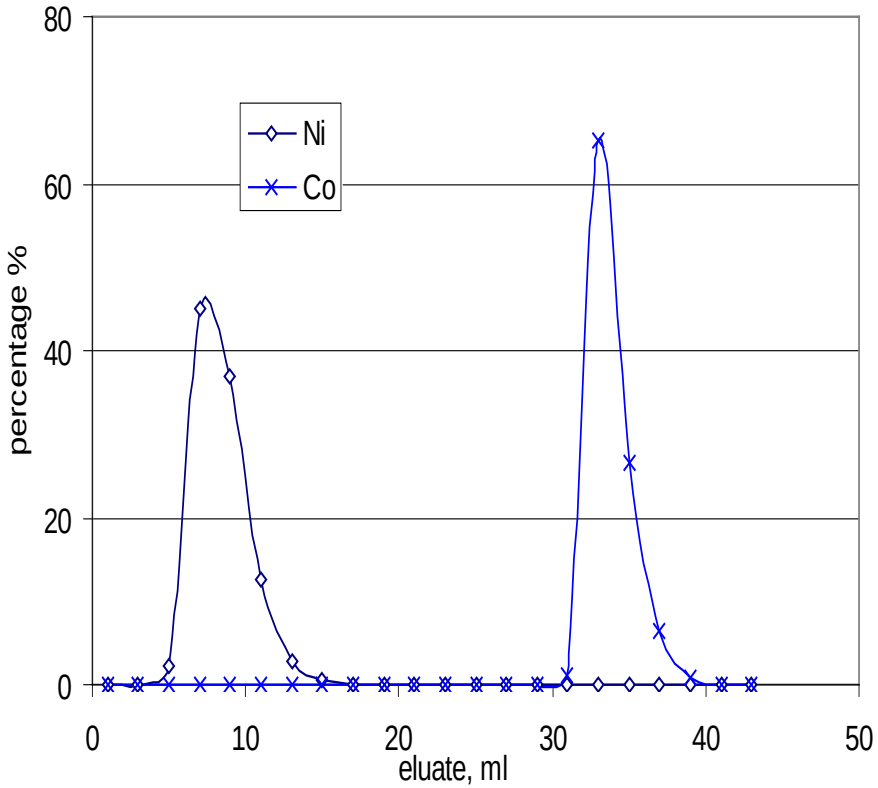
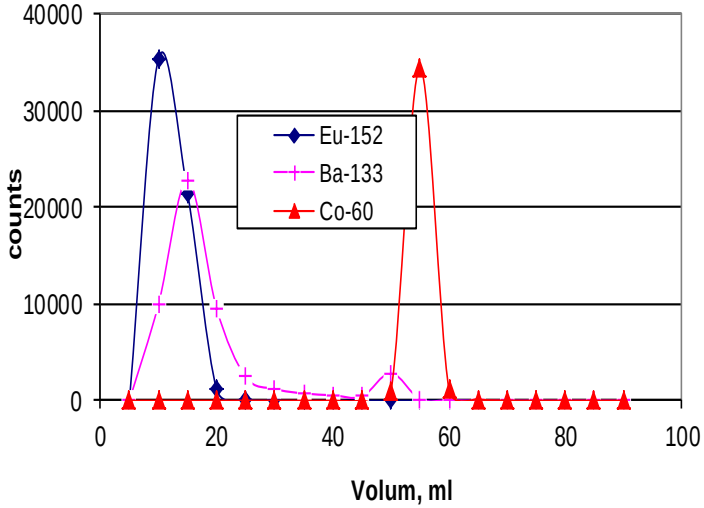


Fig. Separation of Ni from Co by ion exchange, eluted by 9 N HCl (3-20ml) for Ni and 2 N HCl (21-44 ml) for Co. Bio-Rad AG1x4. 1x15 cm column



Separation of Eu, Ba, Co by anion exchange chromatography, Bio-Rad AG1x4, 1x15 cm, 0-40ml:9M HCl, 40-70ml:4M HCl, 70-90ml, 0.05M HCl

NKS STANDMETHOD 2015 Porject meeting

26th March 2015, Copenhagen, Denmark

Participants/Partners:

DTU, Denmark :	Xiaolin Hou
Forsmark AB, Sweden:	Anders Falk/Mattias Olsson
OKG, Sweden:	Sofie Englund,
Ringhals AB, Sweden:	Olof Gottfridsson
Studsvik AB, Sweden:	Charlotta Askeljung
Loviisa NPP, Finland:	Laura Togneri/ Miia Lampen
Olkiluoto NPP,Finland:	Hannele Hirvonen

NKS STANDMETHOS project 2015

The goals of the project:

(1) A Nordic standard method for accurate determination of ^{63}Ni in water samples (especially for water samples from nuclear power plant)

(2) A recommended method for simultaneous determination of ^{55}Fe and ^{63}Ni in water samples.

(3) A proposed chemical procedure for the simultaneous determination of several radionuclides ($^{89}Sr/^{90}Sr$, ^{55}Fe, ^{63}Ni, uranium, plutonium, curium and americium) in waste and environmental samples.

Inter-comparison Samples 2015

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;

Conclusion and perspectives

- It is useful and important for the collaboration among Nordic research labs and the industry in radiochemcial analysis in view of improvement of the radioanalytical capacity and quality in Nordic industry
- Inter-comparison exercise in radiochemcial analysis of radionuclides in environmental and waste is a good way for evaluation of the analytical results, especially those radionculides without suitable standard reference materials
- Establishment of standard/reference method for determination of important radionculides in the Nordic industry is needed for improvement and insurance of analytical quality.
- Besides ^{63}Ni and ^{55}Fe, standard/reference methods for determination of other important radionuclides are expected in near future, which will improve the radioanalytical capacity and competitive in Nordic countries.

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